Supporting Information

Photocatalytic Heck-type coupling reactions of alkyl chlorides mediated by halide-exchange of $CsPbBr_3$ nanocrystals

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1. General information

Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) were recorded in a Bruker Avance instrument equipped with a 500 MHz spectrometer. GC-MS spectrum was obtained on a Thermo Fisher Scientific ISQ 7000/7610 gas chromatograph coupled with a gas chromatograph-mass spectrometer. The GC conditions were as follows: injector temperature, 280 °C; column oven initial temperature, 60 °C; carrier gas flow rate, 1.0 mL/min. XRD spectra were recorded on a Rigaku SmartLab SE equipped with a Cu Kα radiation source (λ = 1.54178 Å) and a scanning range of 10° to 80°. Morphology, microstructure, and elemental mapping of $CsPbBr_3$ nanocrystals ($CsPbBr_3$ NCs) were analyzed using a JEOL JEM-F200 transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ScientificTM ESCALAB 250Xi spectrometer equipped with a monochromatic Al Kα X-ray source (1486.6 eV). Samples were analyzed under vacuum ($P < 10^{-8}$ mbar) at an energy of 100 eV (survey scan) or 50 eV (high-resolution scan). All peaks were calibrated for incidental carbon using the C1s peak binding energy of 284.8 eV. Ultraviolet-visible molecular absorption spectra (UV-Vis) were recorded using a METASH UV-9000. Photoluminescence (PL) spectra were recorded using a HITACHI F-2700 fluorescence spectrometer with an excitation wavelength of 425 nm and an emission wavelength of 580 nm. Electron paramagnetic resonance (EPR) spectrum of alkyl radicals were recorded using a Bruker A300 paramagnetic resonance spectrometer. High-resolution mass spectrometric (HRMS) analysis was conducted on a Bruker SolariX 70 FT-ICR-MS spectrometer with an atmospheric pressure chemical ionization (APCI) source in positive ion mode.

2. Experimental section

2.1 Synthesis of $CsPbBr_3$ NCs

Step 1: Cs_2CO_3 (0.814 g, 2.5 mmol), 2.5 mL Oleic acid (OA) and 30 mL 1-Octadecene (ODE) were added into a 100 mL three-neck flask. The resulted solution was degassed under vacuum until no bubbles generated. Then the temperature was elevated to 120 °C and maintained under N_2 atmosphere until completely dissolved of Cs_2CO_3, obtaining Cs-oleate solution.

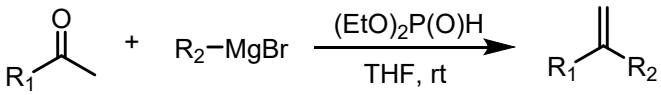
Step 2: $PbBr_2$ (0.069 g, 0.2 mmol) and 10 mL of ODE were mixed in another 100 mL three-neck flask. The resulted solution was degassed under vacuum until no bubbles generated in the system. Then

the temperature was raised to 120 °C under N_2 atmosphere and maintained for 30 min. Subsequently, 1 mL Oleylamine (OAm) and 1 mL OA were added to the solution, and the temperature was further raised to 180 °C. Upon the complete dissolution of $PbBr_2$, 1.2 mL of Cs-oleate solution was rapidly injected. 5 s later, the solution was cooled in an ice water bath. The obtained green solution was washed with n-hexane for three times and collected the precipitate each time by centrifugation at 8000 rpm for 5 min. The precipitates redisperse in 10 mL of n-hexane to obtain a $CsPbBr_3$ NCs suspension, or dry it at 60 °C in vacuum to obtain $CsPbBr_3$ NCs powers[1].

2.2 Synthesis of $CsPbCl_3$

A mixture of CsCl (0.3367 g, 2.0 mmol) and $PbCl_2$ (0.5562 g, 2.0 mmol) was added into a 25 mL agate jar under ambient atmosphere, followed by ball milling at a rotational speed of 500 r/min in a planetary ball mill (Changsha Deco). After 30 min, 1.157 mL of OAm was added into the jar, and the ball milling was continued for another 30 min. Ultimately, $CsPbCl_3$ materials were obtained, which were established by XRD (**Fig.S7**)[2].

2.3 A typical procedure for the synthesis of alkenes



A solution of Grignard reagents (8.8 mL, 1.0 M in THF, 8.8 mmol) was added dropwise to a solution of carbonyl compounds (4.0 mmol) in dry THF (12 mL) at room temperature under N_2 atmosphere. The mixed solution was stirred for 0.5 h, then diethylphosphite (0.62 mL, 4.8 mmol) was added. After the complete conversion of carbonyl compounds, using water to quench the reaction. Removing THF by rotary evaporator and the obtained system was extracted with EtOAc (3×20 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The residues were purified by silica gel column chromatography (eluent: petroleum ether (60-90 ^oC)) to afford target alkenes[3].

2.4 General procedure for conducing Heck coupling reactions

Alkene (0.2 mmol, 36.0 mg, 1.0 equiv), Aceclidine (0.1 mmol, 16.9 mg, 0.5 equiv), $CsPbBr_3$ (1 mol%, 5 mg), and dry 1,2-dichloroethane (2 mL) were added into a dry 25 mL Schlenk tube equipped with a magnetic bar. The mixture was frozen with liquid nitrogen and evacuated three times under N_2 atmosphere. The reaction system was then illuminated by 50 W blue LEDs (λ = 425~430 nm) with

distance of approximately 5 cm. After complete conversion of alkene, removing DCE and photocatalyst, the residues were purified by flash silica gel column chromatography using petroleum ether as the sole eluent to afford the desired product.

3. Calculation Details

Calculations were performed by Density Functional Theory (DFT) as implemented in Vienna Ab-initio Simulation Package (VASP) with Perdew-Burke-Ernzerhof (PBE) functional and projector augmented Wave (PAW) basis set [4-7]. As valence electrons, the following electronic configurations were used respectively: Cs ($5s^25p^66s^1$), Pb($6s^26p^2$), Cl($4s^22p^5$) and Br ($4s^22p^5$). Energy cut off of 450 eV with 3×3×2 Γ centered k-mesh was taken for geometrical relaxations by conjugate-gradient method with an energy threshold of 1.0×10^{-6} eV and atomic forces below 0.02 eV/Å. The recommended k-point path was generated by the VASPKIT package[8].

References

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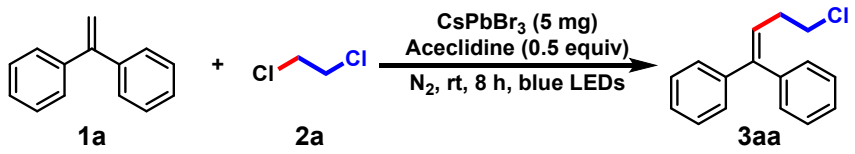
4. Optimization of reaction conditions

Table S1. Reaction conditions optimization for the Heck coupling of alkyl chloride over $CsPbBr_3$ NCs[a]



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

Entry	Variations from the standard conditions	Yield of **3aa** (%)[b]
1	**None**	69
2	MeCN	ND[c]
3	EtOH	ND
4	EtOAc	51
5	Acetone	43
6	365 nm instead of 425 nm	48
7	457 nm instead of 425 nm	54
8	No Aceclidine	ND
9	DABCO instead of Aceclidine	ND
10	No $CsPbBr_3$	NR[d]
11	Under air	25
12	$CsPbCl_3$ instead of $CsPbBr_3$	54
13	1.0 equivalent aceclidine	56
14	1.5 equivalent aceclidine	48
15	2.0 equivalent aceclidine	37

[a]Reaction conditions: **1a** (0.2 mmol, 36.0 mg), **2a** (2 mL), $CsPbBr_3$ (1 mol %, 5 mg), Aceclidine (0.1 mmol, 16.9 mg), 50 W 425 nm LED, N_2, rt, 8 h. [b]Isolated yield. [c]No product detected. [d]No reaction.

5. Lattice parameters of $CsPbBr_3$

Table S2. Lattice parameters for pristine and halide-exchanged $CsPbBr_3$

Structures	**a (Å)**	**b (Å)**	**c (Å)**	**α (°)**	**β (°)**	**γ (°)**
$CsPbBr_3$[a]	8.207	8.255	11.759	90.0	90.0	90.0
$CsPbBr_3$[b]	8.320	8.435	11.998	90.0	90.0	90.0
$CsPbCl_xBr_{3-x}$[b]	8.189	8.437	11.359	89.1	89.9	91.3

[a]Experimental parameters; [b]Calculated parameters.

6. *I-t* curves of $CsPbBr_3$ under light irradiation with different wavelengths

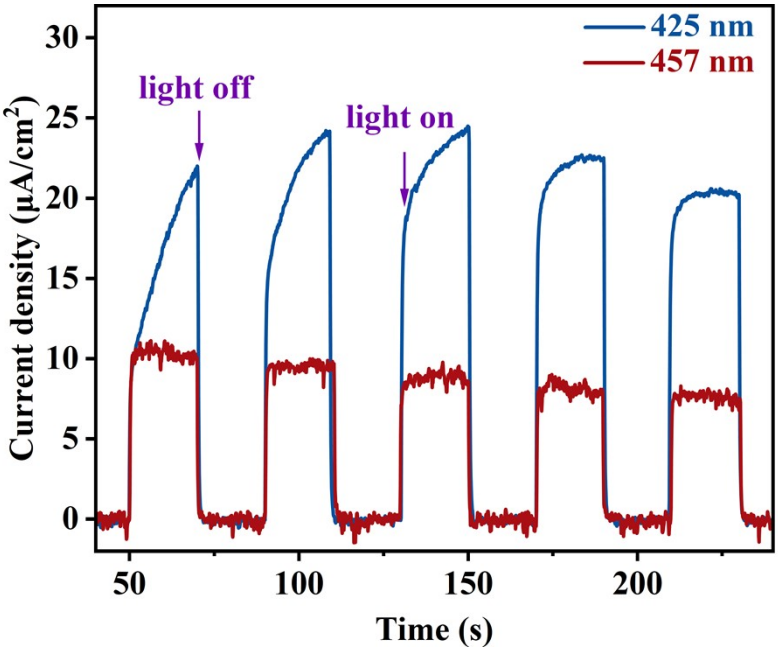


Fig. S1. *I-t* curves of $CsPbBr_3$ at 425 nm and 457 nm irradiation

7. Hammett plot

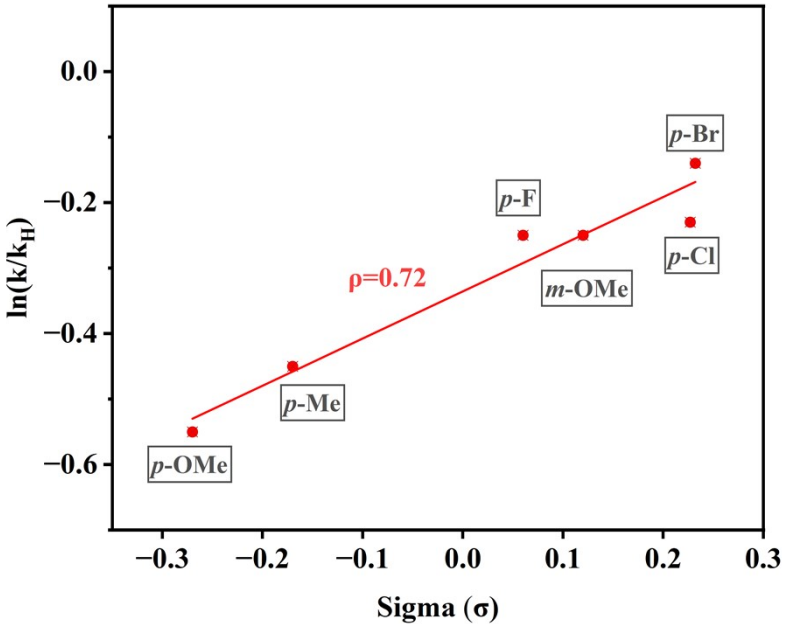


Fig. S2. Hammett plot for the coupling reaction

8. Configuration analysis the target products

As we known, the coupling constant (^3J) between olefinic hydrogens can offer critical information for the configuration of alkenes. Herein, the product **3qa** was used as an example to determine the *trans/cis* configuration of final products. As shown in the ^{1}H NMR of **3qa** (**Fig.S3**), the ^3J can was calculated as 15 Hz according to the coupling constant of H_a, indicating the product has a *trans* configuration, which was further confirmed by the H-H COSY spectra as a COSY signal of H_a and H_c was detected successfully (**Fig.S4**).

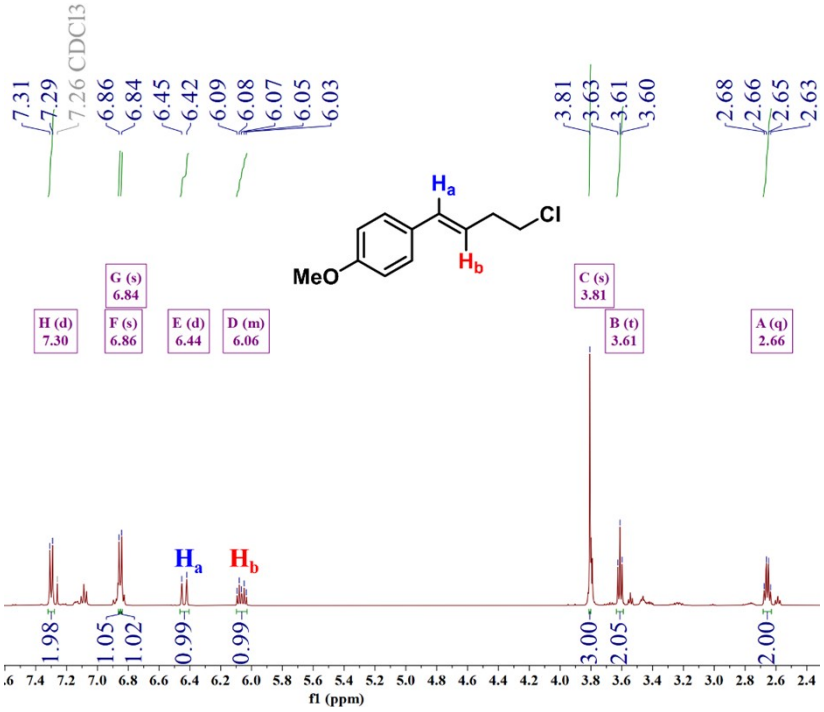


Fig. S3. ^{1}H NMR spectrum of **3qa**

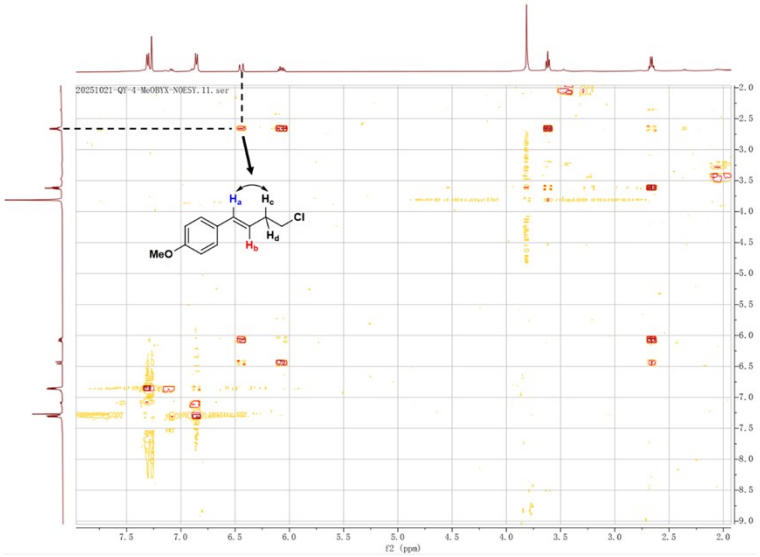


Fig. S4. ^{1}H-^{1}H COSY 2D NMR spectrum of **3qa**

9. Reaction kinetic curve

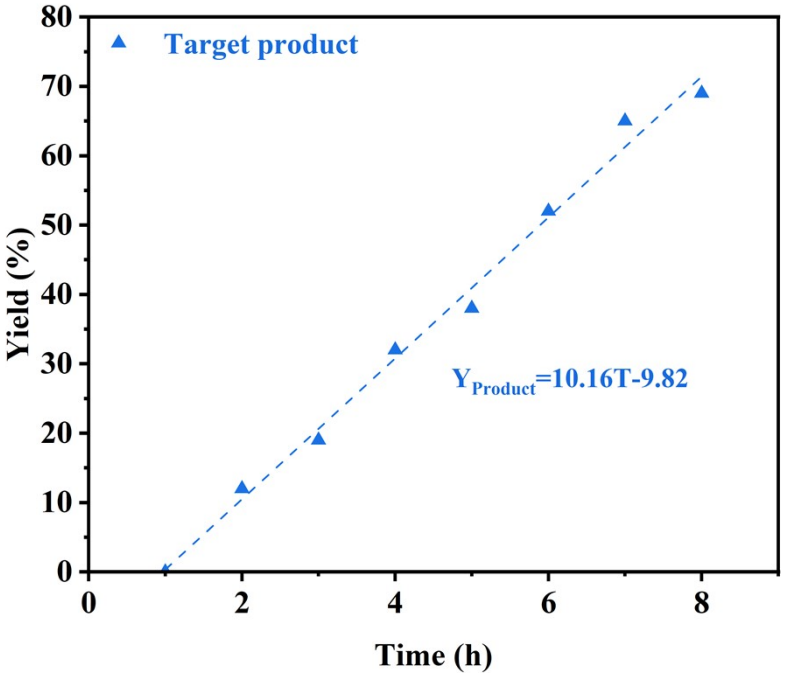


Fig. S5. Kinetic curve for the reaction of **1a**

10. XRD patterns of the recycled catalyst and $CsPbCl_3$

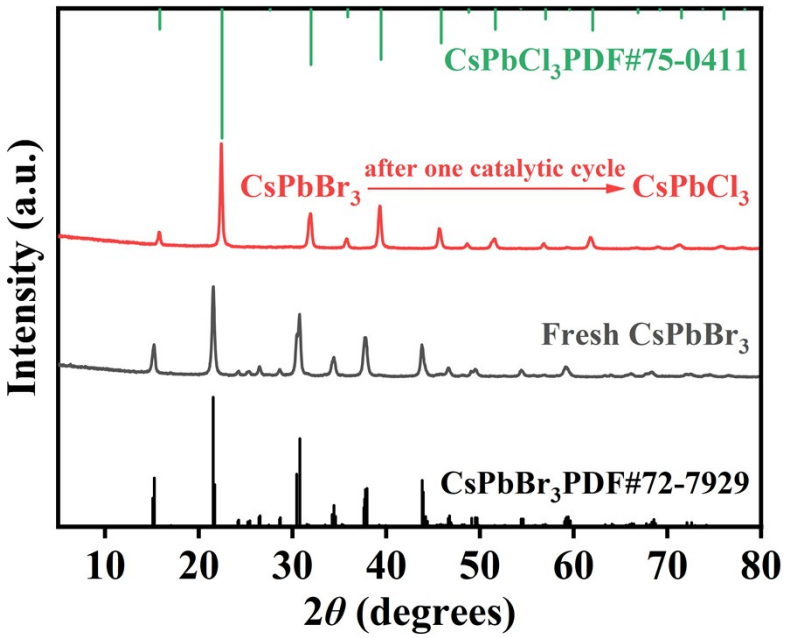


Fig. S6. XRD patterns of $CsPbBr_3$ before and after the reaction

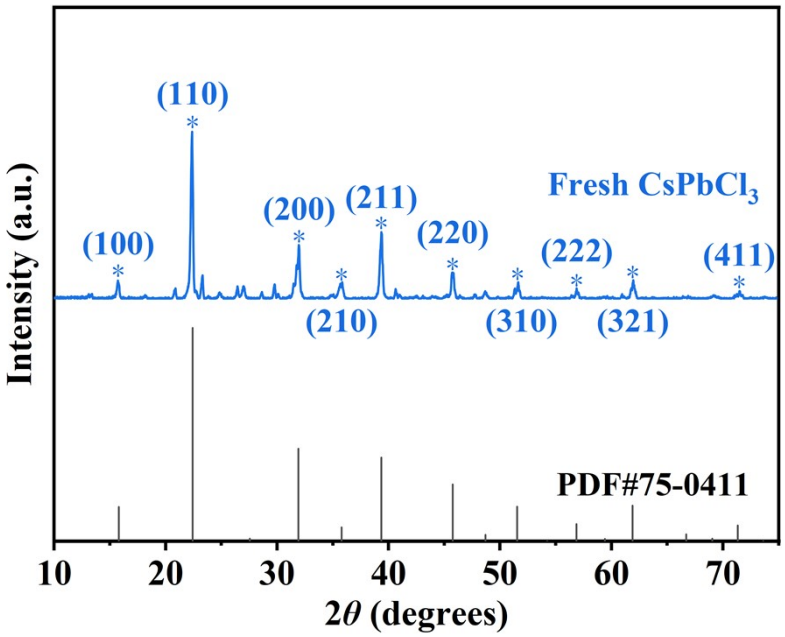


Fig. S7. XRD pattern of $CsPbCl_3$ prepared by mechanochemical synthesis method

11. Stern-Volmer quenching experiments of aceclidine and $CsPbBr_3$ NCs

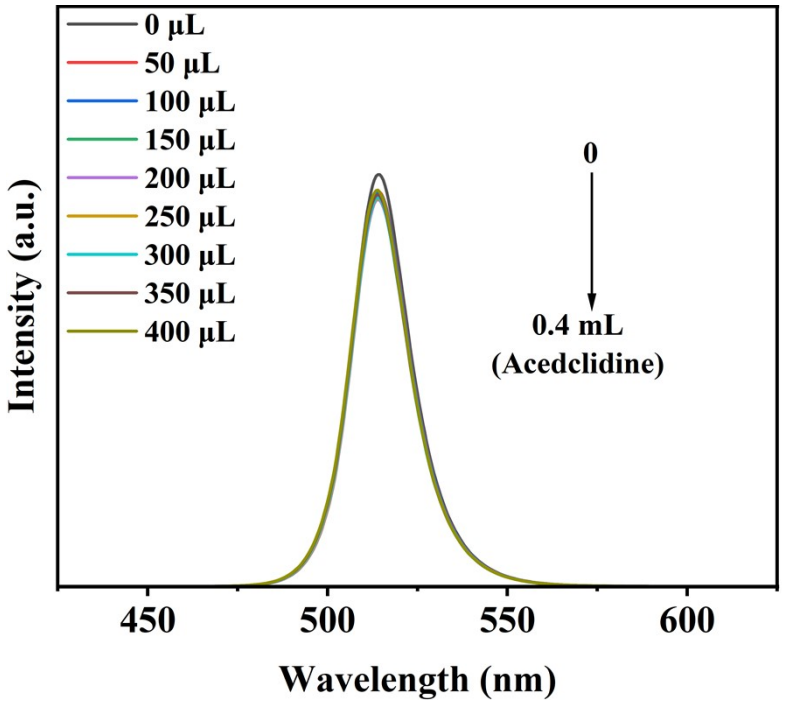


Fig. S8. Stern-Volmer quenching experiments of aceclidine and $CsPbBr_3$ NCs

12. Detection of Cl·

1,3,5-trimethoxybenzene (33.3 mg, 0.2 mmol, 1.0 equiv.), diisopropylethylamine (DIPEA, 2 equiv), $CsPbBr_3$ (1 mol%, 5 mg), and DCM (2 mL) were added into a dry 25 mL Schlenk tube equipped with a magnetic bar. The resulted reaction system was illuminated by 50 W blue LEDs (λ = 425~430 nm) with distance of approximately 5 cm. After complete conversion of alkene, removing DCM and photocatalyst, the residues were purified by flash silica gel column chromatography using petroleum ether as the sole eluent to afford the desired product and subjected to ^{1}H NMR and GC-MS analysis.

