Supporting Information

Controllable Mono/Di- Alkenylation of Aryl Alkyl Thioether Tuned by Oxidants via Pd-catalysis

Xi-Sha Zhang,[a] Yun-Fei Zhang,[a] Kang Chen,[a] and Zhang-Jie Shi[a,b*]

[a] Beijing National Laboratory of Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and PKU Green Chemistry Center, Peking University, Beijing 100871 (China) .[b] State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032 (China).

zshi@pku.edu.cn

Contents

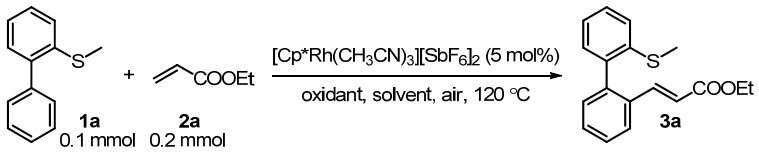
General:

$Pd(OAc)_2$ was purchased from SINOCOMPOUND Co.,Ltd.. AgOTFA was purchssed from Strem. NaOTFA was purchased from TCI. The sulfide derivatives[1] (**1**) except **1a** were prepared according to literature methods. Other reagents were commercially available and were used directly without further purification unless otherwise specified. All the solvents were directly used unless otherwise specified. NMR data were collected on Bruker 400 M or Bruker 500 M nuclear resonance spectrometers in the solvents indicated unless otherwise specified. Chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm and the central peak of $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. The data of ^1H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Column chromatography was performed on 200-300 mesh silica gels with the indicated solvent systems. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). HRMS (ESI) were performed on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer by Analytical Instrumentation Center, Peking University.

Conditions Screening Tables:

Initial screening of the Rh-catalysts, oxidants and solvents were listed below. At that initial stage, the reactions were detected by TLC and GC-MS.

Table S1. Initial screening of the catalysts and oxidants



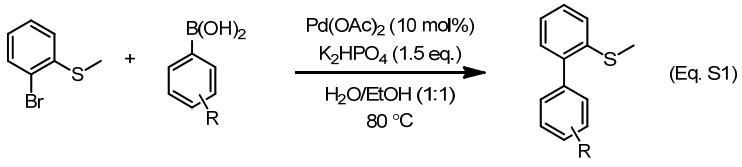
1a 0.1 mmol **2a** 0.2 mmol **3a**

Entry	Catalyst	Oxidant	Solvent	**Results**
1	no change	$Cu(OAc)_2$	MeOH	No
2	no change	$Cu(OAc)_2$	*t*-AmylOH	< 10%
3	no change	$Cu(OAc)_2$	DCE	No
4	no change	AgOAc	DCE	No
5	$Pd(OAc)_2$	$Cu(OAc)_2$	DCE	< 10%
6	$Pd(OAc)_2$	AgOAc	DCE	> 80% conversion (GC-MS)

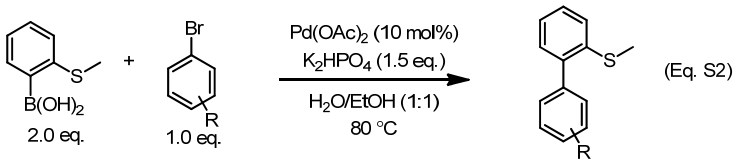
Synthesis Procedures:

1. The general procedure for synthesis of the sulfide substrates (1)

The procedure for the synthesis of the sulfides was followed the literature. [1] Most of the substrates were synthesized according to Eq. S1, and some substrates like **1b** and **1c** were synthesized according to Eq. S2.



(Eq. S1)



(Eq. S2)

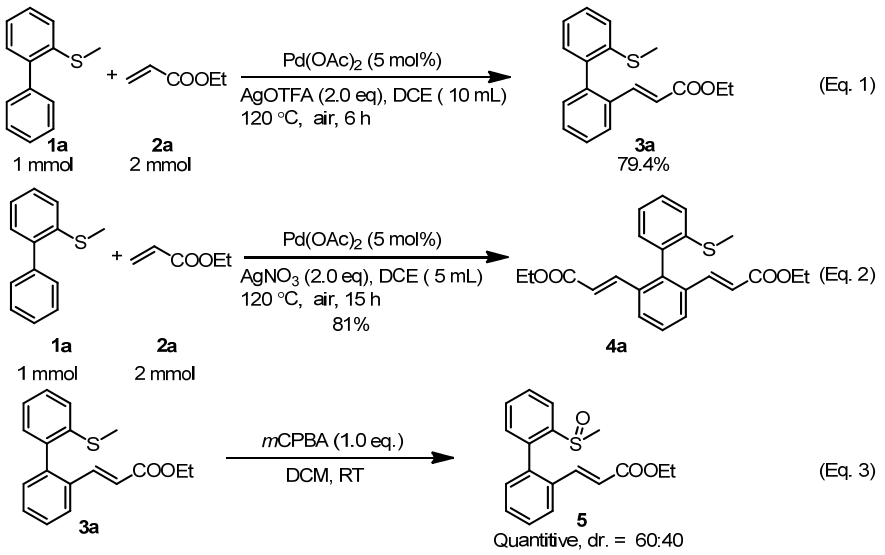
2. The general procedure for the mono-alkenylation: the synthesis of compound 3 (Table 2):

To a 50 mL Wattecs Schlenk tube, the catalyst $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), AgOTFA (88.0 mg, 0.4 mmol), substrate **1** (0.2 mmol) were added in sequence to the tube under air atmosphere. After the addition of substituted alkenes **2** (0.40 mmol, 2.0 eq.) by microinjector, DCE (2.0 mL, 0.1 M) was injected, the reaction mixture was sealed and subjected to stirring at 120 ℃ in a Wattecs Parallel Reactor for 6 h. After cooling to rt., the product was purified by column chromatography on silica gel with petroleum ether/EtOAc (20:1 to 10:1) to afford compound **3** as white solid or colorless oil.

3. The general procedure for the di-alkenylation: synthesis of compound 4 (Table 3)

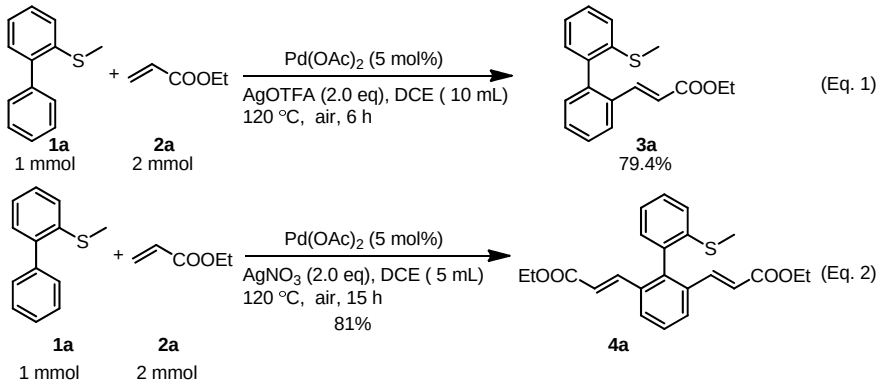
To a 50 mL Wattecs Schlenk tube, the catalyst $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $AgNO_3$ (68.0 mg, 0.4 mmol), substrate **1** (0.2 mmol) were added in sequence to the tube under air atmosphere. After the addition of substituted alkenes **2** (0.40 mmol, 2.0 eq.) by microinjector, DCE (2.0 mL, 0.1 M) was injected, the reaction mixture was sealed and subjected to stirring at 120 ℃ in a Wattecs Parallel Reactor for 6 h. After cooling to rt., the product was purified by column chromatography on silica gel with petroleum ether/EtOAc (20:1 to 10:1) to afford compound **4** as white solid.

4. The procedure for the large scale reaction and product transformation: (Scheme 2)



Scheme 2. Large scale reaction and transformation of the product to synthesize ligand.

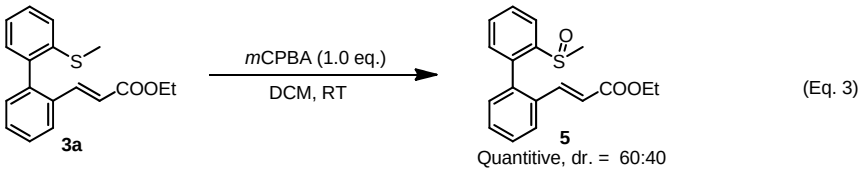
4.1 The procedure for the large scale reaction: (Eq. 1 and Eq. 2)



For Eq. 1: To a 50 mL round bottom Schlenk flask, the catalyst $Pd(OAc)_2$ (11.0 mg, 0.05 mmol), AgOTFA (440.0 mg, 2.0 mmol), substrate **1a** (200.0 mg, 1.0 mmol) were added in sequence to the tube under air atmosphere. After the addition of ethyl acrylate **2a** (200.2 mg, 217 uL, 2.0 mmol, 2.0 eq.) by microinjector, DCE (10.0 mL, 0.1 M) was injected, the reaction mixture was sealed and subjected to stirring at 120 ℃ in a Wattecs Parallel Reactor for 6 h. After cooling to rt., the product was purified by column chromatography on silica gel with petroleum ether/EtOAc (20:1 to 10:1) to afford compound **3a** as white solid in 79% yield (236.8 mg).

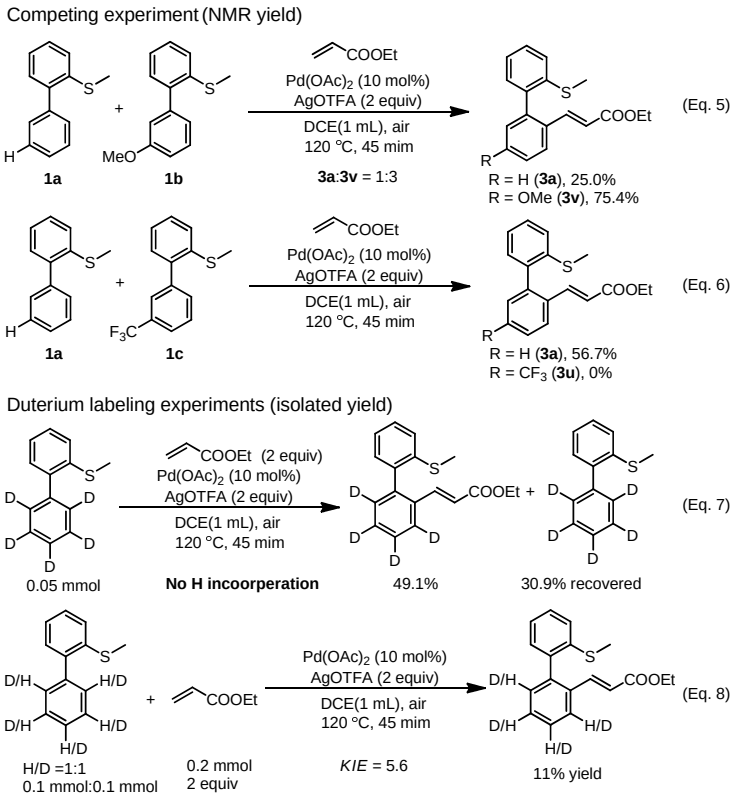
For Eq. 2: To a 50 mL Wattecs Schlenk tube, the catalyst $Pd(OAc)_2$ (11.0 mg, 0.05 mmol), $AgNO_3$ (340.0 mg, 2.0 mmol), substrate **1a** (200.0 mg, 1.0 mmol) were added in sequence to the tube under air atmosphere. After the addition of ethyl acrylate **2a** (200.2 mg, 217 uL, 2.0 mmol, 2.0 eq.) by microinjector, DCE (5.0 mL, 0.2 M) was injected, the reaction mixture was sealed and subjected to stirring at 120 ℃ in a Wattecs Parallel Reactor for 15 h for good conversion and di-functionalization selectivity. After cooling to rt., the product was purified by column chromatography on silica gel with petroleum ether/EtOAc (10:1) to afford compound **4a** as white solid in 81% yield (322.2 mg).

4.2 The procedure for the product transformation to synthesize sulfoxide-olefin ligand: (Eq. 3)



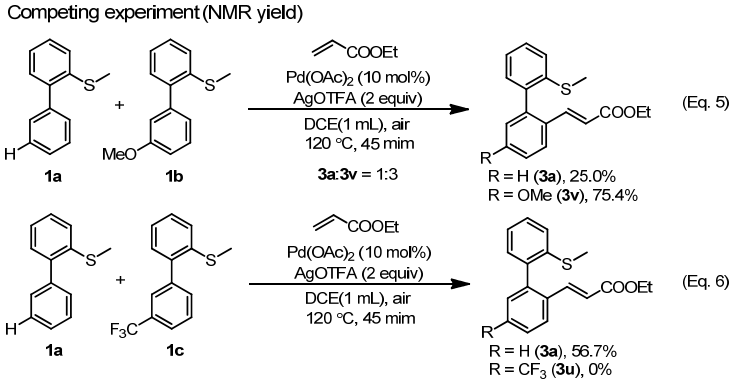
In a 50 mL reaction tube, thioether **3a**（0.1 mmol, 29.8 mg） was dissolved in 3 mL DCM. Then *m*-CPBA solution (in 3 ml DCM, 0.1 mmol, 20.4 mg) was injected into the system at room temperature. The reaction was monitored by TLC for the full conversion. Then the solvent was removed under vcumm and the product was purified by column chromatography (PE/EA = 1:1) in quantitive yield as a white solid.

5. The procedure for the mechanistic study: (Scheme 4)



Scheme 4. Mechanistic studies

5.1 The procedure for the competing experiment. (Eq 5 and Eq 6)

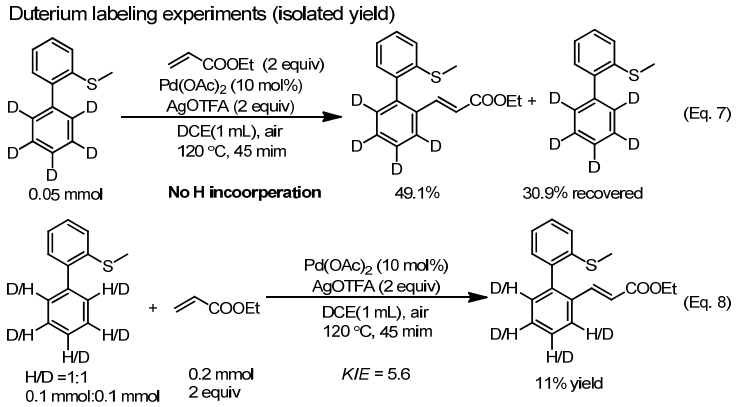


The competing experiments were conducted according to the standard procedure with two different electron characteristic phenol derivatives in the same reaction system. Take the mixture of **1a** and **1b** for example: To a 50 mL Wattecs Schlenk tube, the catalyst $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), AgOTFA (44.2 mg, 0.2 mmol), substrate **1a** (0.1 mmol), substrate **1b** (0.1 mmol) were added in sequence to the tube under air atmosphere. After the addition of ethyl acrylate **2a** (0.20 mmol) by microinjector, DCE (1.0 mL) was injected, the reaction mixture was sealed and subjected to stirring at 120 ℃ in a Wattecs Parallel Reactor for 45 min. After cooling to room temperature, the solvent was removed under reduced pressure and the yield and ratio of the products (**3**) were determined by crude NMR with CH_2Br_2 as internal standard.

The characteristic peaks in the crude NMR of the mixture of **3a** and **3v**: ^{1}H NMR(400MHz, $CDCl_3$): δ = 4.916 (s, 2.00H, CH_2 of CH_2Br_2), 6.24 (d, J = 16.0 Hz, 0.87H, alkenyl CH of **3v**), 6.35 (d, J = 16.0 Hz, 0.29H, alkenyl CH of **3a**).

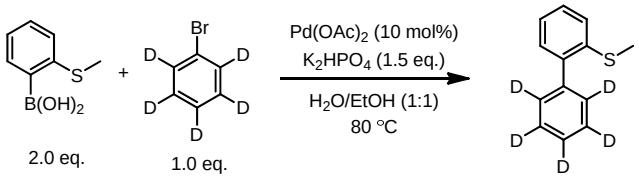
The characteristic peaks in the crude NMR of the mixture of **3a** and **3u**: ^{1}H NMR(400MHz, $CDCl_3$): δ = 4.924 (s, 2.00H, CH_2 of CH_2Br_2), 6.39 (d, J = 16.0 Hz, 0.64H, alkenyl CH of **3a**).

5.2 The procedure for the deuterium labeling experiment. (Eq 7 and Eq 8)



5.2.1 The synthesis of deuterium starting materials

The deuterium labeled substrate d5-**1a** was synthesized according to Eq. S1.



5.2.2 The procedure for the H/D exchange experiment (Eq 7)

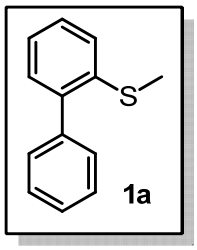
The procedure was following the standard fashion with ***d5*-1a** as the substrate except that the reaction time was reduced to 45 min. After the reaction, the starting material was recovered and the ^{1}HNMR detection showed that no deuterium exchange was present.

5.2.3 The procedure for the KIE experiment (Eq 8)

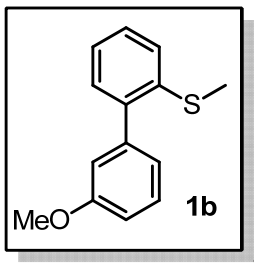
The reaction was conducted in the presence of **1a** and **d5-1a**, according to the standard procedure except that the reaction time was reduced to 45 min, in order to make sure a proper conversion. To a 50 mL Wattecs Schlenk tube, the catalyst $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), AgOTFA (44.2 mg, 0.2 mmol), substrate **1a** (0.1 mmol), substrate d5-**1a** (0.1 mmol) were added in sequence to the tube under air atmosphere. After the addition of ethyl acrylate **2a** (0.20 mmol) by microinjector, DCE (1.0 mL) was injected, the reaction mixture was sealed and subjected to stirring at 120 ℃ in a Wattecs Parallel Reactor for 45 min. After the reaction, the product was isolated and characterized by ^{1}HNMR. The ^{1}HNMR of the product was: ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.93-7.91 (m, 0.85H), 7.49-7.37 (m, 4.65H), 7.28-7.24 (m, 1.85 H), 7.11 (dd, J = 7.6, 1.2 Hz, 1H), 6.44 (d, J = 16.0 Hz, 1H), 4.11 (q, J = 3.2 Hz, 2H), 2.38 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H). H% = 85%, KIE = 5.6.

Characterization data

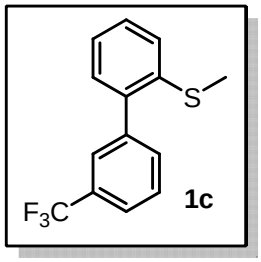
1.Characterization of some sulfide substrates 1



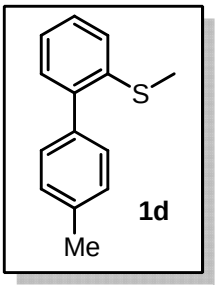
1a. White solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.43-7.32 (m, 6H), 7.28 (d, J = 7.6 Hz, 1H), 7.23-7.18 (m, 2H), 2.37 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 141.0, 140.6, 137.1, 130.0, 129.3, 128.1, 127.9, 127.5, 125.4, 124.8, 16.0.



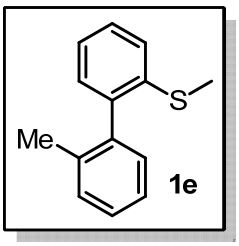
1b. White solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.34 (t, J = 8.0 Hz, 2H), 7.28 (d, J = 7.6 Hz, 1H), 7.24-7.17 (m, 2H), 7.00 (d, J = 7.6 Hz, 1H), 6.97 (br, 1H), 6.92 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 3.84 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 159.3, 141.8, 140.7, 137.1, 129.8, 129.1, 128.0, 125.1, 124.6, 121.7, 114.8, 113.2, 55.2, 16.0. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{14}H_{15}OS$: 231.08381, found: 231.08364.



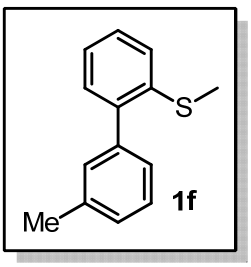
1c. Colorless oil. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.69 (s, 1H), 7.64-7.61 (m, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.40-7.35 (m, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.23-7.21 (m, 2H), 2.38 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 141.2, 139.4, 137.1, 132.8, 130.6 (q, J = 32.6 Hz), 129.969, 128.552, 128.500, 126.2 (q, J = 3.8 Hz), 125.611, 124.962, 124.2 (q, J = 2.6 Hz), 124.2 (q, J = 272.8 Hz), 15.9. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{14}H_{12}F_3S$: 269.06063, found: 269.06143.



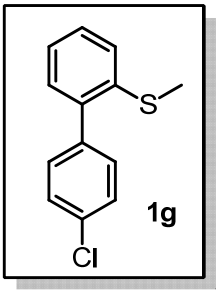
1d. White solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.34-7.18 (m, 8H), 2.40 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =140.9, 137.6, 137.2, 137.1, 129.9, 129.1, 128.8, 127.7, 125.2, 124.7, 21.2, 16.0. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{14}H_{15}S$: 215.08890, found: 215.08892.



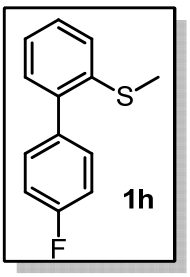
1e. White solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.35 (dt, J = 7.2, 0.8 Hz, 1H), 7.30-7.28 (m, 2H), 7.25-7.22 (m, 2H), 7.19 (dt, J = 7.4, 1.2 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.10 (dd, J = 7.4, 1.2 Hz, 1H), 2.36 (s, 3H), 2.11 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 140.3, 140.0, 137.8, 136.4, 129.9, 129.6, 129.5, 127.8, 125.6, 124.4, 19.7, 15.3. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{14}H_{15}S$: 215.08890, found: 215.08876.



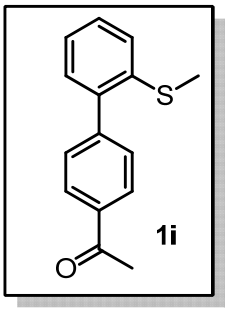
1f. Colorless oil. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.33-7.18 (m, 8H), 2.40 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 141.0, 140.4, 137.7, 137.1, 130.0, 129.9, 128.2, 127.9, 127.8, 126.3, 125.1, 124.6, 21.4, 15.9. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{14}H_{15}S$: 215.08890, found: 215.08878.



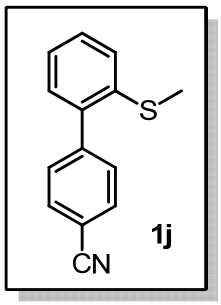
1g. White solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.41-7.33 (m, 5H), 7.28 (d, J = 7.5 Hz, 1H), 7.22-7.16 (m, 2H), 2.37 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 139.7, 138.9, 137.1, 133.5, 130.7, 129.9, 128.3, 128.2, 125.5, 124.9, 16.0. **HRMS (ESI)**: m/z: $[M]^+$ caculated for $C_{13}H_{11}ClS$: 234.02645, found: 234.02715.



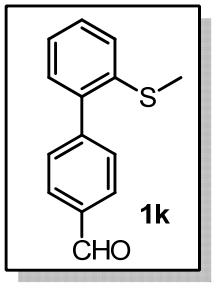
1h. White solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.39-7.32 (m, 3H), 7.28 (br, 1H), 7.20-7.19 (m, 2H), 7.13-7.08 (m, 2H), 2.37 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 162.2 (d, J = 247.0 Hz), 139.9, 137.2, 136.4 (d, J = 3.5 Hz) 131.0 (d, J = 7.8 Hz), 130.0, 128.1, 125.3, 124.8, 115.0 (d, J = 21.3 Hz), 15.9. **HRMS (ESI)**: m/z: $[M]^+$ caculated for $C_{13}H_{11}FS$: 218.05600, found: 218.05622.



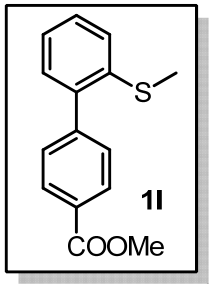
1i. Light yellow solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 8.0 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.38-7.34 (m, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.25-7.19 (m, 2H), 2.63 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 197.6, 145.4, 139.8, 136.9, 136.050, 1.725, 129.6, 128.5, 128.1, 125.6, 124.9, 26.6, 16.0. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{15}H_{15}OS$: 243.08381, found: 243.08439.



1j. White solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.71 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.40-7.37 (m, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.25-7.21 (m, 1H), 7.17 (dd, J = 7.6, 1.2 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 145.2, 139.0, 136.8, 131.8, 130.1, 129.7, 128.8, 125.8, 125.0, 118.8, 111.2, 15.9. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{14}H_{12}NS$: 226.06850, found: 226.06846.

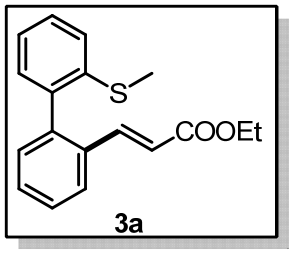


1k. Light yellow solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 10.07 (s, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.41-7.36 (m, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.24-7.22 (m, 2H), 2.38 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 191.8, 146.9, 139.7, 136.9, 135.4, 130.1, 129.8, 129.5, 128.7, 125.8, 125.0, 16.1. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{14}H_{13}OS$: 229.06816, found: 229.06825.

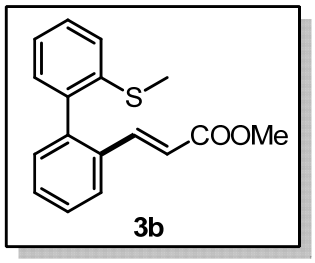


1l. White solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 8.09 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.74-7.33 (m, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.21-7.20 (m, 2H), 3.93 (s, 3H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.8, 145.2, 139.9, 136.9, 129.8, 129.4, 129.4, 129.1, 128.4, 125.7, 124.9, 52.0, 16.0. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{15}H_{15}O_2S$: 259.07873, found: 259.07919.

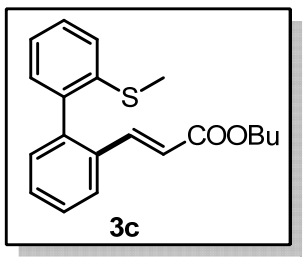
2. Characterization of mono-alkenylation product 3



(E)-ethyl 3-(2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. According to the general procedure, **3a** was obtained as a white solid in 81% yield (48.0 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (500MHz, $CDCl_3$)**: δ = 7.74-7.71 (m, 1H), 7.45-7.35 (m, 4H), 7.28-7.25 (m, 2H), 7.18 (dt, J = 7.5, 1.0 Hz, 1H), 7.08 (dd, J = 7.5, 1.0 Hz, 1H), 6.34 (d, J = 16.0 Hz, 1H), 4.15 (q, J = 7.0 Hz, 2H), 2.33 (s, 3H), 1.24 (t, J = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 166.8, 142.8, 141.2, 138.3, 137.9, 133.1, 130.8, 130.2, 129.6, 128.5, 128.1, 126.1, 125.0, 124.6, 118.9, 60.2, 15.6, 14.1. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{18}H_{19}O_2S$: 299.11003, found: 299.11064.

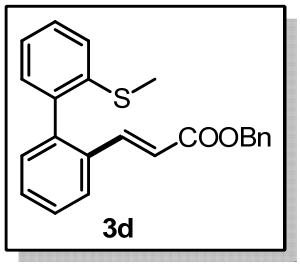


(E)-methyl 3-(2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. According to the general procedure, **3b** was obtained as a white solid in 78% yield (44.0 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (500MHz, $CDCl_3$)**: δ = 7.73-7.71 (m, 1H), 7.45-7.35 (m, 4H), 7.28-7.26 (m, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 6.34 (d, J = 16.0 Hz, 1H), 3.68 (s, 3H), 2.33 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 167.3, 143.1, 141.3, 138.4, 138.0, 133.1, 130.9, 130.2, 129.8, 128.6, 128.3, 126.3, 125.1, 124.7, 118.6, 51.5, 15.7. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{17}H_{17}O_2S$: 285.09438, found: 285.09514.



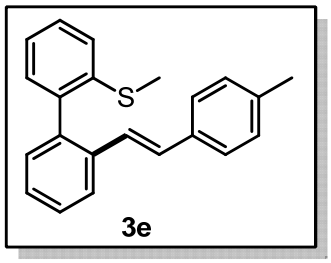
(E)-butyl 3-(2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. According to the general procedure, **3c** was obtained as a white solid in 73% yield (48.2 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.75-7.73 (m, 1H), 7.45-7.35 (m, 4H), 7.27-7.26 (m, 2H), 7.19 (dt, J = 7.6, 0.8 Hz, 1H), 7.08 (dd, J = 7.2, 1.2 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 4.10 (t, J = 6.4 Hz, 2H), 2.34 (s, 3H), 1.62-1.55 (m, 2H), 1.38-1.26 (m,

2H), 0.90 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.9, 142.7, 141.2, 138.2, 137.9, 133.0, 130.7, 130.2, 129.7, 128.5, 128.2, 126.0, 124.9, 124.5, 118.8, 64.1, 30.6, 19.1, 15.6, 13.7. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{20}H_{23}O_2S$: 327.14133, found: 327.14158.



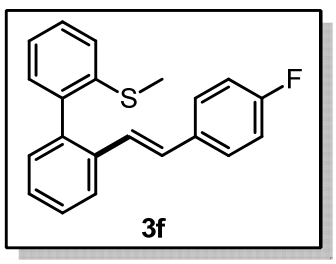
3d

(E)-benzyl 3-(2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. According to the general procedure, **3d** was obtained as a white solid in 82% yield (59.3 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.74-7.72 (m, 1H), 7.50 (d, J = 16.0 Hz, 1H), 7.42-7.25 (m, 10H), 7.18 (t, J = 7.6 Hz, 1H), 7.07 (dd, J = 7.6, 1.2 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 5.14 (s, 2H), 2.31 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.5, 143.4, 141.3, 138.1, 137.9, 136.1, 132.9, 130.7, 130.2, 129.8, 128.5, 128.4, 128.2, 128.0, 127.8, 126.0, 124.8, 124.5, 118.4, 65.9, 15.5. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{23}H_{21}O_2S$: 361.12568, found: 361.12597.



3e

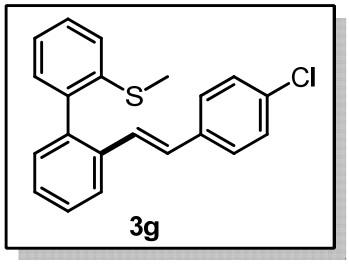
(E)-methyl(2'-(4-methylstyryl)-[1,1'-biphenyl]-2-yl)sulfane. According to the general procedure, **3e** was obtained as a White solid in 41% yield (25.7 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.79 (d, J = 8.0 Hz, 1H), 7.38 (q, J = 8.0Hz, 2H), 7.30-7.28 (m, 2H), 7.24-7.14 (m, 5H), 7.07-6.99 (m, 3H), 6.75 (d, J = 16.0 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 139.5, 139.3, 138.2, 137.3, 136.0, 134.9, 130.4, 129.3, 129.2, 128.1, 127.1, 126.5, 125.9, 124.9, 124.9, 124.5, 21.2, 15.7. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{22}H_{21}S$: 317.13585, found: 317.13604.



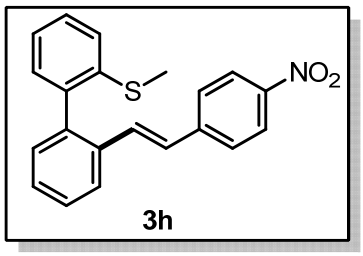
3f

(E)-(2'-(4-fluorostyryl)-[1,1'-biphenyl]-2-yl)(methyl)sulfane. According to the general procedure, **3f** was obtained as a White solid in 49% yield (31.3 mg) by column chromatography

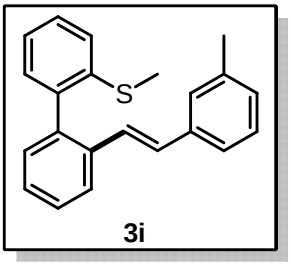
(Petroleum ether: Ethyl acetate = 2 0: 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.77 (d, J = 7.6 Hz, 1H), 7.39 (dq, J = 8.0, 1.2 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.25-7.19 (m, 4H), 7.14 (dd, J = 7.2, 1.2 Hz, 1H), 7.00-6.92 (m, 3H), 6.71 (d, J = 16.0 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 162.2 (d, J = 247.5 Hz), 139.4 (d, J = 16.3 Hz), 138.12, 135.6, 133.8, 130.5, 130.4, 128.2, 128.1, 128.1, 128.0, 128.0, 127.3, 126.6, 124.8 (d, J = 8.6 Hz), 124.5, 115.5, 115.3, 15.6. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{21}H_{18}FS$: 321.11078, found: 321.11058.



(E)-(2'-(4-chlorostyryl)-[1,1'-biphenyl]-2-yl)(methyl)sulfane. According to the general procedure, **3g** was obtained as a White solid in 42% yield (28.3 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **H NMR (400MHz, $CDCl_3$)**: δ = 7.70 (d, J = 7.6 Hz, 1H), 7.32 (dq, J = 8.0, 1.6 Hz, 2H), 7.26-7.21 (m, 2H), 7.18-7.11 (m, 6H), 7.07 (dd, J = 7.6, 1.6 Hz, 1H), 6.90 (d, J = 16.4 Hz, 1H), 6.69 (d, J = 16.4 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 139.6, 139.2, 138.2, 136.1, 135.5, 133.0, 130.5, 130.4, 128.7, 128.2, 128.2, 128.0, 127.7, 127.5, 127.5, 125.0, 124.8, 124.5, 15.6. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{21}H_{18}ClS$: 337.08123, found: 337.08105.

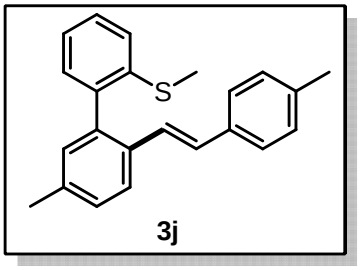


(E)-methyl(2'-(4-nitrostyryl)-[1,1'-biphenyl]-2-yl)sulfane. According to the general procedure, **3h** was obtained as a White solid in 71% yield (49.4 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 8.10 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 7.6 Hz, 1H), 7.44-7.30 (m, 5H), 7.32-7.21 (m, 3H), 7.14 (dd, J = 7.6, 1.6 Hz, 1H), 7.06 (d, J = 16.4 Hz, 1H), 6.96 (d, J = 16.4 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 146.6, 144.1, 140.2, 138.7, 138.2, 134.7, 131.5, 130.6, 130.3, 128.4, 128.3, 126.9, 126.8, 125.2, 124.8, 124.5, 123.9, 15.6. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{21}H_{18}NO_2S$: 348.10528, found: 348.10551.



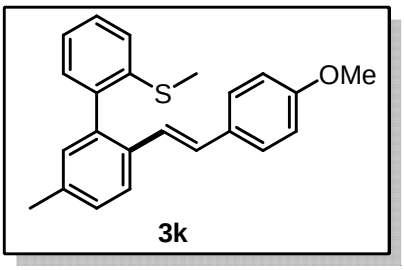
3i

(E)-methyl(2'-(3-methylstyryl)-[1,1'-biphenyl]-2-yl)sulfane. According to the general procedure, **3i** was obtained as a White solid in 50% yield (31.3 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.78 (d, J = 8.0 Hz, 1H), 7.42-7.35 (m, 2H), 7.33-7.28 (m, 2H), 7.25-7.09 (m, 6H), 7.02-6.98 (m, 2H), 6.78 (d, J = 16.0 Hz, 1H), 2.34 (s, 3H), 2.29 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 139.4, 138.1, 138.0, 137.6, 135.9, 130.4, 129.6, 128.4, 128.2, 128.1, 127.5, 127.2, 126.7, 125.0, 124.9, 124.5, 123.5, 21.3, 15.7. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{22}H_{21}S$: 317.13585, found: 317.13607.



3j

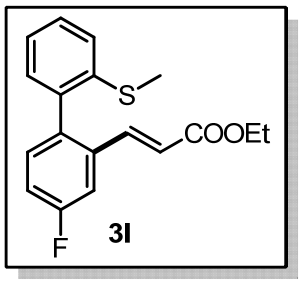
(E)-methyl(5'-methyl-2'-(4-methylstyryl)-[1,1'-biphenyl]-2-yl)sulfane. (In 0.1 mmol scale) According to the general procedure, **3j** was obtained as a White solid in 65% yield (21.3 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.69 (d, J = 7.2 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.22-7.12 (m, 5H), 7.05 (d, J = 7.6 Hz, 3H), 6.95 (d, J = 16.4 Hz, 1H), 6.72 (d, J = 16.4 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 139.4, 139.2, 138.1, 137.0, 136.9, 135.0, 133.1, 130.9, 130.3, 129.2, 129.0, 128.3, 128.0, 126.4, 125.8, 124.7, 124.5, 124.3, 21.2, 15.6. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{23}H_{23}S$: 331.15150, found: 331.15160.



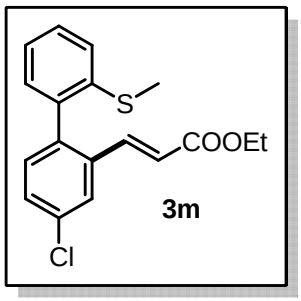
3k

(E)-(2'-(4-methoxystyryl)-5'-methyl-[1,1'-biphenyl]-2-yl)(methyl)sulfane. (In 0.1 mmol scale) According to the general procedure, **3k** was obtained as a White solid in 54% yield (18.6 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.67 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 6.8 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.24-7.13 (m, 5H), 7.03 (s, 1H), 6.94 (d, J = 16.4 Hz, 1H), 6.78 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 16.4 Hz, 1H), 3.762 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ =159.0, 139.5,

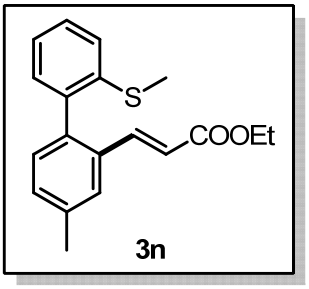
139.1, 138.1, 136.7, 133.2, 130.9, 130.6, 130.3, 129.0, 128.0, 127.8, 127.6, 124.7, 124.5, 124.3, 113.9, 55.2, 21.2, 15.6. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{23}H_{23}OS$: 347.14641, found: 347.14669.



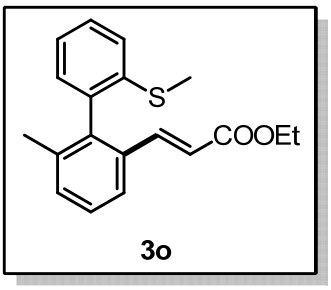
(E)-ethyl 3-(4-fluoro-2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. (In 0.1 mmol scale) According to the general procedure, **3l** was obtained as a White solid in 64% yield (20.1 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.43-7.33 (m, 3H), 7.27-7.18 (m, 3H), 7.13 (dt, *J* = 8.0, 2.8 Hz, 1H), 7.06 (dd, *J*= 7.6, 1.2 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.5, 162.4 (d, *J* = 245.6 Hz), 141.7, 137.6 (d, *J* = 97.7 Hz), 135.1 (d, *J* = 7.7 Hz), 132.5 (d, *J* = 8.1 Hz), 130.4, 128.8, 124.9, 124.6, 120.060, 116.9, 116.7, 112.6, 112.4, 60.4, 15.6, 14.2. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{18}H_{18}FO_2S$: 317.10061, found: 317.10096.



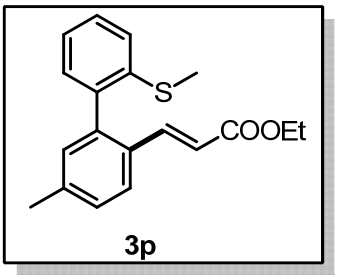
(E)-ethyl 3-(4-chloro-2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. (In 0.1 mmol scale) According to the general procedure, **3m** was obtained as a White solid in 79% yield (26.4 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.70 (d, *J* = 2.0 Hz, 1H), 7.40-7.35 (m, 3H), 7.30 (d, *J* = 12.8 Hz, 1H), 7.21 (q, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.5, 141.4, 139.5, 137.9, 137.1, 134.9, 134.2, 132.2, 130.2, 129.6, 128.8, 126.1, 125.2, 124.7, 120.2, 60.4, 15.6, 14.2. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{18}H_{18}ClO_2S$: 333.07105, found: 333.07173.



(E)-ethyl 3-(4-methyl-2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. (In 0.1 mmol scale) According to the general procedure, **3n** was obtained as a White solid in 82% yield (25.6 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.56 (br, 1H), 7.41 (d, J = 16.0 Hz, 1H), 7.36 (dt, J = 7.2, 0.8 Hz, 1H), 7.27-7.24 (m, 2H), 7.21-7.16 (m, 2H), 7.07 (dd, J = 7.2, 1.2 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.9, 142.9, 138.5, 138.2, 138.0, 137.9, 132.8, 130.7, 130.6, 130.3, 128.4, 126.7, 124.8, 124.5, 118.6, 60.2, 21.3, 15.6, 14.2. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{19}H_{21}O_2S$: 313.12568, found: 313.12633.

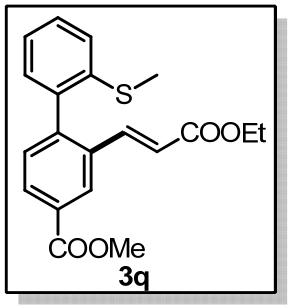


(E)-ethyl 3-(6-methyl-2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. (in 0.1 mmol scale) According to the general procedure, **3o** was obtained as a White solid in 86% yield (26.7 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.60-7.57 (m, 1H), 7.38 (dt, J = 8.0, 1.2 Hz, 1H), 7.33-7.30 (m, 2H), 7.27-7.25 (m, 2H), 7.21 (dt, J = 7.2, 1.2 Hz, 1H), 7.00 (dd, J = 7.6, 1.2 Hz, 1H), 6.30 (d, J = 16.0 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 2.35 (s, 3H), 2.03 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.9, 143.2, 140.6, 137.9, 137.6, 136.8, 133.4, 131.5, 129.6, 128.4, 128.0, 124.7, 124.3, 123.6, 118.8, 60.2, 20.1, 15.1, 14.2. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{19}H_{21}O_2S$: 313.12568, found: 313.12624.



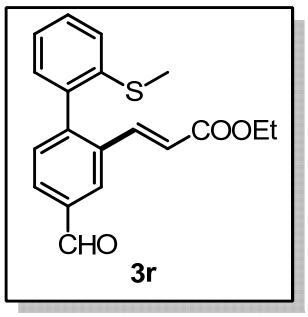
(E)-ethyl 3-(5-methyl-2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. (in 0.1 mmol scale)

According to the general procedure, **3p** was obtained as a White solid in 86% yield (26.8 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.64 (d, J = 8.0 Hz, 1H), 7.42-7.35 (m, 2H), 7.27-7.19 (m, 3H), 7.08 (br, 2H), 6.31 (d, J = 16.0 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 2.39 (s, 3H), 2.35 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.1, 142.8, 141.3, 140.1, 138.4, 137.9, 131.3, 130.3, 130.1, 129.1, 128.4, 126.1, 124.8, 124.5, 117.8, 60.2, 21.4, 15.6, 14.2. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{19}H_{21}O_2S$: 313.12568, found: 313.12614.



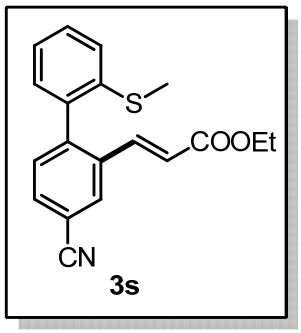
3q

(E)-methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-2'-(methylthio)-[1,1'-biphenyl]-4-carboxylate. (IN 0.1 mmol scale) According to the general procedure, **3q** was obtained as a White solid in 55% yield (19.6 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 8.43 (d, J = 1.2 Hz, 1H), 8.07 (dd, J = 8.0, 1.2 Hz, 1H), 7.44-7.35 (m, 3H), 7.30 (d, J = 7.6 Hz, 1H), 7.22 (dt, J = 7.2, 0.8 Hz, 1H), 7.07 (dd, J = 7.2, 1.2 Hz, 1H), 6.48 (d, J = 16.0 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.96 (s, 3H), 2.36 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.6, 166.4, 145.5, 141.8, 137.6, 137.5, 133.5, 131.1, 130.3, 130.0, 129.9, 129.0, 127.5, 125.4, 124.8, 120.2, 60.4, 52.3, 15.7, 14.2. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{20}H_{21}O_4S$: 357.11551, found: 357.11629.



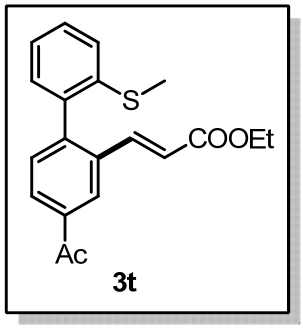
3r

(E)-ethyl 3-(4-formyl-2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. (In 0.1 mmol scale) According to the general procedure, **3r** was obtained as a White solid in 75% yield (24.5 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 10.09 (s, 1H), 8.24 (d, J = 1.2 Hz, 1H), 7.93 (dd, J = 8.0, 1.2 Hz, 1H), 7.47-7.40 (m, 3H), 7.31 (d, J = 7.6 Hz, 1H), 7.23 (dt, J = 7.2, 0.8 Hz, 1H), 7.07 (dd, J = 7.2, 1.2 Hz, 1H), 6.50 (d, J = 16.0 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 191.4, 166.4, 146.9, 141.3, 137.5, 137.2, 136.0, 134.3, 131.8, 130.0, 129.7, 129.1, 127.6, 125.4, 124.9, 120.7, 60.5, 15.7, 14.2. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{19}H_{19}O_3S$: 327.10494, found: 327.10548.



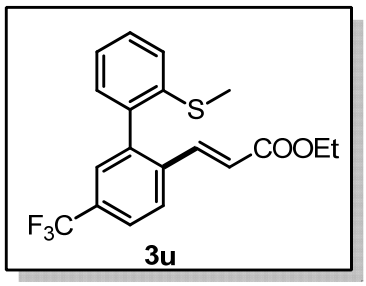
3s

(E)-ethyl 3-(4-cyano-2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. (In 0.1 mmol scale) According to the general procedure, **3s** was obtained as a White solid in 85% yield (27.6 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 8.00 (d, J = 1.2 Hz, 1H), 7.68 (dd, J = 8.0, 1.2 Hz, 1H), 7.43-7.30 (m, 4H), 7.23 (t, J = 7.2 Hz, 1H), 7.04 (dd, J = 7.6, 1.2 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.1, 145.4, 140.4, 137.5, 136.5, 134.7, 132.3, 131.9, 130.0, 129.7, 129.3, 125.5, 124.9, 121.4, 118.2, 112.4, 60.6, 15.7, 14.1. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{19}H_{18}NO_2S$: 324.10528, found: 324.10560.



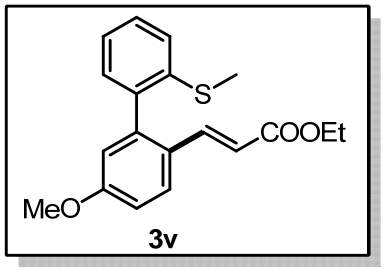
3t

(E)-ethyl 3-(4-acetyl-2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate. (In 0.1 mmol scale) According to the general procedure, **3t** was obtained as a White solid in 56% yield (18.9 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 8.34 (d, J = 1.2 Hz, 1H), 8.00 (dd, J = 8.0, 2.0 Hz, 1H), 7.45-7.38 (m, 3H), 7.30 (d, J = 8.0 Hz, 1H), 7.23 (dt, J = 7.2, 0.8 Hz, 1H), 7.07 (dd, J = 7.2, 1.2 Hz, 1H), 6.48 (d, J = 16.0 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.67 (s, 3H), 2.37 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 197.2, 166.5, 145.6, 141.8, 137.5, 137.4, 136.8, 133.7, 1313, 129.8, 129.1, 129.0, 126.2, 125.4, 124.8, 120.3, 60.5, 26.6, 15.7, 14.2. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{20}H_{21}O_3S$: 341.12059, found: 341.12085.



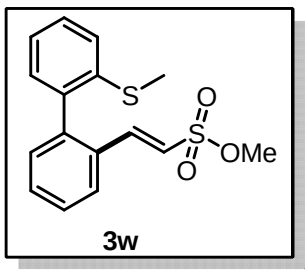
3u

(E)-ethyl 3-(2'-(methylthio)-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)acrylate. (In 0.1 mmol scale) According to the general procedure, **3u** was obtained as a White solid in 40% yield (14.5 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.82 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.55 (s, 1H), 7.43-7.39 (m, 2H), 7.30 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 166.4, 141.5, 141.3, 137.9, 136.9, 136.7, 131.3 (q, J = 32.9 Hz), 130.1, 129.1, 127.9 (q, J = 3.7 Hz), 126.6, 125.2, 124.9 (q, J = 3.3 Hz), 124.8, 122.3 (q, J = 272.9 Hz), 121.2, 60.6, 15.7, 14.2. **HRMS (ESI)**: m/z: $[M+Na]^+$ caculated for $C_{19}H_{17}F_3NaO_2S$: 389.07936, found: 389.07933.



3v

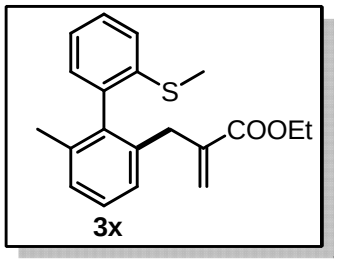
(E)-ethyl 3-(5-methoxy-2'-(methylthio)-[1,1'-biphenyl]-2-yl)acrylate (3v). ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.70 (d, J = 8.8 Hz, 1H), 7.40-7.34 (m, 2H), 7.28-7.26 (m, 1H), 7.20 (J = 7.6 Hz, 1H), 7.09 (dd, J = 7.6, 1.2 Hz, 1H), 6.95 (dd, J = 8.8, 2.7 Hz, 1H), 6.79 (d, J = 2.8 Hz, 1H), 6.24 (d, J = 16.0 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 2.36 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.2, 160.6, 143.0, 142.4, 138.2, 137.9, 130.1, 128.6, 127.7, 125.7, 125.0, 124.6, 116.4, 115.4, 114.6, 60.1, 55.4, 15.6, 14.2. **HRMS (ESI)**: m/z: $[M+Na]^+$ caculated for $C_{19}H_{20}NaO_3S$: 351.10254, found: 351.10286.



3w

(E)-methyl 2-(2'-(methylthio)-[1,1'-biphenyl]-2-yl)ethenesulfonate. (In 0.1 mmol scale) According to the general procedure, **3w** was obtained as a White solid in 58% yield (18.4 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (500MHz, $CDCl_3$)**: δ = 7.64 (d, J = 8.0 Hz, 1H), 7.51-7.45 (m, 2H), 7.40 (dt, J = 8.0, 1.5 Hz, 1H), 7.34 (d, J

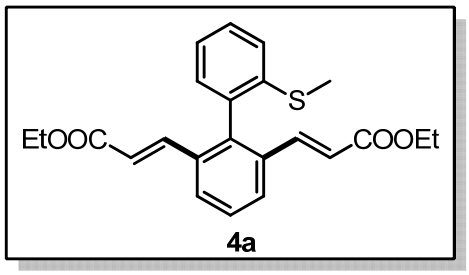
=15.5 Hz, 1H), 7.30 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.22 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.09 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.49 (d, *J* = 15.5 Hz, 1H), 372 (s, 3H), 2.35 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 143.9, 141.5, 137.9, 137.6, 131.1, 131.0, 130.9, 130.0, 129.0, 128.5, 127.0, 125.1, 124.9, 121.1, 56.0, 15.5. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{16}H_{17}O_3S_2$: 321.06136, found: 321.06193.



3x

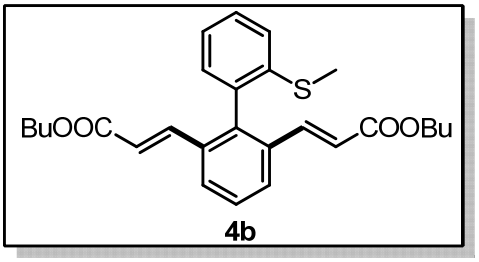
(S)-ethyl 2-((6-methyl-2'-(methylthio)-[1,1'-biphenyl]-2-yl)methyl)acrylate. According to the general procedure, **3x** was obtained as a oil in 30% yield (9.8 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1 to 10:1). **^{1}H NMR (400MHz, $CDCl_3$)**: *δ* = 7.33 (t, *J* = 7.2 Hz, 1H), 7.24-7.21 (m, 2H), 7.16 (d, *J* = 6.8 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.13 (s, 1H), 5.17 (d, *J* = 1.2 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.38 (d, *J* = 16.4, Hz, 1H), 3.27 (d, *J* = 16.4 Hz, 1H), 2.36 (s, 3H), 2.00 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.0, 139.9, 139.5, 138.1, 138.0, 137.3, 136.9, 129.6, 128.0, 127.9, 127.8, 127.1, 126.4, 124.4, 123.9, 60.5, 35.4, 20.2, 14.9, 14.1. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{20}H_{23}O_2S$: 327.14133, found: 327.14177.

3. Characterization of di-alkenylation product 4



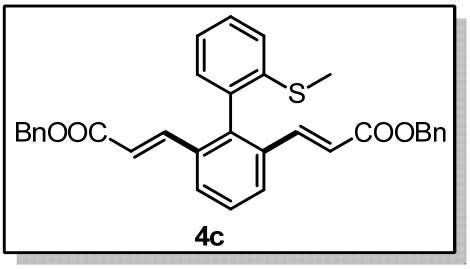
4a

(2E,2'E)-diethyl 3,3'-(2'-(methylthio)-[1,1'-biphenyl]-2,6-diyl)diacrylate. According to the general procedure, **4a** was obtained as a White solid in 80% yield (63.1 mg) by column chromatography (Petroleum ether: Ethyl acetate = 20 : 1). **^{1}H NMR (400MHz, $CDCl_3$)**: *δ* = 7.74 (d, *J* = 8.0 Hz, 2H), 7.42 (q, *J* = 8.0 Hz, 2H), 7.30-7.20 (m, 4H), 7.00 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 4H), 2.34 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.5, 142.3, 141.2, 138.2, 134.9, 134.4, 130.3, 129.1, 128.4, 127.5, 124.8, 124.8, 119.8, 60.2, 15.3, 14.1. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{23}H_{25}O_4S$: 397.14681, found: 397.14749.



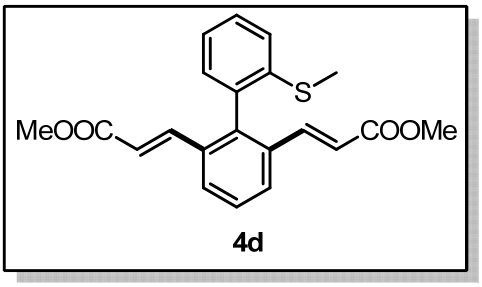
4b

(2E,2'E)-dibutyl 3,3'-(2'-(methylthio)-[1,1'-biphenyl]-2,6-diyl)diacrylate. According to the general procedure, **4b** was obtained as a White solid in 86% yield (78.0 mg) by column chromatography (Petroleum ether: Ethyl acetate = 10 : 1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.67 (d, J = 8.0 Hz, 2H), 7.34 (q, J = 8.0 Hz, 2H), 7.22-7.14 (m, 4H), 6.91 (d, J = 7. 2 Hz, 1H), 6.25 (d, J = 16.0 Hz, 2H), 4.00 (t, J = 7.2 Hz, 4H), 2.25 (s, 3H), 1.50-1.45 (m, 4H), 1.26-1.21 (m, 4H), 0.81 (t, J = 7.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.5, 142.2, 141.2, 138.2, 134.9, 134.3, 130.3, 129.0, 128.4, 127.4, 124.7, 119.7, 64.1, 30.5, 19.0, 15.3, 13.6. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{27}H_{33}O_4S$: 453.20941, found: 453.20958.



4c

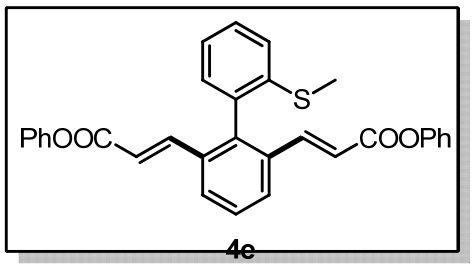
(2E,2'E)-dibenzyl 3,3'-(2'-(methylthio)-[1,1'-biphenyl]-2,6-diyl)diacrylate. According to the general procedure, **4c** was obtained as a White solid in 82% yield (84.9 mg) by column chromatography (Petroleum ether: Ethyl acetate = 10 : 1 to 5:1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.72 (d, J = 8.0 Hz, 2H), 7.42-7.37 (m, 3H), 7.33-7.21 (m, 13H), 6.98 (d, J = 7. 2 Hz, 1H), 6.37 (d, J = 16.0 Hz, 2H), 5.11 (s, 4H), 2.27 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.1, 142.8, 141.4, 138.3, 135.9, 134.7, 134.2, 130.3, 129.0, 128.4, 128.4, 127.9, 127.7, 127.6, 124.7, 124.6, 119.3, 65.9, 15.2. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{33}H_{29}O_4S$: 521.17811, found: 521.17763.