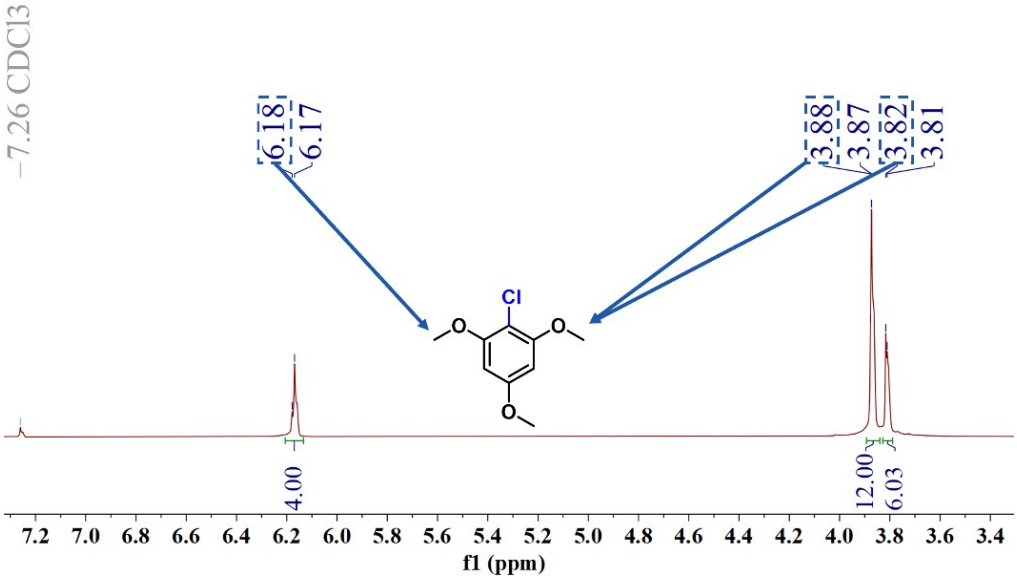


Fig. S9. ^{1}H NMR spectrum of 2-Chloro-1,3,5-trimethoxybenzene

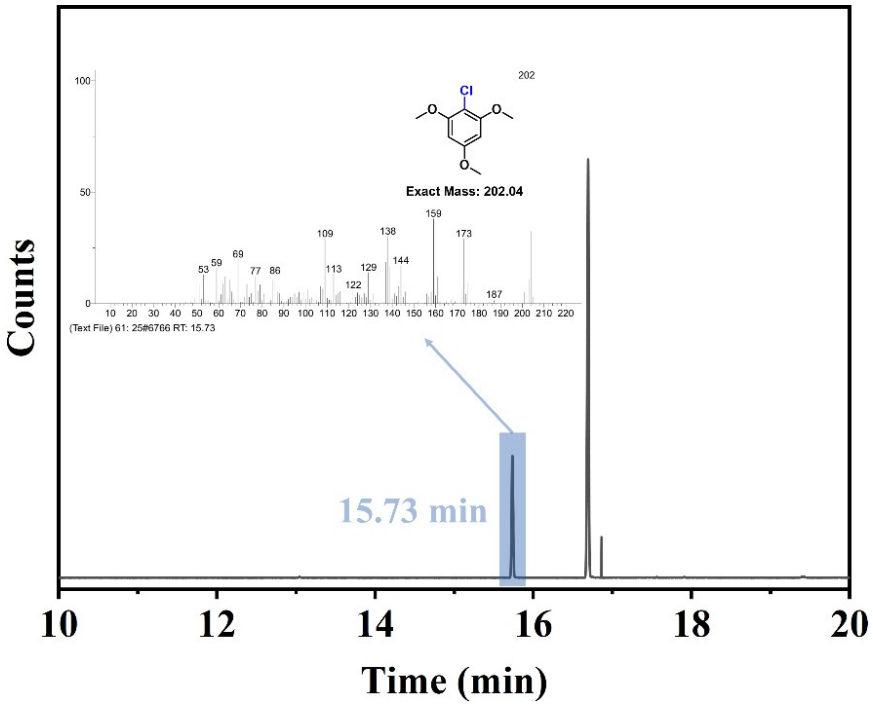


Fig. S10. GC-MS spectrum of 2-chloro-1,3,5-trimethoxybenzene

13. Detection of Br•

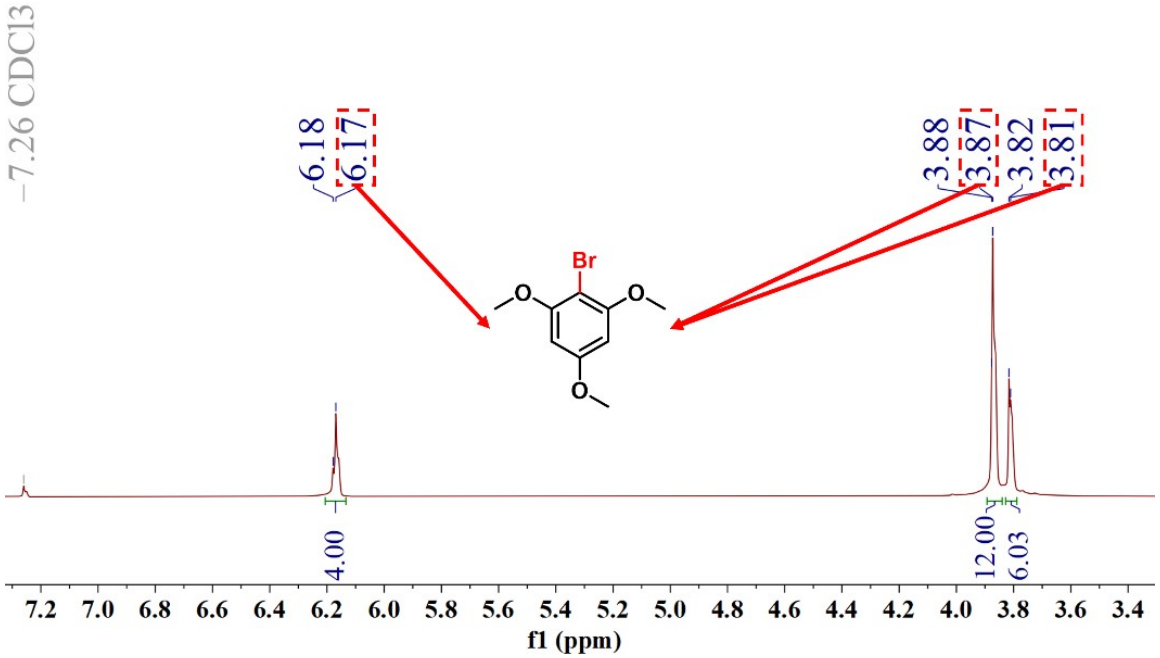


Fig. S11. ^{1}H NMR spectrum of 2-bromo-1,3,5-trimethoxybenzene

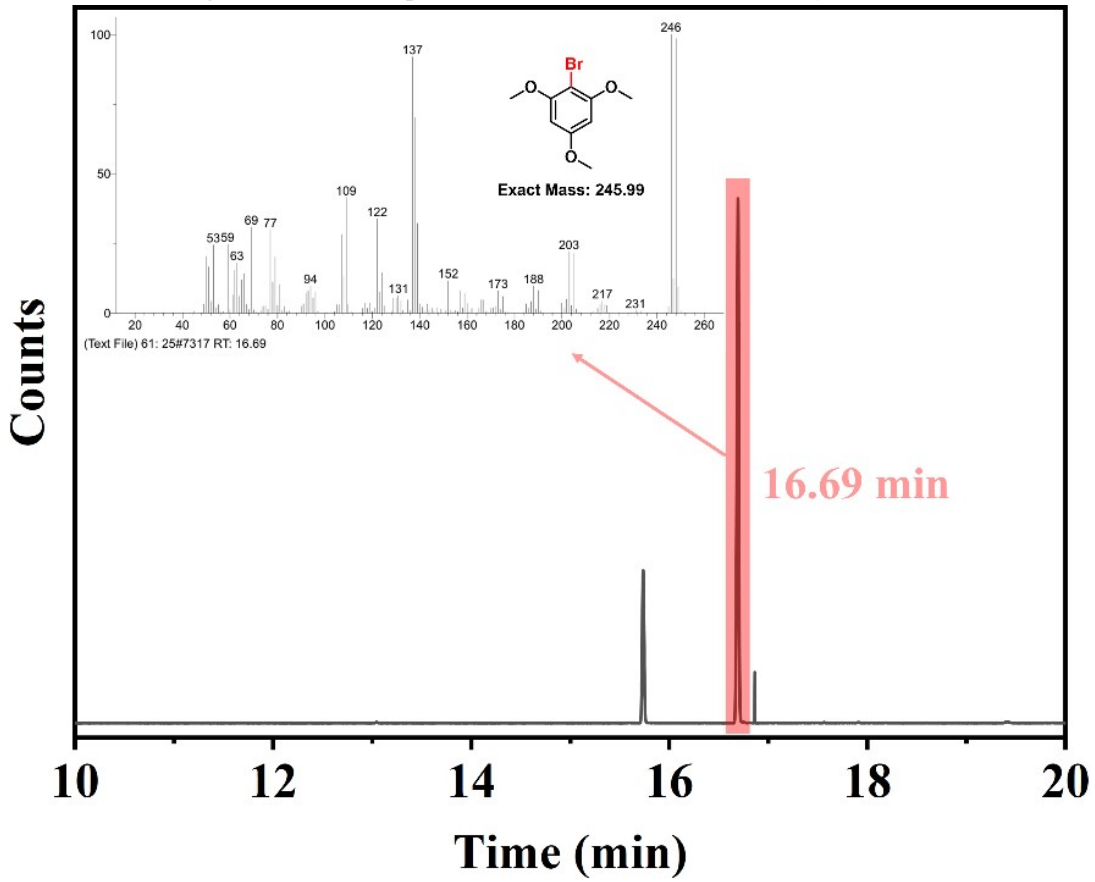


Fig. S12. GC-MS spectrum of 2-bromo-1,3,5-trimethoxybenzene

14. Detection of C-centered radical

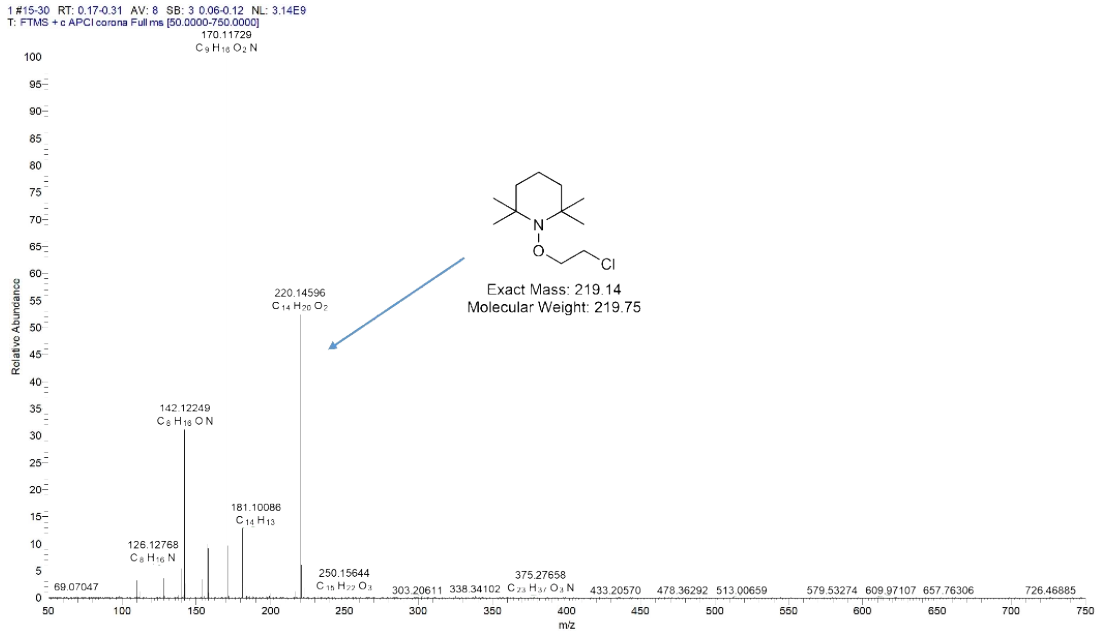


Fig. S13. HRMS spectrum of the C-centered radical

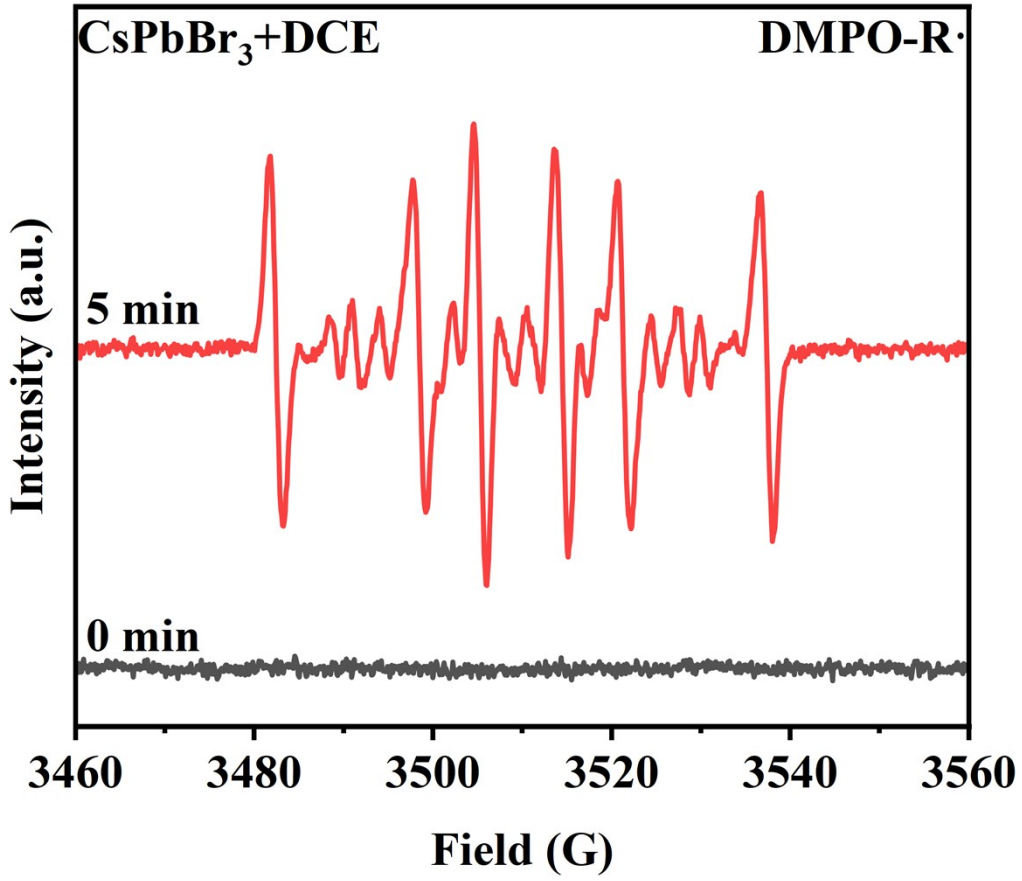


Fig. S14. EPR spectrum of the C-centered radical

15. NMR data of final products

3aa: colorless oil (33 mg, 69%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.20 (q, *J* = 6.5 Hz, 5H), 7.13 (d, *J* = 6.7 Hz, 2H), 6.07 (t, *J* = 7.3 Hz, 1H), 3.52 (t, *J* = 6.9 Hz, 2H), 2.54 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.35, 141.06, 138.56, 128.68, 127.30, 127.11, 126.24, 123.74, 43.34, 31.86.

3ba: yellow oil (28 mg, 54%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.16 – 7.11 (m, 2H), 7.08 (dd, *J* = 7.8, 6.3 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 1H), 6.88 (t, *J* = 8.7 Hz, 1H), 6.01 (dt, *J* = 27.0, 7.3 Hz, 1H), 3.51 (td, *J* = 6.8, 4.3 Hz, 2H), 2.51 (q, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.43, 131.37, 129.66, 128.93, 128.86, 128.45, 128.24, 127.47, 127.43, 127.27, 125.24, 124.68, 115.43, 115.26, 115.08, 114.91, 44.39, 44.28, 32.88, 32.86.

3ca: colorless oil (30 mg, 55%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 3H), 7.23 – 7.11 (m, 4H), 7.07 (dd, *J* = 15.9, 8.4 Hz, 3H), 6.03 (q, *J* = 7.3 Hz, 1H), 3.50 (td, *J* = 6.8, 3.5 Hz, 2H), 2.50 (qd, *J* = 6.9, 2.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.24, 133.17, 131.17, 129.68, 128.64, 128.59, 128.50, 128.32, 128.28, 127.55, 127.51, 127.29, 125.44, 125.34, 44.31, 44.24, 32.86.

3da: colorless oil (32 mg, 50%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.19 (d, *J* = 3.5 Hz, 2H), 7.13 (d, *J* = 6.8 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 7.01 (dd, *J* = 14.7, 8.2 Hz, 2H), 6.08 – 5.98 (m, 1H), 3.50 (td, *J* = 6.7, 3.4 Hz, 2H), 2.50 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.53, 130.44, 130.20, 128.62, 127.87, 127.44, 127.22, 126.50, 126.46, 126.22, 124.36, 120.35, 120.31, 43.20, 43.17, 31.81, 31.79.

3ea: colorless oil (25 mg, 48%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.29 (d, *J* = 6.2 Hz, 2H), 7.27 (s, 2H), 7.20 – 7.14 (m, 3H), 6.29 (t, *J* = 7.3 Hz, 1H), 3.60 (t, *J* = 6.7 Hz, 2H), 2.53 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.90, 131.87, 129.54, 129.47, 129.16, 128.34, 128.25, 127.51, 126.95, 126.62, 124.22, 124.19, 115.96, 115.79, 43.95, 33.20.

3fa: colorless oil (28 mg, 50%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 1H), 7.35 – 7.29 (m, 3H), 7.28 (d, *J* = 7.3 Hz, 3H), 7.23 (d, *J* = 8.3 Hz, 4H), 6.30 (t, *J* = 7.2 Hz, 1H), 3.59 (t, *J* = 6.9 Hz, 2H), 2.45 (dp, *J* = 33.8, 7.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.36, 139.98, 138.19, 133.75, 131.55, 129.84, 128.95, 128.37, 127.48, 126.93, 126.36, 126.03, 43.90, 33.03.

3ga: colorless oil (26 mg, 45%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.28 (dd, *J* = 7.2, 1.9 Hz, 3H), 7.23 (dd, *J* = 9.5, 7.6 Hz, 6H), 6.30 (td, *J* = 7.2, 2.4 Hz, 1H), 3.60 (t, *J* = 6.7 Hz, 2H), 2.44 (ddt, *J* = 39.0, 15.0, 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.95, 140.24, 139.73, 133.06, 131.53, 129.08, 128.38, 127.56, 127.48, 126.42, 125.76, 123.99, 43.88, 33.04.

3ha: colorless oil (24 mg, 43%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 1H), 7.33 – 7.26 (m, 1H), 7.22 (dd, *J* = 8.8, 4.0 Hz, 2H), 7.16 – 7.13 (m, 2H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 9.0 Hz, 1H), 6.01 (dt, *J* = 16.5, 7.3 Hz, 1H), 3.78 (d, *J* = 25.7 Hz, 3H), 3.54 (dt, *J* = 9.0, 6.9 Hz, 2H), 2.56 (dq, *J* = 28.7, 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.05, 143.86, 142.58, 139.89, 134.83, 131.90, 130.95, 129.73, 128.44, 128.36, 128.16, 127.43, 127.30, 127.24, 124.60, 123.01, 113.74, 113.55, 55.31, 55.28, 44.54, 44.47, 33.03, 32.94.

3ia: colorless oil (22 mg, 40%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.16 (m, 3H), 7.12 – 7.09 (m, 1H), 6.80 – 6.65 (m, 3H), 6.04 (td, *J* = 7.3, 4.6 Hz, 1H), 3.71 (d, *J* = 18.5 Hz, 3H), 3.53 – 3.47 (m, 2H), 2.51 (p, *J* = 7.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.29, 144.28, 143.67, 141.84, 141.03, 139.51, 129.72, 129.42, 129.13, 128.38, 128.21, 127.37, 127.33, 127.21, 125.04, 124.81, 122.20, 119.97, 115.30, 113.37, 112.75, 112.47, 55.26, 55.23, 44.45, 44.37, 32.94, 32.92.

3ja: colorless oil (21 mg, 44%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 4.6 Hz, 2H), 7.20 – 7.15 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.08 (q, *J* = 6.5 Hz, 2H), 6.07 (t, *J* = 7.4 Hz, 1H), 3.56 (td, *J* = 6.9, 3.6 Hz, 2H), 2.58 (dq, *J* = 14.3, 7.1 Hz, 2H), 2.35 (d, *J* = 30.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.38, 144.27, 142.39, 139.81, 139.35, 137.14, 136.96, 136.64, 129.75, 129.66, 129.07, 128.90, 128.34, 128.16, 127.37, 127.28, 127.22, 127.20, 124.61, 123.91, 44.47, 32.99, 32.94, 29.75.

3ka: colorless oil (20 mg, 39%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 2.1 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 5H), 7.13 (s, 1H), 7.04 – 7.01 (m, 1H), 6.17 (t, *J* = 7.1 Hz, 1H), 3.46 (t, *J* = 6.8 Hz, 2H), 2.33 (dt, *J* = 13.8, 6.9 Hz, 2H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.57, 140.63, 138.79, 136.43, 130.32, 129.94, 128.36, 127.56,

127.29, 126.32, 125.87, 124.62, 44.24, 32.90, 19.64.

3la: colorless oil (20 mg, 37%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 4H), 6.06 (t, *J* = 7.3 Hz, 1H), 3.58 (t, *J* = 6.9 Hz, 2H), 2.60 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.21, 139.60, 137.06, 136.86, 136.80, 129.64, 129.03, 128.86, 127.24, 123.70, 44.51, 32.99, 21.28, 21.12.

3ma: colorless oil (25 mg, 43%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.13 – 7.07 (m, 3H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.12 – 6.03 (m, 1H), 3.57 (t, *J* = 6.8 Hz, 2H), 2.57 (dq, *J* = 16.7, 7.0 Hz, 2H), 2.36 (d, *J* = 28.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.32, 140.87, 131.14, 129.57, 129.17, 128.63, 128.26, 127.16, 125.11, 124.50, 44.35, 32.91, 32.86, 21.27.

3na: colorless oil (32 mg, 45%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 1H), 7.38 (dd, *J* = 15.3, 8.4 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.08 (ddd, *J* = 28.4, 16.1, 8.5 Hz, 4H), 6.10 (td, *J* = 7.3, 2.6 Hz, 1H), 3.58 (t, *J* = 6.7 Hz, 2H), 2.56 (q, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.68, 130.37, 130.33, 130.04, 127.84, 127.73, 127.50, 127.38, 43.08, 28.68.

3oa: yellow oil (22 mg, 38%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.71 (m, 4H), 7.61 – 7.36 (m, 4H), 7.29 (d, *J* = 3.5 Hz, 4H), 6.25 (dt, *J* = 25.7, 7.3 Hz, 1H), 3.67 – 3.56 (m, 2H), 2.66 (q, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.38, 142.07, 137.13, 133.30, 132.60, 129.87, 128.59, 128.47, 128.25, 128.04, 128.03, 127.99, 127.77, 127.45, 126.27, 126.11, 125.28, 44.46, 32.98.