4d

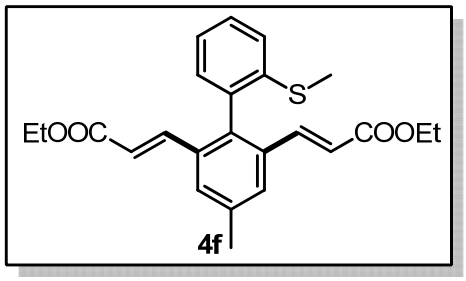
(2E,2'E)-dimethyl 3,3'-(2'-(methylthio)-[1,1'-biphenyl]-2,6-diyl)diacrylate. According to the general procedure, **4d** was obtained as a White solid in 56% yield (41.2 mg) by column chromatography (Petroleum ether: Ethyl acetate = 10 : 1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.74 (d, J = 7.6 Hz, 2H), 7.44 (q, J = 8.0 Hz, 2H), 7.30-7.21 (m, 4H), 7.00 (dd, J = 7.6, 1.2 Hz, 1H), 6.32 (d, J = 16.0 Hz, 2H), 3.68 (s, 6H), 2.34 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 166.9,

142.5, 141.2, 138.3, 134.9, 134.5, 130.3, 129.2, 128.5, 127.7, 125.0, 124.9, 119.5, 51.5, 15.4. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{21}H_{21}O_4S$: 369.11551, found: 369.11601.



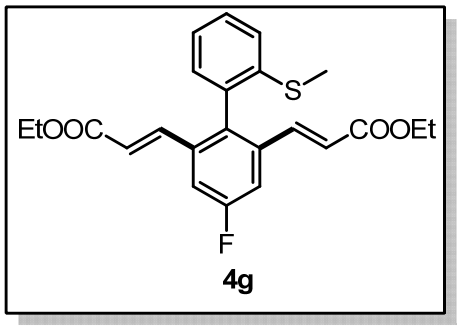
4e

(2E,2'E)-diphenyl 3,3'-(2'-(methylthio)-[1,1'-biphenyl]-2,6-diyl)diacrylate. According to the general procedure, **4e** was obtained as a White solid in 86% yield (84.5 mg) by column chromatography (Petroleum ether: Ethyl acetate = 10 : 1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.86 (d, J = 8.0 Hz, 2H), 7.52-7.17 (m, 13H), 7.06 (d, J = 8.0 Hz, 4H), 6.54 (d, J = 16.0 Hz, 2H), 2.26 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 164.9, 150.7, 144.2, 141.8, 138.2, 134.4, 134.2, 130.3, 129.4, 129.2, 128.6, 128.2, 125.6, 124.9, 124.8, 121.5, 118.9, 15.3. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{31}H_{25}O_4S$: 493.14681, found: 493.14801.



4f

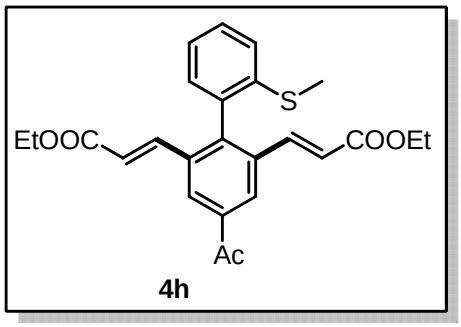
(2E,2'E)-diethyl 3,3'-(4-methyl-2'-(methylthio)-[1,1'-biphenyl]-2,6-diyl)diacrylate. (0.1 mmol scale) According to the general procedure, **4f** was obtained as a White solid in 87% yield (35.7 mg) by column chromatography (Petroleum ether: Ethyl acetate = 10 : 1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.58 (s, 2H), 7.40 (t, J = 7.2 Hz, 1H), 7.28-7.19 (m, 4H), 6.98 (d J = 7.6 Hz, 1H), 6.32 (d, J = 16.0 Hz, 2H), 4.14 (q, J = 7.2 Hz, 4H), 2.44 (s, 3H), 2.34 (s, 3H), 1.23 (t, J = 7.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.6, 142.5, 138.7, 138.4, 138.1, 134.9, 134.2, 130.6, 129.0, 128.4, 124.8, 119.5, 60.3, 21.3, 15.4, 14.2. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{24}H_{27}O_4S$: 411.16246, found: 411.16325.



4g

(2E,2'E)-diethyl 3,3'-(4-fluoro-2'-(methylthio)-[1,1'-biphenyl]-2,6-diyl)diacrylate. (In 0.1

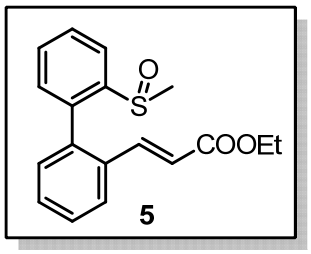
mmol scale) According to the general procedure, **4g** was obtained as a White solid in 89% yield (36.9 mg) by column chromatography (Petroleum ether: Ethyl acetate = 10 : 1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.44-7.42 (m, 3H), 7.28 (d, J = 8.0 Hz, 1H), 7.24-7.19 (m, 3H), 6.97 (d, J = 6.8 Hz, 1H), 6.32 (d, J = 16.0 Hz, 2H), 4.15 (q, J = 7.2 Hz, 4H), 2.35 (s, 3H), 1.24 (t, J = 7.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 166.2, 162.3 (d, J = 245.7 Hz), 141.2 (d, J = 2.5 Hz), 138.6, 137.3 (d, J = 2.9 Hz), 136.6 (d, J = 7.8 Hz), 134.0, 130.6, 129.4, 124.9, 124.8, 120.9, 114.1 (d, J = 22.3 Hz), 60.5, 15.3, 14.1. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{23}H_{24}FO_4S$: 415.13738, found: 415.13735.



4h

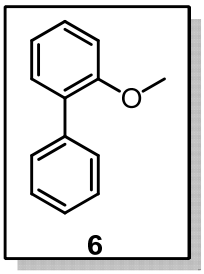
(2E,2'E)-diethyl 3,3'-(4-acetyl-2'-(methylthio)-[1,1'-biphenyl]-2,6-diyl)diacrylate. (In 0.1 mmol scale) According to the general procedure, **4h** was obtained as a White solid in 68% yield (29.9 mg) by column chromatography (Petroleum ether: Ethyl acetate = 10 : 1). **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 8.30 (s, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.33-7.24 (m, 4H), 6.97 (d J = 7.2 Hz, 1H), 6.44 (d, J = 16.0 Hz, 2H), 4.16 (q, J = 7.2 Hz, 4H), 2.70 (s, 3H), 2.36 (s, 3H) 1.26 (t, J = 7.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 196.8, 166.3, 145.2, 141.5, 137.8, 136.9, 135.2, 134.3, 129.9, 129.6, 127.0, 125.3, 125.1, 121.1, 60.5, 26.6, 15.5, 14.1. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{25}H_{27}O_5S$: 439.15737, found: 439.15869.

4. Characterization of transformation product 5 and ether directing groups

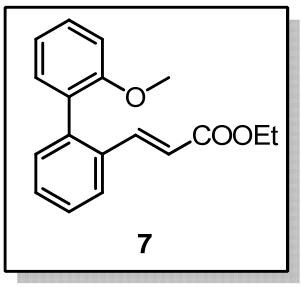


5

(E)-ethyl 3-(2'-(methylsulfinyl)-[1,1'-biphenyl]-2-yl)acrylate (5). Colorless oil. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 8.17-8.12 (m, 1H), 7.78-7.66 (m, 2H), 7.61-7.54 (m, 1H), 7.49-7.36 (m, 4H), 7.25-7.14 (m, 1H), 6.39 (d, J = 16.0 Hz, 0.59H), 6.32 (d, J = 16.0 HZ, 0.40H), 4.18-4.14 (m, 2H), 2.41 (s, 1.16H), 2.38 (s, 1.75H), 1.28-1.24 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 166.4, 166.2, 144.7, 144.4, 141.6, 141.2, 138.0, 137.9, 136.8, 133.3, 132.9, 131.2, 131.0, 130.8, 130.6, 130.2, 129.9, 129.7, 129.6, 129.5, 129.0, 126.9, 126.7, 123.9, 123.3, 120.7,2, 60.6, 60.5, 42.4, 41.4, 14.2, 14.1. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{18}H_{19}O_3S$: 315.10494, found: 315.10505.

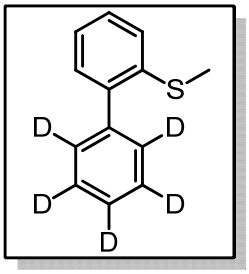


2-methoxy-1,1'-biphenyl (6). Colorless oil. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.53 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.34-7.24 (m, 3H), 7.05-6.97 (m, 2H), 3.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 156.5, 138.5, 130.9, 130.7, 129.5, 128.6, 128.0, 126.9, 120.8, 111.2, 55.5.



(E)-ethyl 3-(2'-methoxy-[1,1'-biphenyl]-2-yl)acrylate (7). White solid. **^{1}H NMR (400MHz, $CDCl_3$)**: δ = 7.68 (d, J = 16.0 Hz, 1H), 7.52-7.49 (m, 4H), 7.42 (t, J = 7.2 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.3, 158.2, 144.1, 137.7, 131.2, 130.5, 129.4, 129.0, 128.1, 127.3, 127.2, 116.1, 111.3, 60.3, 55.7, 14.3. **HRMS (ESI)**: m/z: $[M+H]^+$ caculated for $C_{18}H_{19}O_3$: 283.13287, found: 283.13340.

5. Characterization of mechanism study



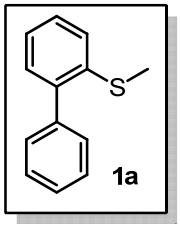
D5-1a. White solid.
^{1}H NMR (400MHz, $CDCl_3$): δ = 7.35-7.29 (m, 2H), 7.23-7.19 (m, 2H), 2.36 (s, 3H).
^{1}H NMR (400MHz, CD_3COCD_3): δ = 7.23-7.21 (m, 2H), 7.08-7.06 (m, 2H), 2.23 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.0, 140.4, 137.2, 130.0, 129.3, 129.2, 128.9, 128.7, 128.1, 127.9, 127.9, 127.6, 127.4, 127.0, 126.9, 125.3, 124.8, 16.0.

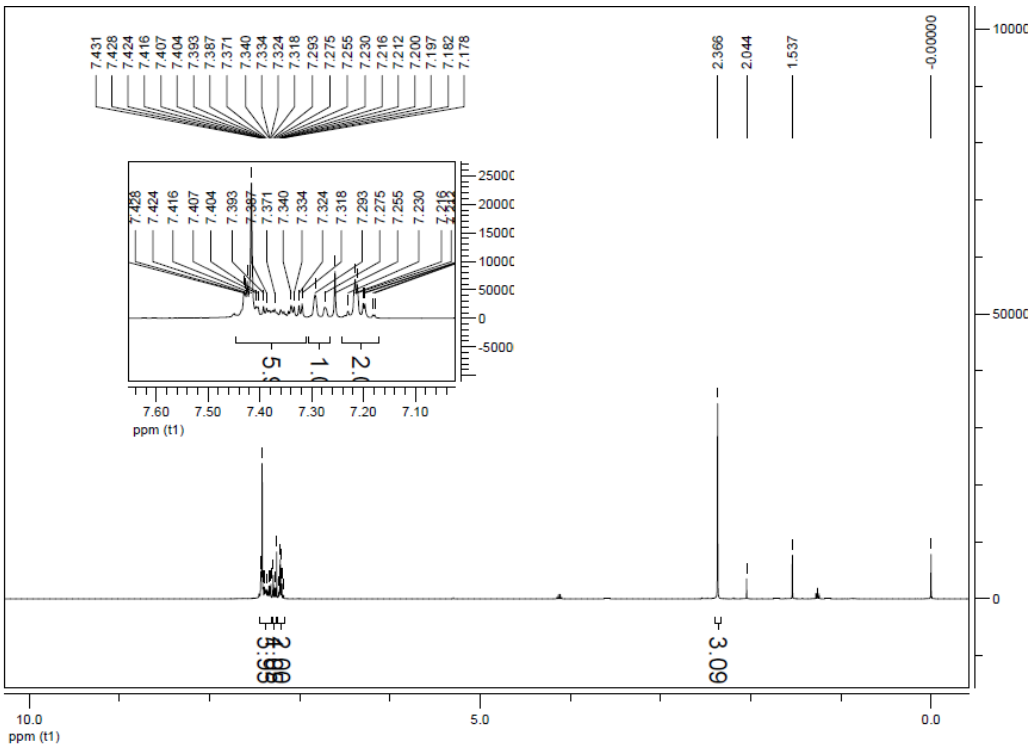
References:

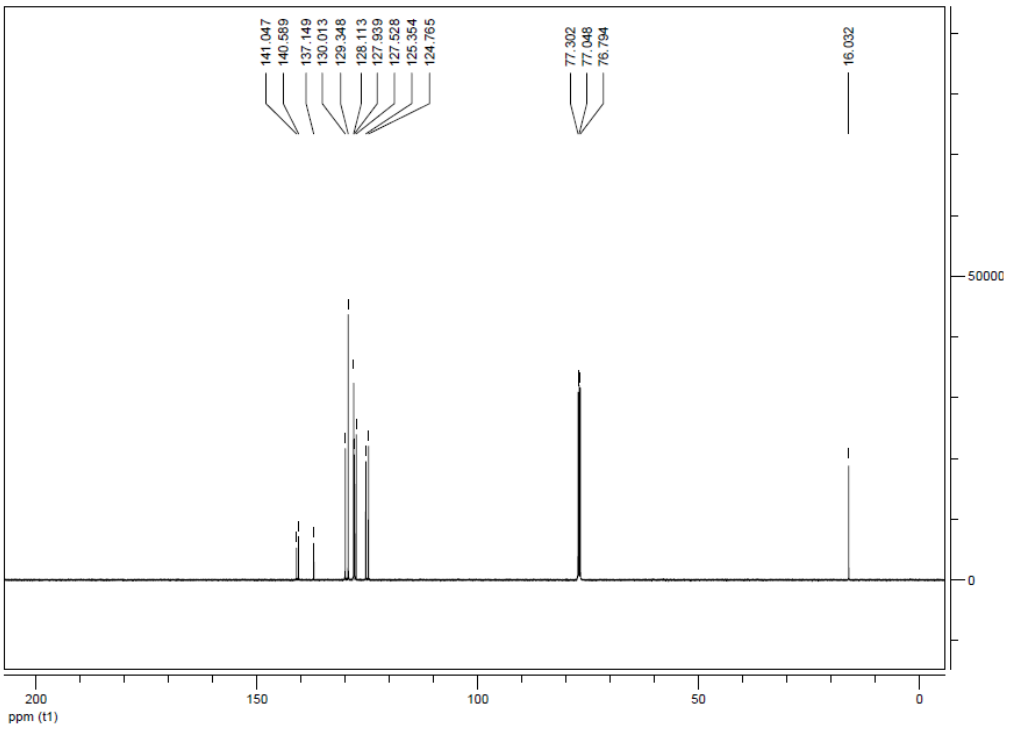
[1] S.-R. Guo and Y.-Q. Yuan, *Journal of Chemical Research*, 2009, **2009**, 745.

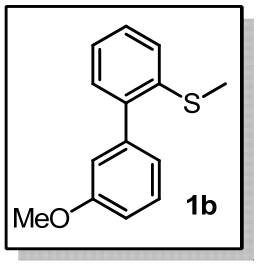
NMR Spectrum

1.Characterization of some sulfide substrates 1





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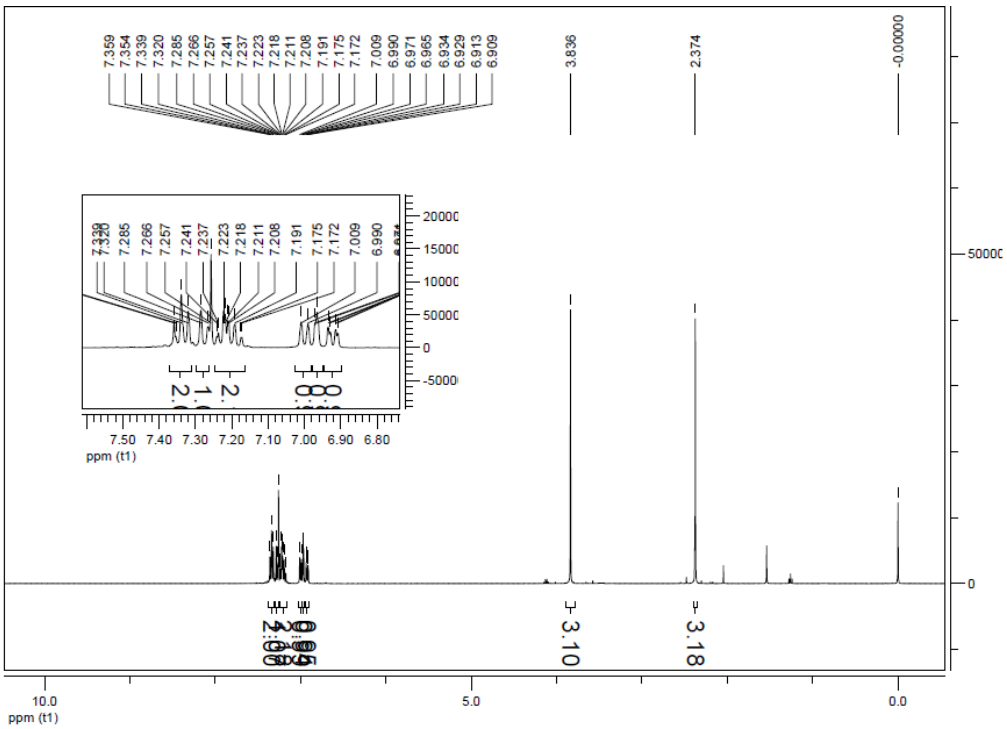
MeO
1b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7.172
7.009
6.990
6.971
6.965
6.934
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ppm (t1)
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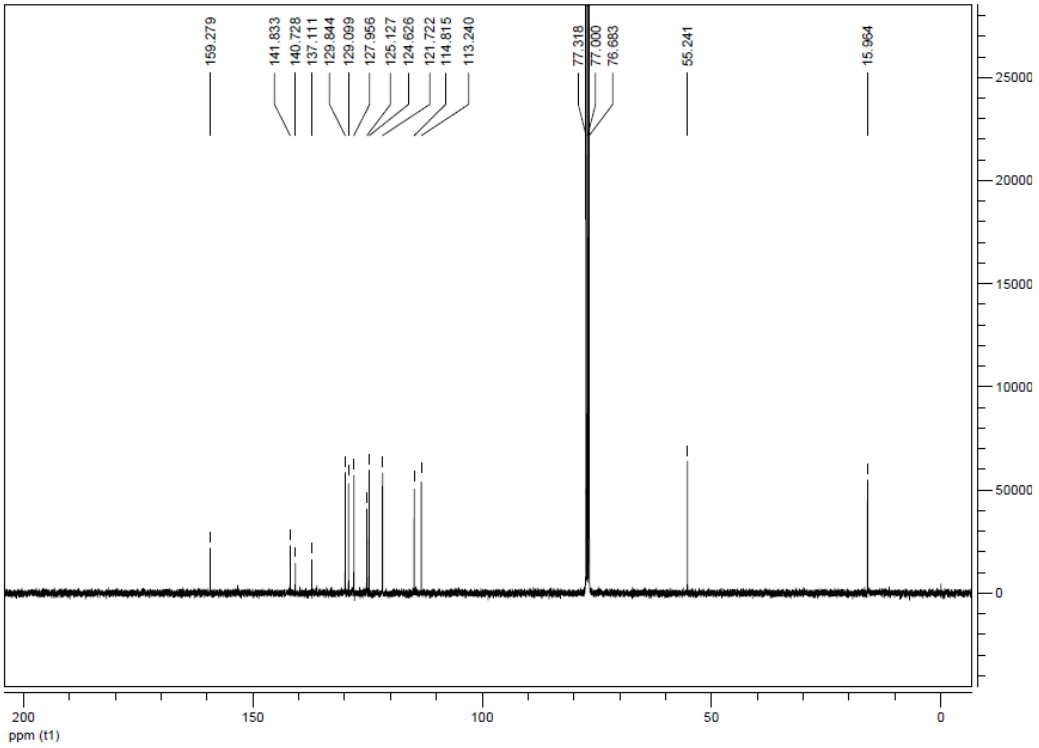
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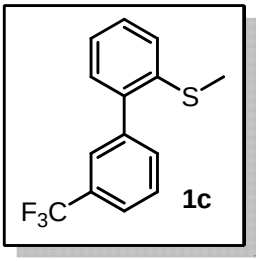
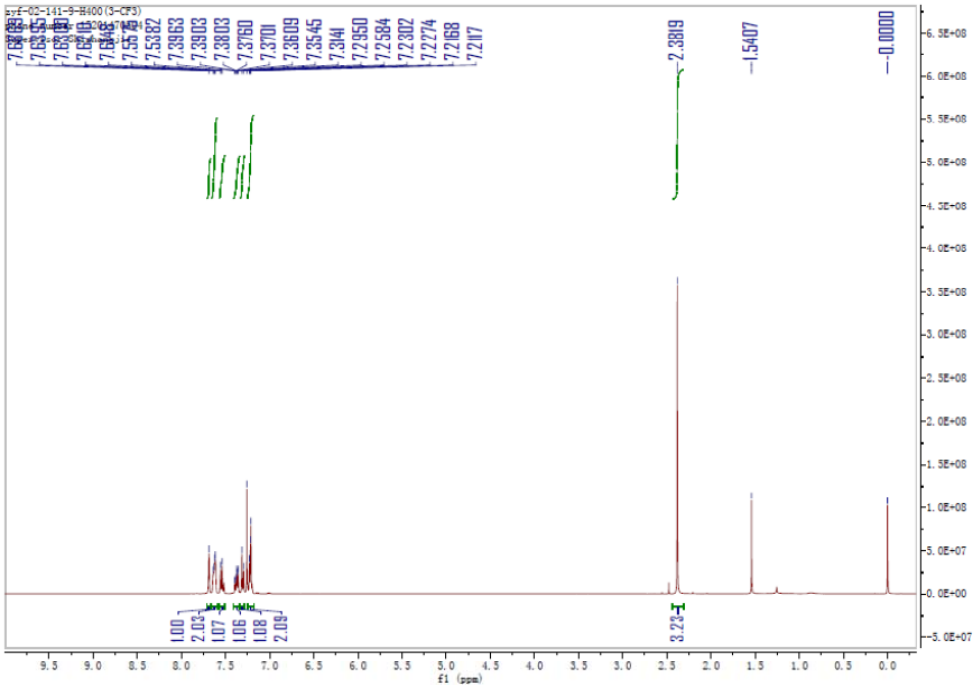

S
F3C
1c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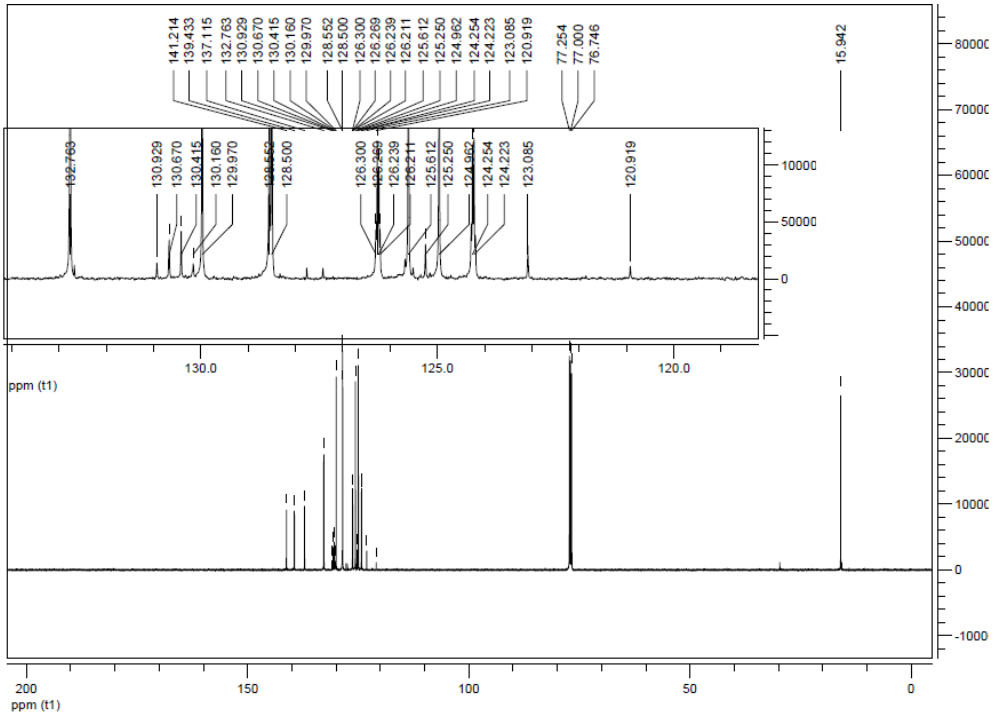
0.0000
f1 (ppm)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126.239
126.211
125.612
125.250
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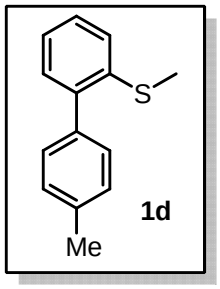
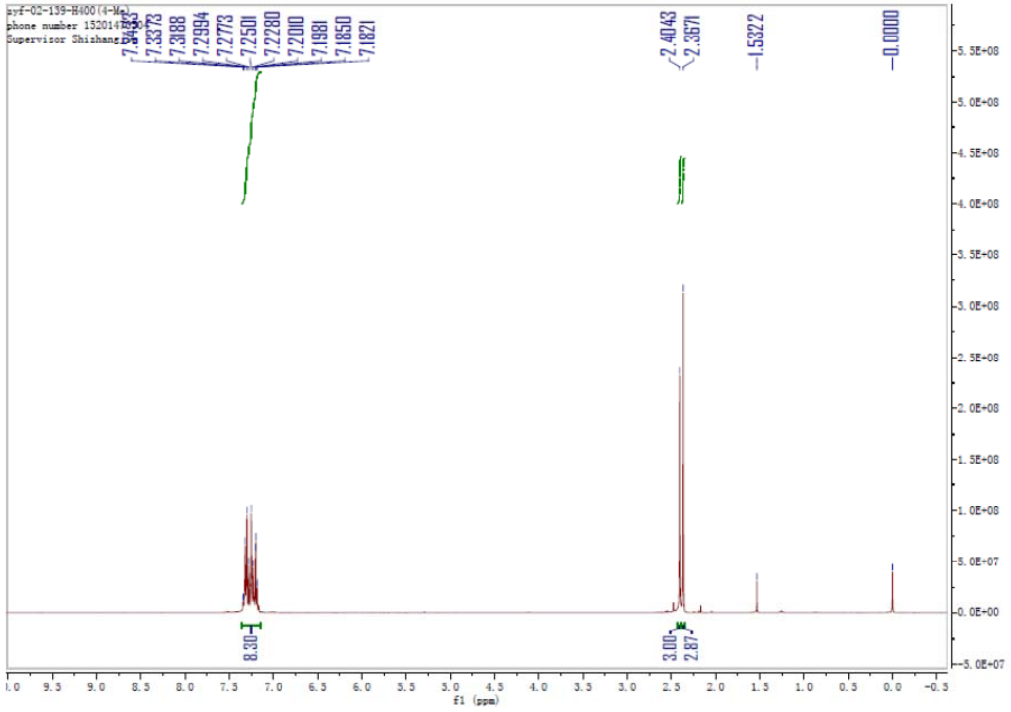
ppm (t1)
ppm (t1)