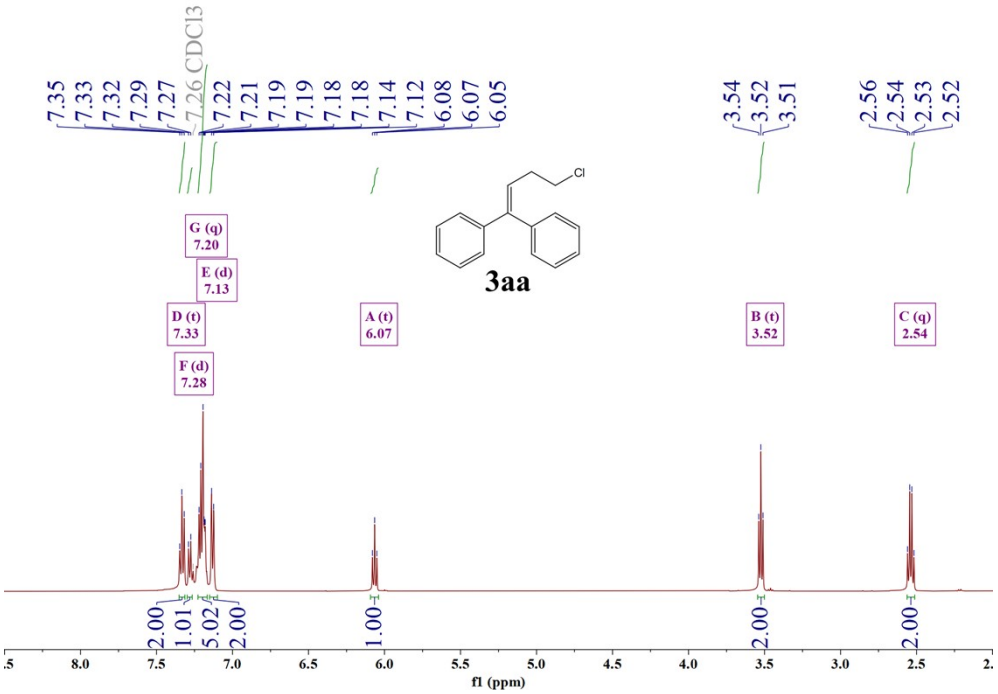
3pa: colorless oil (20 mg, 40%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.23 (dd, *J* = 9.5, 3.9 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.10 – 6.97 (m, 1H), 6.88 – 6.80 (m, 1H), 6.03 (dt, *J* = 51.4, 7.3 Hz, 1H), 3.52 (dt, *J* = 52.2, 6.9 Hz, 2H), 2.58 (dq, *J* = 154.9, 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.40, 128.43, 128.16, 128.02, 127.69, 127.67, 127.59, 127.51, 127.28, 126.87, 125.93, 125.63, 124.33, 123.31, 44.22, 44.08, 33.16, 32.59, 29.72.

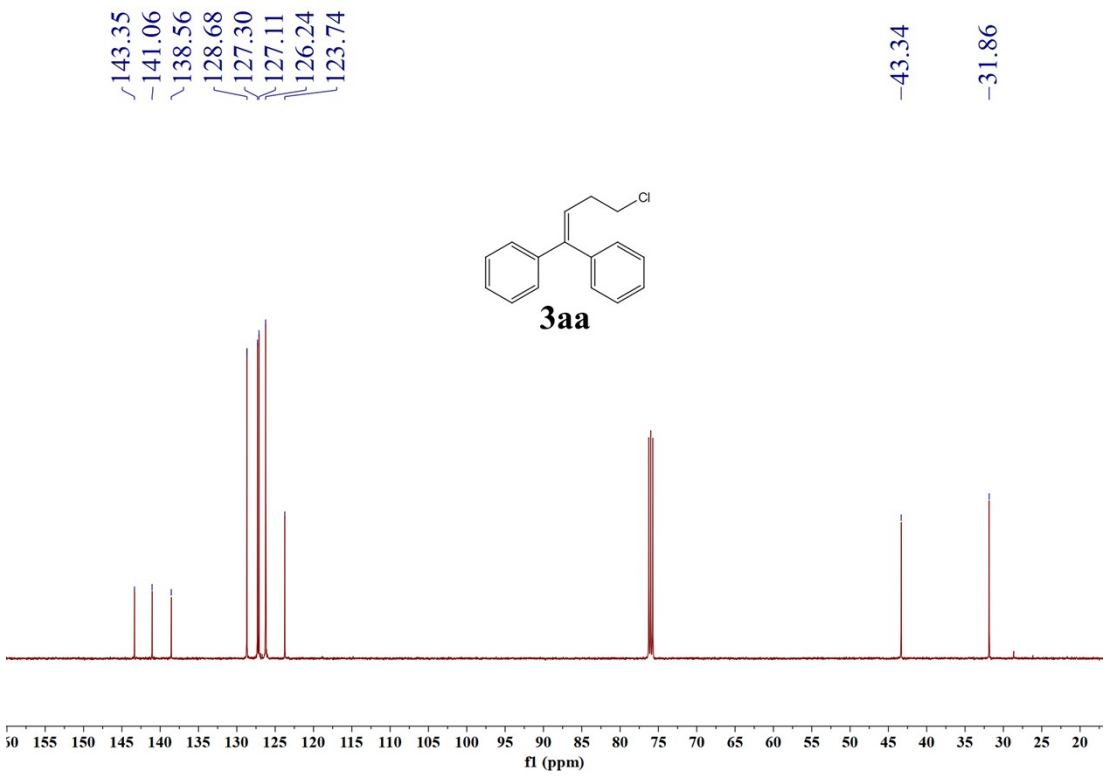
3qa: colorless oil (18 mg, 47%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.86 (s, 1H), 6.84 (s, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.10 – 6.03 (m, 1H), 3.81 (s, 3H), 3.61 (t, *J* = 7.0 Hz, 2H), 2.66 (q, *J* = 6.9 Hz, 2H). ^{13}C NMR

(126 MHz, $CDCl_3$) δ 159.09, 132.19, 128.52, 127.33, 123.58, 113.98, 55.32, 44.28, 36.25.

3ab: yellow oil (21 mg, 47%), purified by silica gel flash chromatography (EtOAc/PE = 1/20). ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 6.5 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 6H), 7.19 (s, 3H), 7.17 (s, 1H), 6.61 (d, *J* = 89.7 Hz, 1H), 4.25 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.83, 128.63, 127.99, 127.39, 127.33, 127.17, 127.06, 126.68, 126.59, 124.97, 114.83, 42.44.

16. Copies of NMR spectra of final products

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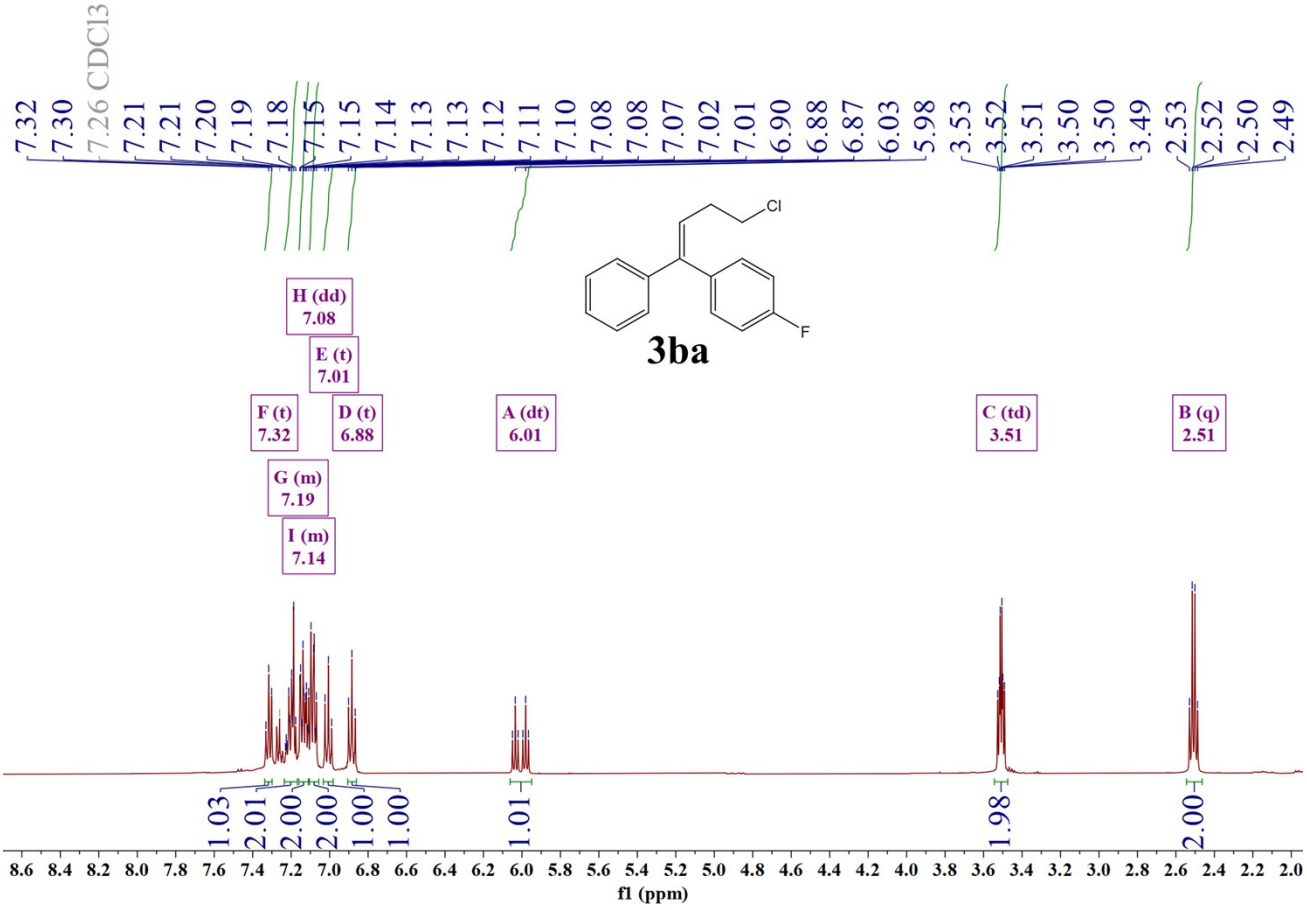
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7.08
7.08
7.07
7.02
7.01
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5.98
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3.52
3.51
3.50
3.50
3.49
2.53
2.52
2.50
2.49
Cl
F
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E (t) 7.01
F (t) 7.32
D (t) 6.88
A (dt) 6.01
C (td) 3.51
B (q) 2.51
G (m) 7.19
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1.01
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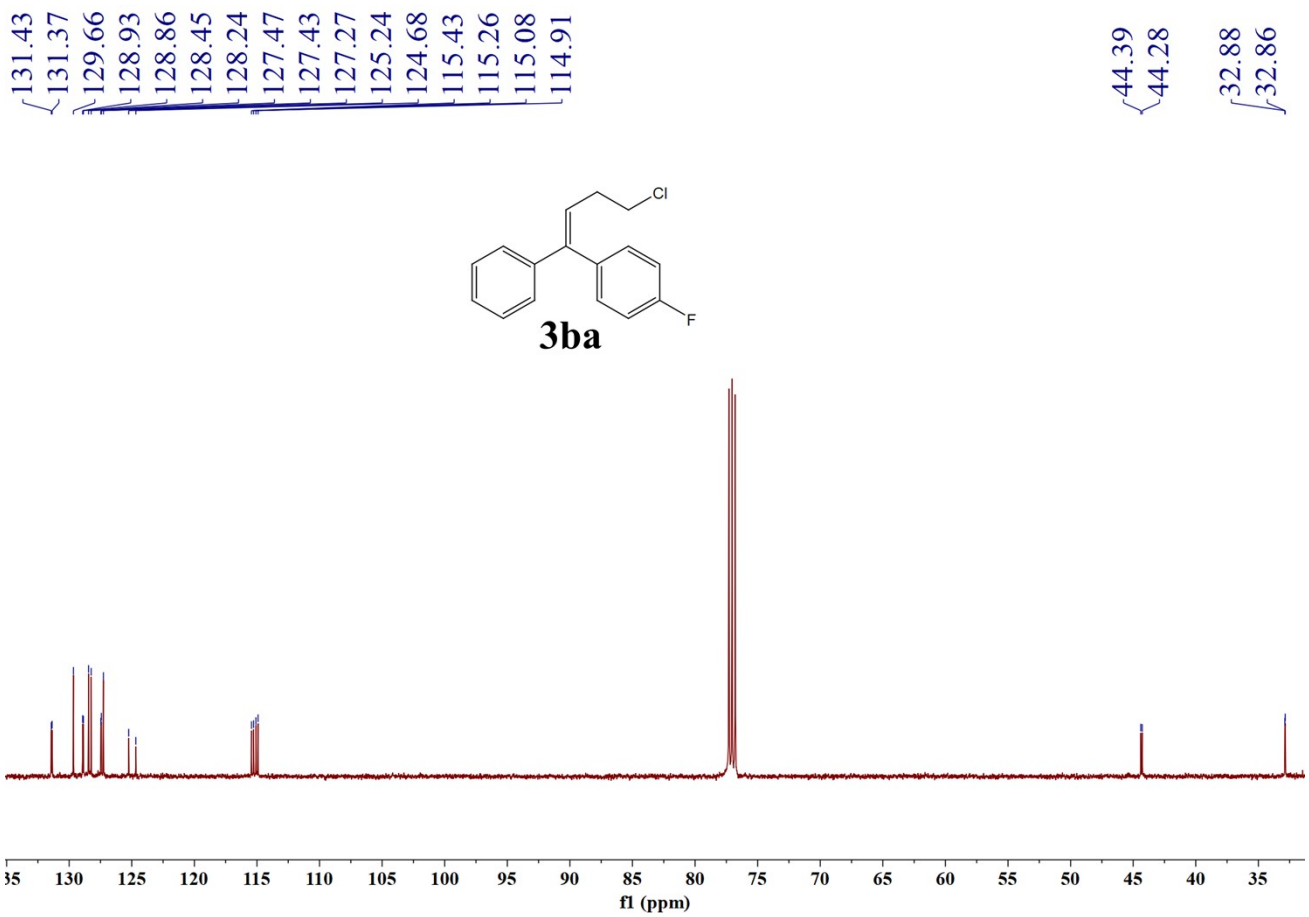
2.00
fl (ppm)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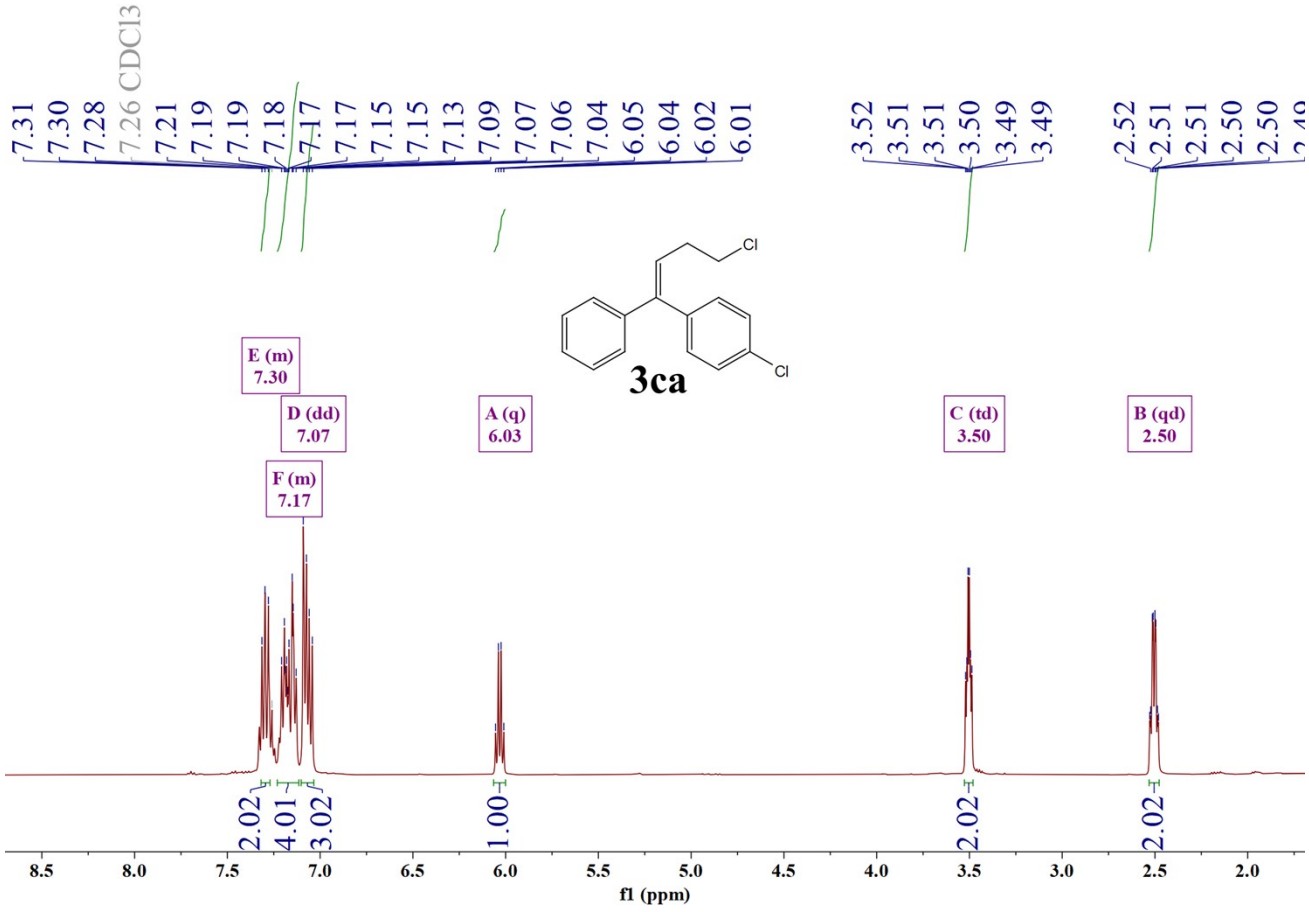
114.91
44.39
44.28
32.88
32.86
Cl
F
3ba
f1 (ppm)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7.04
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2.50
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Cl
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D (dd)
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F (m)
7.17
A (q)
6.03
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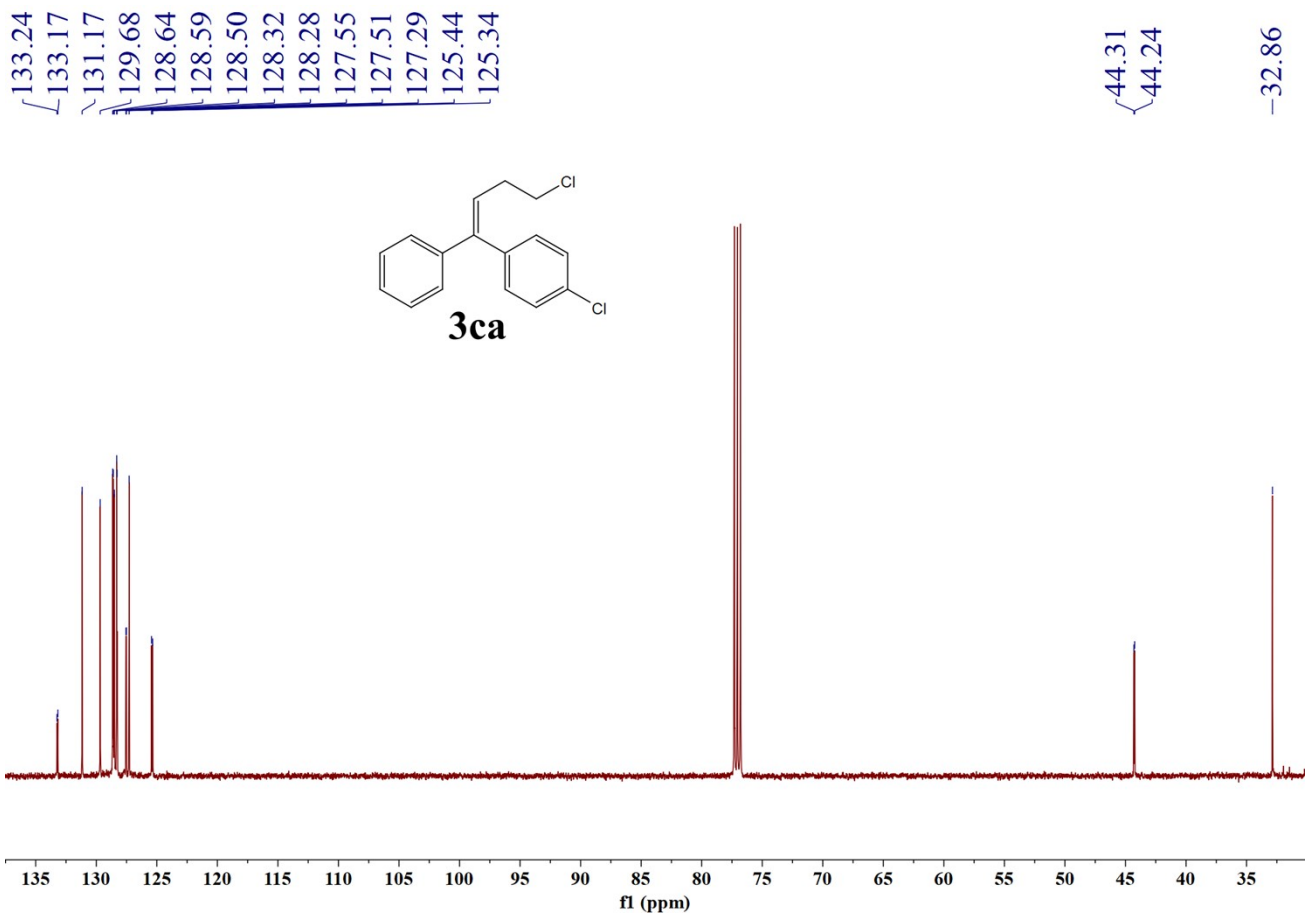
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127.29
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32.86
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Cl
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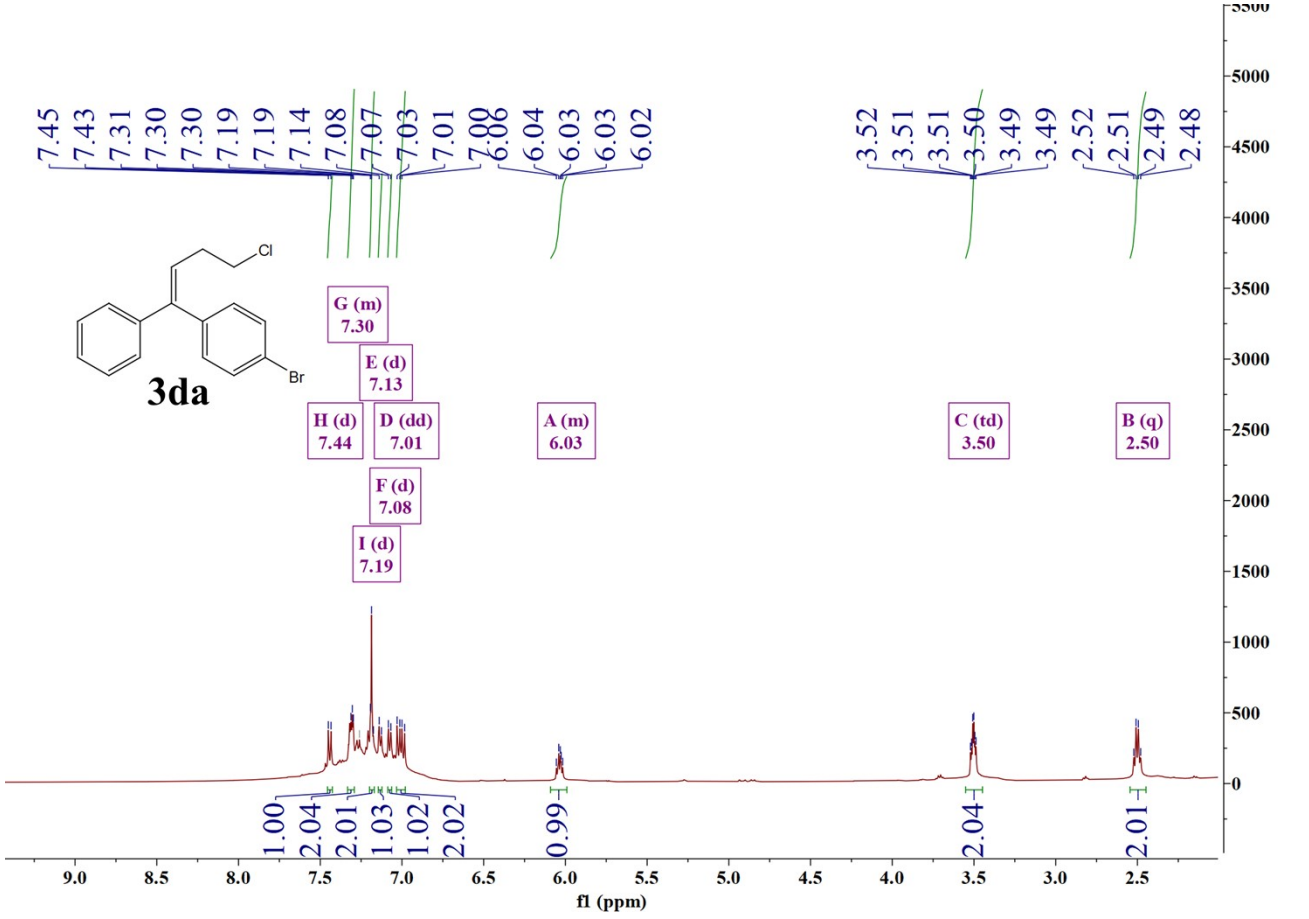
f1 (ppm)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6.03
6.02
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3.50
3.49
3.49
2.52
2.51
2.49
2.48
Cl
Br
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E (d)
7.13
H (d)
7.44
D (dd)
7.01
A (m)
6.03
C (td)
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B (q)
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F (d)
7.08
I (d)
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2.04
2.01
1.03
1.02
2.02
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2.04
2.01
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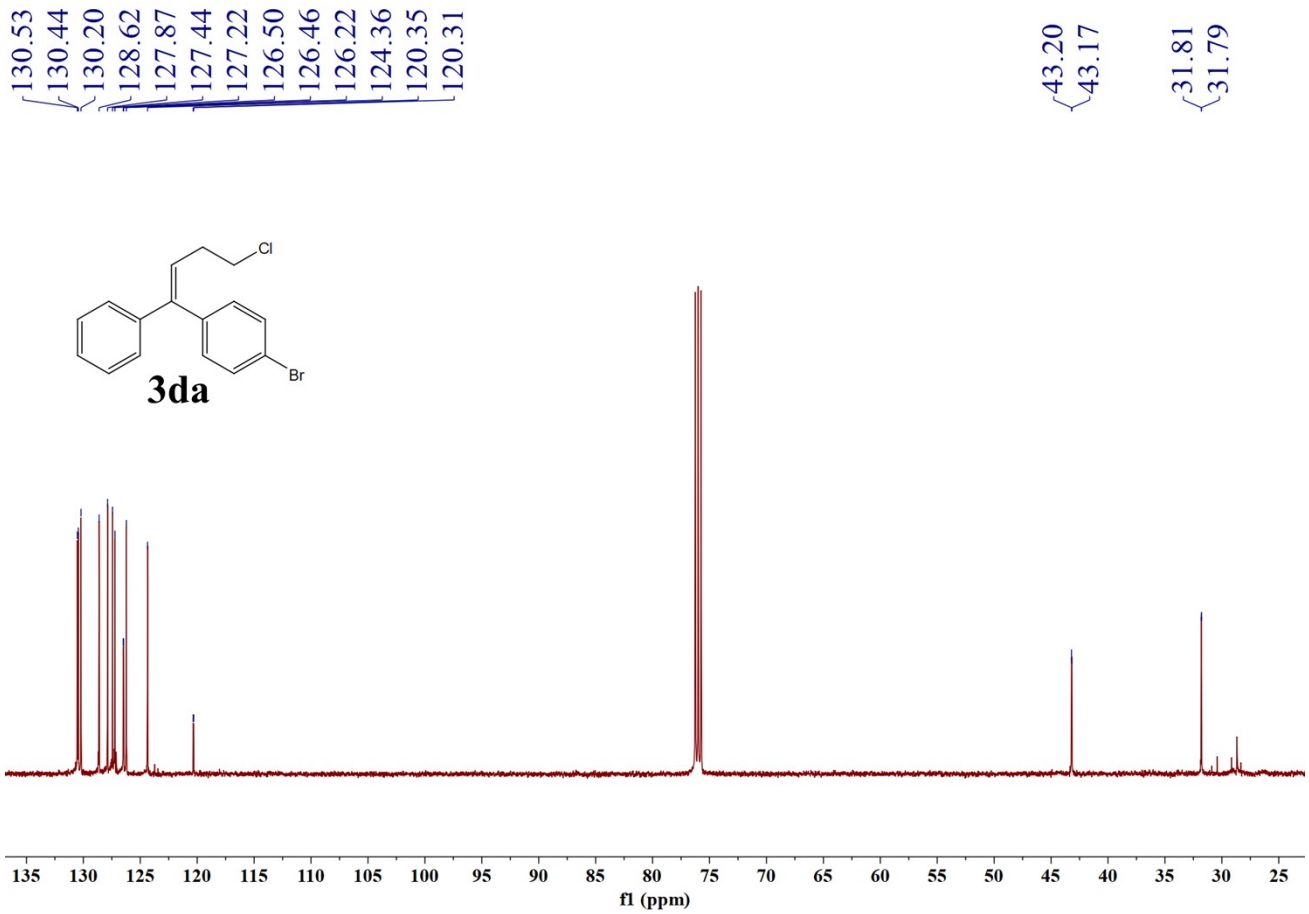
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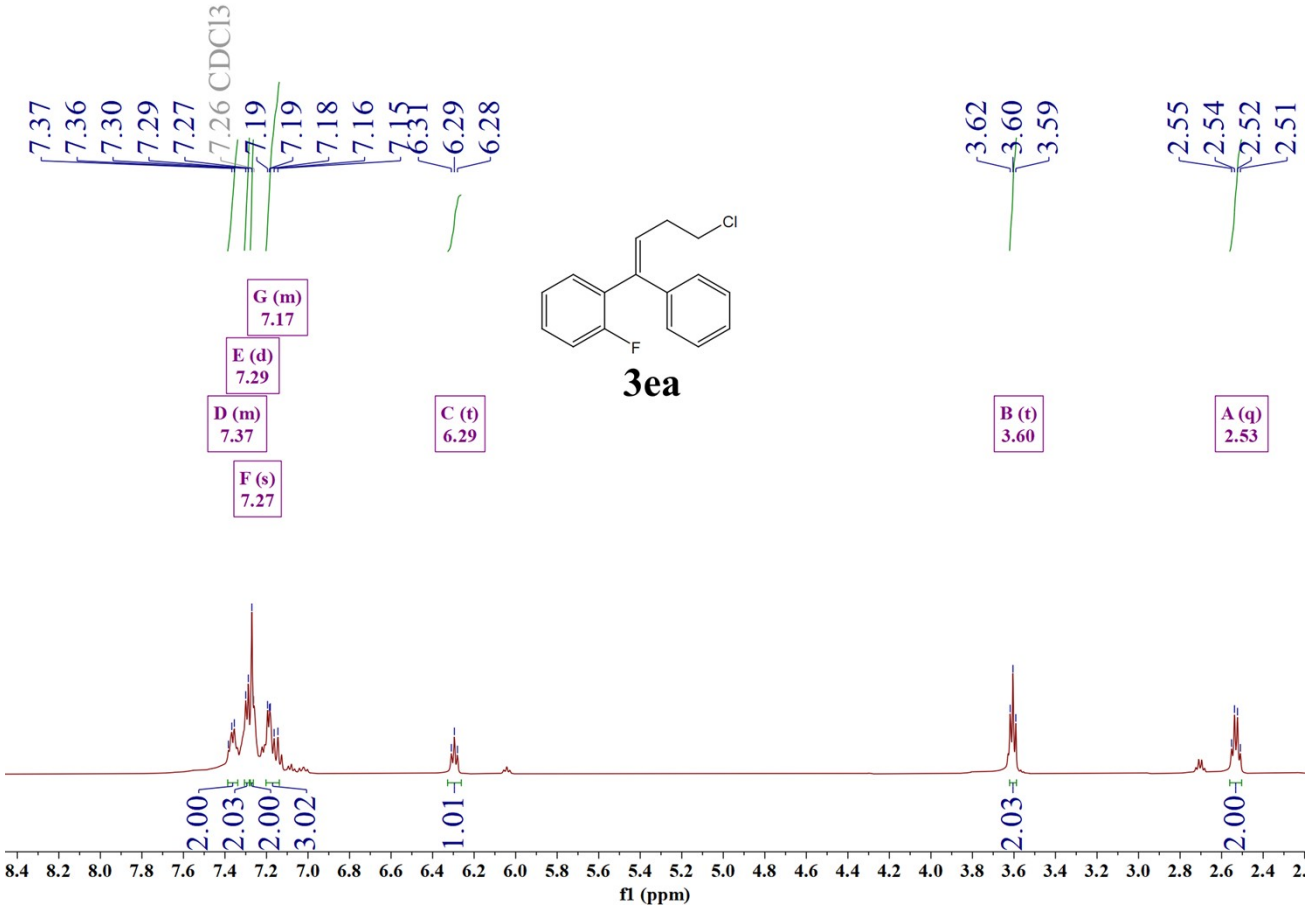
f1 (ppm)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2.55
2.54