S
Me

1d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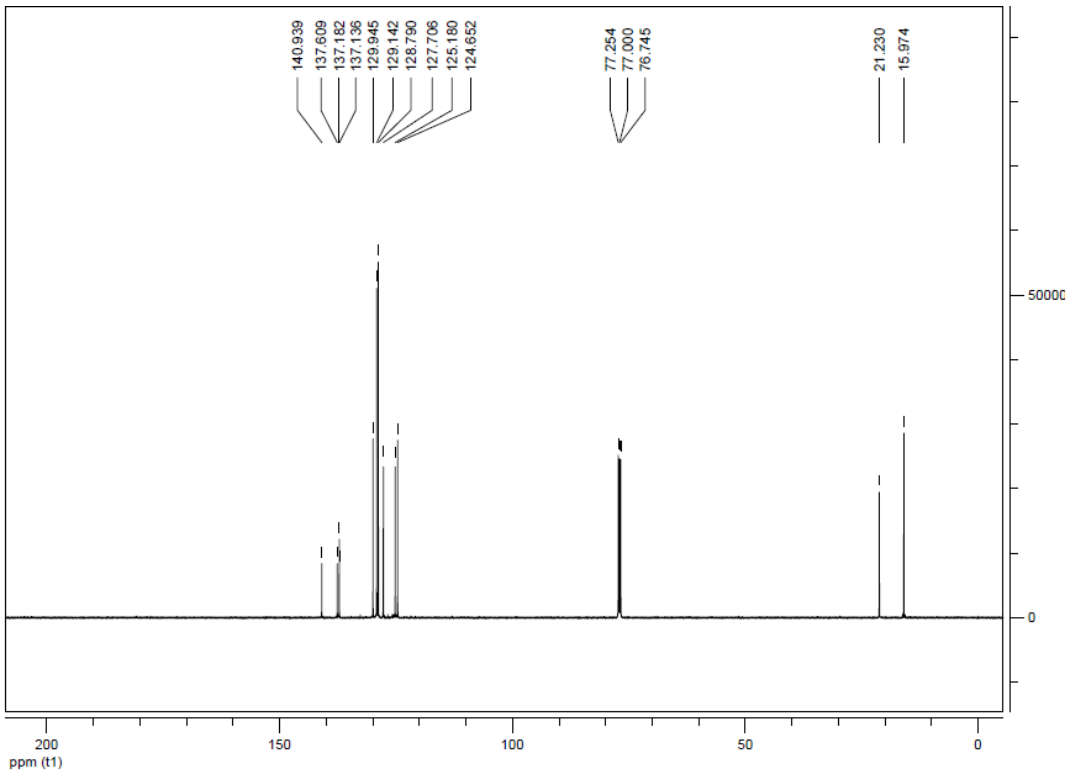
2.87
f1 (ppm)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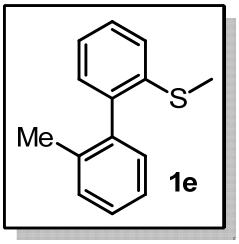
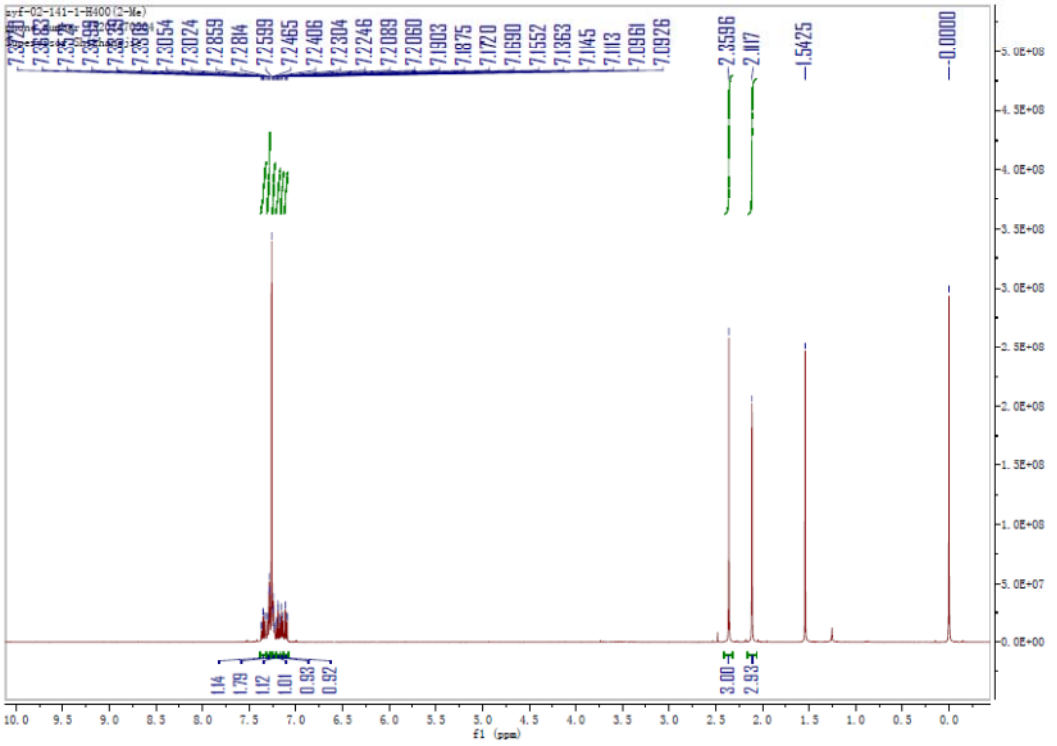
ppm (t1)


S
Me
1e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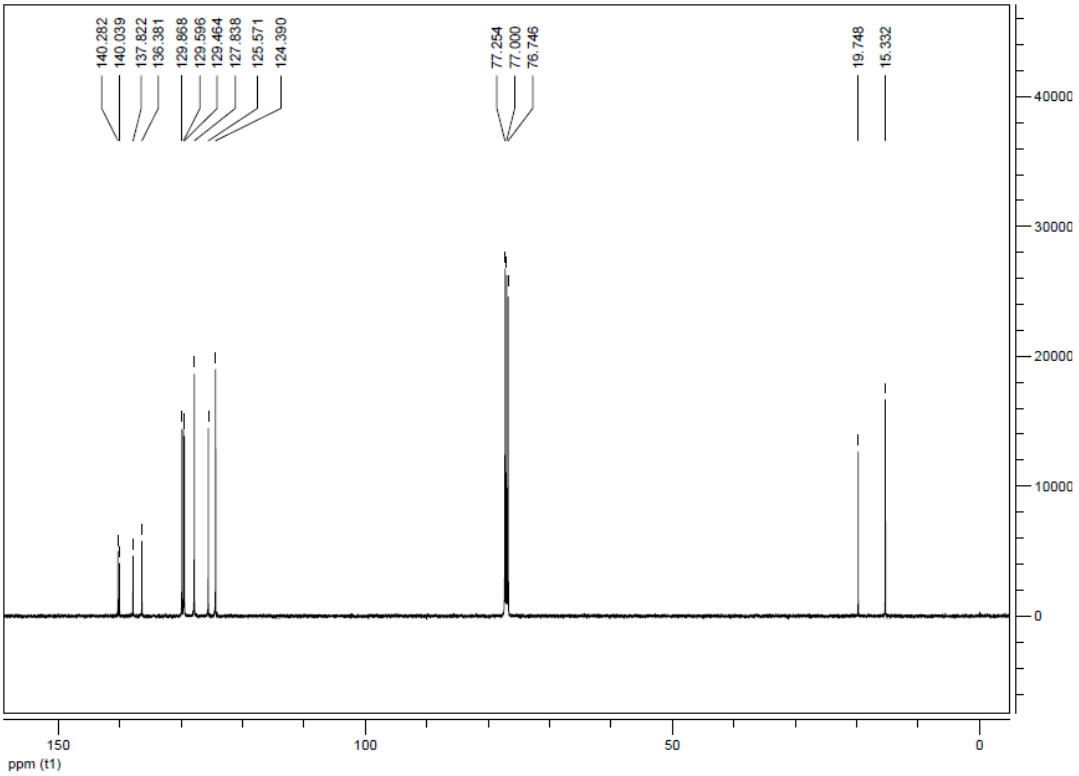
f1 (ppm)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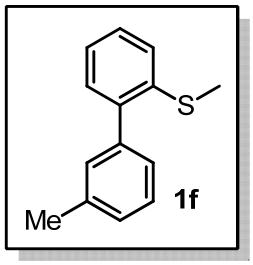
ppm (t1)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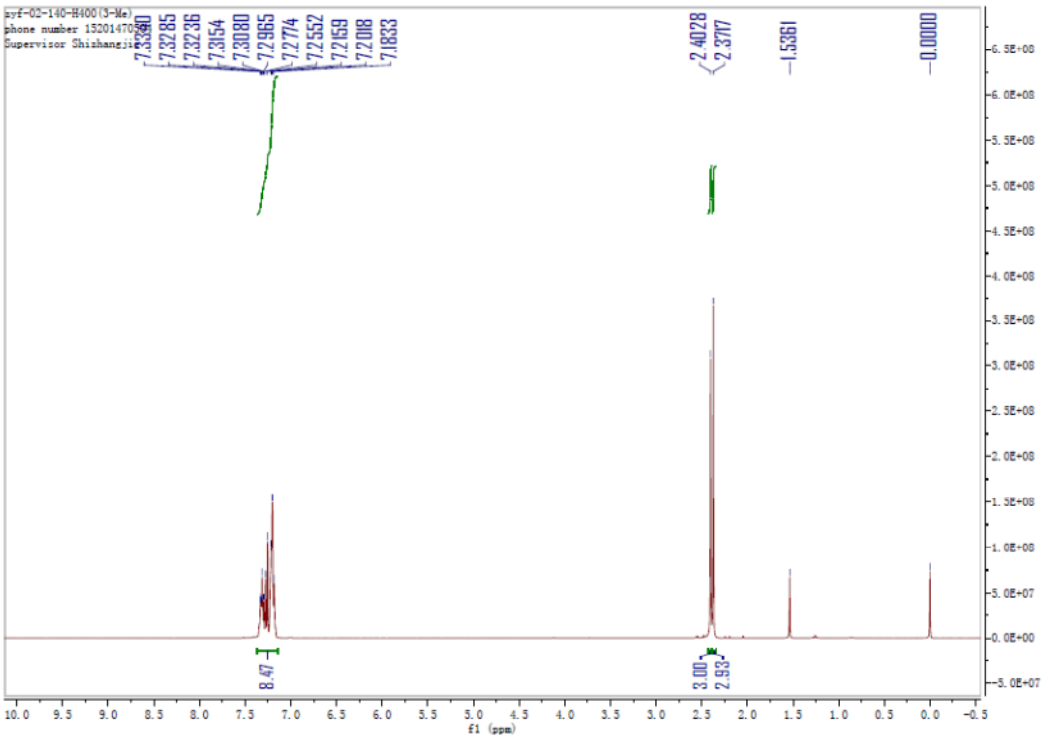
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Supervisor Shizhangji
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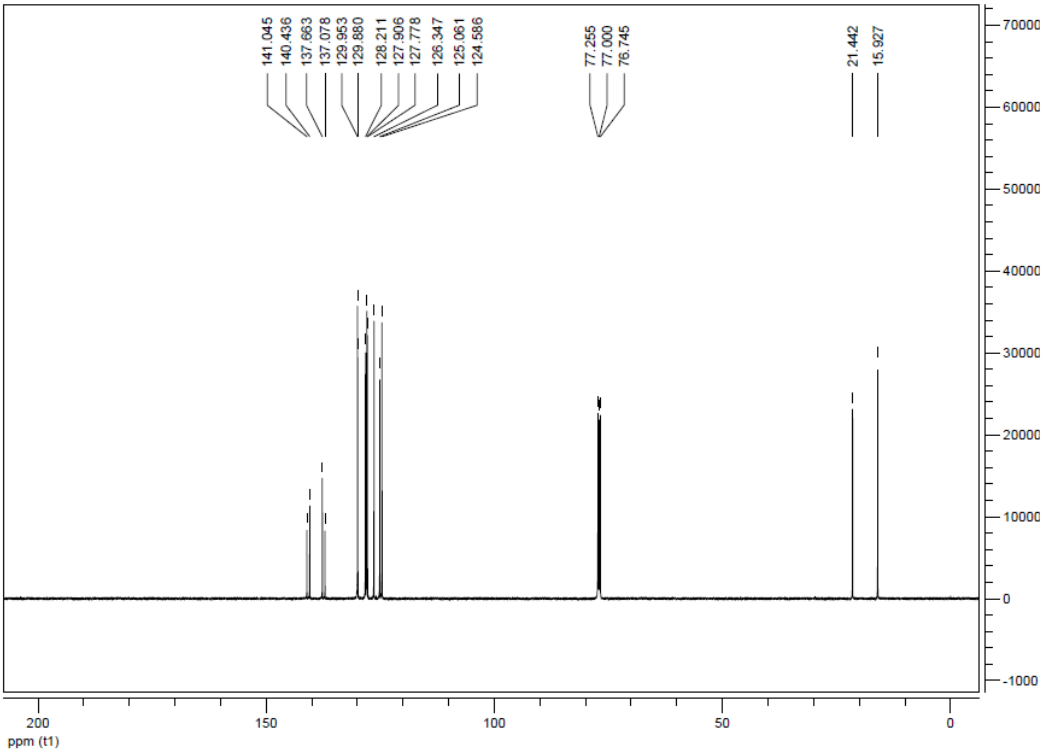
f1 (ppm)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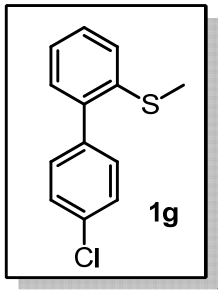
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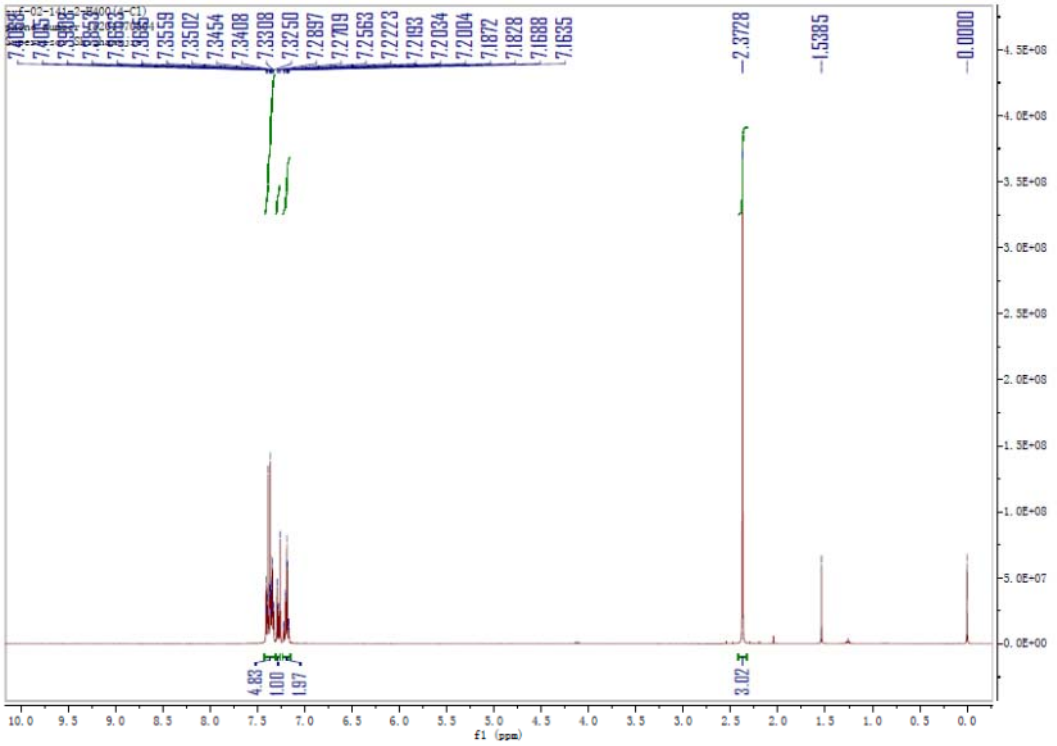
1g
Cl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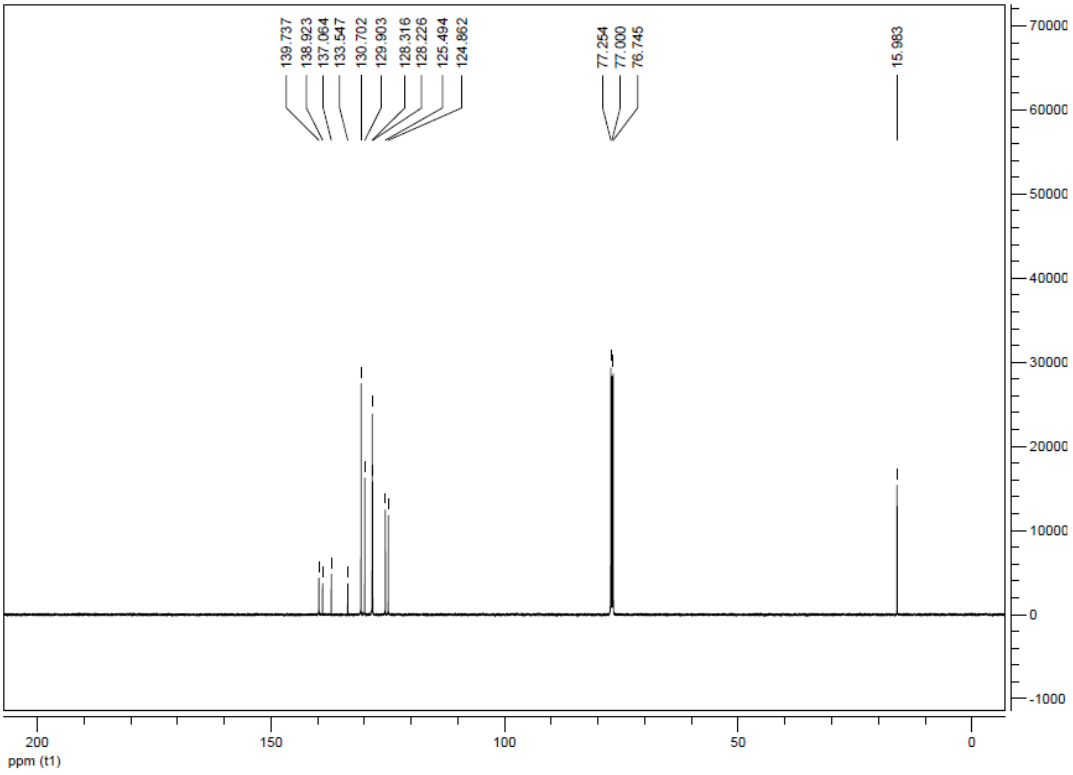
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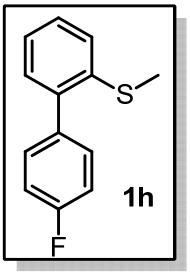
S
1h
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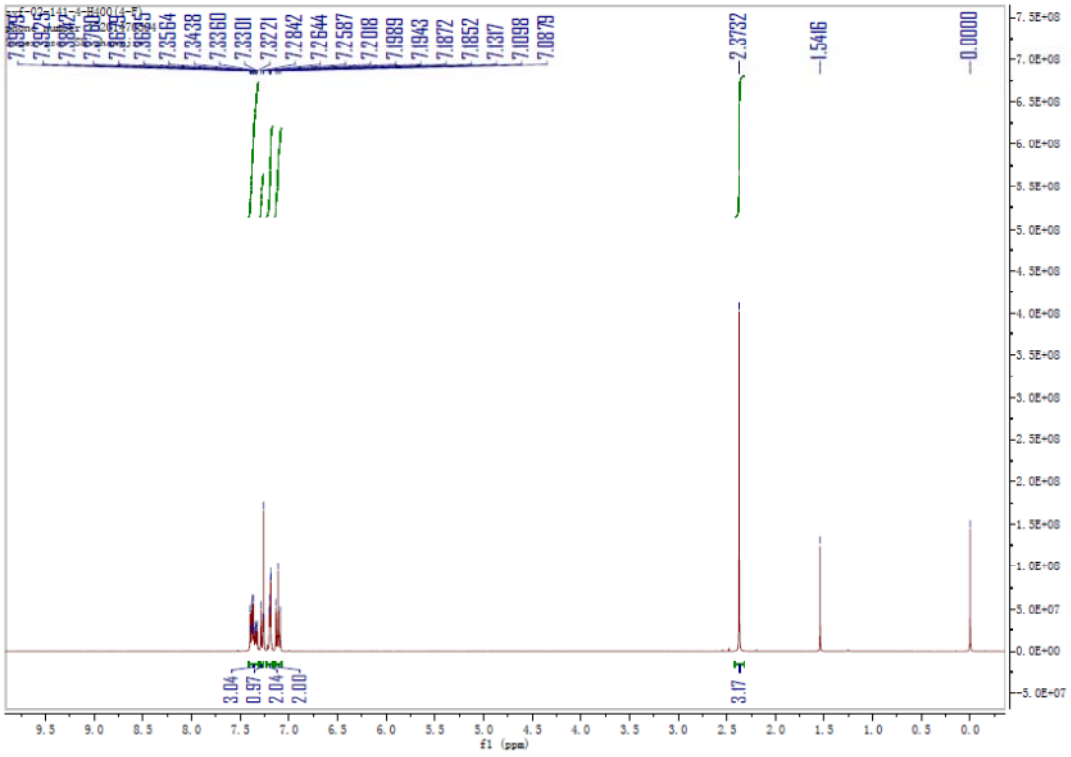
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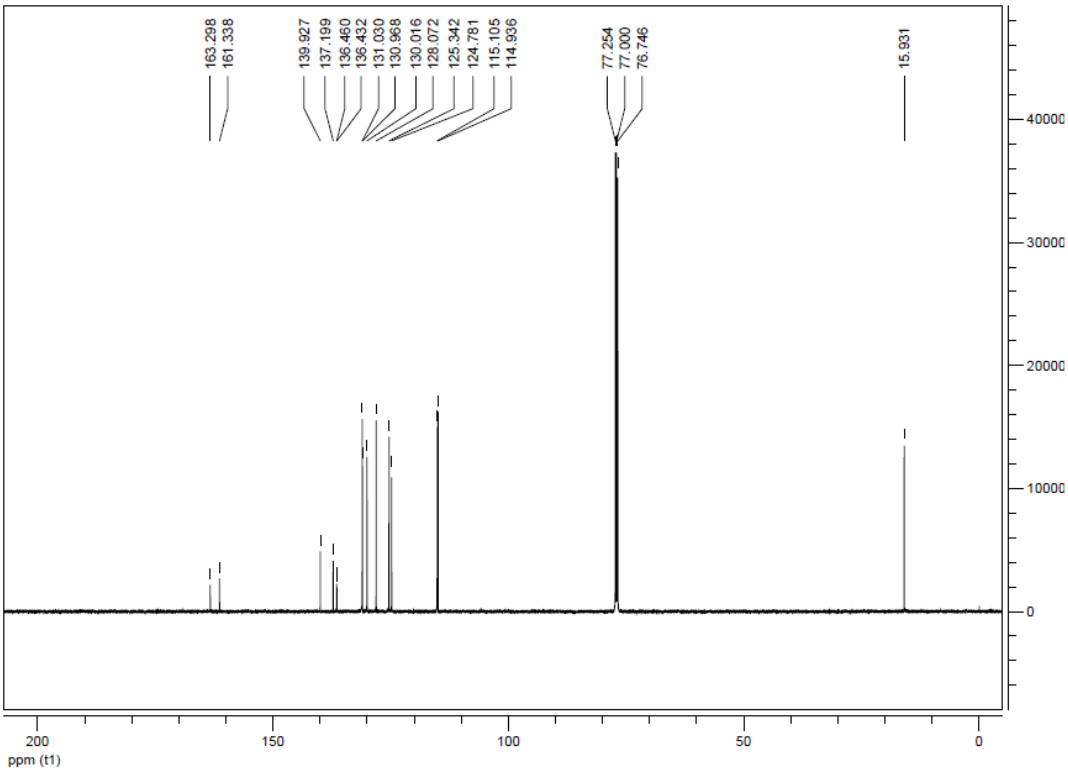
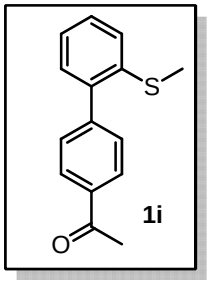
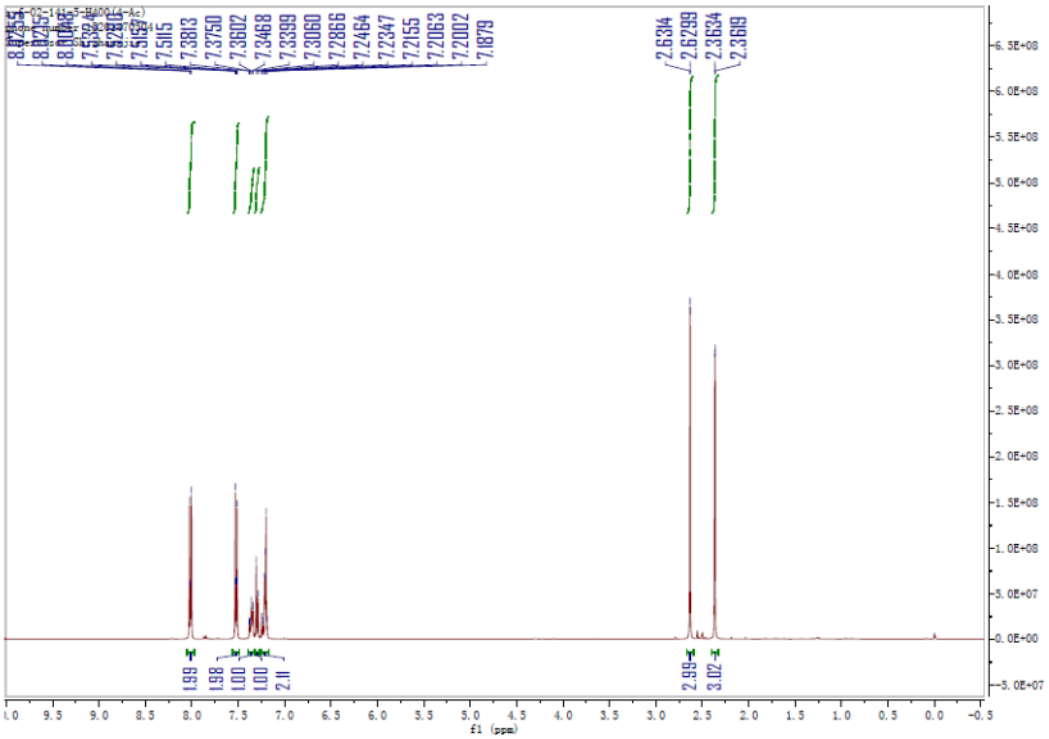
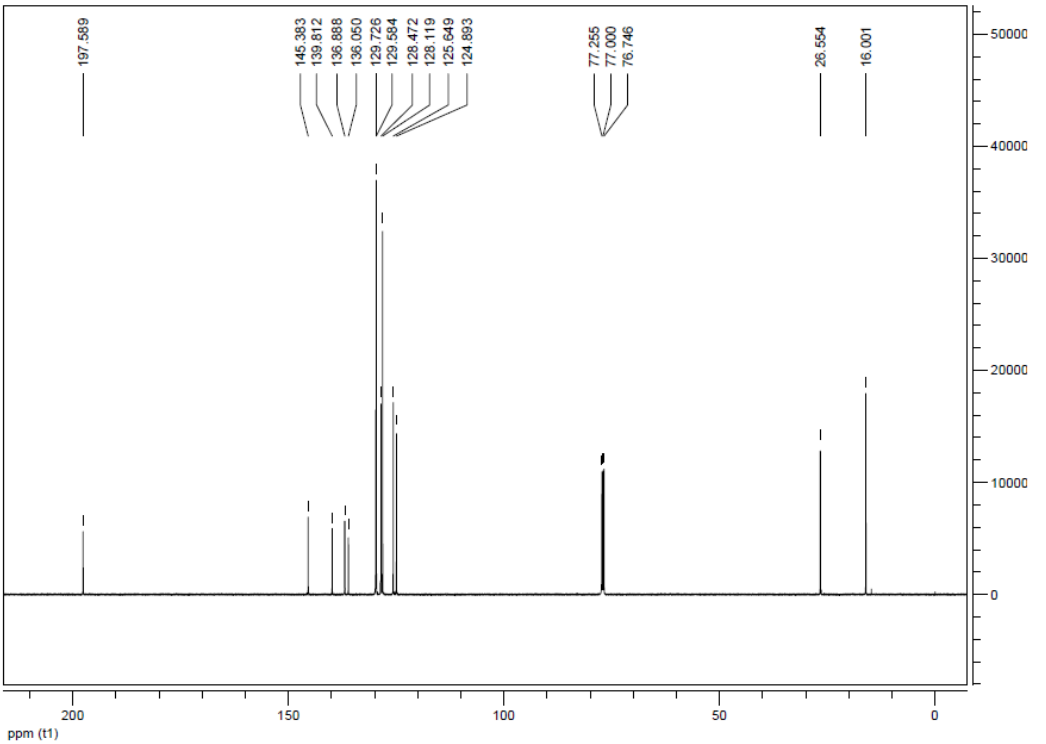
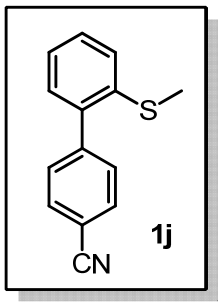
2.00
3.17
f1 (ppm)

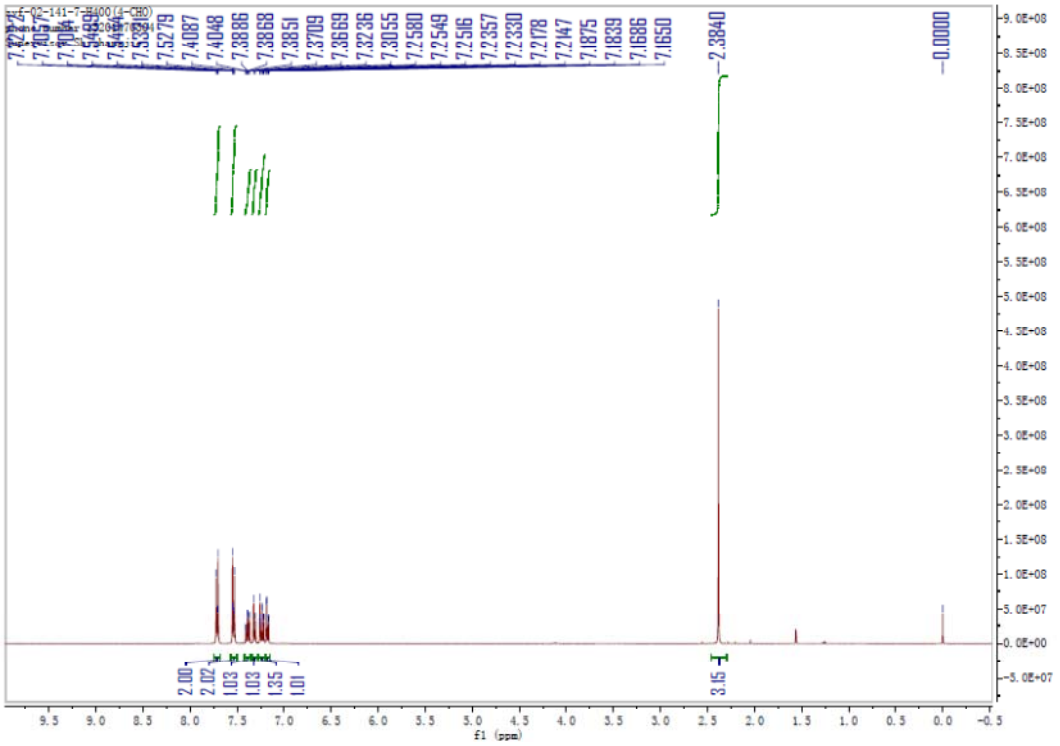

163.298
161.338
139.927
137.199
136.460
136.432
131.030
130.968
130.016
128.072
125.342
124.781
115.105
114.936
77.254
77.000
76.746
15.931
ppm (t1)

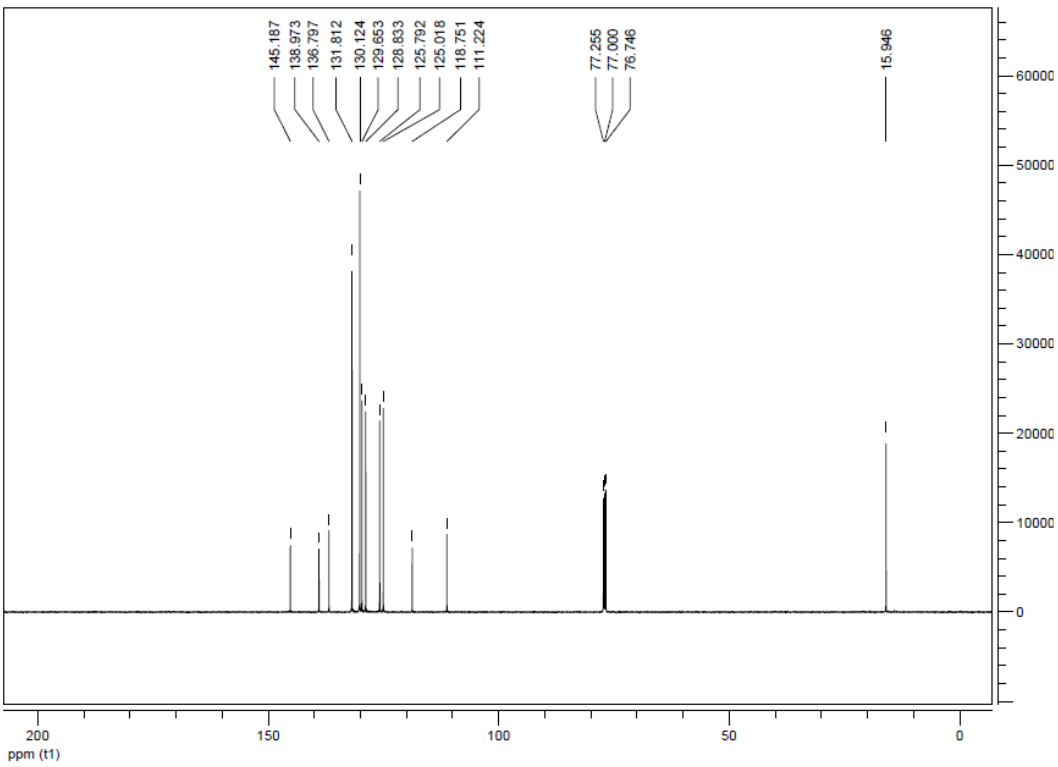

S
O
1i

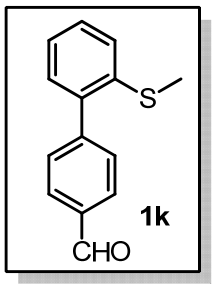

7.3813
7.3750
7.3602
7.3468
7.3399
7.3060
7.2866
7.2464
7.2347
7.2155
7.2063
7.2002
7.1879
2.6314
2.6299
2.3634
2.3619
1.99
1.98
1.00
1.00
2.11
2.99
3.02
f1 (ppm)

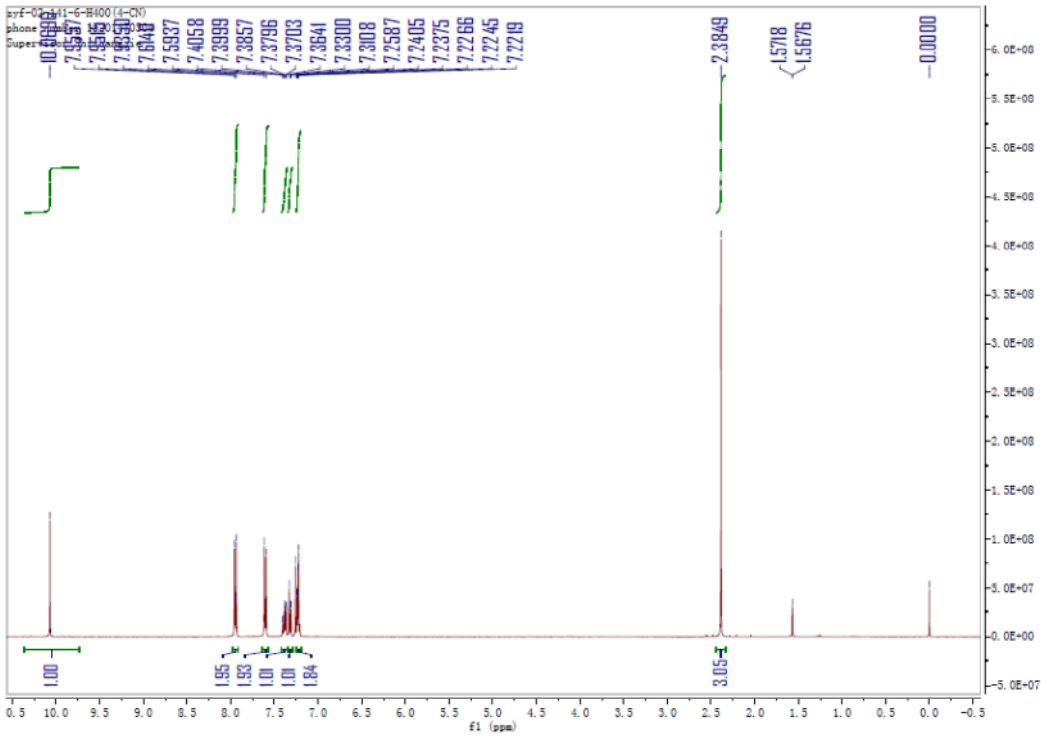

197.589
145.383
139.812
136.888
136.050
129.726
129.584
128.472
128.119
125.649
124.893
77.255
77.000
76.746
26.554
16.001
ppm (t1)

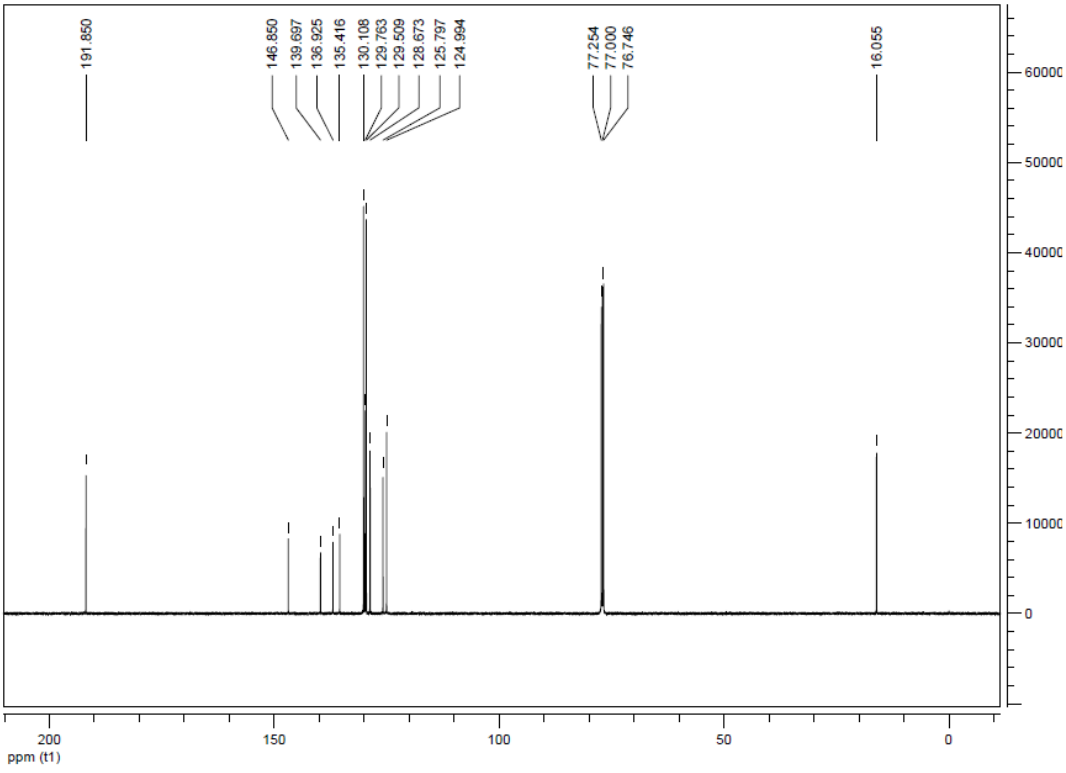

S
1j
CN

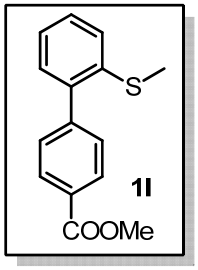

7.5279
7.4087
7.4048
7.3886
7.3868
7.3851
7.3709
7.3669
7.3236
7.3055
7.2580
7.2549
7.2516
7.2357
7.2330
7.2178
7.2147
7.1875
7.1839
7.1686
7.1650
2.3840
0.0000
2.00
2.02
1.03
1.03
1.35
1.01
3.15
f1 (ppm)

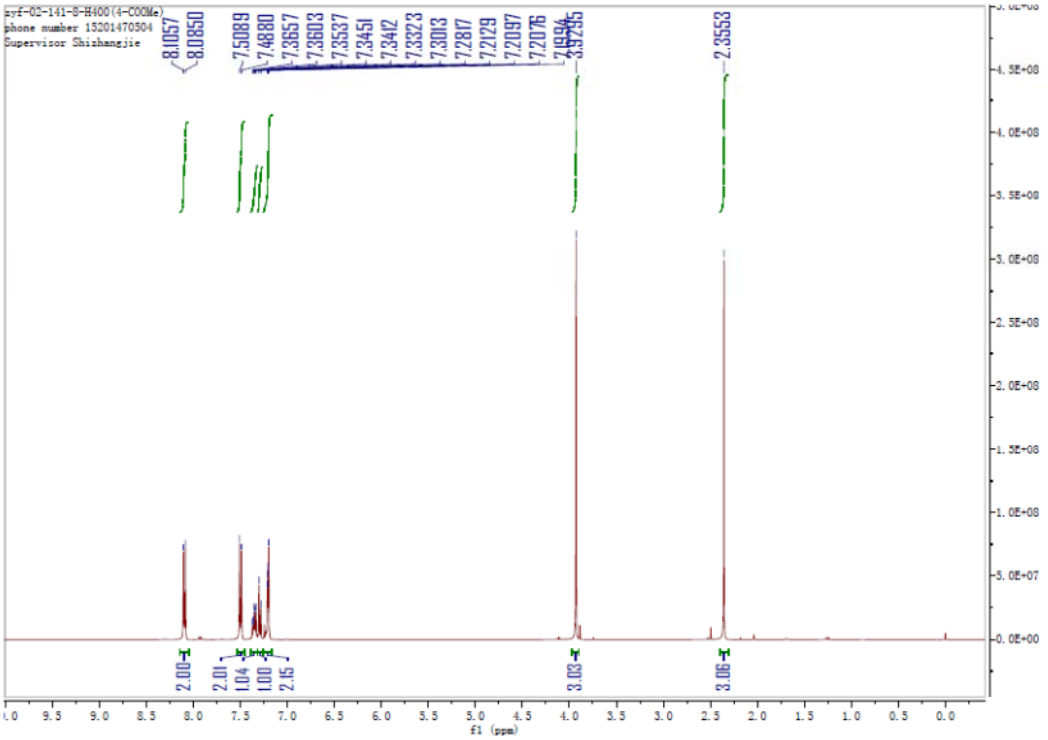

145.187
138.973
136.797
131.812
130.124
129.653
128.833
125.792
125.018
118.751
111.224
77.255
77.000
76.746
15.946
ppm (t1)

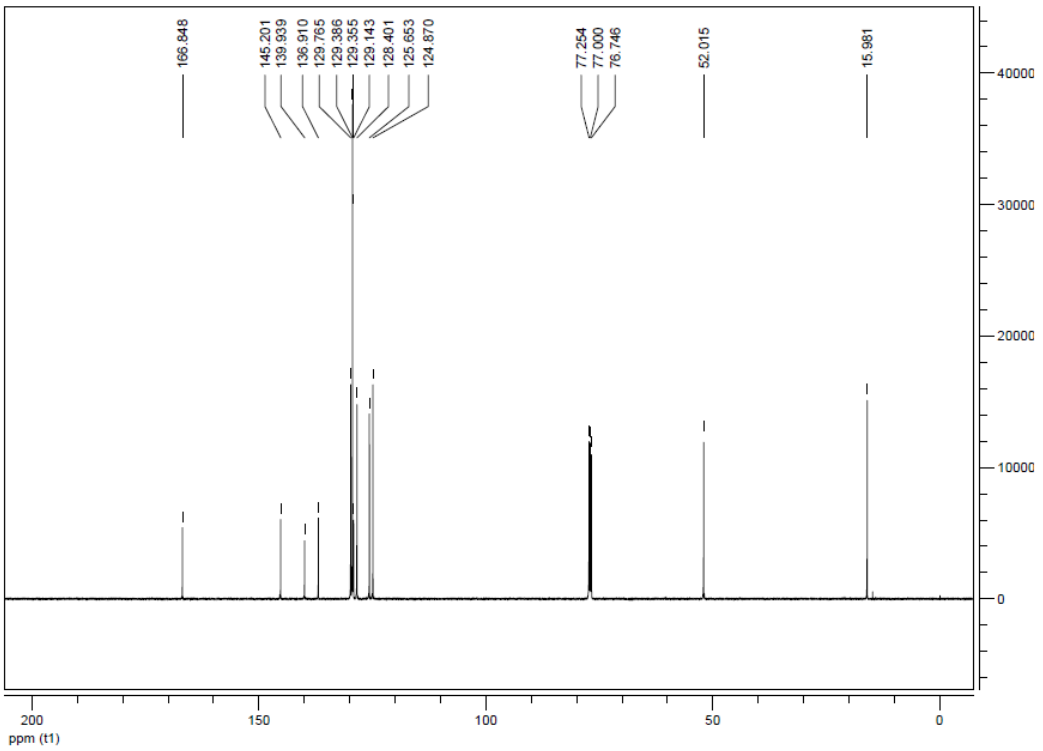

S
1k
CHO


2.3849
1.5718
1.5676
0.0000
1.00
1.95
1.93
1.01
1.01
1.84
3.05
f1 (ppm)

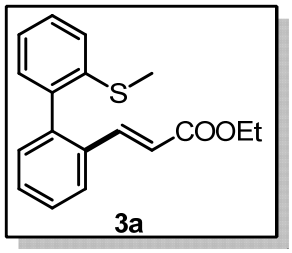

191.850
146.850
139.697
136.925
135.416
130.108
129.763
129.509
128.673
125.797
124.994
77.254
77.000
76.746
16.055
ppm (t1)

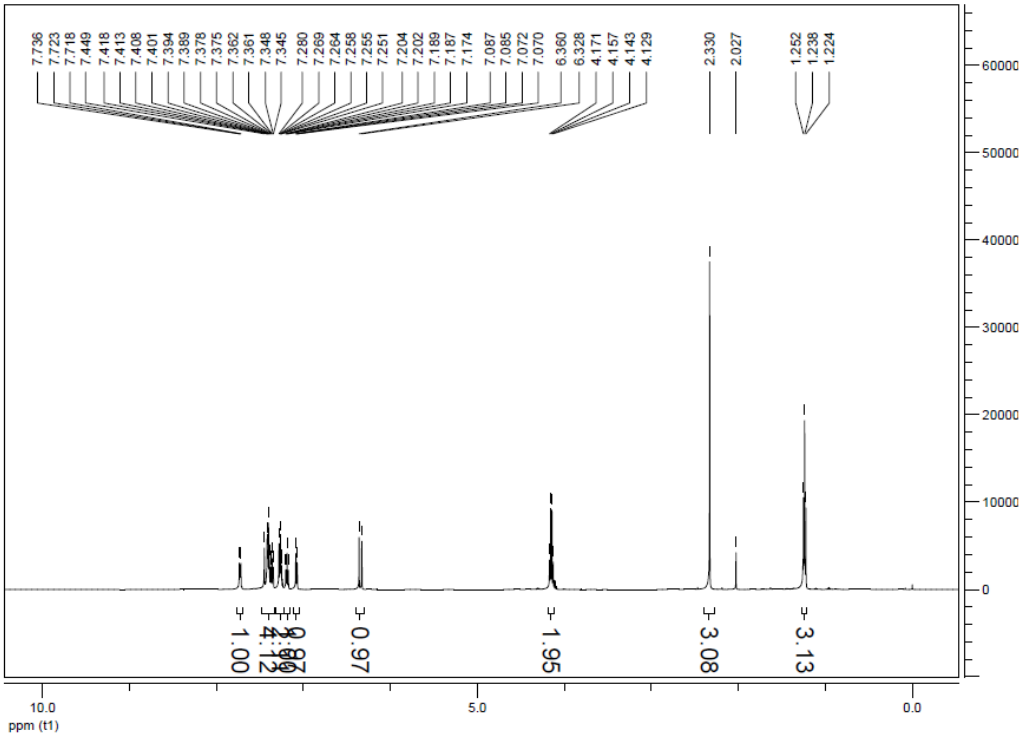

S
1l
COOMe

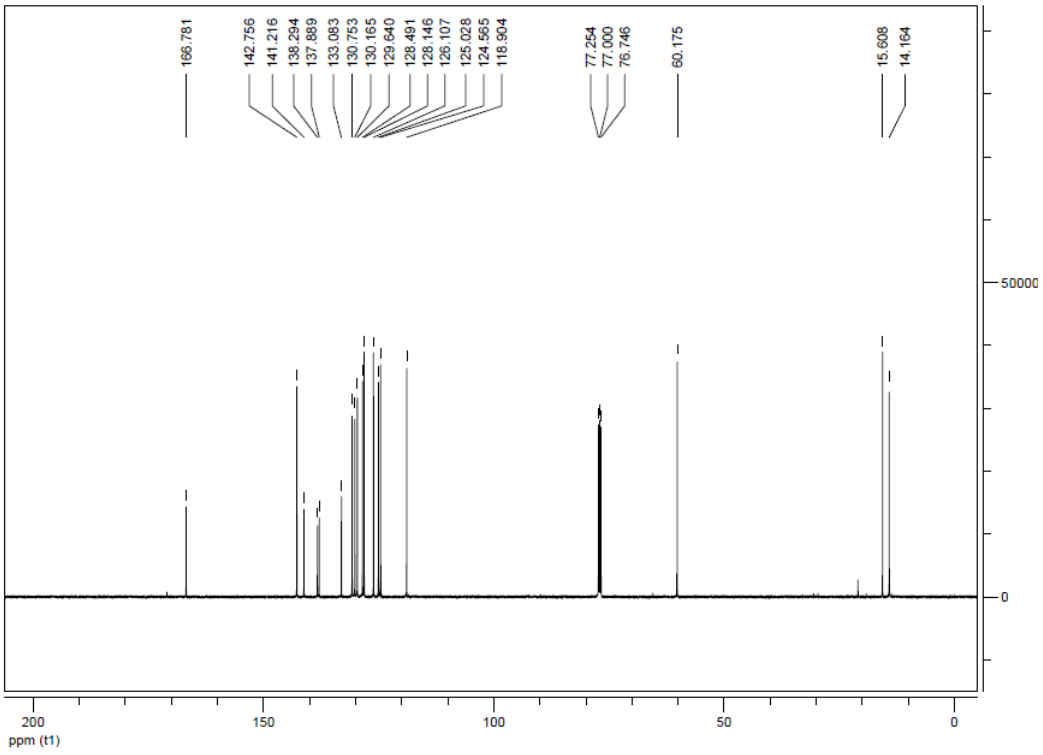

zyf-02-141-8-H400(4-COOMe)
phone number 15201470504
Supervisor Shizhangjie
8.1057
8.0850
7.5089
7.4880
7.3657
7.3603
7.3537
7.3451
7.3412
7.3323
7.3013
7.2817
7.2129
7.2097
7.2076
3.9295
2.3553
2.00
2.01
1.04
1.00
2.15
3.03
3.06
f1 (ppm)

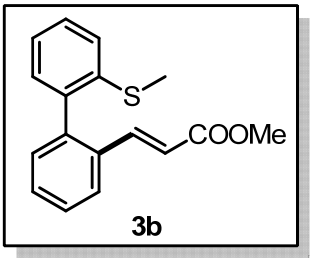

166.848
145.201
139.939
136.910
129.765
129.386
129.355
129.143
128.401
125.653
124.870
77.254
77.000
76.746
52.015
15.981
ppm (t1)

2. Characterization of mono-alkenylation product 3

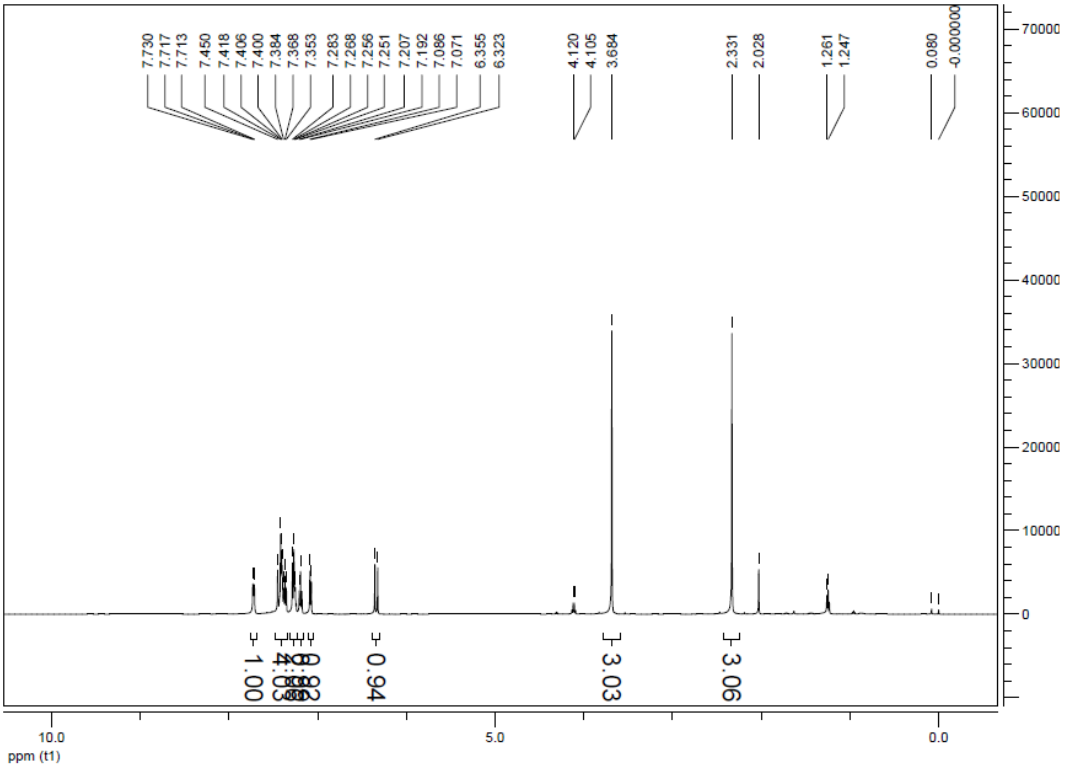


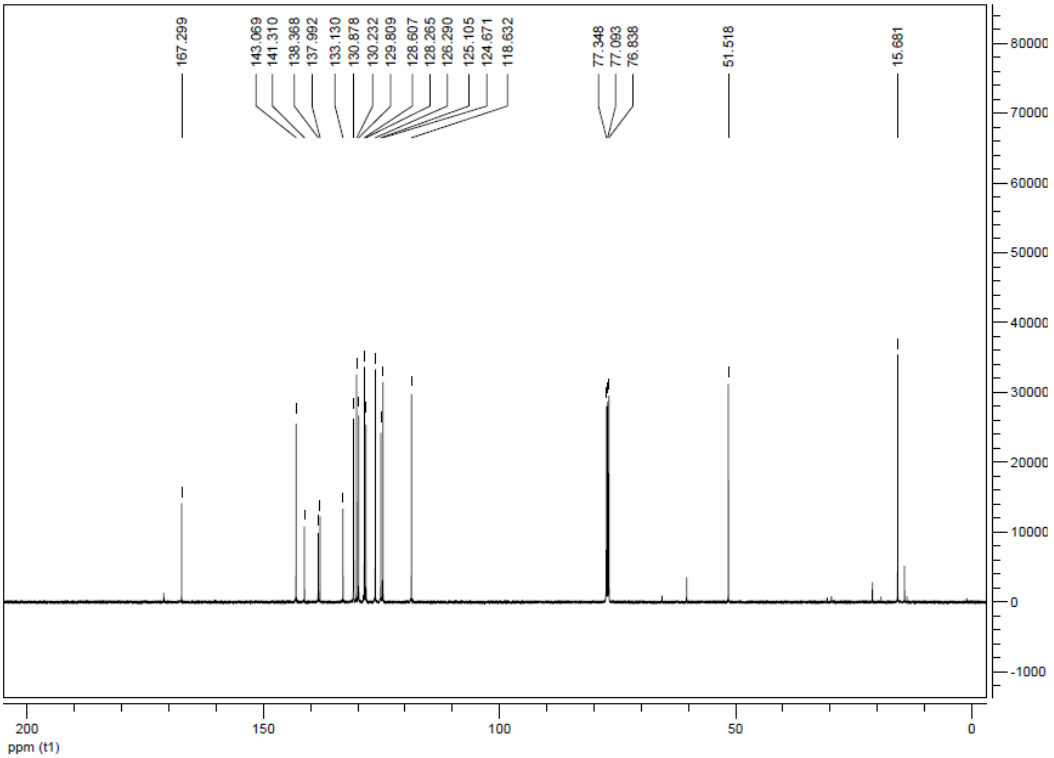


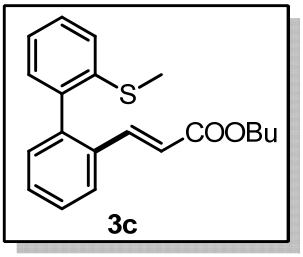



S
COOMe

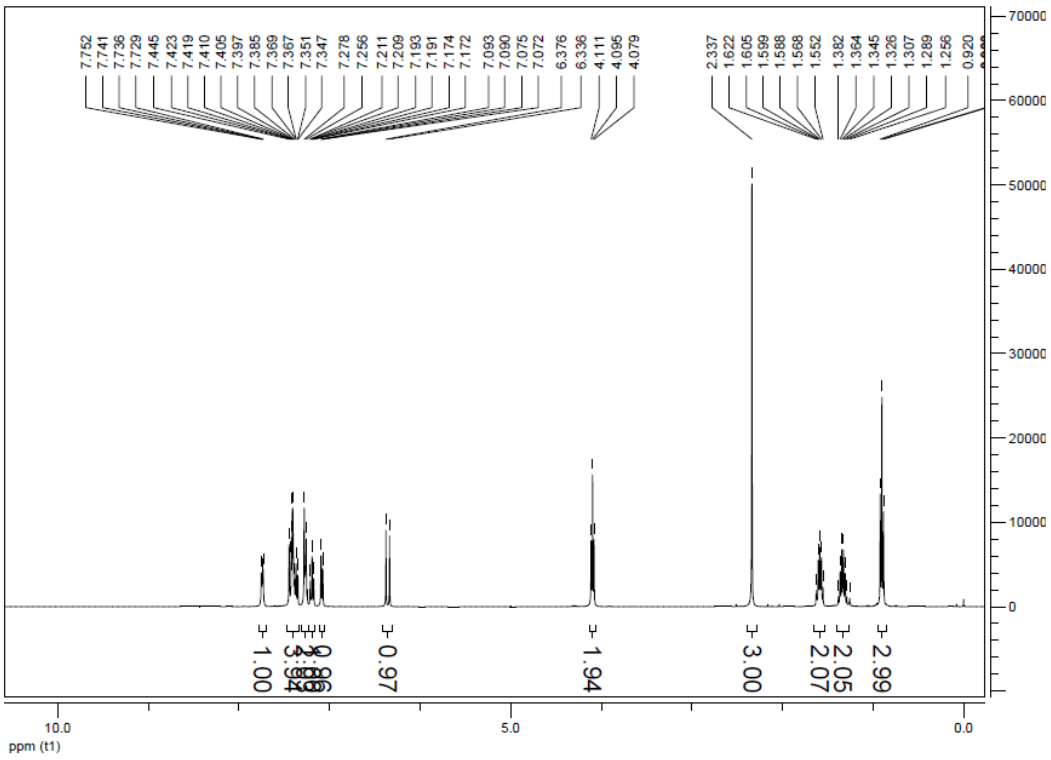
3b

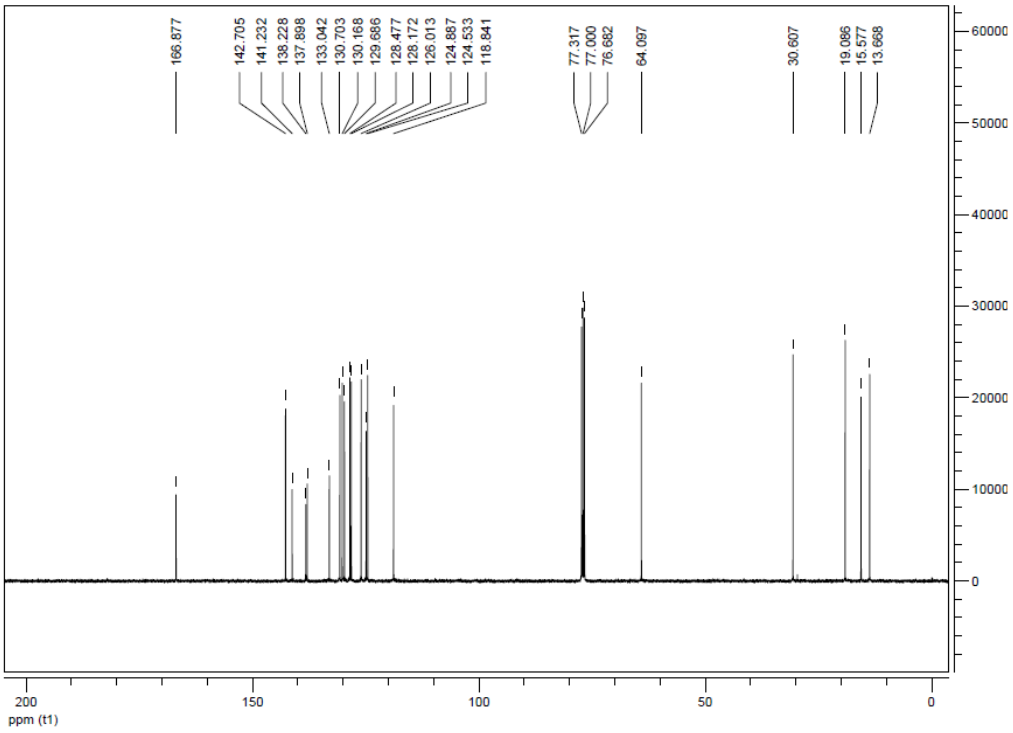

7.730
7.717
7.713
7.450
7.418
7.406
7.400
7.384
7.368
7.353
7.283
7.268
7.256
7.251
7.207
7.192
7.086
7.071
6.355
6.323
4.120
4.105
3.684
2.331
2.028
1.261
1.247
0.080
-0.000000
1.00
0.94
3.03
3.06
10.0
5.0
0.0
ppm (t1)