2.52
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F
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G (m)
7.17
E (d)
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D (m)
7.37
F (s)
7.27
C (t)
6.29
B (t)
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A (q)
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2.03
2.00
3.02
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2.03
2.00
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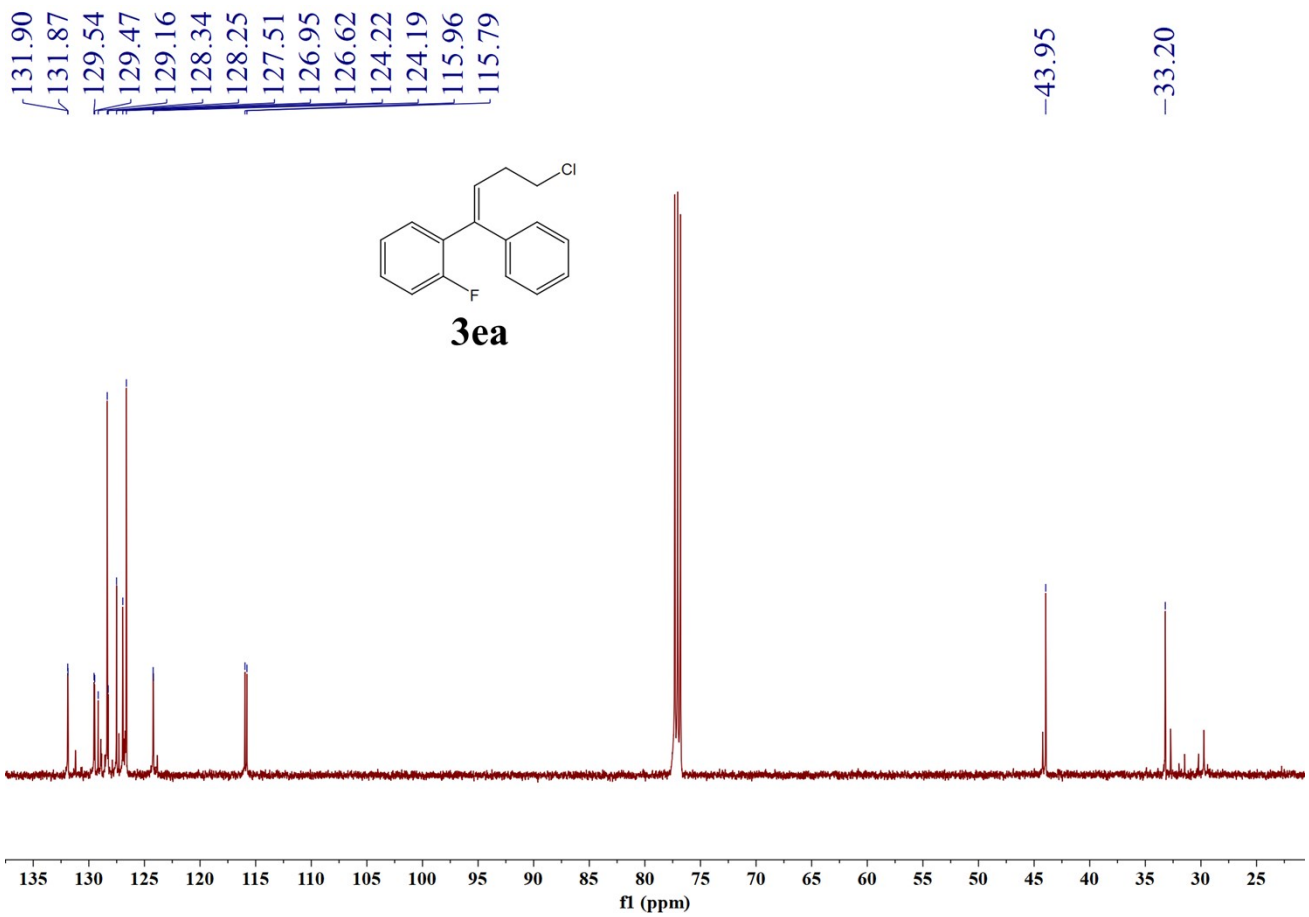
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Cl
F
3ea
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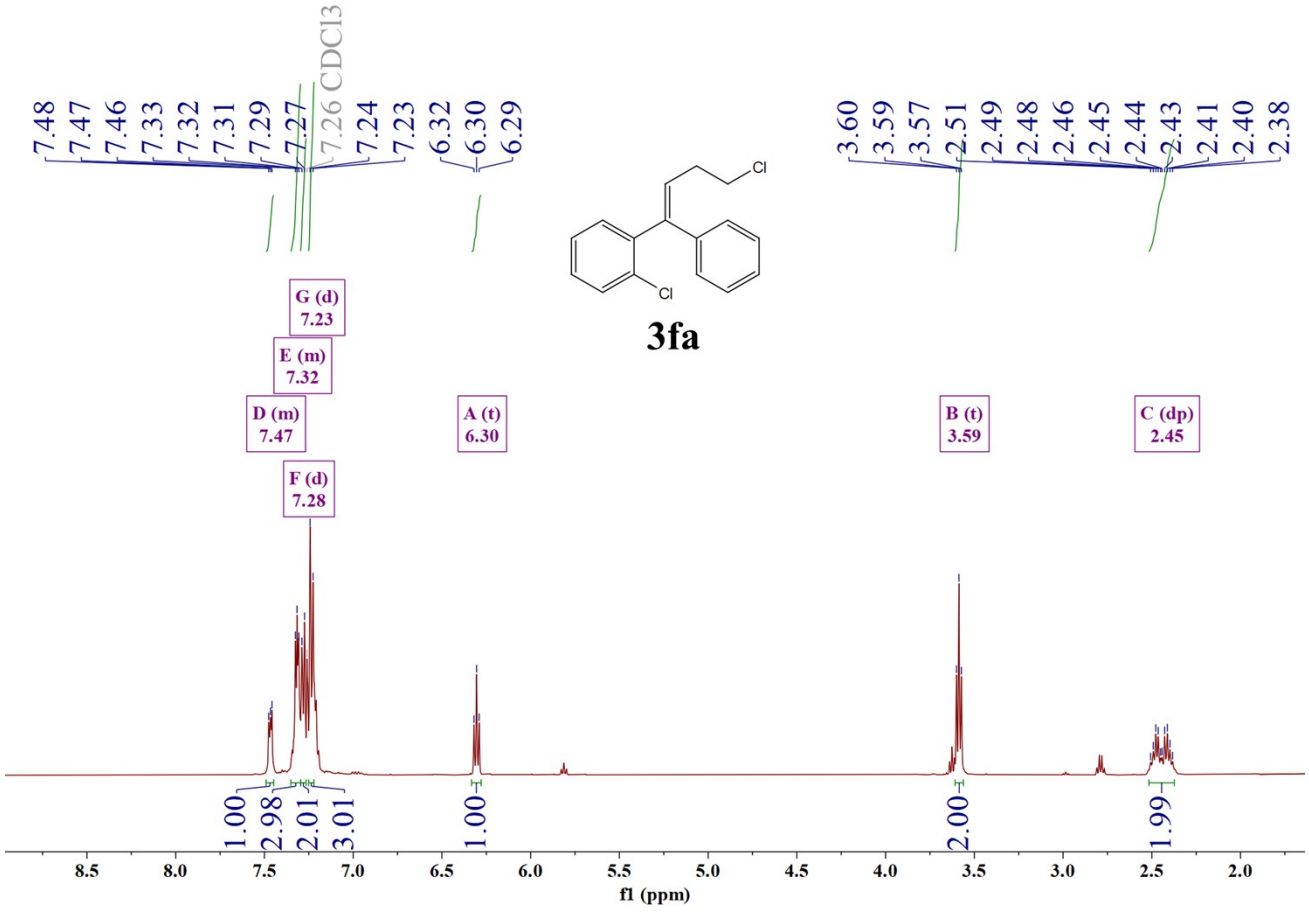
f1 (ppm)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B (t) 3.59
C (dp) 2.45
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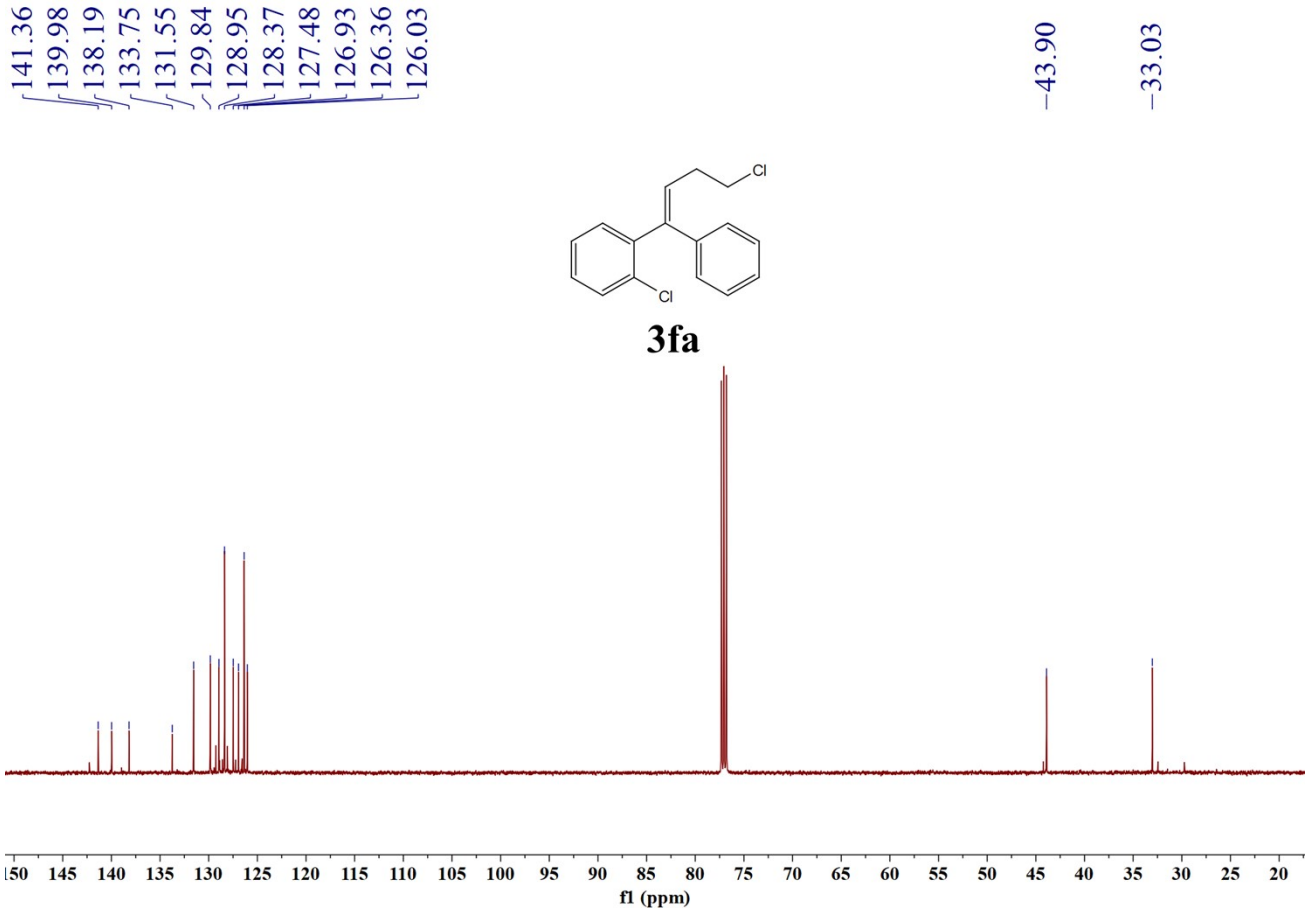
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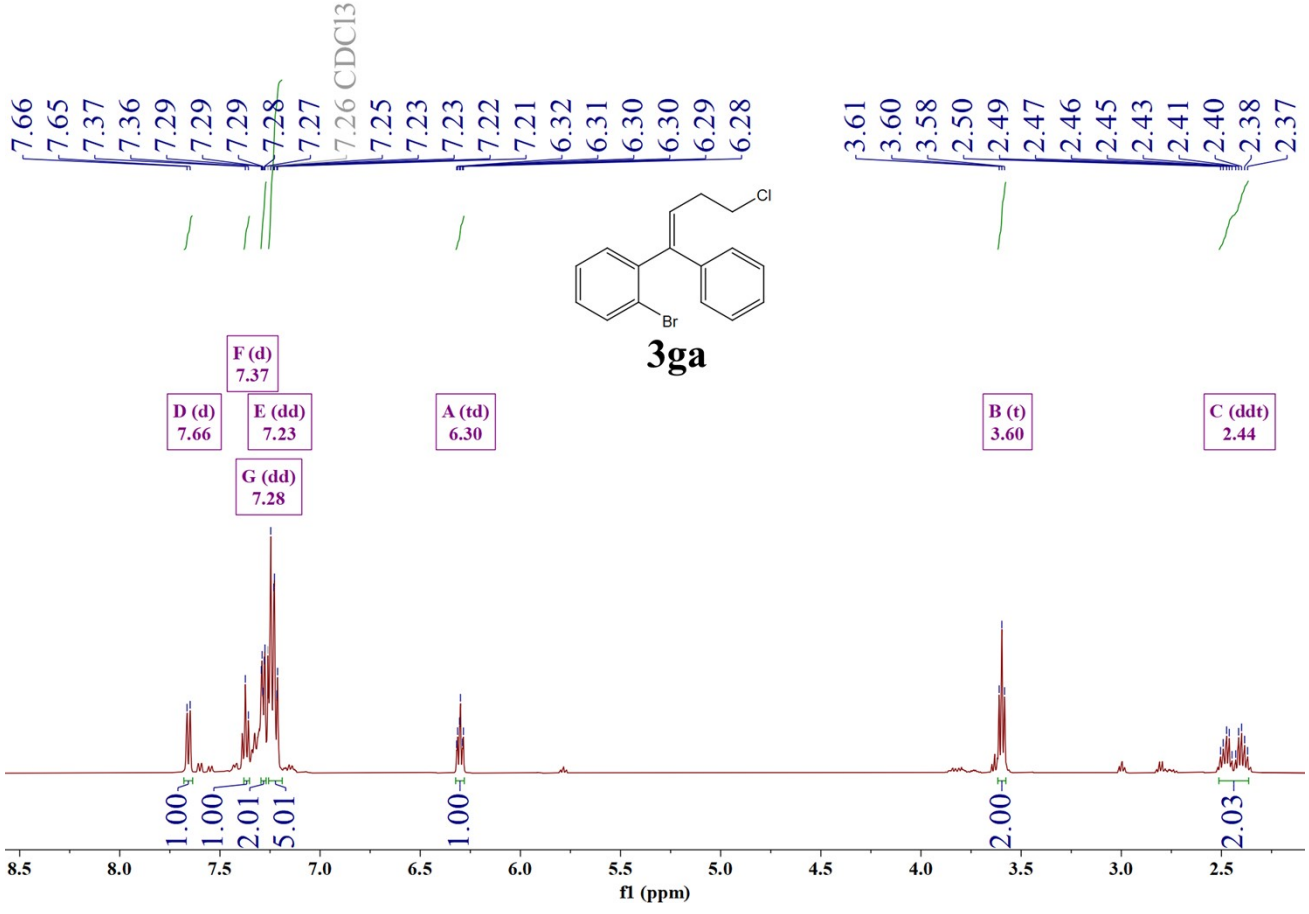
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2.43
2.41
2.40
2.38
2.37
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Br
3ga
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D (d) 7.66
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A (td) 6.30
B (t) 3.60
C (ddt) 2.44
G (dd) 7.28
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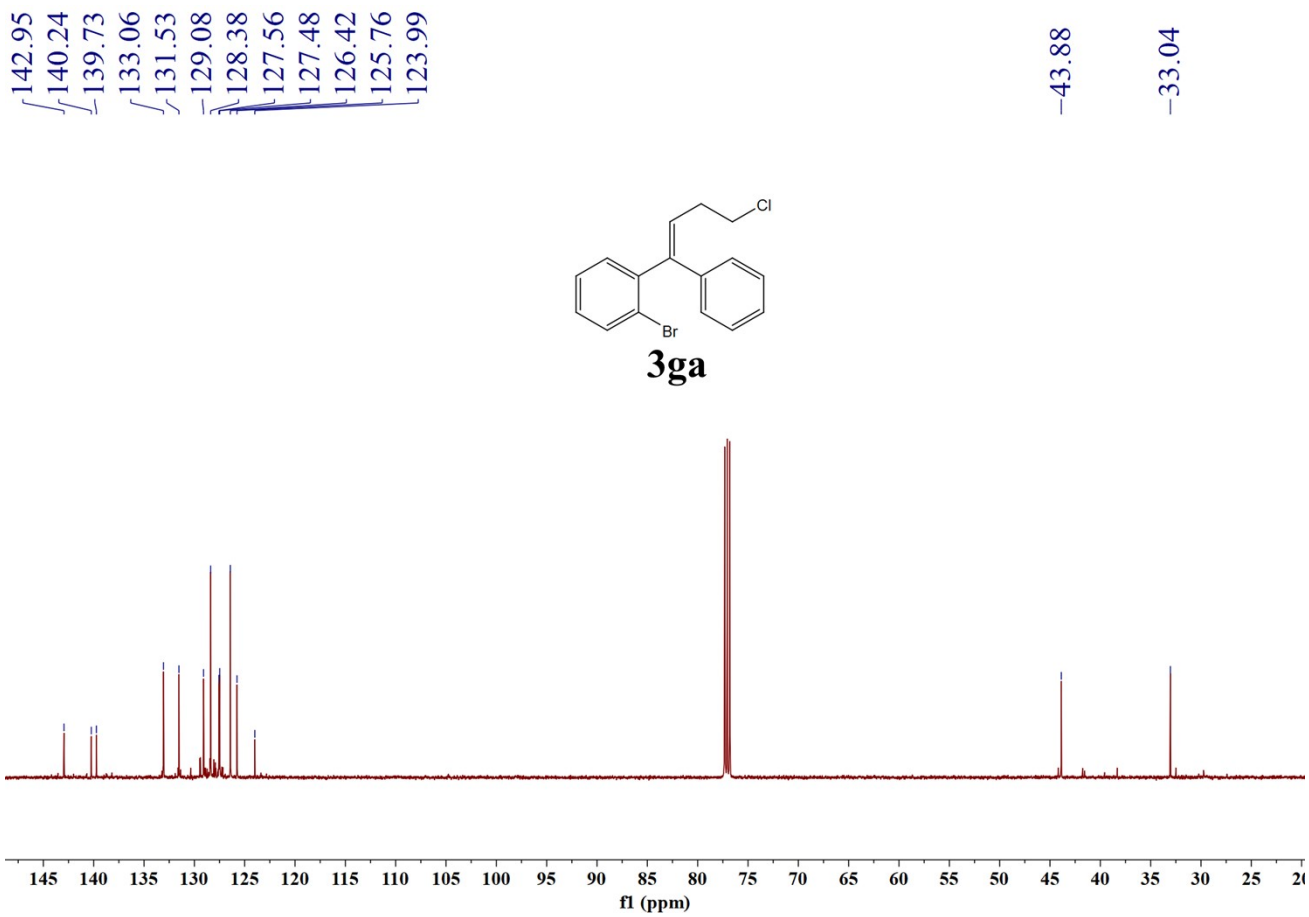
f1 (ppm)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Br
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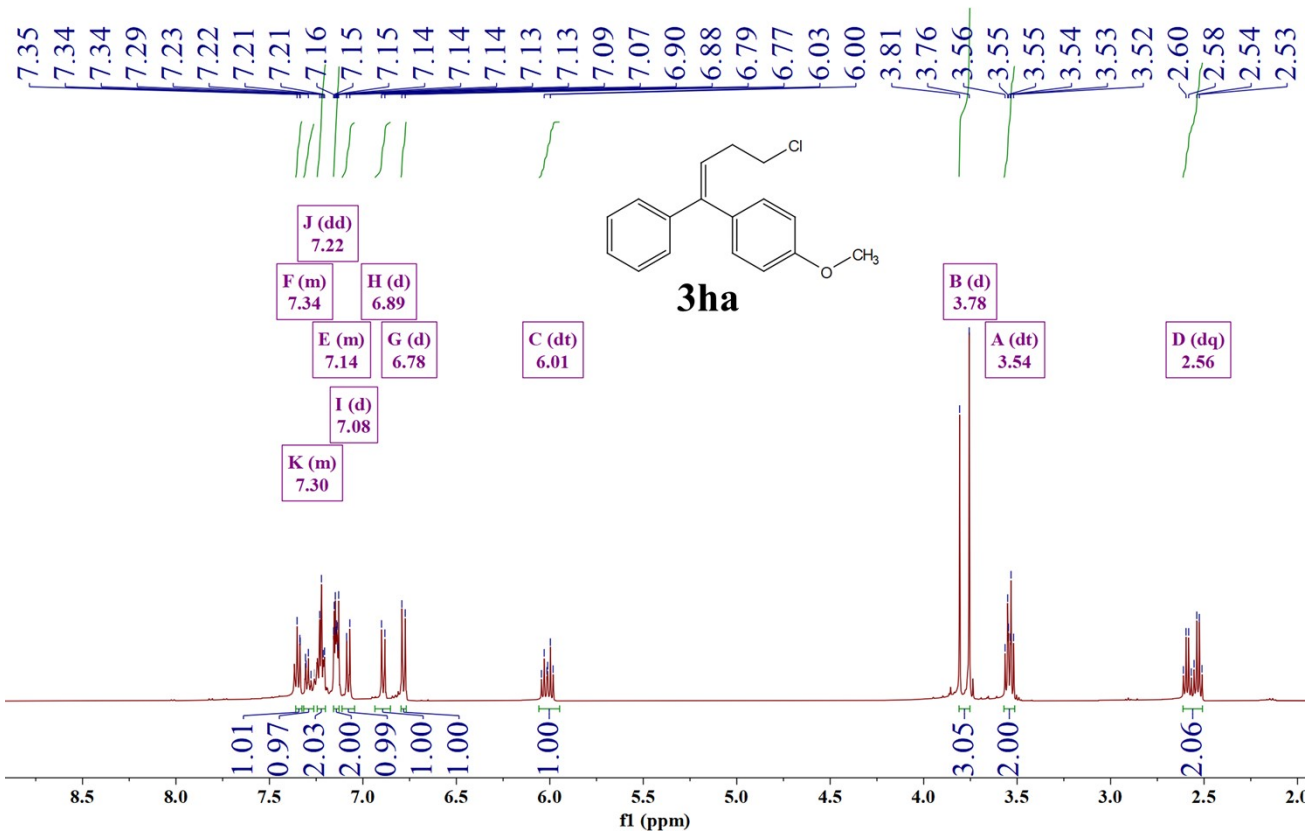
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6.00
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3.76
3.56
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3.54
3.53
3.52
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2.53
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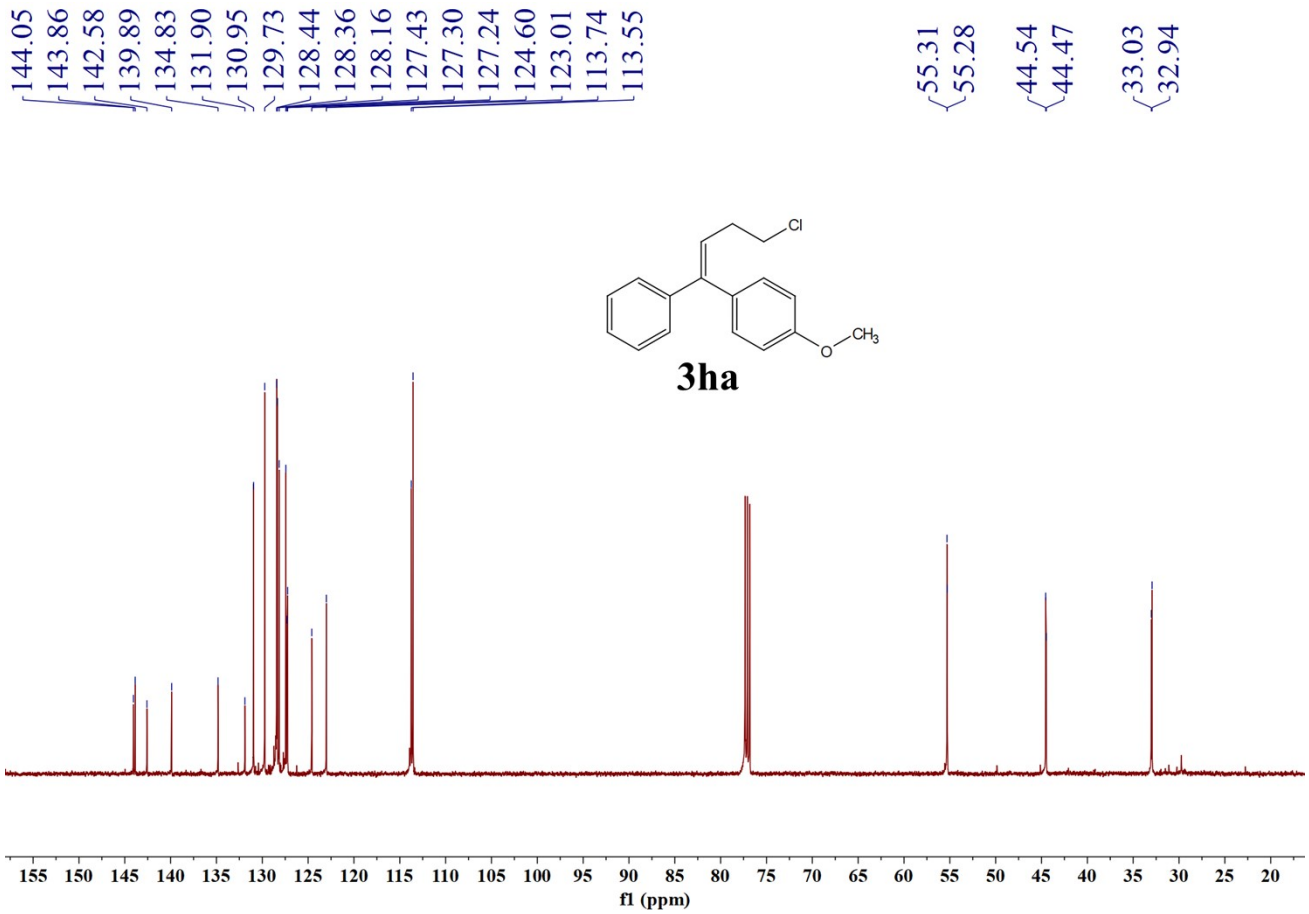
3.05
2.00
2.06
f1 (ppm)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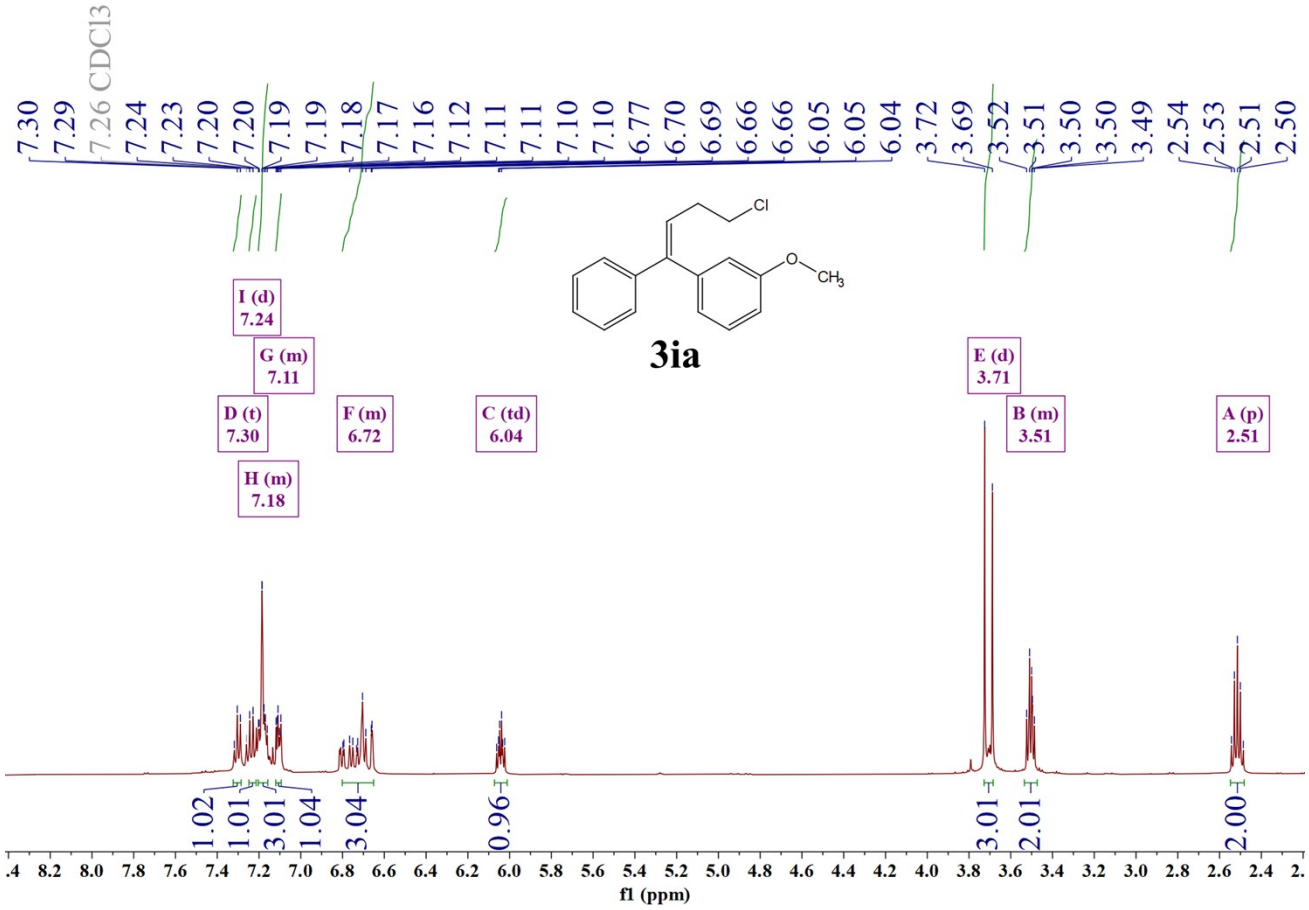
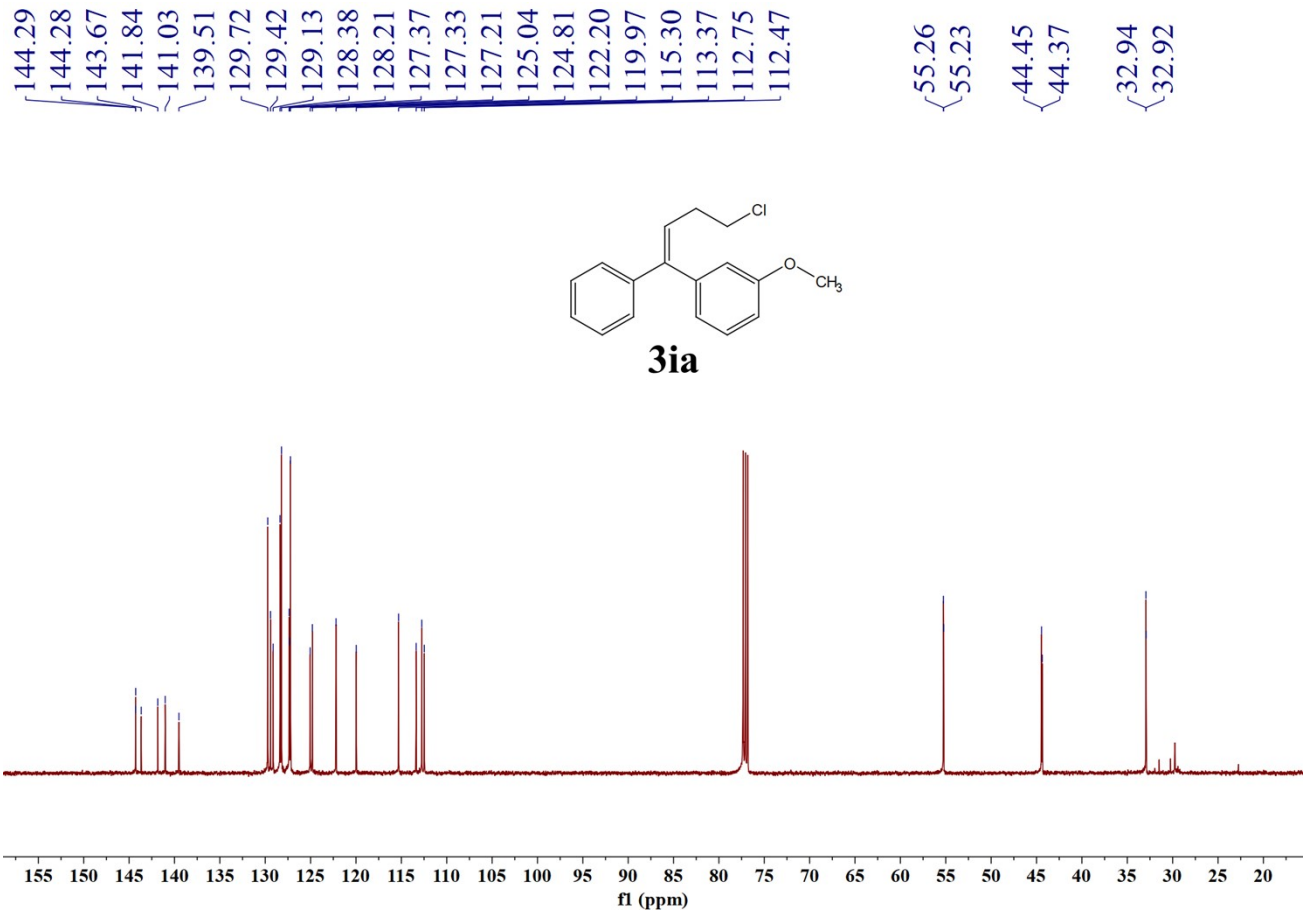
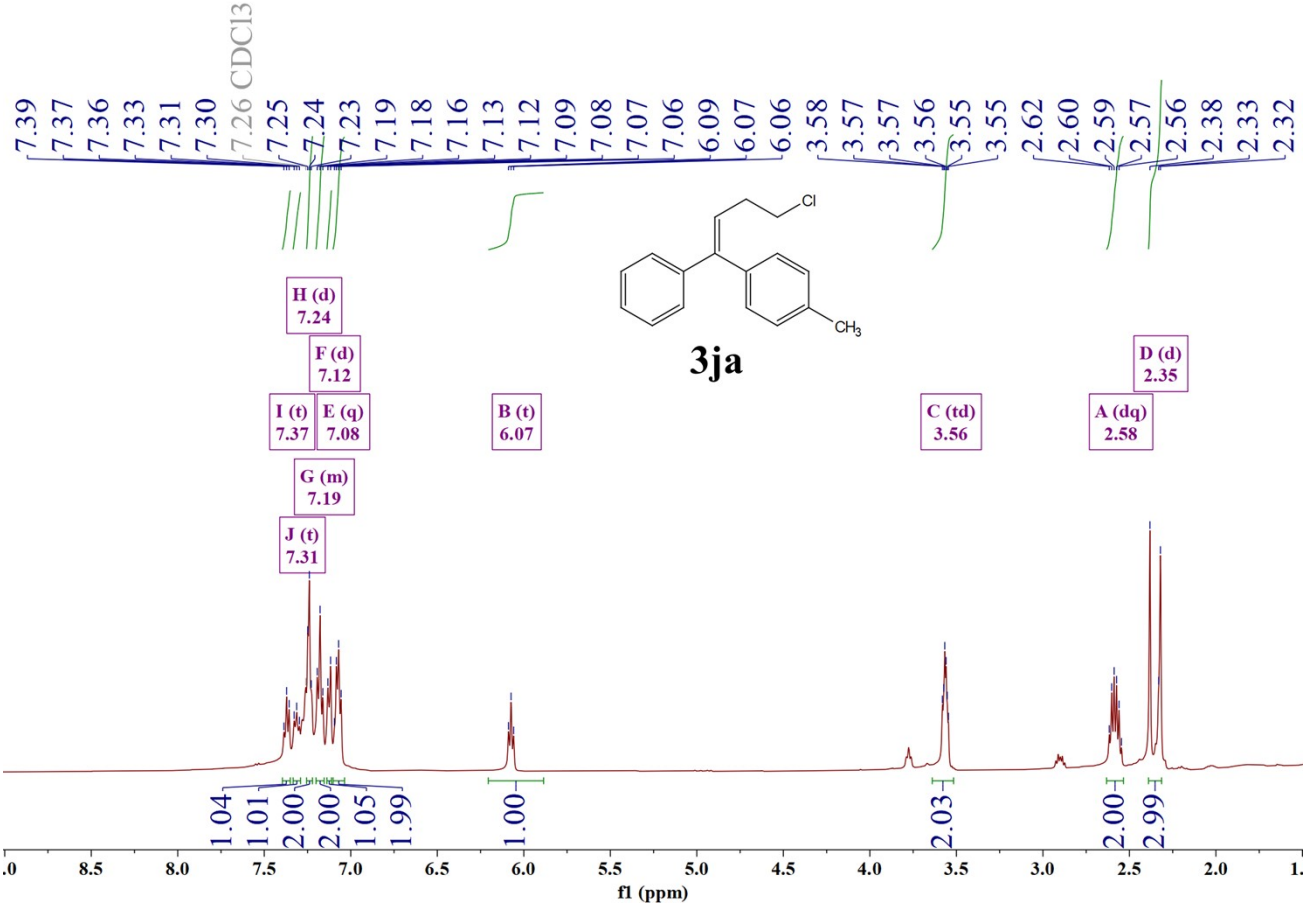
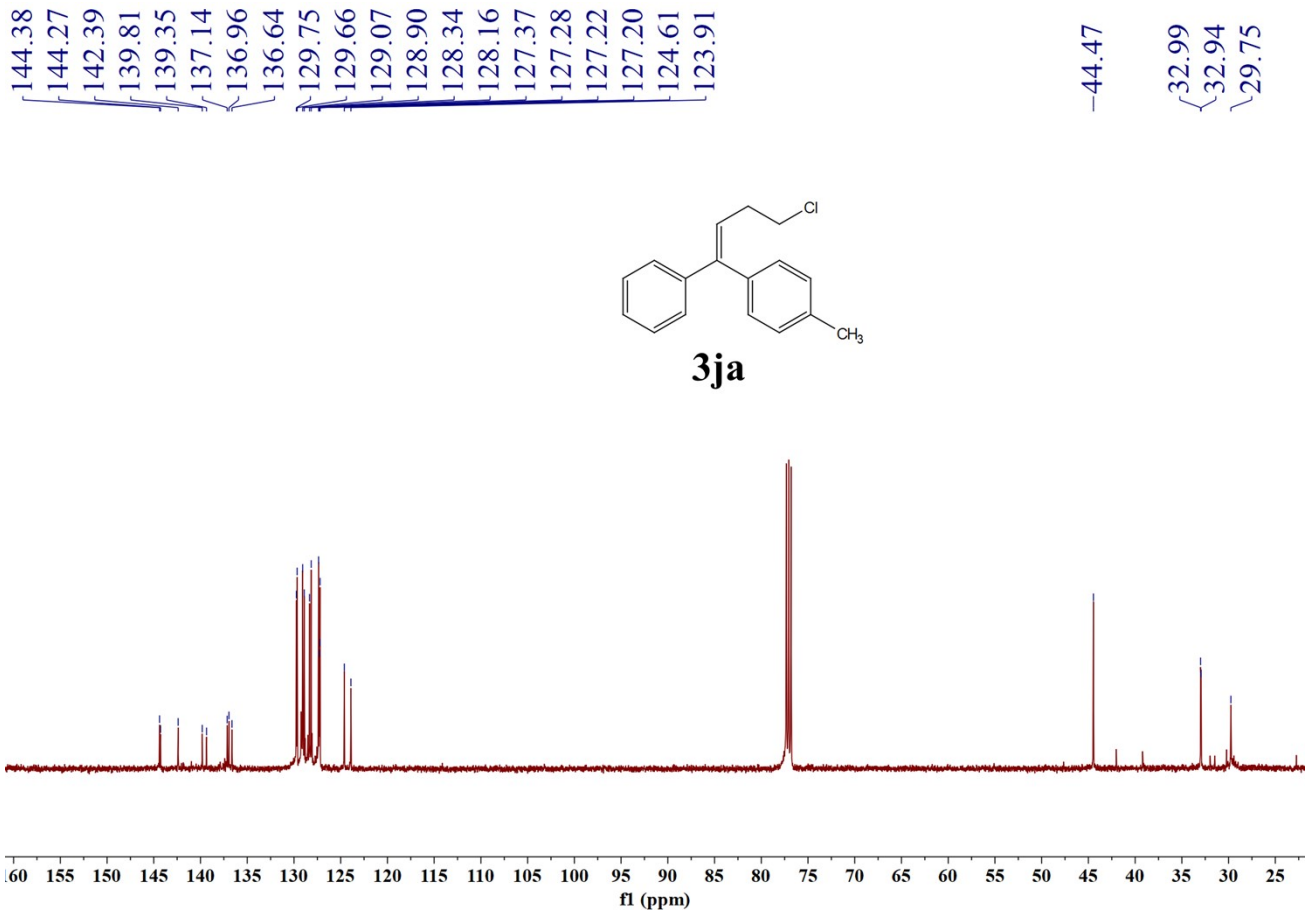
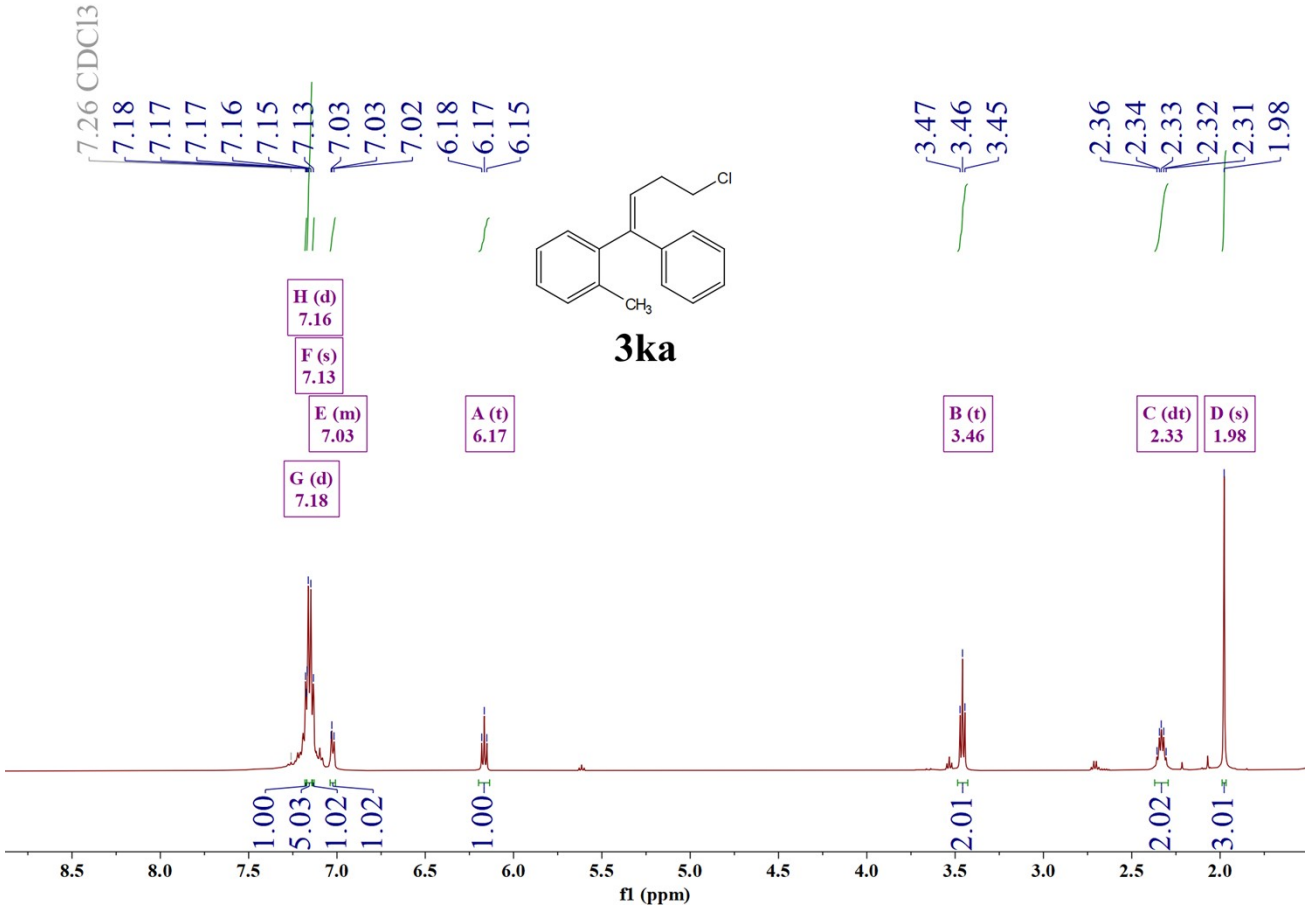
143.86
142.58
139.89
134.83
131.90
130.95
129.73
128.44
128.36
128.16
127.43
127.30
127.24
124.60
123.01
113.74
113.55
55.31
55.28
44.54
44.47
33.03
32.94
Cl
O
CH3
3ha
fl (ppm)