167.299
143.069
141.310
138.368
137.992
133.130
130.878
130.232
129.809
128.607
128.265
126.290
125.105
124.671
118.632
77.348
77.093
76.838
51.518
15.681
200
150
100
50
0
ppm (t1)


S
COOBu

3c


7.752
7.741
7.736
7.729
7.445
7.423
7.419
7.410
7.405
7.397
7.385
7.369
7.367
7.351
7.347
7.278
7.256
7.211
7.209
7.193
7.191
7.174
7.172
7.093
7.090
7.075
7.072
6.376
6.336
4.111
4.095
4.079
2.337
1.622
1.605
1.599
1.588
1.568
1.552
1.382
1.364
1.345
1.326
1.307
1.289
1.256
0.920
1.00
3.00
0.97
1.94
3.00
2.07
2.05
2.99
ppm (t1)


166.877
142.705
141.232
138.226
137.898
133.042
130.703
130.168
129.686
128.477
128.172
126.013
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124.533
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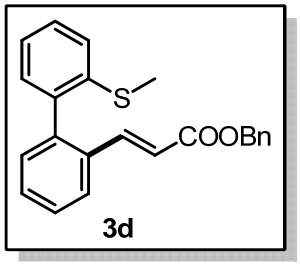
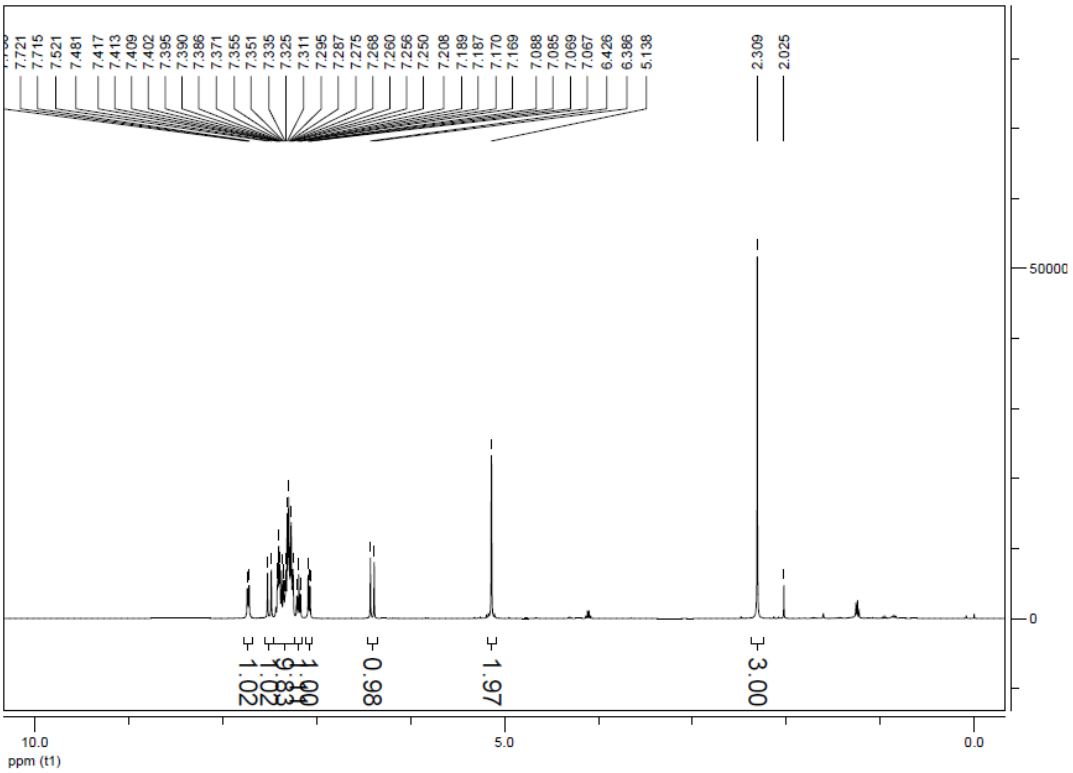
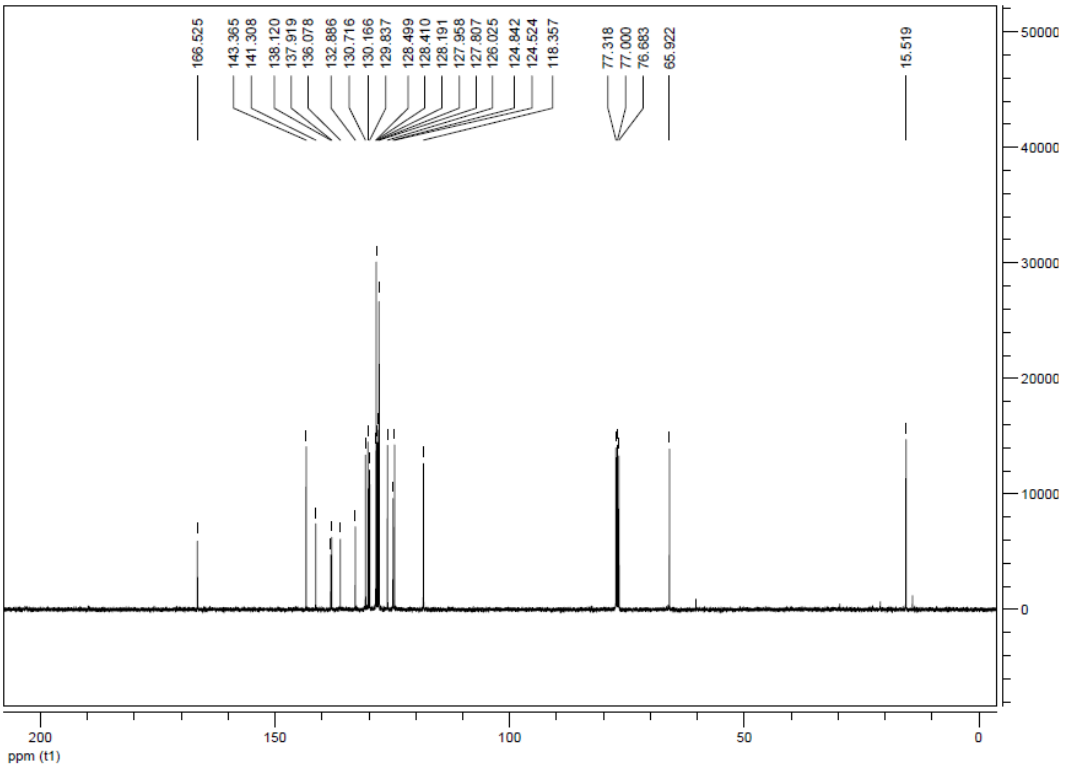
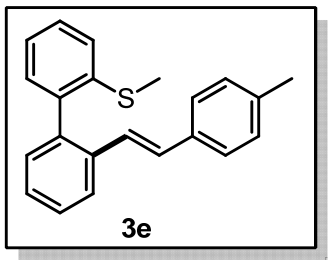
77.317
77.000
76.682
64.097
30.607
19.086
15.577
13.668
ppm (t1)

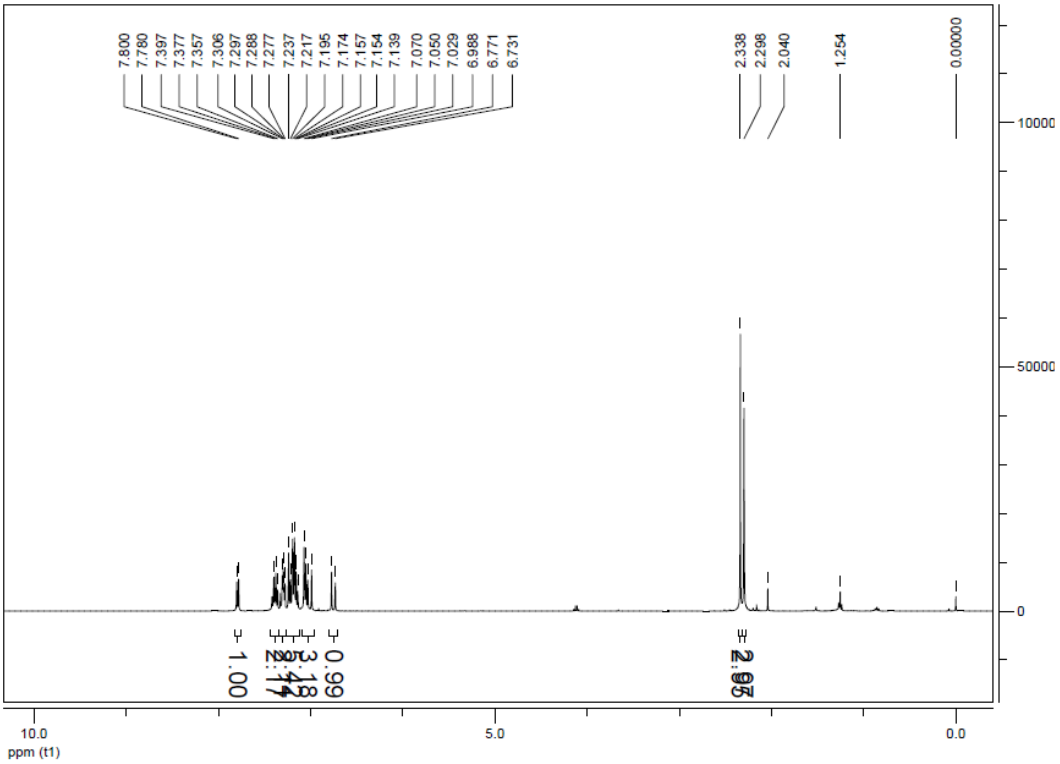

S
COOBn

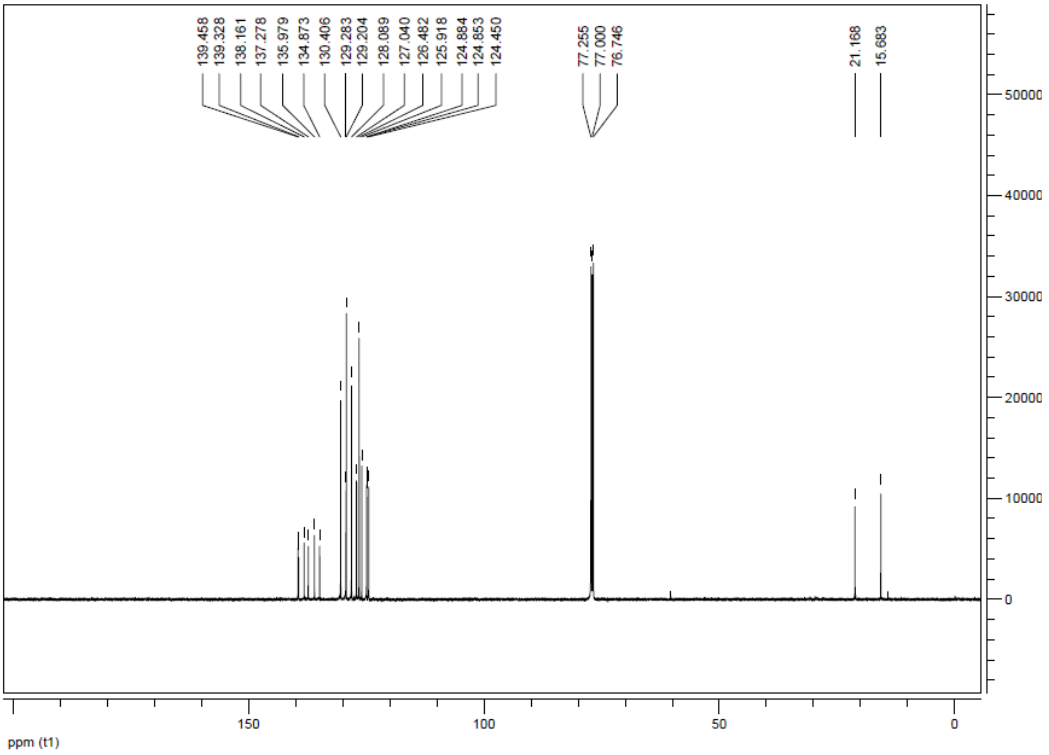
3d

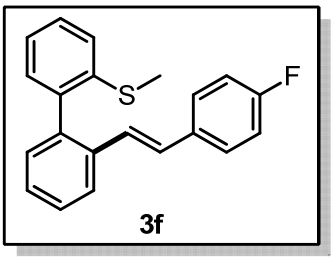

7.721
7.715
7.521
7.481
7.417
7.413
7.409
7.402
7.395
7.390
7.386
7.371
7.355
7.351
7.335
7.325
7.311
7.295
7.287
7.275
7.268
7.260
7.256
7.250
7.208
7.189
7.187
7.170
7.169
7.088
7.085
7.069
7.067
6.426
6.386
5.138
2.309
2.025
1.02
2.83
1.96
1.00
0.98
1.97
3.00
50000
0
10.0
5.0
0.0
ppm (t1)


166.525
143.365
141.308
138.120
137.919
136.078
132.886
130.716
130.166
129.837
128.499
128.410
128.191
127.958
127.807
126.025
124.842
124.524
118.357
77.318
77.000
76.683
65.922
15.519
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

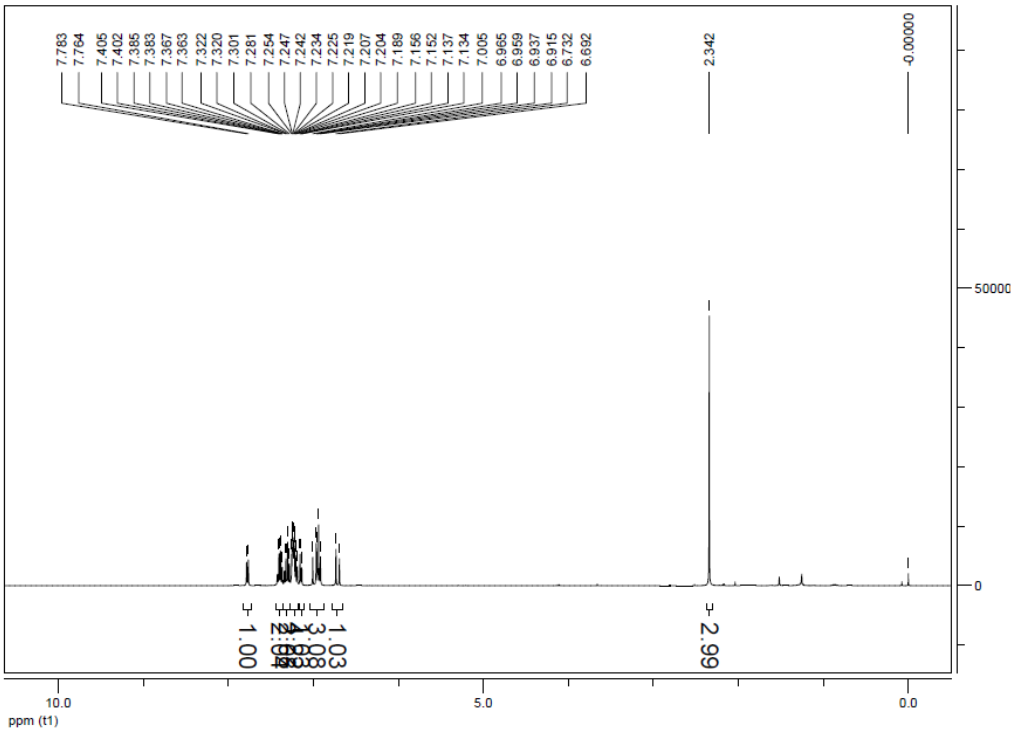

S
3e


7.800
7.780
7.397
7.377
7.357
7.306
7.297
7.288
7.277
7.237
7.217
7.195
7.174
7.157
7.154
7.139
7.070
7.050
7.029
6.988
6.771
6.731
2.338
2.298
2.040
1.254
0.00000
10000
50000
0
1.00
0.99
2.97
10.0
5.0
0.0
ppm (t1)


139.458
139.328
138.161
137.278
135.979
134.873
130.406
129.283
129.204
128.089
127.040
126.482
125.918
124.884
124.853
124.450
77.255
77.000
76.746
21.168
15.683
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)


S
F

3f


7.783
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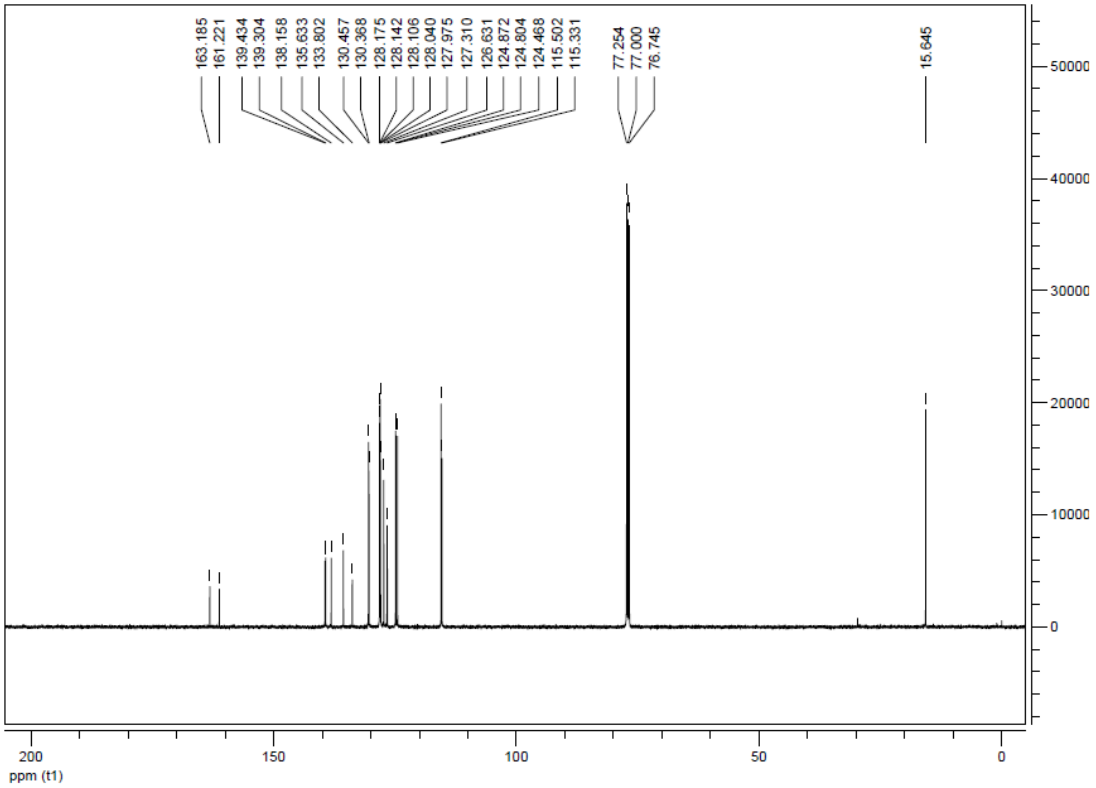
7.405
7.402
7.385
7.383
7.367
7.363
7.322
7.320
7.301
7.281
7.254
7.247
7.242
7.234
7.225
7.219
7.207
7.204
7.189
7.156
7.152
7.137
7.134
7.005
6.965
6.959
6.937
6.915
6.732
6.692
2.342
-0.00000
50000
0
1.00
3.08
1.03
2.99
10.0
5.0
0.0
ppm (t1)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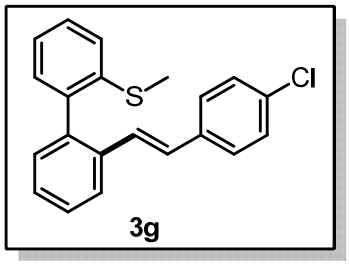
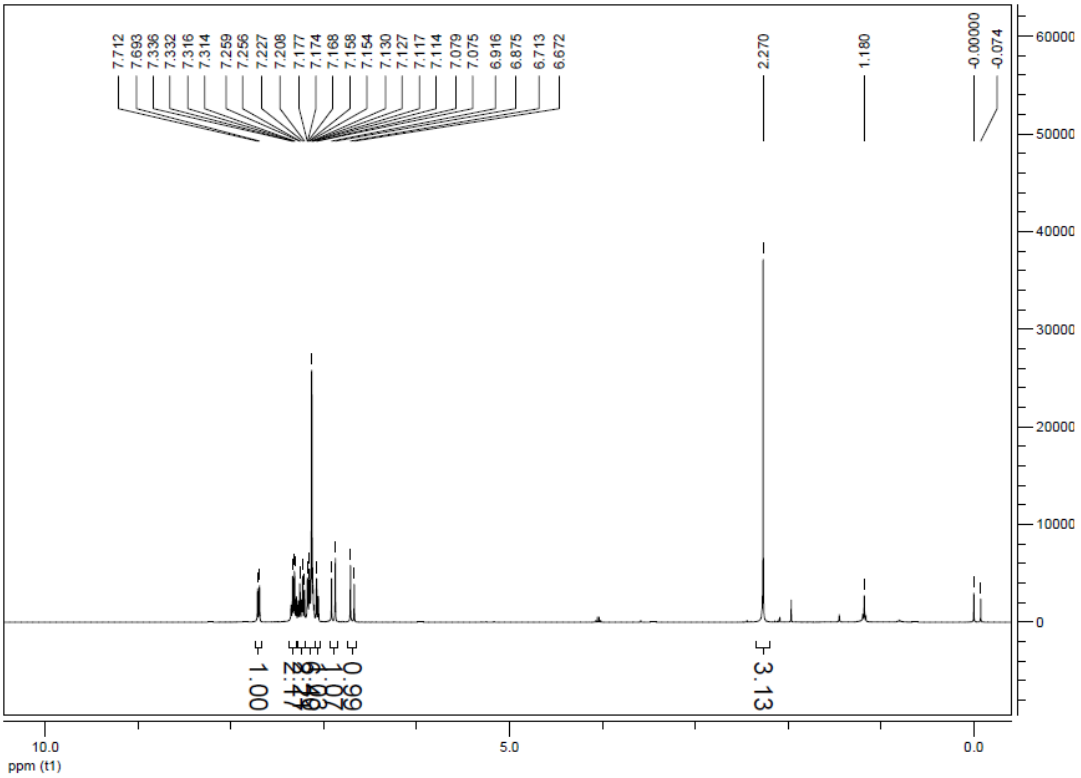
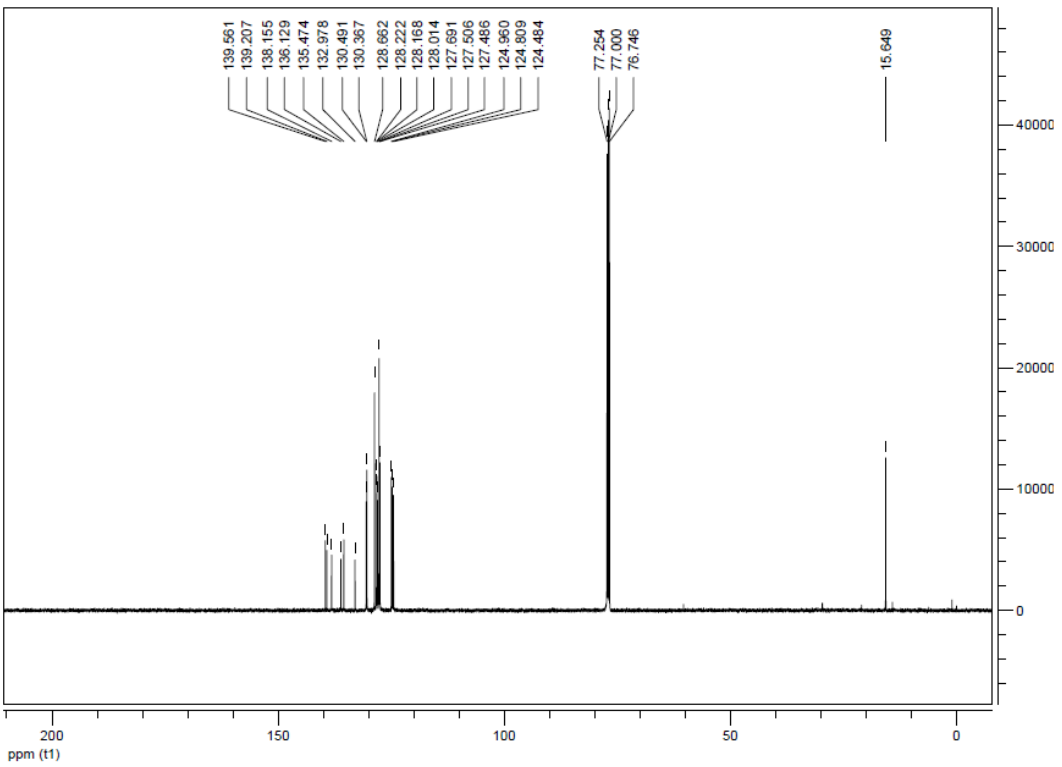
161.221
139.434
139.304
138.158
135.633
133.802
130.457
130.368
128.175
128.142
128.106
128.040
127.975
127.310
126.631
124.872
124.804
124.468
115.502
115.331
77.254
77.000
76.745
15.645
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)