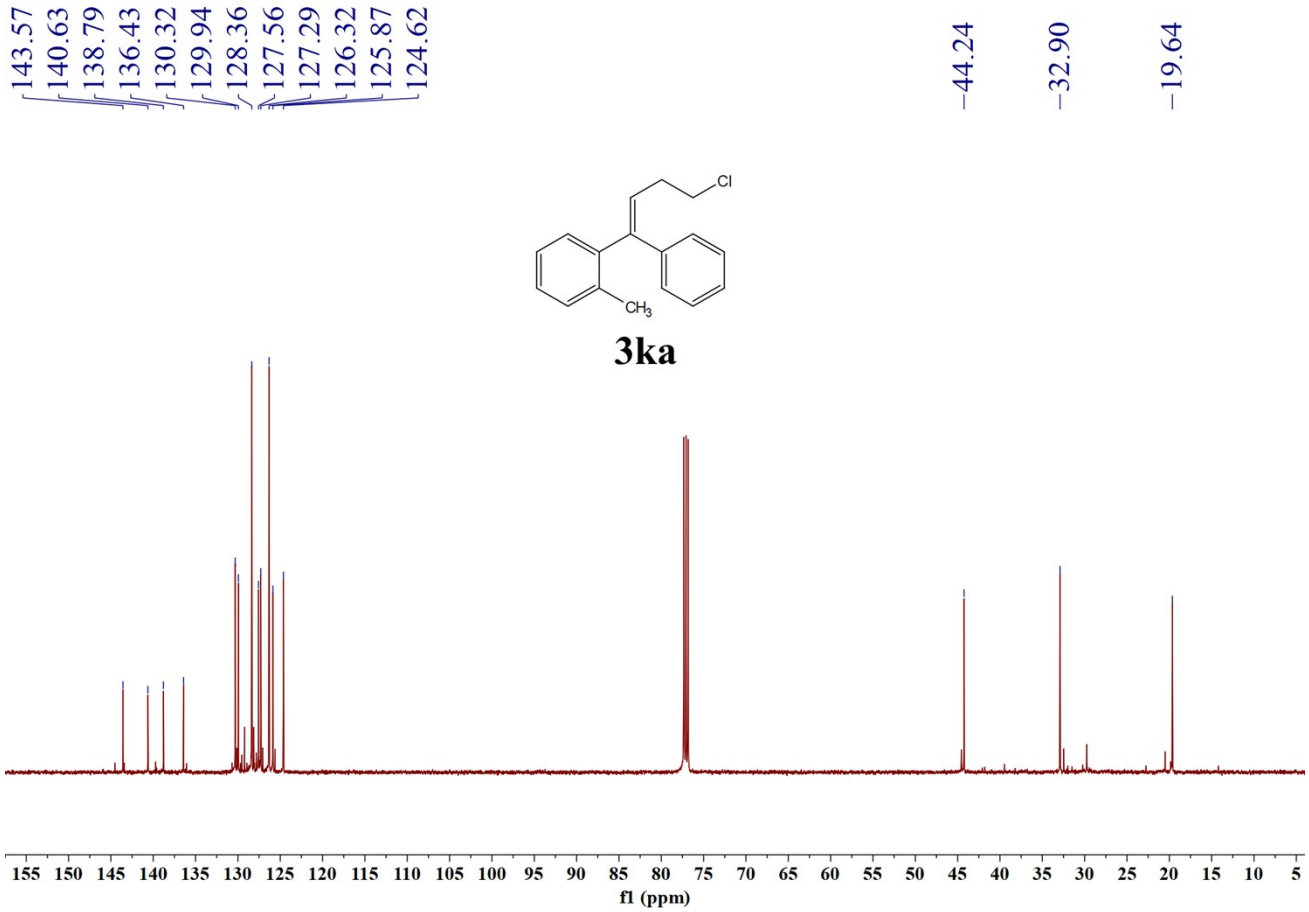

7.30
7.29
7.26 CDCl3
7.24
7.23
7.20
7.20
7.19
7.19
7.18
7.17
7.16
7.12
7.11
7.11
7.10
7.10
6.77
6.70
6.69
6.66
6.66
6.05
6.05
6.04
3.72
3.69
3.52
3.51
3.50
3.50
3.49
2.54
2.53
2.51
2.50
Cl
O
CH3
3ia
I (d) 7.24
G (m) 7.11
D (t) 7.30
F (m) 6.72
C (td) 6.04
H (m) 7.18
E (d) 3.71
B (m) 3.51
A (p) 2.51
1.02
1.01
3.01
1.04
3.04
0.96
3.01
2.01
2.00
fl (ppm)

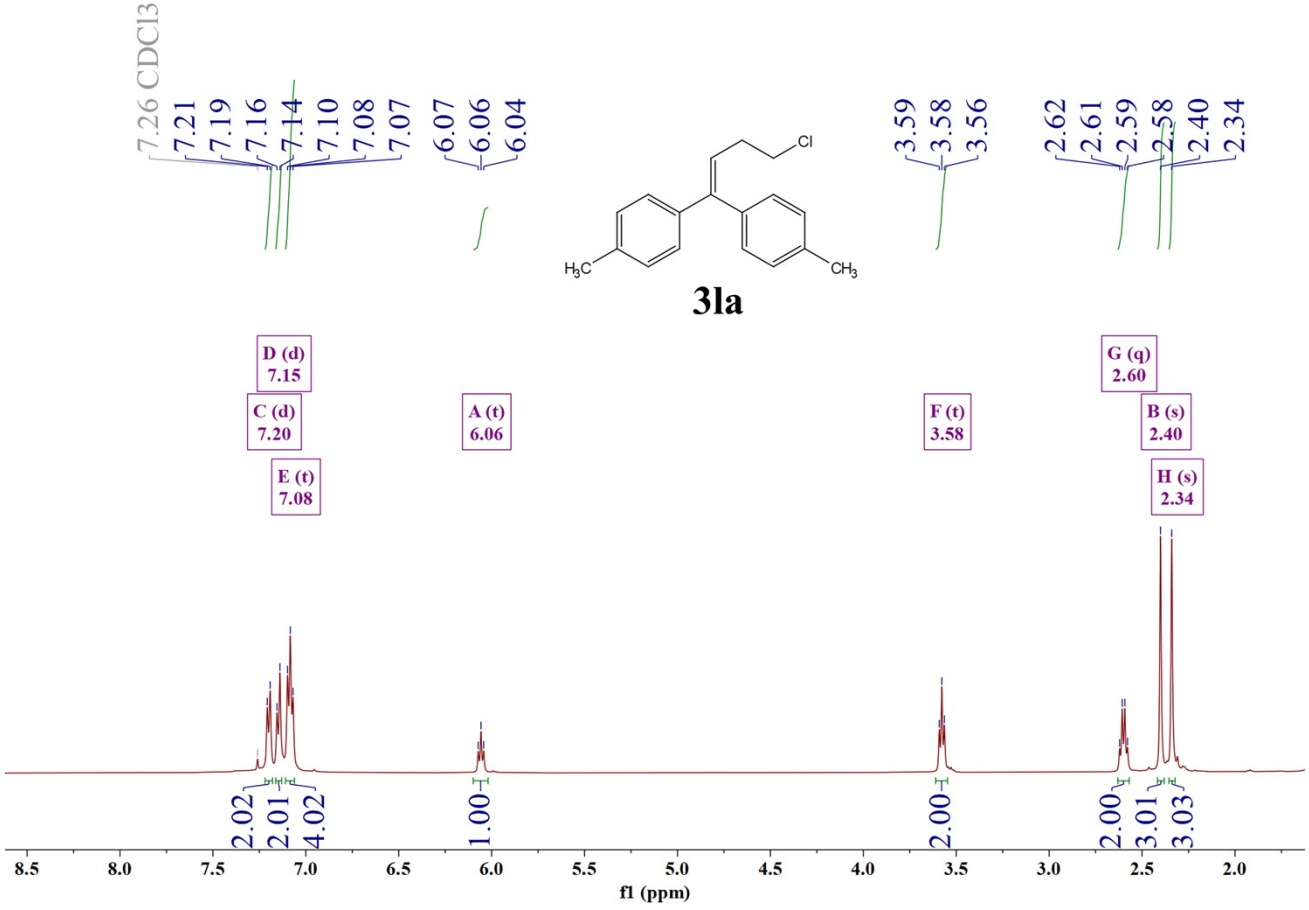

144.29
144.28
143.67
141.84
141.03
139.51
129.72
129.42
129.13
128.38
128.21
127.37
127.33
127.21
125.04
124.81
122.20
119.97
115.30
113.37
112.75
112.47
55.26
55.23
44.45
44.37
32.94
32.92
Cl
O
CH3
3ia
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

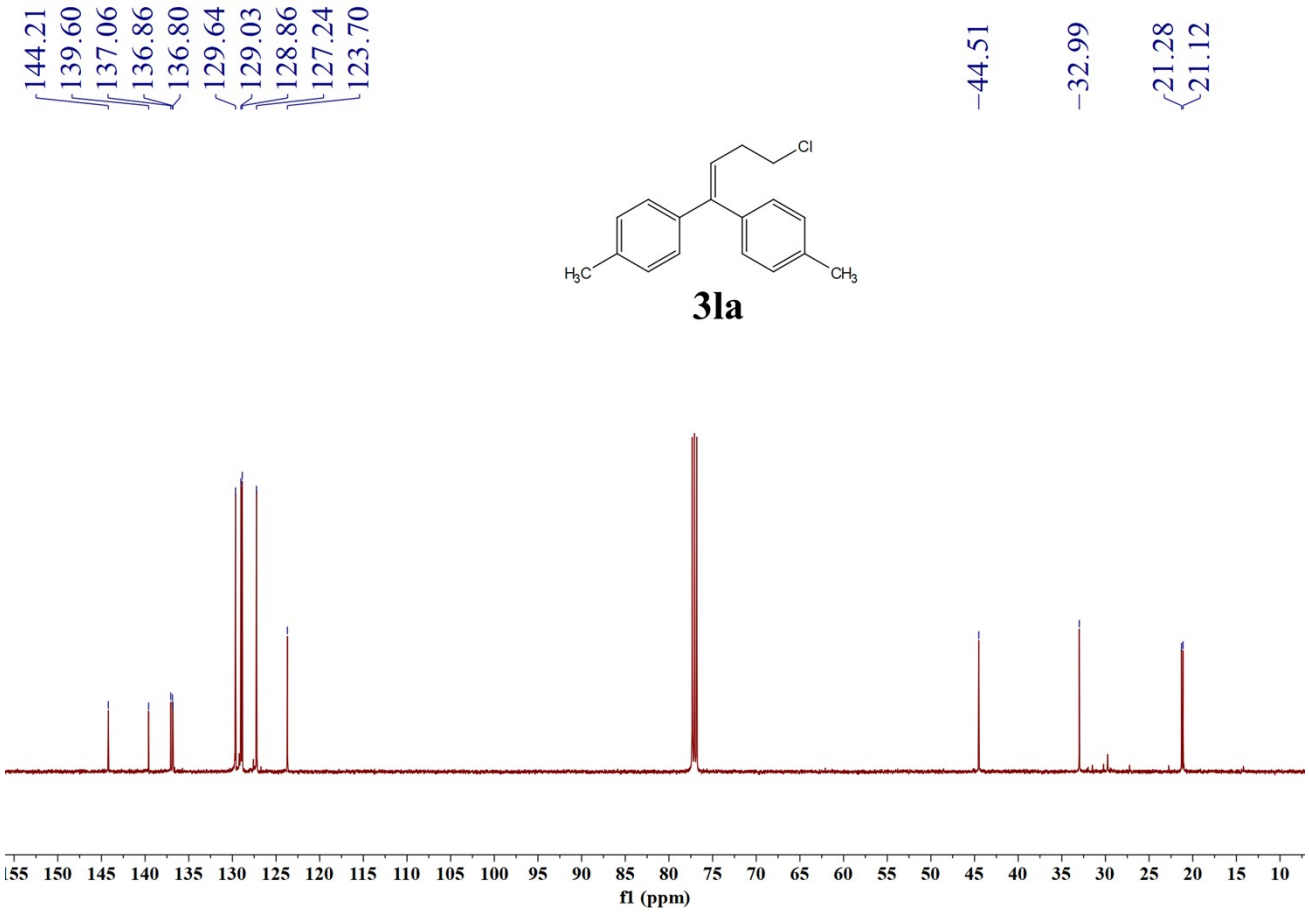

7.39
7.37
7.36
7.33
7.31
7.30
7.26 CDCl3
7.25
7.24
7.23
7.19
7.18
7.16
7.13
7.12
7.09
7.08
7.07
7.06
6.09
6.07
6.06
3.58
3.57
3.57
3.56
3.55
3.55
2.62
2.60
2.59
2.57
2.56
2.38
2.33
2.32
Cl
CH3
3ja
H (d) 7.24
F (d) 7.12
I (t) 7.37
E (q) 7.08
B (t) 6.07
C (td) 3.56
A (dq) 2.58
D (d) 2.35
G (m) 7.19
J (t) 7.31
1.04
1.01
2.00
2.00
1.05
1.99
1.00
2.03
2.00
2.99
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
f1 (ppm)

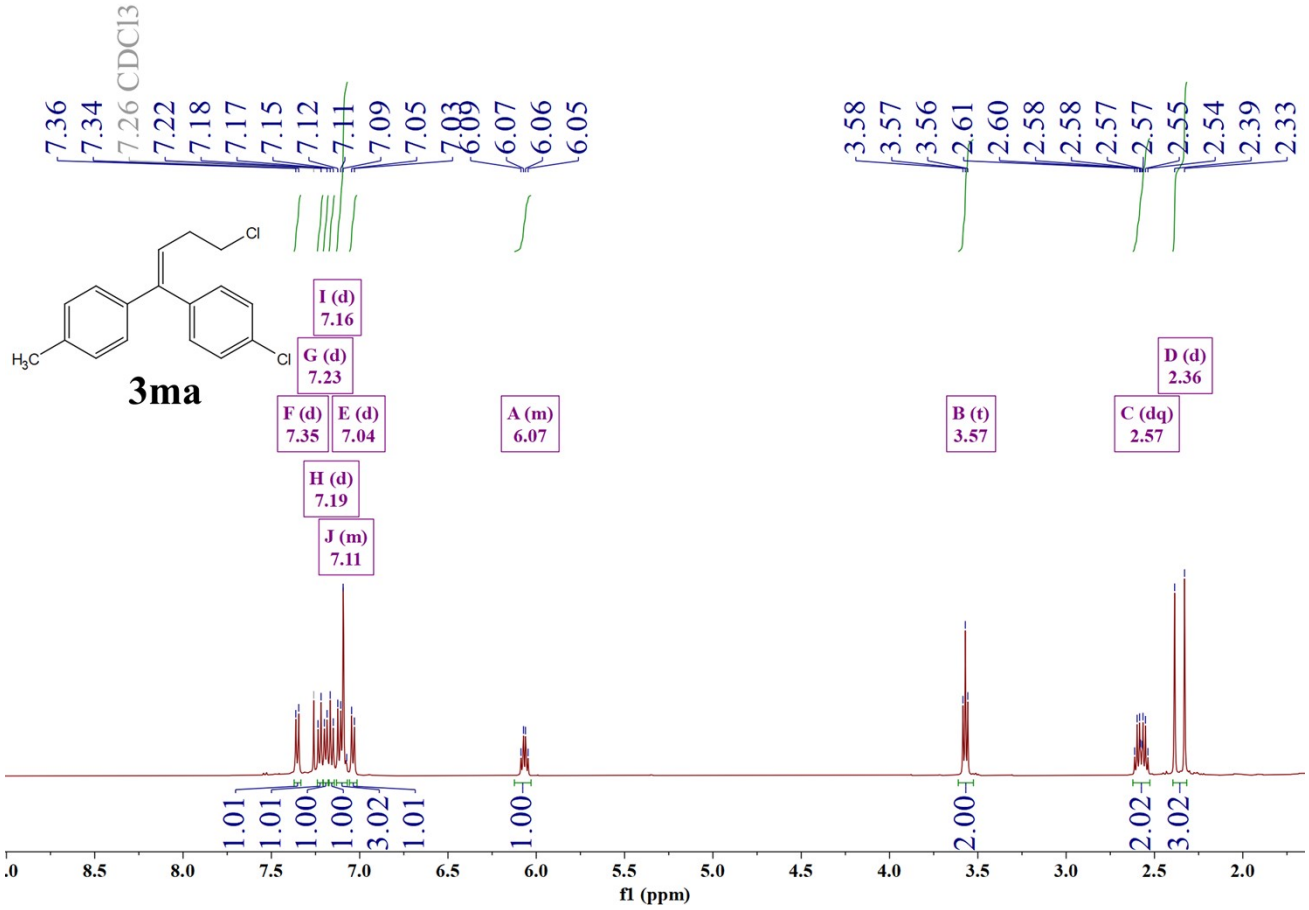

144.38
144.27
142.39
139.81
139.35
137.14
136.96
136.64
129.75
129.66
129.07
128.90
128.34
128.16
127.37
127.28
127.22
127.20
124.61
123.91
44.47
32.99
32.94
29.75
Cl
CH3
3ja
fl (ppm)

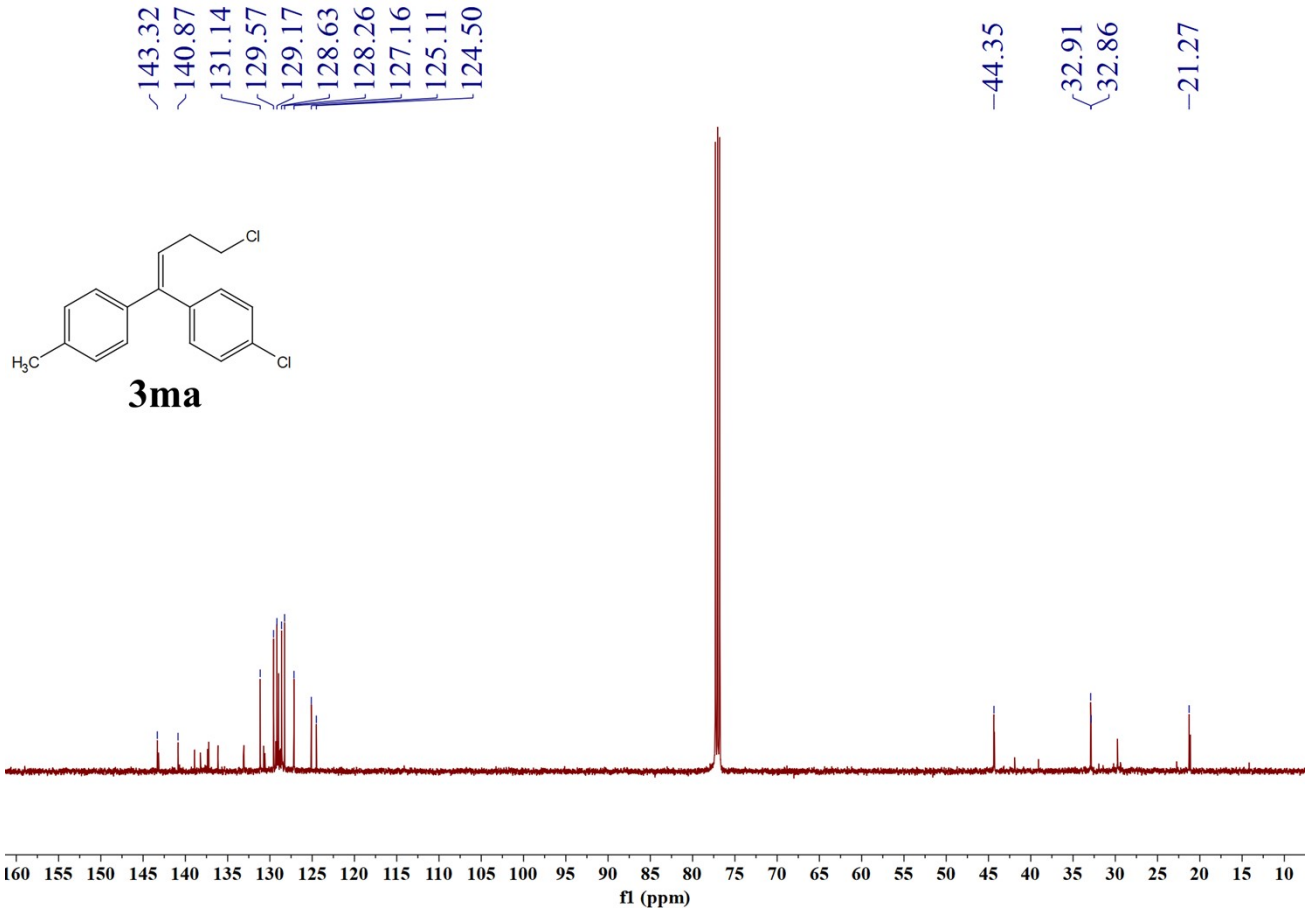

7.26 CDCl3
7.18
7.17
7.17
7.16
7.15
7.13
7.03
7.03
7.02
6.18
6.17
6.15
3.47
3.46
3.45
2.36
2.34
2.33
2.32
2.31
1.98
Cl
CH3
3ka
H (d) 7.16
F (s) 7.13
E (m) 7.03
G (d) 7.18
A (t) 6.17
B (t) 3.46
C (dt) 2.33
D (s) 1.98
1.00
5.03
1.02
1.02
1.00
2.01
2.02
3.01
fl (ppm)

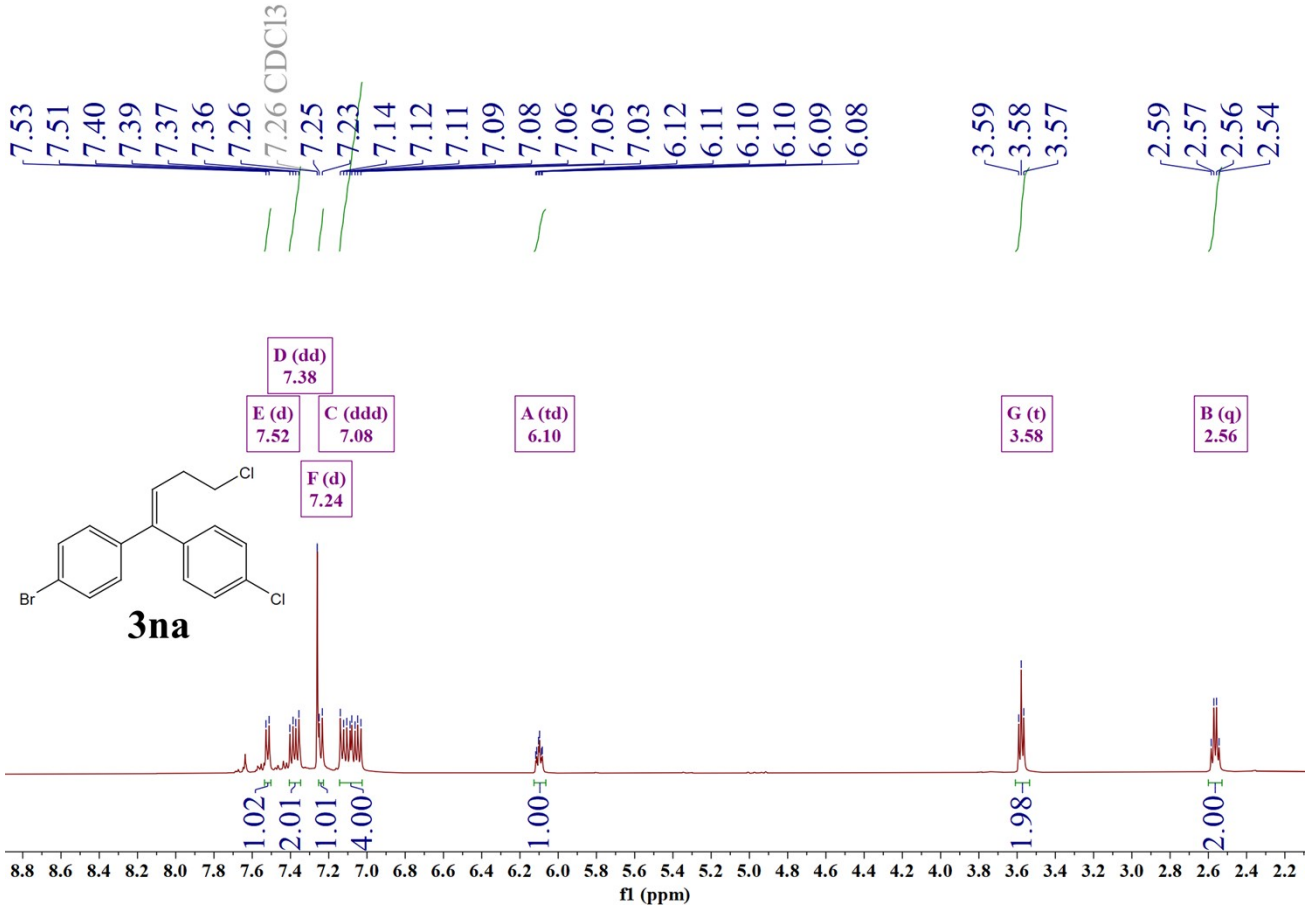

143.57
140.63
138.79
136.43
130.32
129.94
128.36
127.56
127.29
126.32
125.87
124.62
44.24
32.90
19.64
Cl
CH3
3ka
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

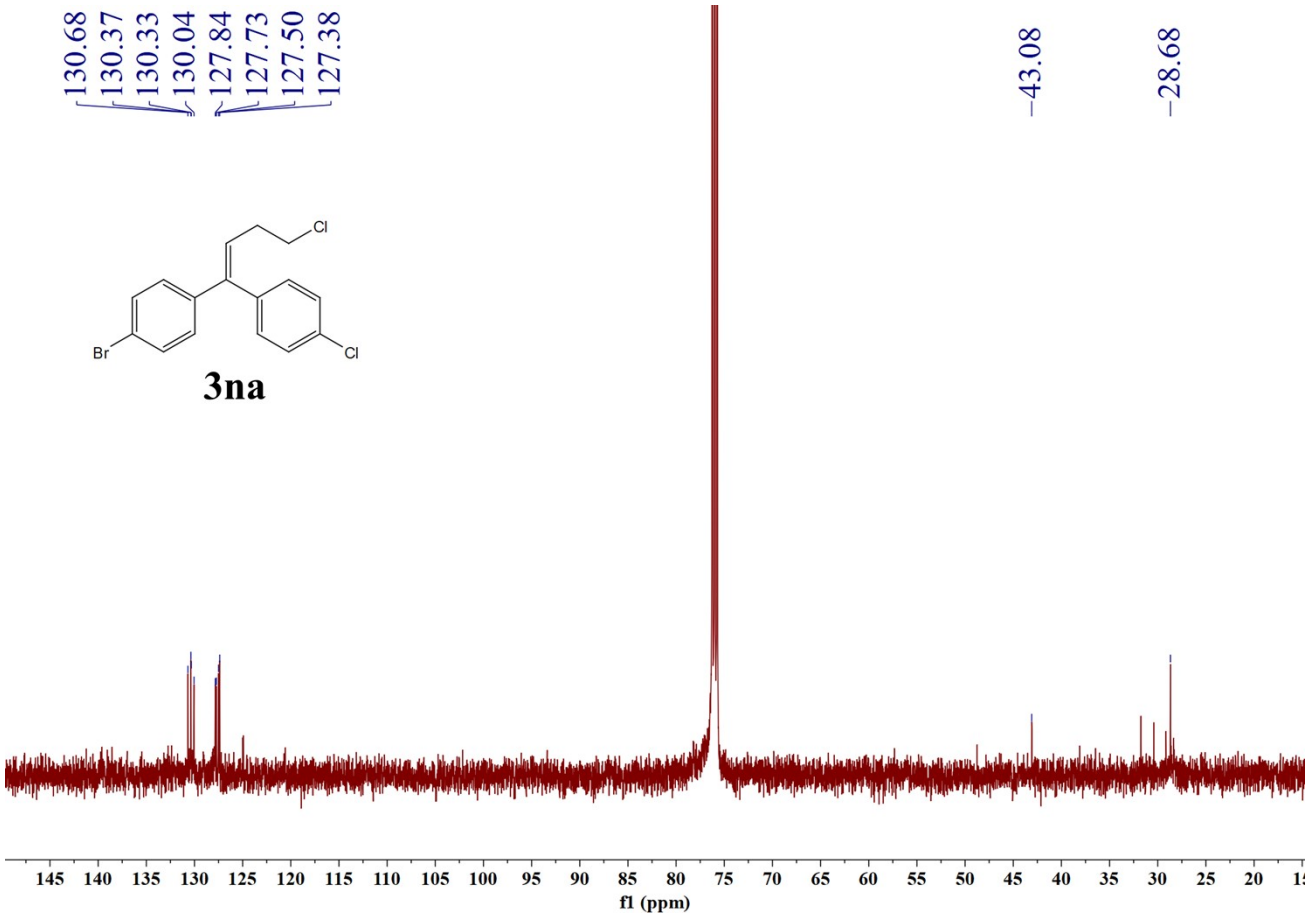

7.26 CDCl3
7.21
7.19
7.16
7.14
7.10
7.08
7.07
6.07
6.06
6.04
3.59
3.58
3.56
2.62
2.61
2.59
2.58
2.40
2.34
Cl
H3C
CH3
3la
D (d) 7.15
C (d) 7.20
E (t) 7.08
A (t) 6.06
F (t) 3.58
G (q) 2.60
B (s) 2.40
H (s) 2.34
2.02
2.01
4.02
1.00
2.00
2.00
3.01
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)

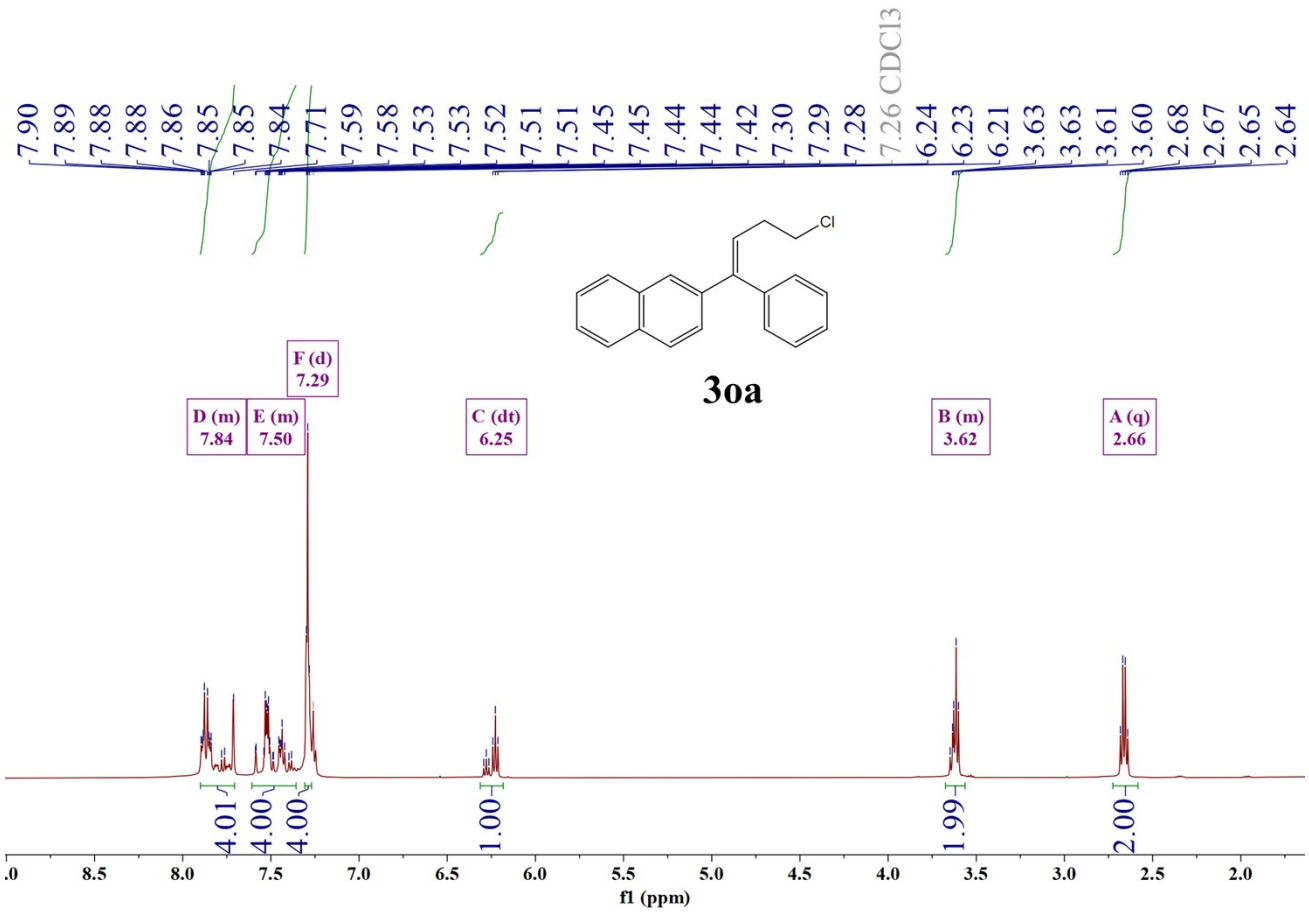

144.21
139.60
137.06
136.86
136.80
129.64
129.03
128.86
127.24
123.70
44.51
32.99
21.28
21.12
Cl
H3C
CH3
3la
fl (ppm)

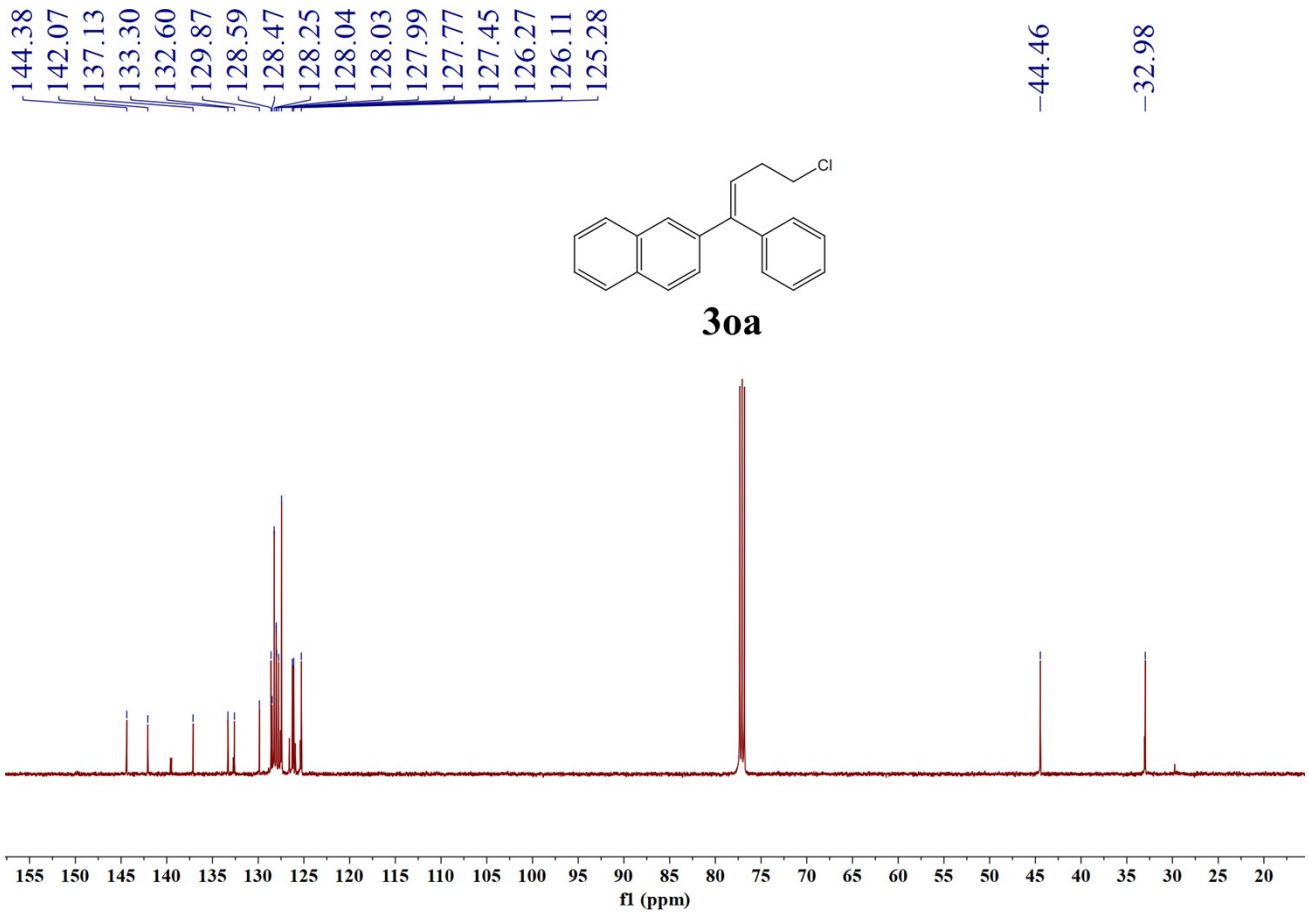

7.36
7.34
7.26 CDCl3
7.22
7.18
7.17
7.15
7.12
7.11
7.09
7.05
7.03
6.09
6.07
6.06
6.05
3.58
3.57
3.56
2.61
2.60
2.58
2.58
2.57
2.57
2.55
2.54
2.39
2.33
Cl
H3C
Cl
3ma
I (d) 7.16
G (d) 7.23
F (d) 7.35
E (d) 7.04
A (m) 6.07
H (d) 7.19
J (m) 7.11
B (t) 3.57
D (d) 2.36
C (dq) 2.57
1.01
1.01
1.00
1.00
3.02
1.01
1.00
2.00
2.02
3.02
fl (ppm)