S
Cl

3g


7.712
7.693
7.336
7.332
7.316
7.314
7.259
7.256
7.227
7.208
7.177
7.174
7.168
7.158
7.154
7.130
7.127
7.117
7.114
7.079
7.075
6.916
6.875
6.713
6.672
2.270
1.180
-0.00000
-0.074
1.00
3.13
60000
50000
40000
30000
20000
10000
0
10.0
5.0
0.0
ppm (t1)


139.561
139.207
138.155
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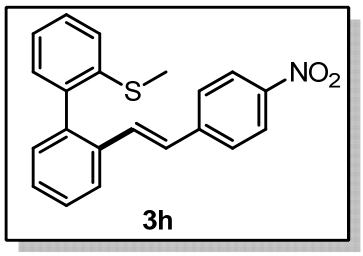
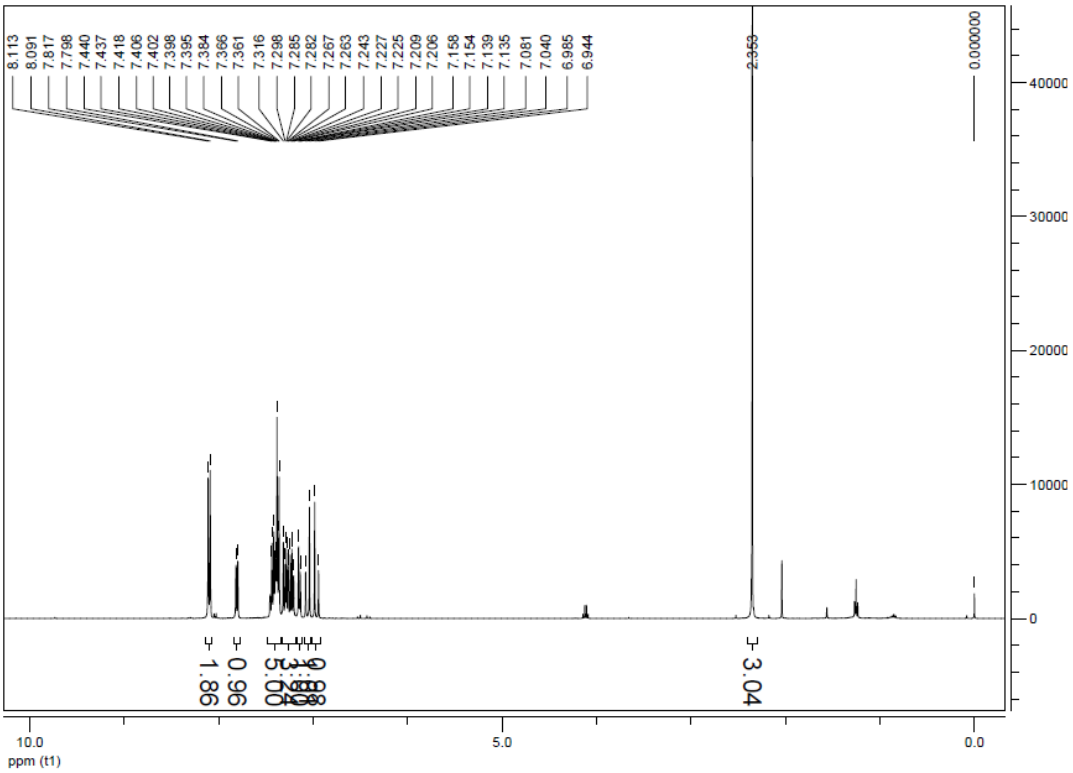
135.474
132.978
130.491
130.367
128.662
128.222
128.168
128.014
127.691
127.506
127.486
124.960
124.809
124.484
77.254
77.000
76.746
15.649
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)


S
NO2

3h


8.113
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7.440
7.437
7.418
7.406
7.402
7.398
7.395
7.384
7.366
7.361
7.316
7.298
7.285
7.282
7.267
7.263
7.243
7.227
7.225
7.209
7.206
7.158
7.154
7.139
7.135
7.081
7.040
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6.944
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0.96
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10.0
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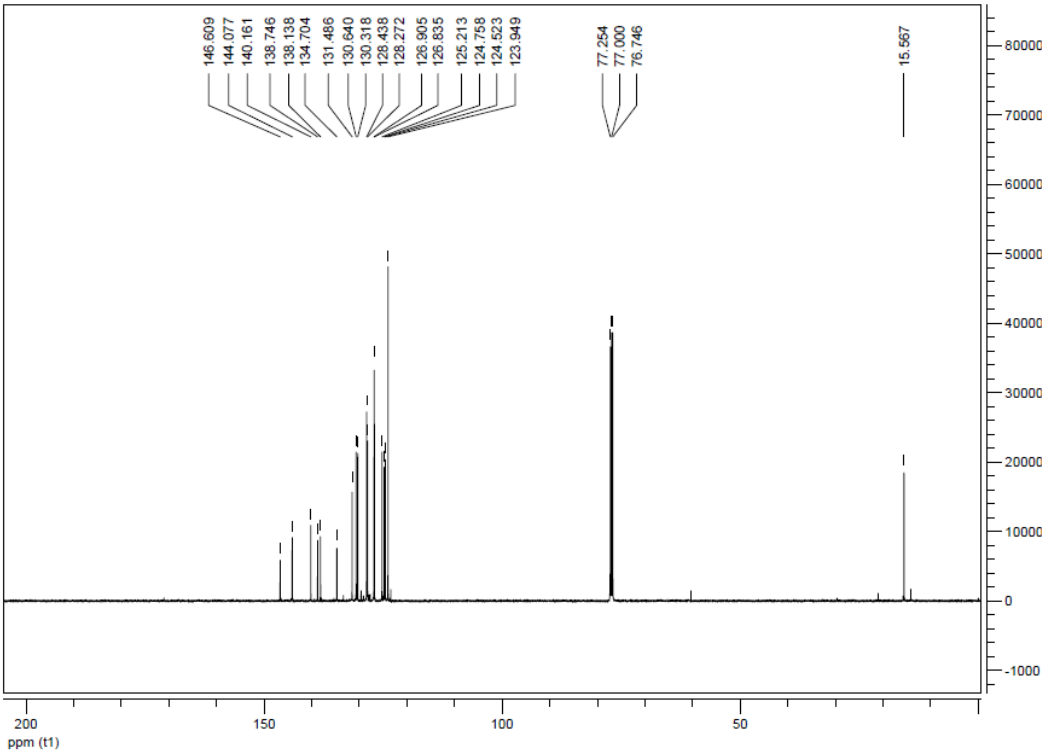
0.0
ppm (t1)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130.640
130.318
128.438
128.272
126.905
126.835
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124.523
123.949
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77.000
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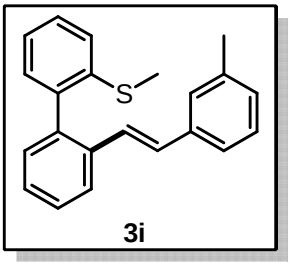
15.567
200
150
100
50
ppm (t1)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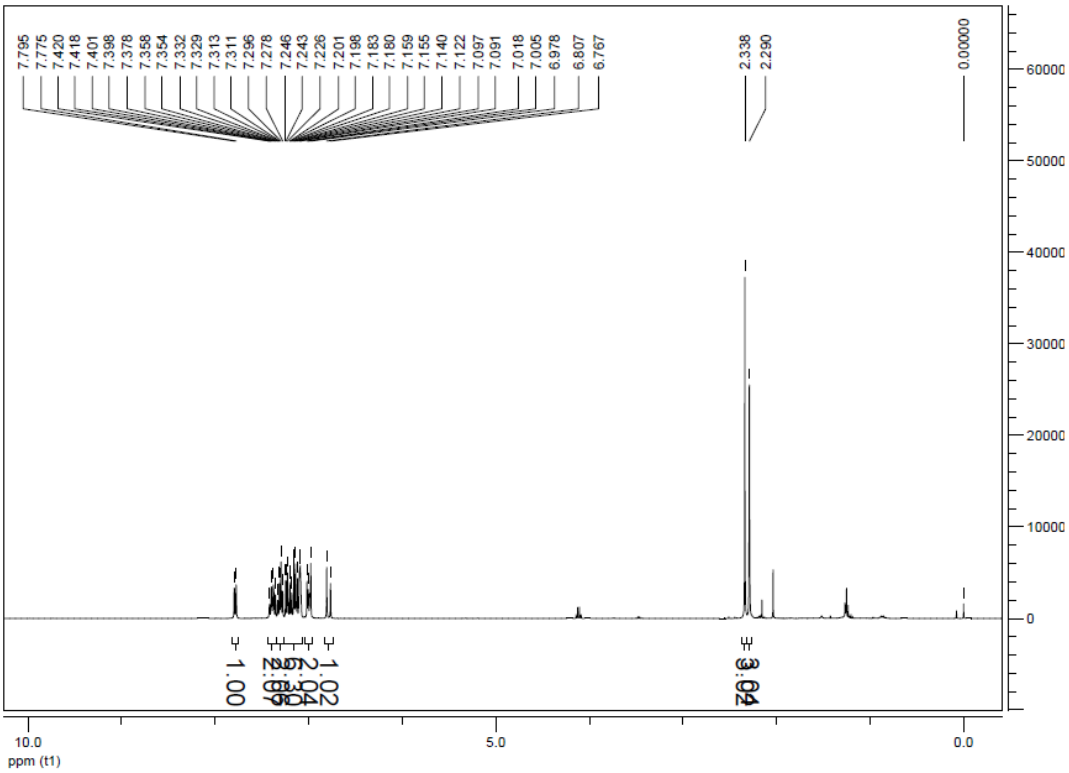
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7.332
7.329
7.313
7.311
7.296
7.278
7.246
7.243
7.226
7.201
7.198
7.183
7.180
7.159
7.155
7.140
7.122
7.097
7.091
7.018
7.005
6.978
6.807
6.767
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2.290
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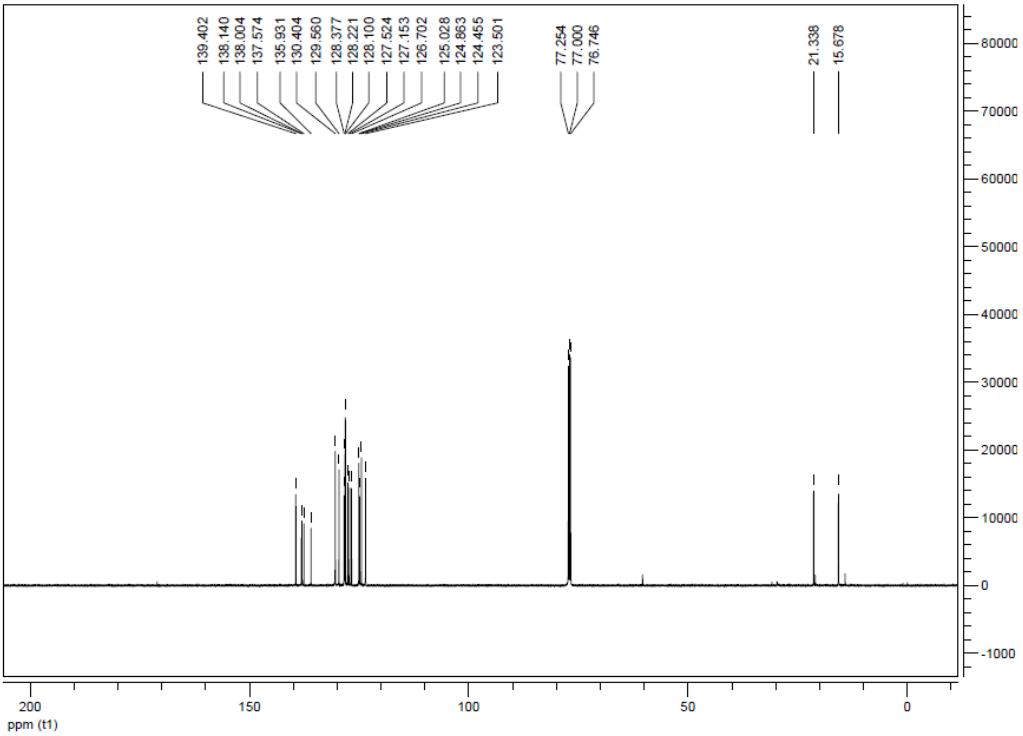
1.02
3.04
10.0
ppm (t1)
5.0
0.0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127.524
127.153
126.702
125.028
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77.000
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200
ppm (t1)
150
100
50
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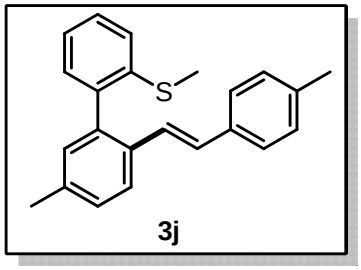
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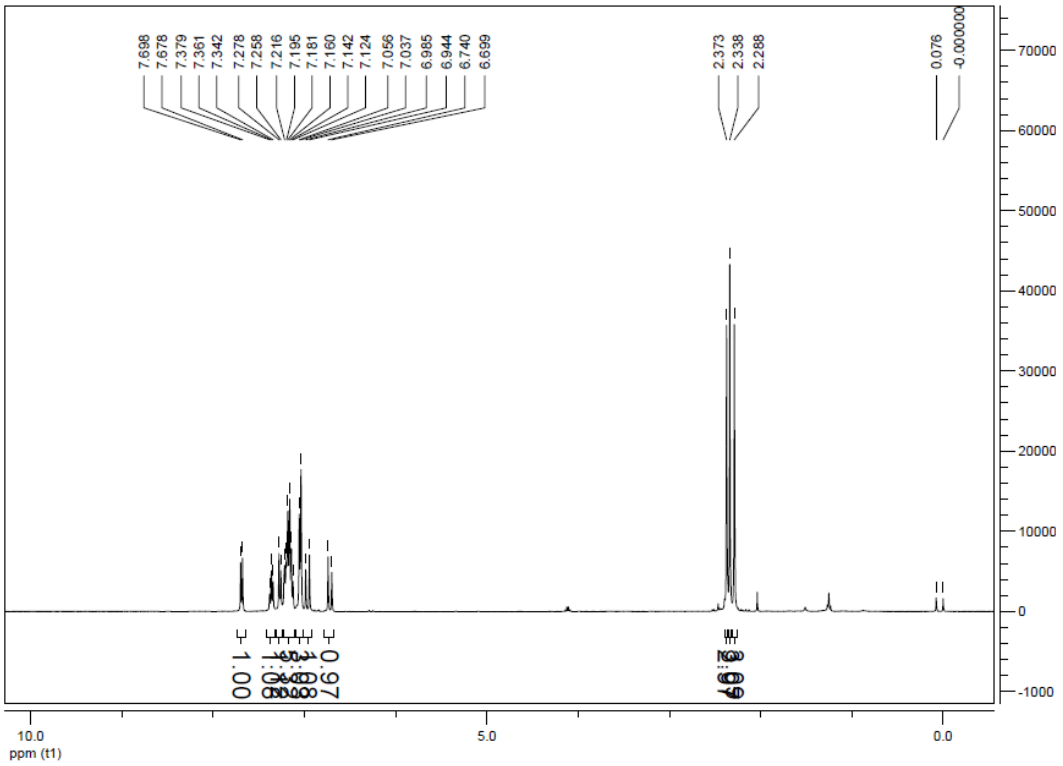
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7.361
7.342
7.278
7.258
7.216
7.195
7.181
7.160
7.142
7.124
7.056
7.037
6.985
6.944
6.740
6.699
2.373
2.338
2.288
0.076
-0.000000
70000
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20000
10000
0
-1000
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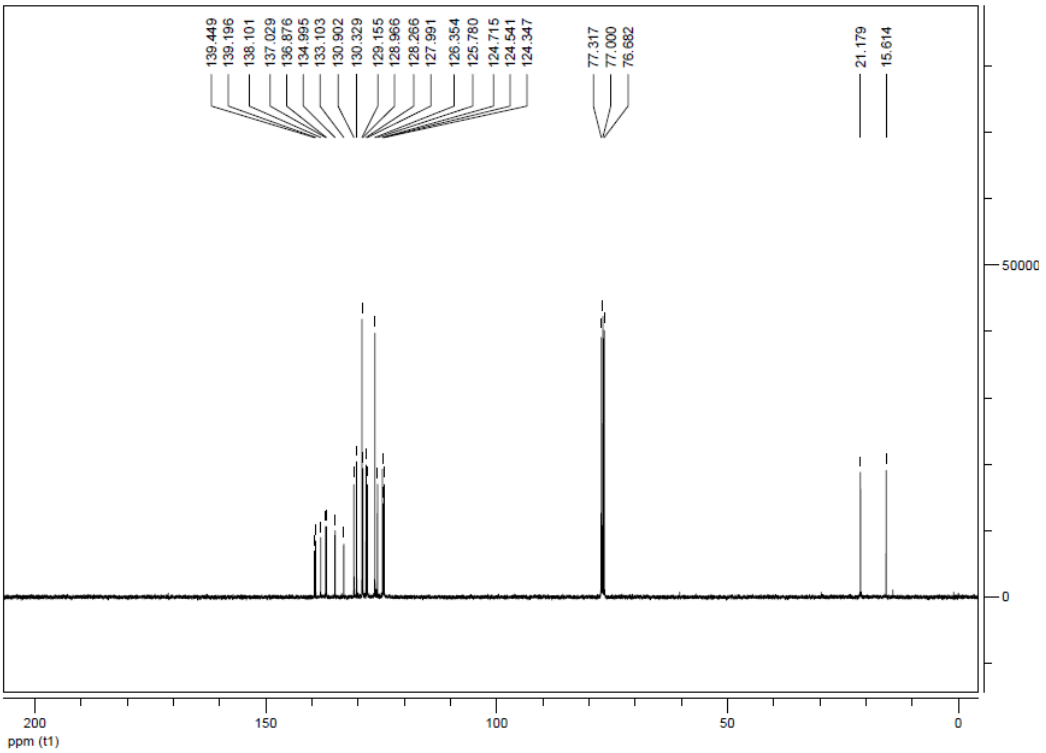
5.0
0.0
ppm (t1)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134.995
133.103
130.902
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129.155
128.966
128.266
127.991
126.354
125.780
124.715
124.541
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77.000
76.682
21.179
15.614
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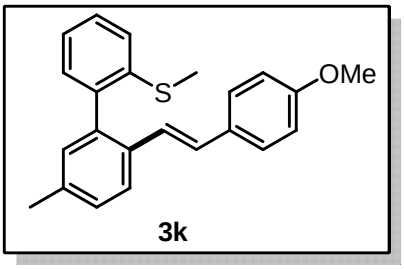
0
200
150
100
50
0
ppm (t1)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OMe

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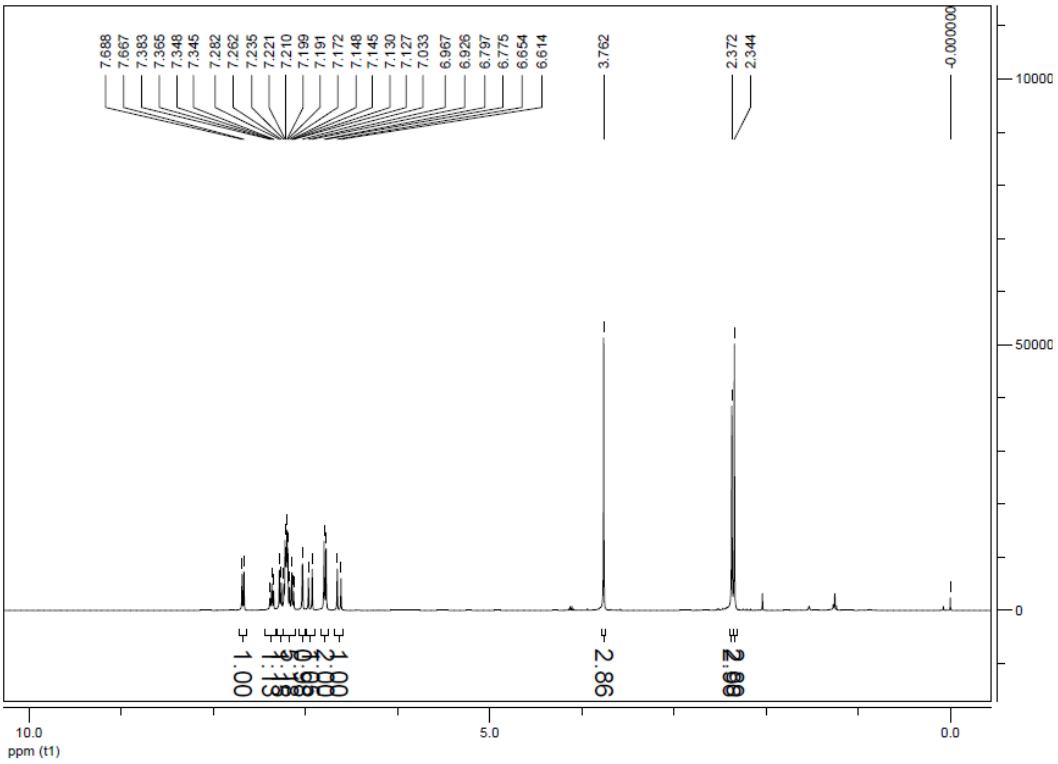
7.688
7.667
7.383
7.365
7.348
7.345
7.282
7.262
7.235
7.221
7.210
7.199
7.191
7.172
7.148
7.145
7.130
7.127
7.033
6.967
6.926
6.797
6.775
6.654
6.614
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0
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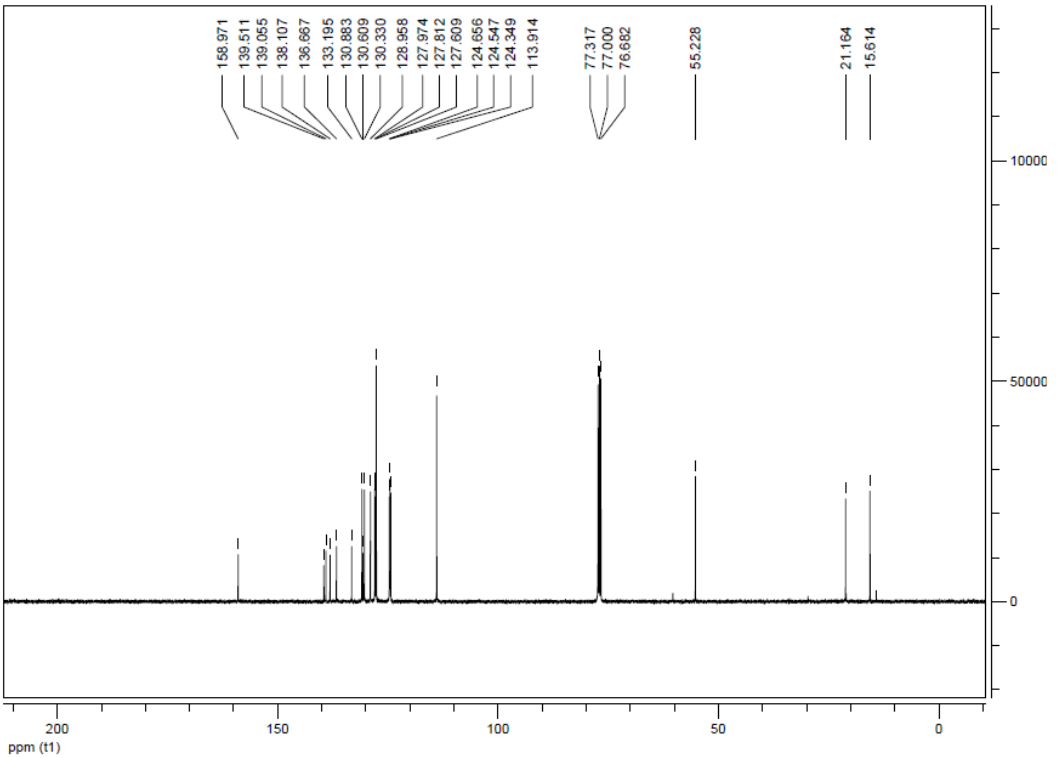
10.0
5.0
0.0
ppm (t1)