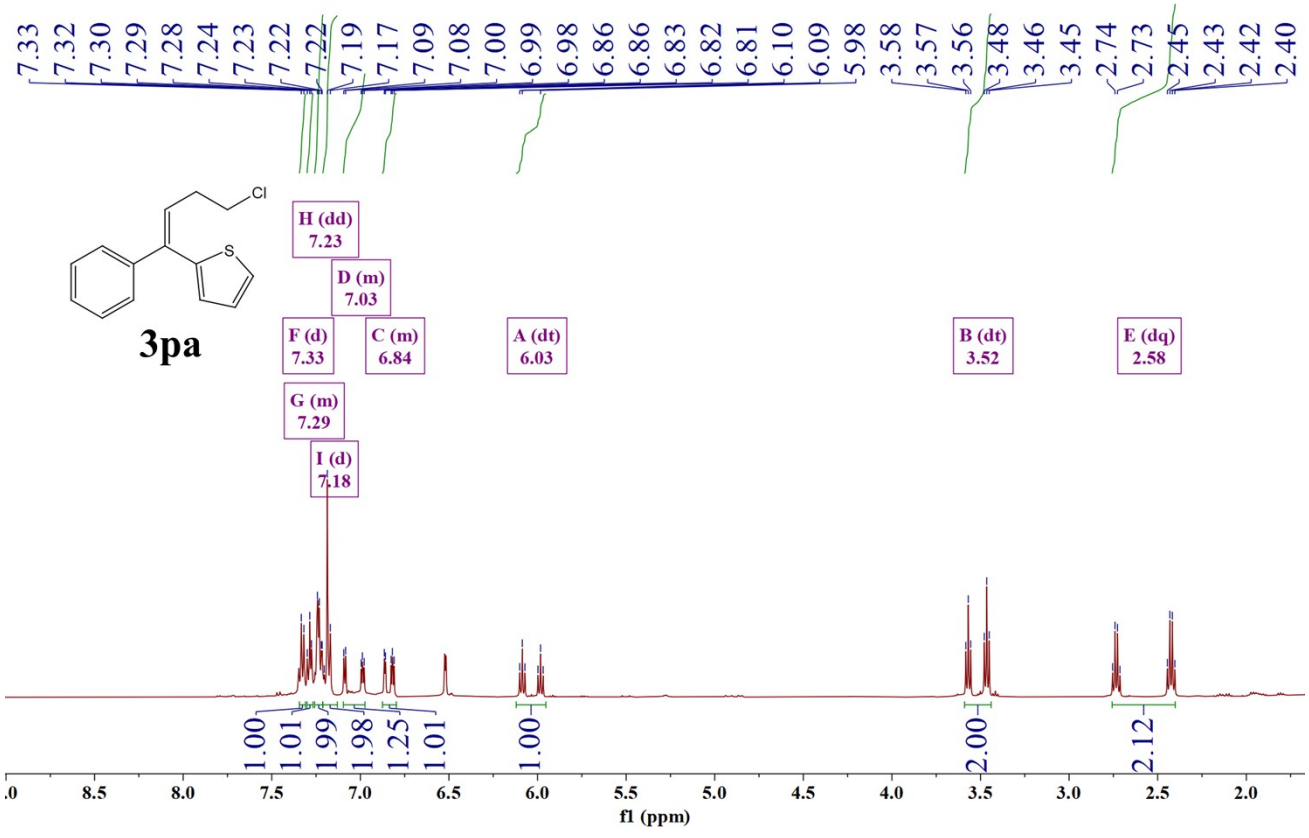

143.32
140.87
131.14
129.57
129.17
128.63
128.26
127.16
125.11
124.50
44.35
32.91
32.86
21.27
Cl
H3C
Cl
3ma
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

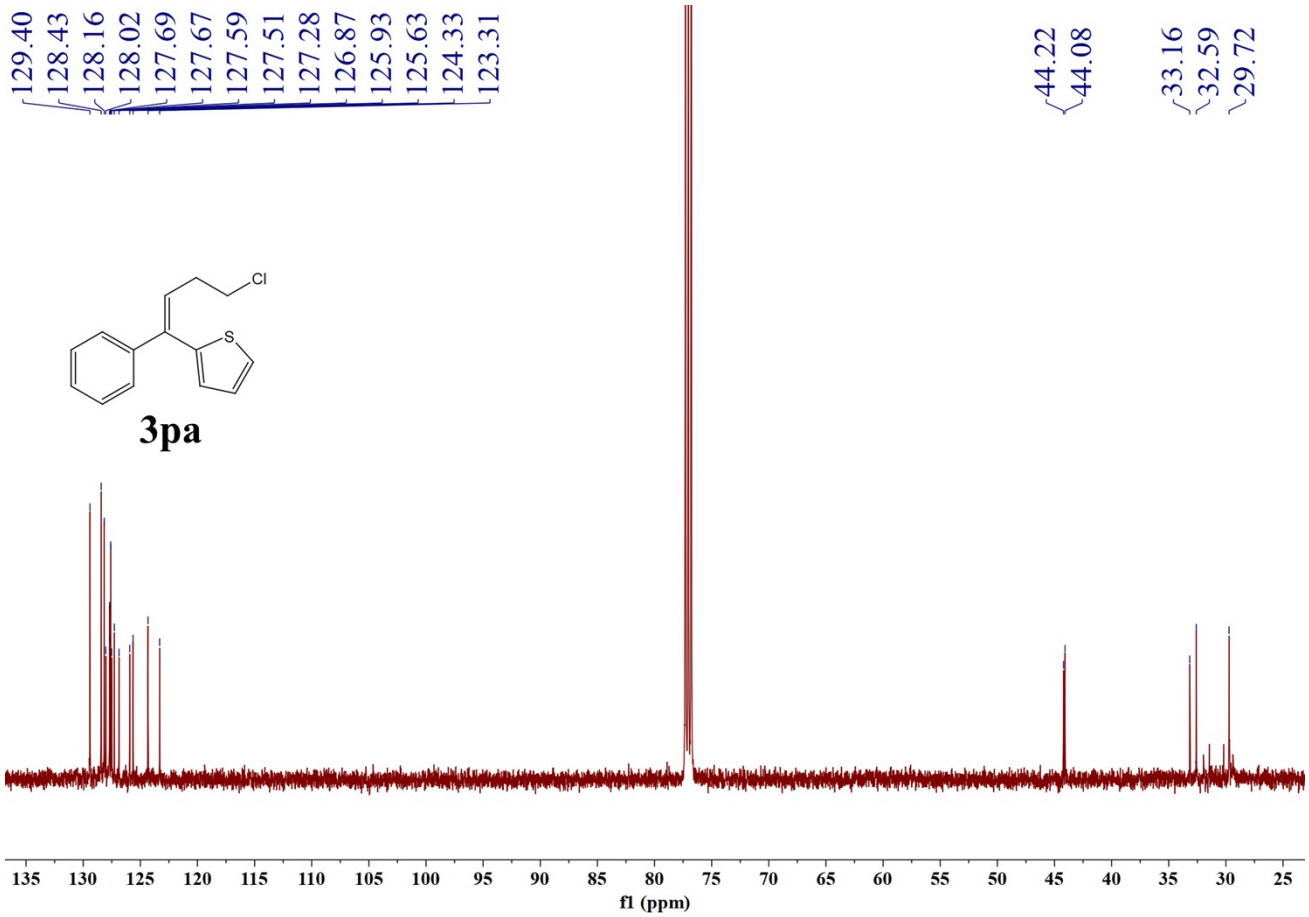

7.53
7.51
7.40
7.39
7.37
7.36
7.26
7.26 CDCl3
7.25
7.23
7.14
7.12
7.11
7.09
7.08
7.06
7.05
7.03
6.12
6.11
6.10
6.10
6.09
6.08
3.59
3.58
3.57
2.59
2.57
2.56
2.54
D (dd) 7.38
E (d) 7.52
C (ddd) 7.08
A (td) 6.10
G (t) 3.58
B (q) 2.56
F (d) 7.24
Cl
Br
Cl
3na
1.02
2.01
1.01
4.00
1.00
1.98
2.00
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2
f1 (ppm)

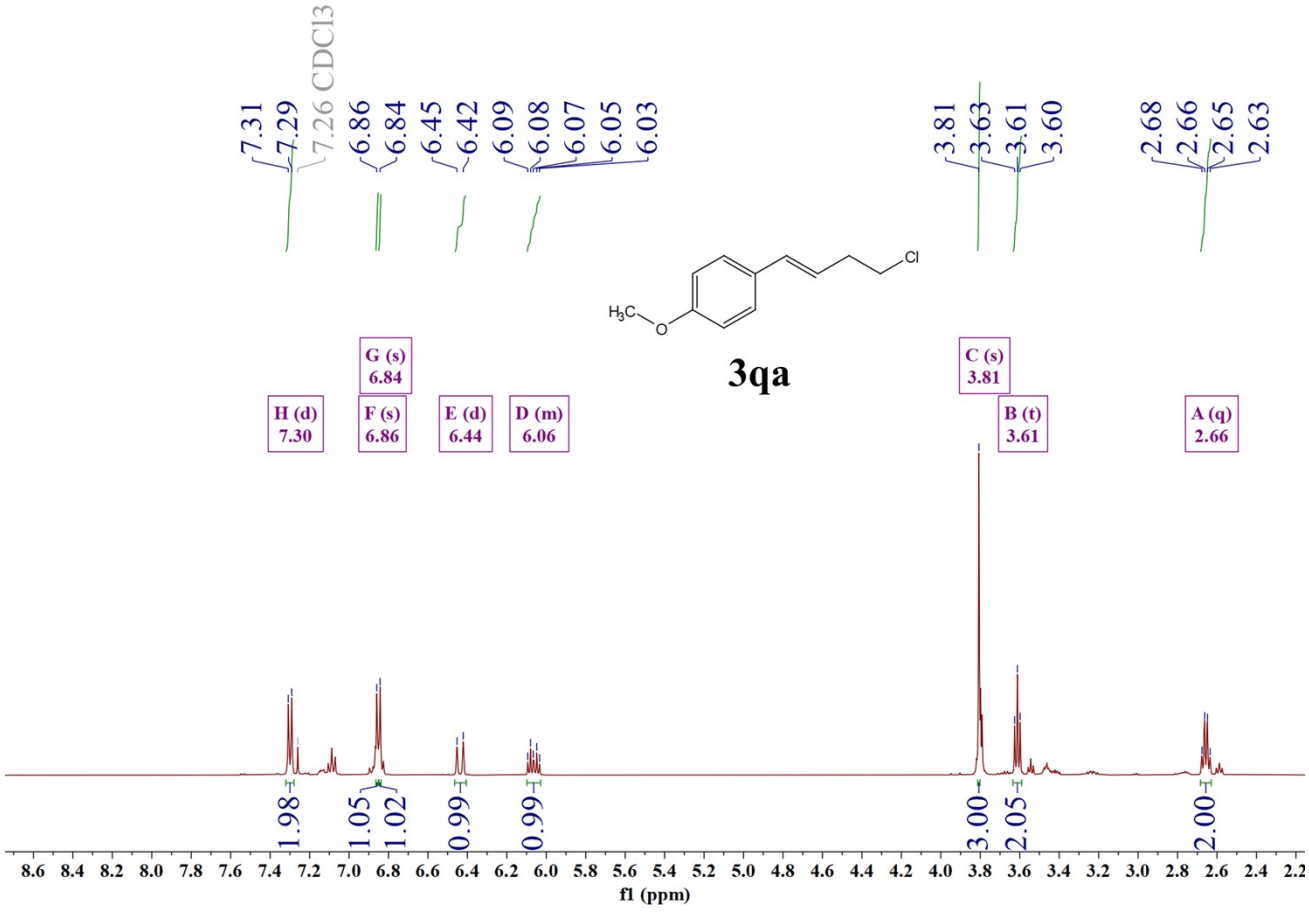

130.68
130.37
130.33
130.04
127.84
127.73
127.50
127.38
43.08
28.68
Cl
Br
Cl
3na
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

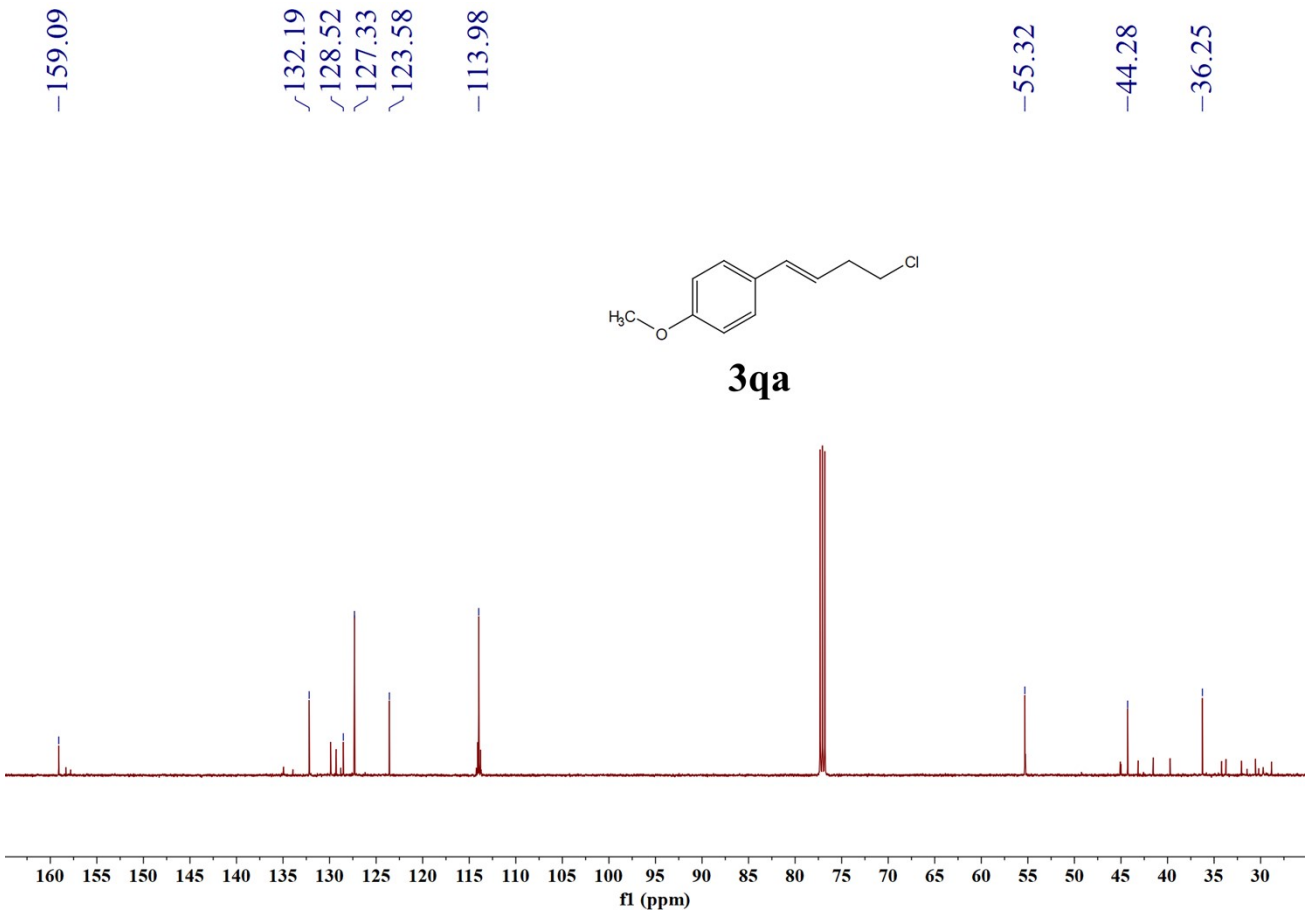

7.90
7.89
7.88
7.88
7.86
7.85
7.85
7.84
7.71
7.59
7.58
7.53
7.53
7.52
7.51
7.51
7.45
7.45
7.44
7.44
7.42
7.30
7.29
7.28
7.26 CDCl3
6.24
6.23
6.21
3.63
3.63
3.61
3.60
2.68
2.67
2.65
2.64
Cl
3oa
F (d)
7.29
D (m)
7.84
E (m)
7.50
C (dt)
6.25
B (m)
3.62
A (q)
2.66
4.01
4.00
4.00
1.00
1.99
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)

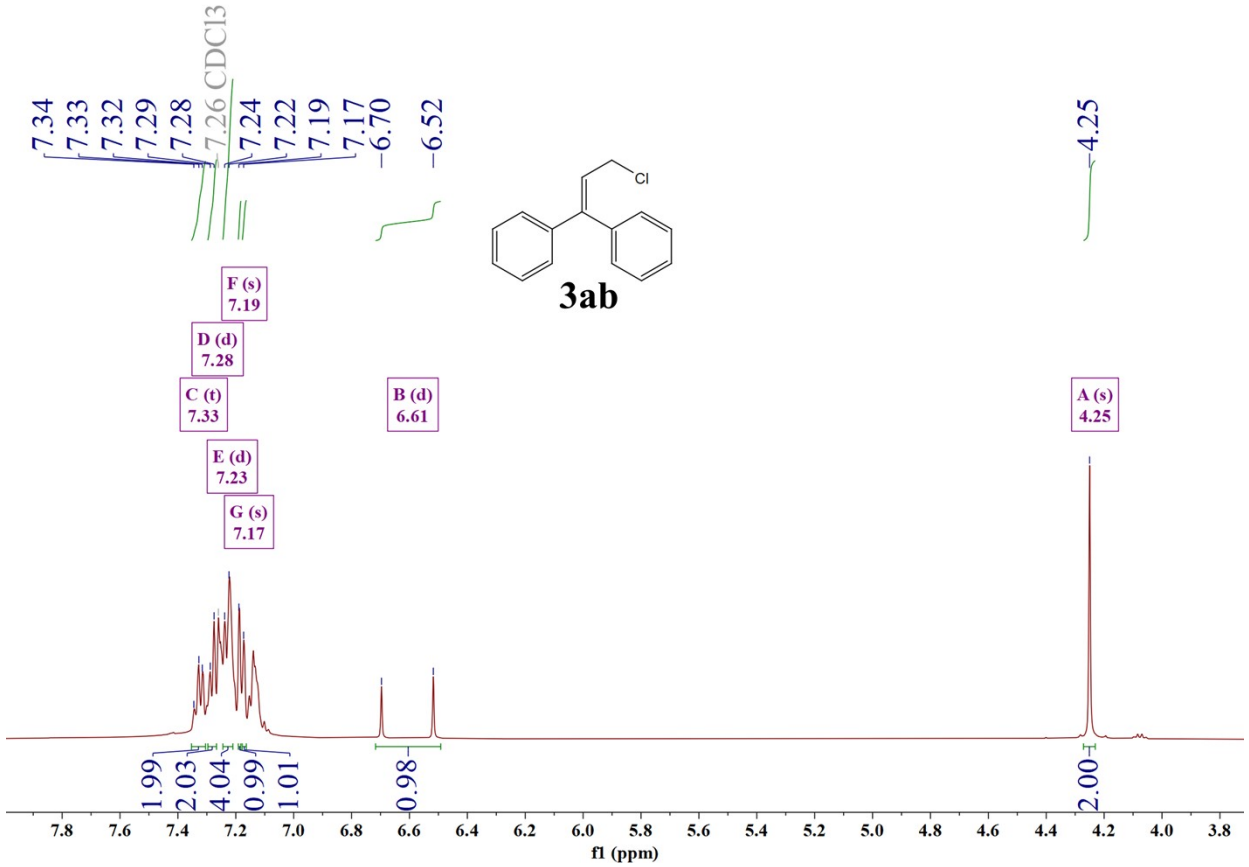

144.38
142.07
137.13
133.30
132.60
129.87
128.59
128.47
128.25
128.04
128.03
127.99
127.77
127.45
126.27
126.11
125.28
44.46
32.98
Cl
3oa
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

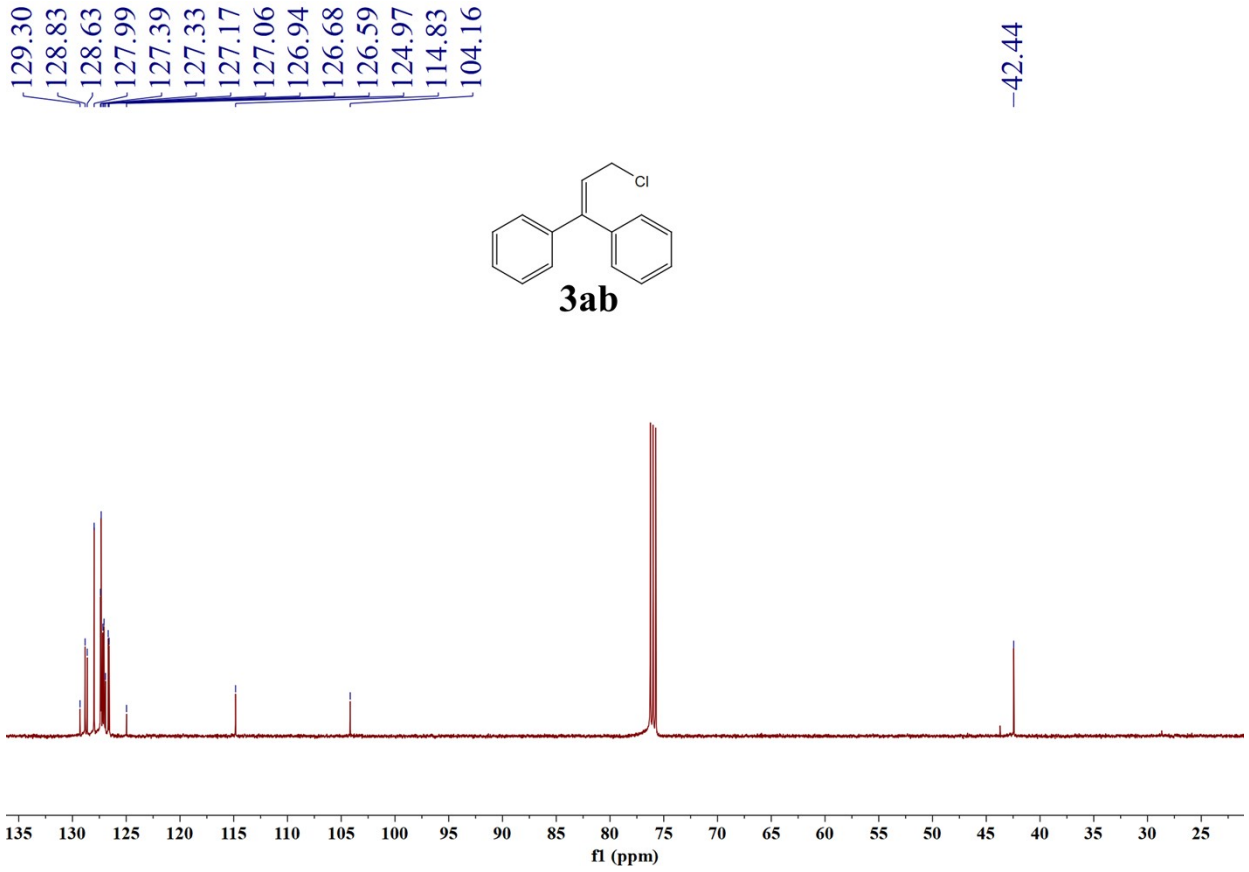

7.33
7.32
7.30
7.29
7.28
7.24
7.23
7.22
7.22
7.19
7.17
7.09
7.08
7.00
6.99
6.98
6.86
6.86
6.83
6.82
6.81
6.10
6.09
5.98
3.58
3.57
3.56
3.48
3.46
3.45
2.74
2.73
2.45
2.43
2.42
2.40
Cl
S
3pa
H (dd) 7.23
D (m) 7.03
F (d) 7.33
C (m) 6.84
A (dt) 6.03
B (dt) 3.52
E (dq) 2.58
G (m) 7.29
I (d) 7.18
1.00
1.01
1.99
1.98
1.25
1.01
1.00
2.00
2.12
.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
f1 (ppm)


129.40
128.43
128.16
128.02
127.69
127.67
127.59
127.51
127.28
126.87
125.93
125.63
124.33
123.31
44.22
44.08
33.16
32.59
29.72
Cl
S
3pa
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)


7.31
7.29
7.26 CDCl3
6.86
6.84
6.45
6.42
6.09
6.08
6.07
6.05
6.03
3.81
3.63
3.61
3.60
2.68
2.66
2.65
2.63
Cl
H3C
O
3qa
G (s) 6.84
H (d) 7.30
F (s) 6.86
E (d) 6.44
D (m) 6.06
C (s) 3.81
B (t) 3.61
A (q) 2.66
1.98
1.05
1.02
0.99
0.99
3.00
2.05
2.00
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2
f1 (ppm)


159.09
132.19
128.52
127.33
123.58
113.98
55.32
44.28
36.25
Cl
H3C
O
3qa
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30
f1 (ppm)


7.34
7.33
7.32
7.29
7.28
7.26 CDCl3
7.24
7.22
7.19
7.17
6.70
6.52
4.25
Cl
3ab
F (s) 7.19
D (d) 7.28
C (t) 7.33
E (d) 7.23
G (s) 7.17
B (d) 6.61
A (s) 4.25
1.99
2.03
4.04
0.99
1.01
0.98
2.00
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8
f1 (ppm)


129.30
128.83
128.63
127.99
127.39
127.33
127.17
127.06
126.94
126.68
126.59
124.97
114.83
104.16
42.44
Cl
3ab
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)