158.971
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139.055
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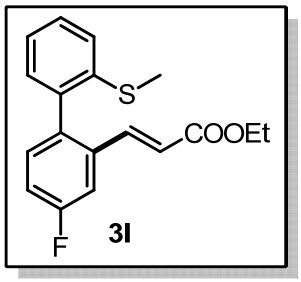
136.667
133.195
130.883
130.609
130.330
128.958
127.974
127.812
127.609
124.656
124.547
124.349
113.914
77.317
77.000
76.682
55.228
21.164
15.614
10000
50000
0
200
150
100
50
0
ppm (t1)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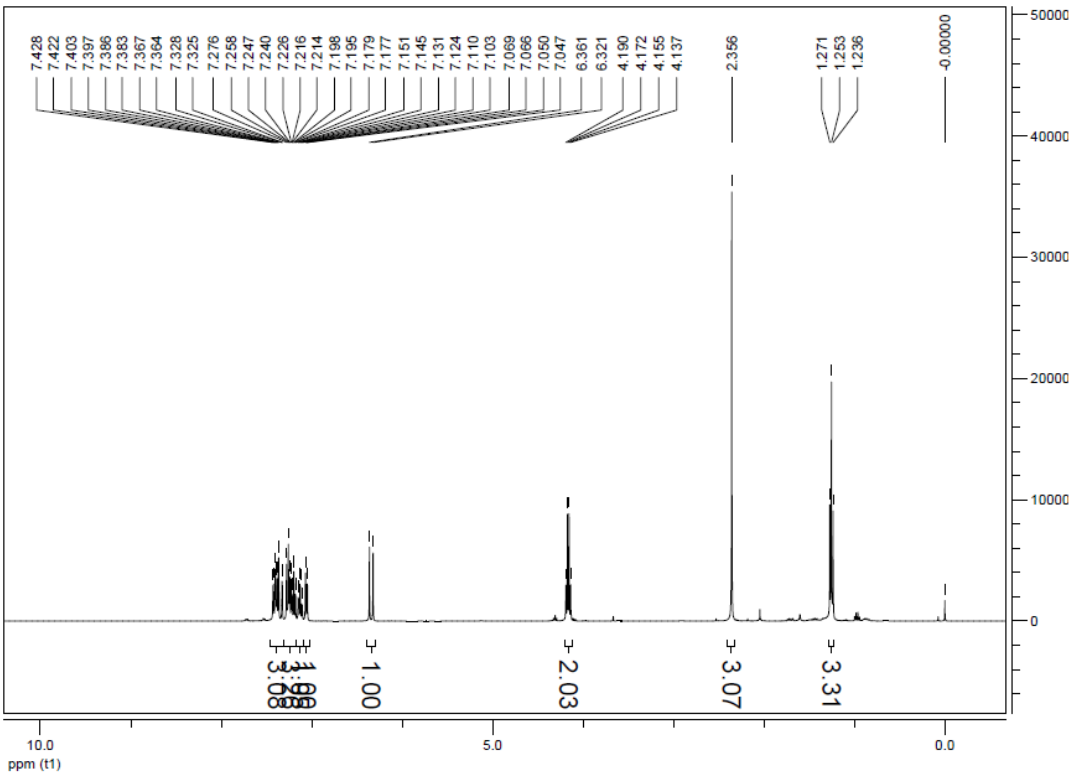
COOEt
F
3l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7.403
7.397
7.386
7.383
7.367
7.364
7.328
7.325
7.276
7.258
7.247
7.240
7.226
7.216
7.214
7.198
7.195
7.179
7.177
7.151
7.145
7.131
7.124
7.110
7.103
7.069
7.066
7.050
7.047
6.361
6.321
4.190
4.172
4.155
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1.271
1.253
1.236
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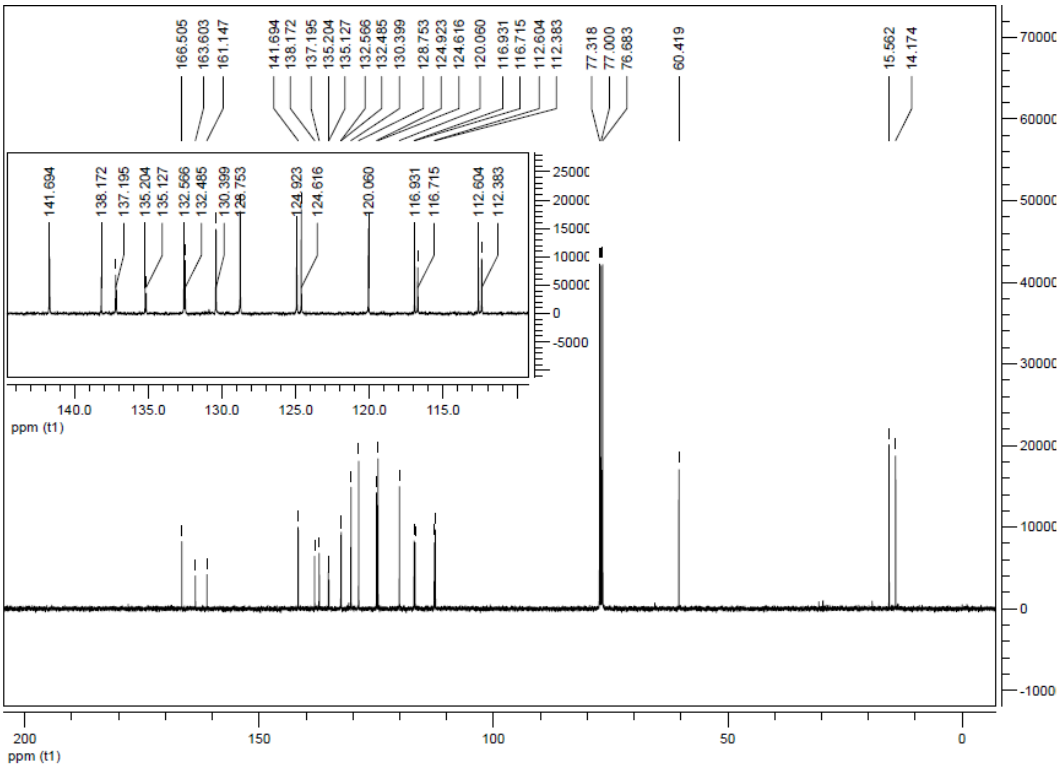
1.00
2.03
3.07
3.31
ppm (t1)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163.603
161.147
141.694
138.172
137.195
135.204
135.127
132.566
132.485
130.399
128.753
124.923
124.616
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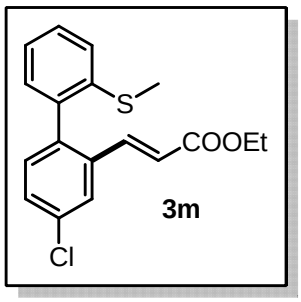
116.715
112.604
112.383
77.318
77.000
76.683
60.419
15.562
14.174
ppm (t1)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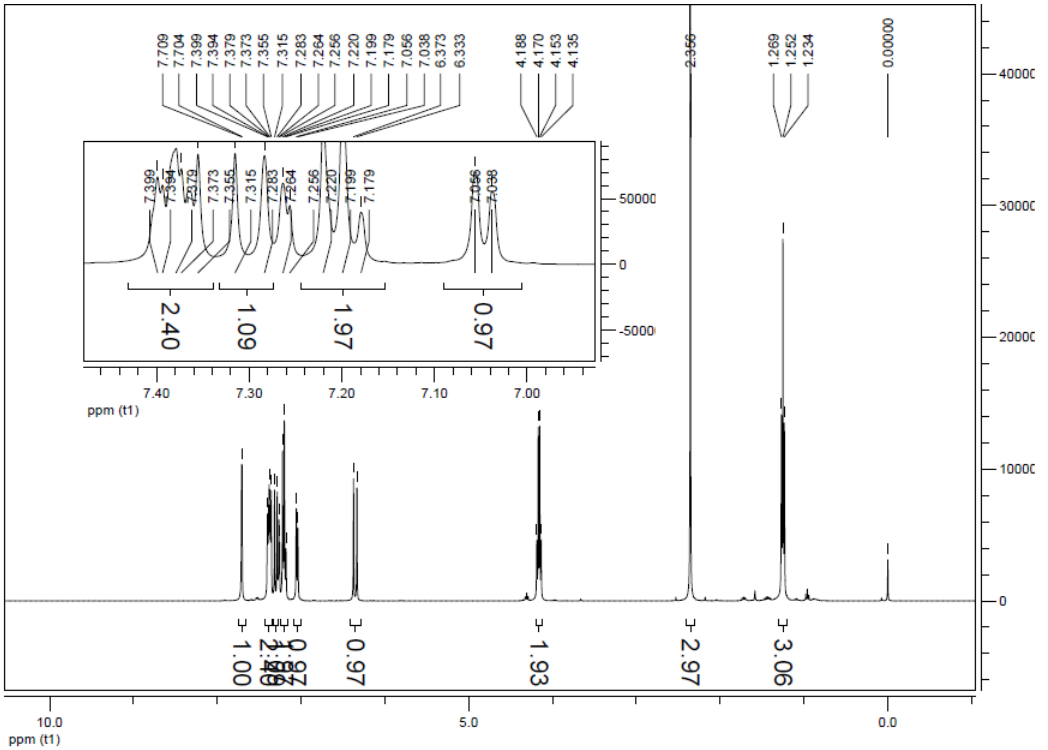
COOEt
Cl

3m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7.704
7.399
7.394
7.379
7.373
7.355
7.315
7.283
7.264
7.256
7.220
7.199
7.179
7.056
7.038
6.373
6.333
4.188
4.170
4.153
4.135
2.356
1.269
1.252
1.234
0.00000
2.40
1.09
1.97
0.97
ppm (t1)
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0.97
1.93
2.97
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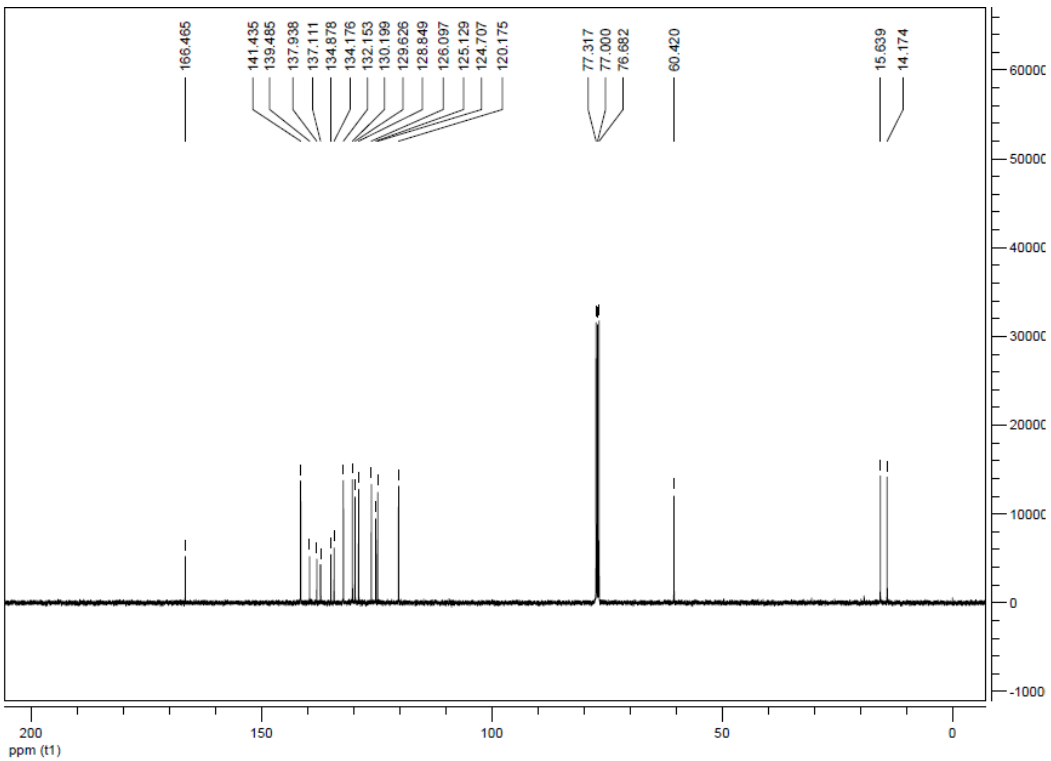
10.0
5.0
0.0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134.176
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130.199
129.626
128.849
126.097
125.129
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77.000
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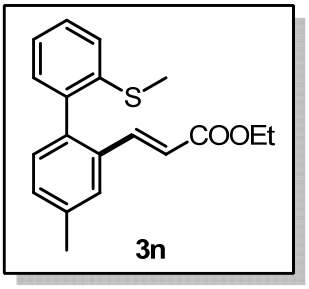
200
150
100
50
0
ppm (t1)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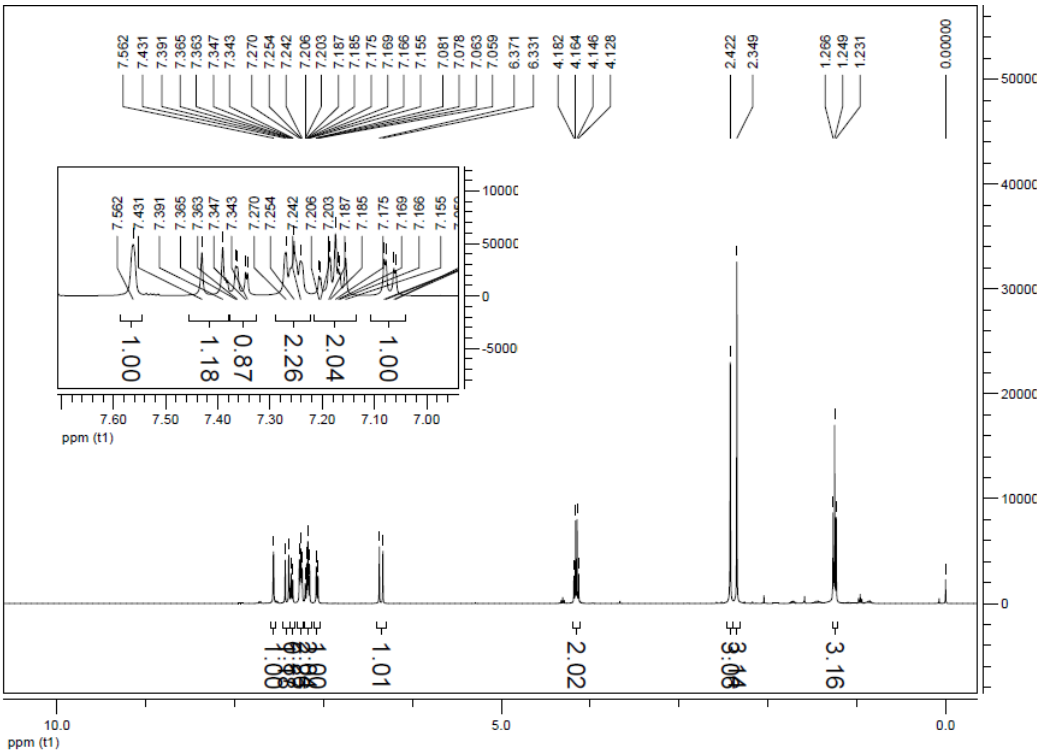
3n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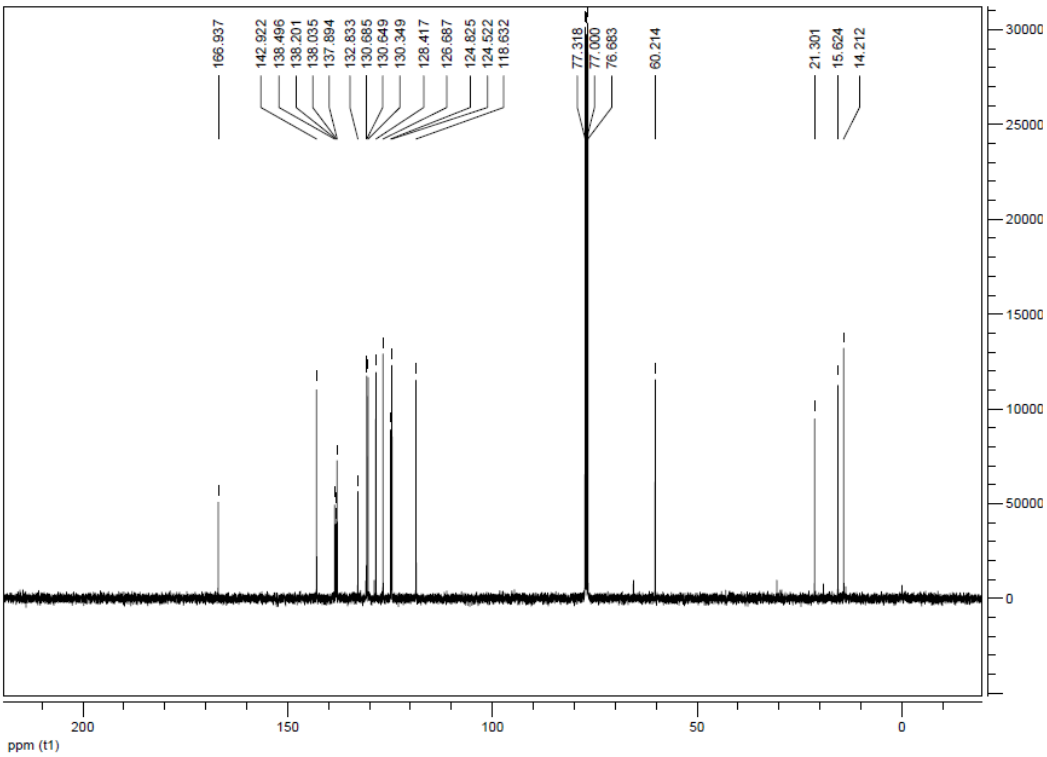
7.365
7.363
7.347
7.343
7.270
7.254
7.242
7.206
7.203
7.187
7.185
7.175
7.169
7.166
7.155
7.081
7.078
7.063
7.059
6.371
6.331
4.182
4.164
4.146
4.128
2.422
2.349
1.266
1.249
1.231
0.00000
1.00
1.18
0.87
2.26
2.04
1.00
ppm (t1)
1.01
2.02
3.16
10.0
5.0
0.0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130.685
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130.349
128.417
126.687
124.825
124.522
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77.000
76.683
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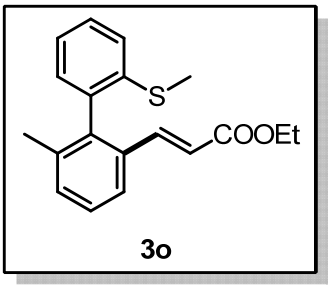
15.624
14.212
200
150
100
50
0
ppm (t1)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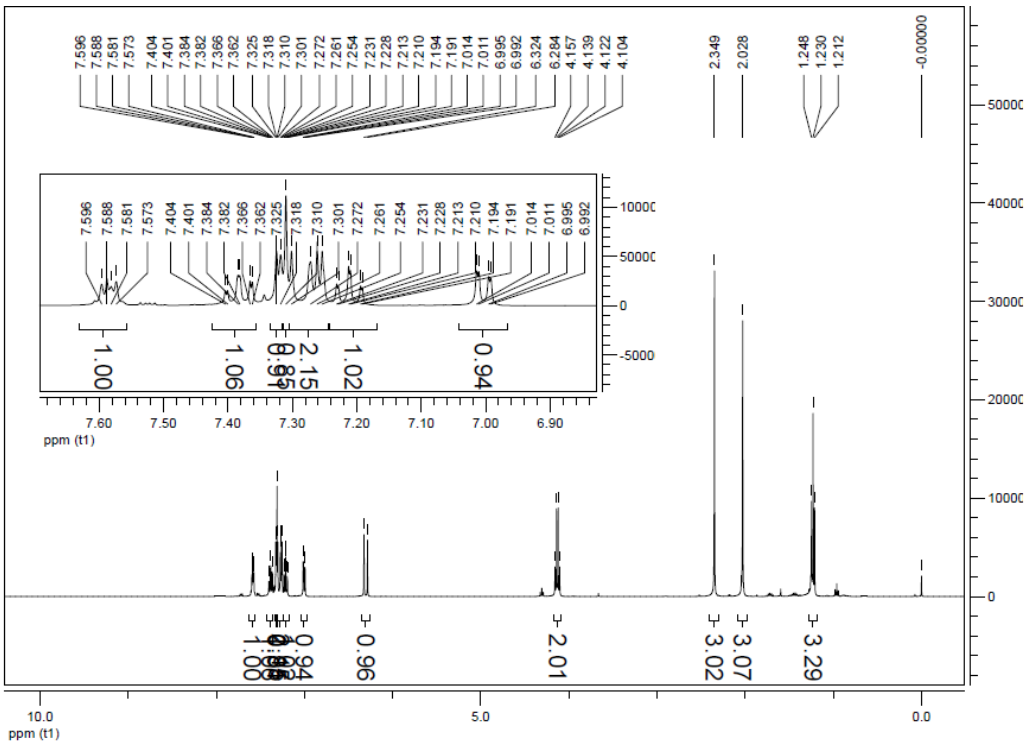
COOEt

3o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7.401
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7.382
7.366
7.362
7.325
7.318
7.310
7.301
7.272
7.261
7.254
7.231
7.228
7.213
7.210
7.194
7.191
7.014
7.011
6.995
6.992
6.324
6.284
4.157
4.139
4.122
4.104
2.349
2.028
1.248
1.230
1.212
-0.00000
1.00
1.06
0.85
2.15
1.02
0.94
ppm (t1)
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0.94
0.96
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3.07
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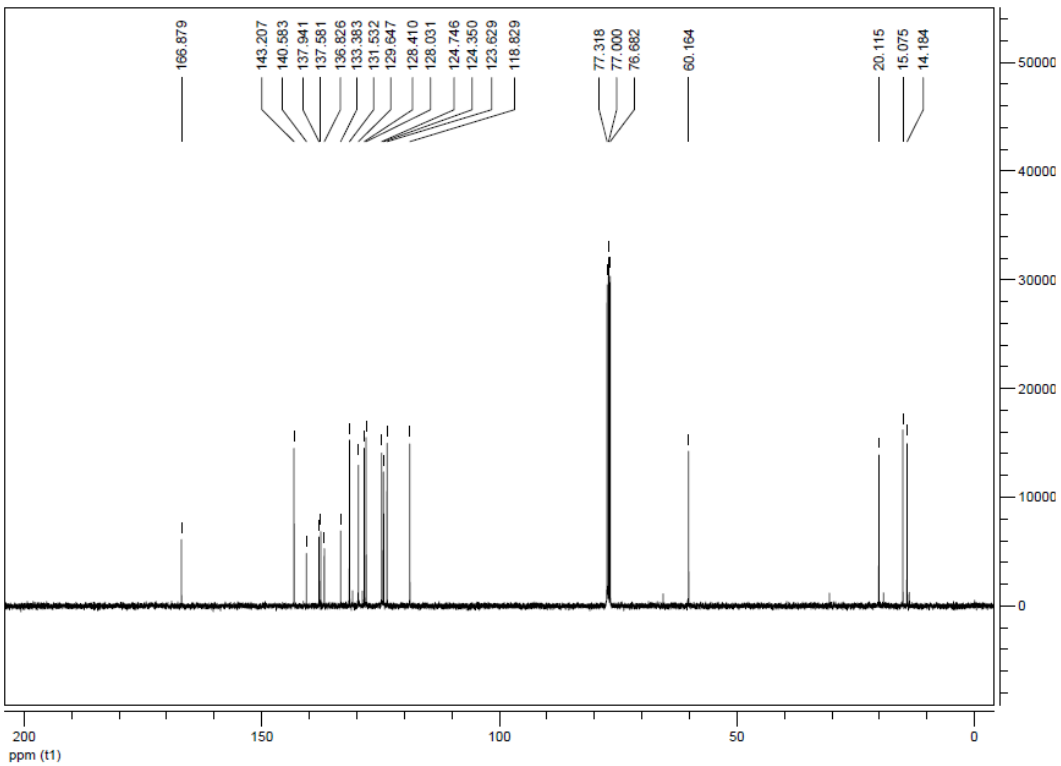
5.0
0.0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140.583
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133.383
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129.647
128.410
128.031
124.746
124.350
123.629
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77.000
76.682
60.164
20.115
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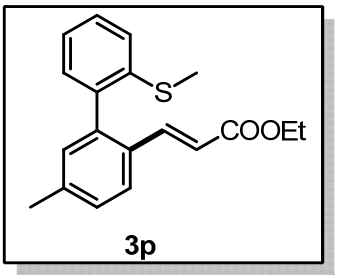
200
150
100
50
0
ppm (t1)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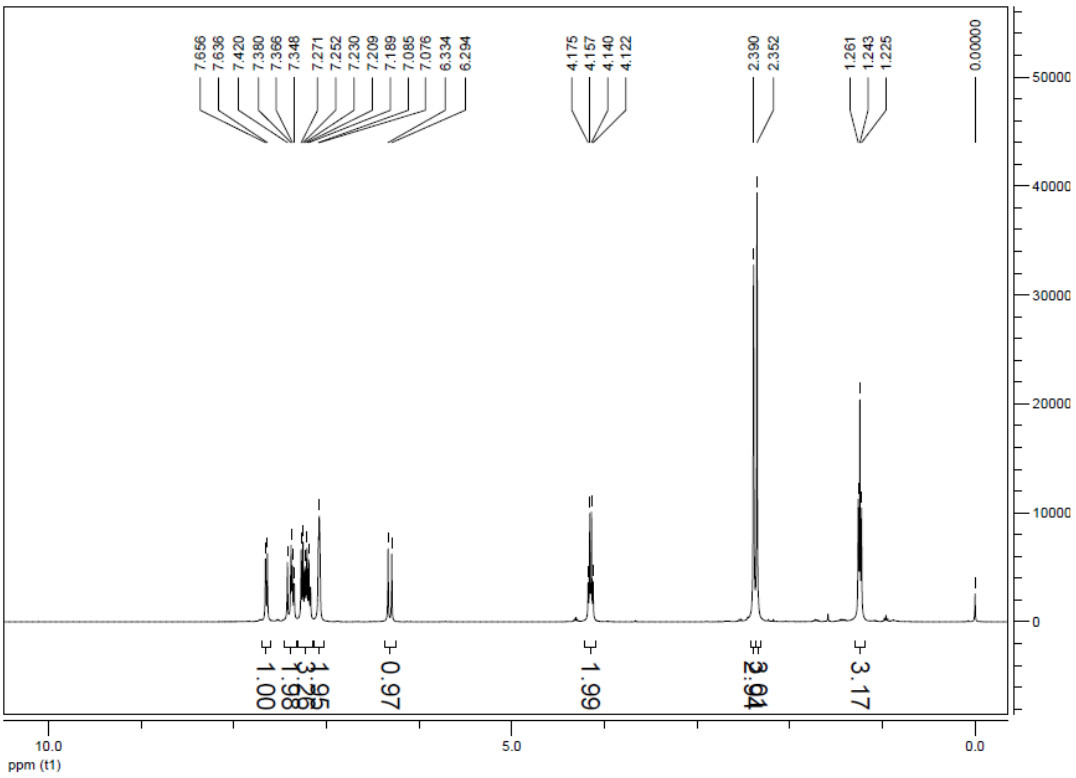
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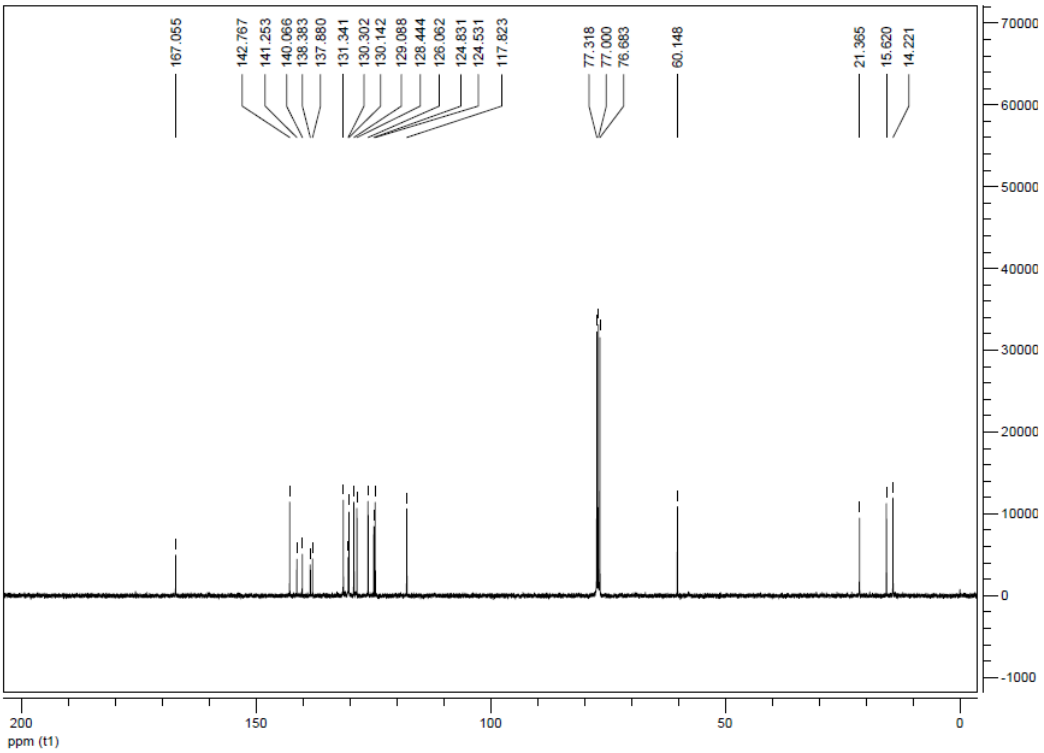
7.366
7.348
7.271
7.252
7.230
7.209
7.189
7.085
7.076
6.334
6.294
4.175
4.157
4.140
4.122
2.390
2.352
1.261
1.243
1.225
0.00000
1.00
1.98
3.25
1.95
0.97
1.99
3.04
3.17
10.0
5.0
0.0
ppm (t1)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140.066
138.383
137.880
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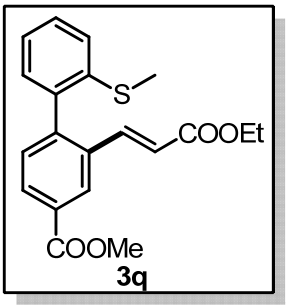
130.302
130.142
129.088
128.444
126.062
124.831
124.531
117.823
77.318
77.000
76.683
60.148
21.365
15.620
14.221
200
150
100
50
0
ppm (t1)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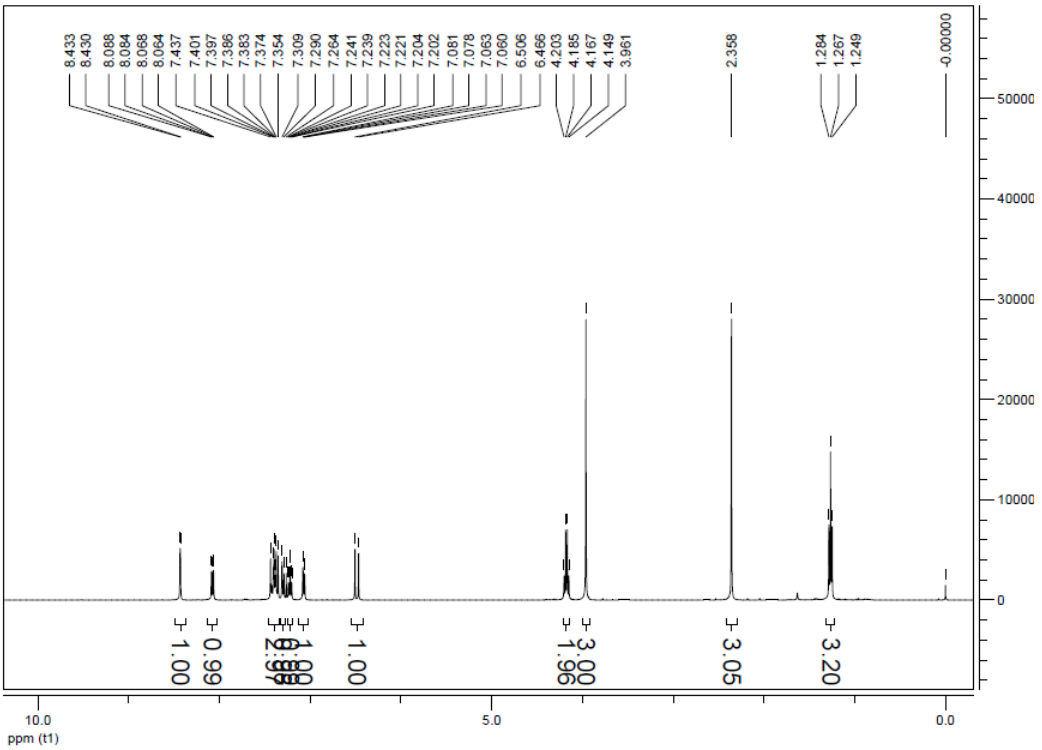
COOEt
COOMe
3q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7.401
7.397
7.386
7.383
7.374
7.354
7.309
7.290
7.264
7.241
7.239
7.223
7.221
7.204
7.202
7.081
7.078
7.063
7.060
6.506
6.466
4.203
4.185
4.167
4.149
3.961
2.358
1.284
1.267
1.249
-0.00000
1.00
0.99
1.00
1.00
3.00
1.96
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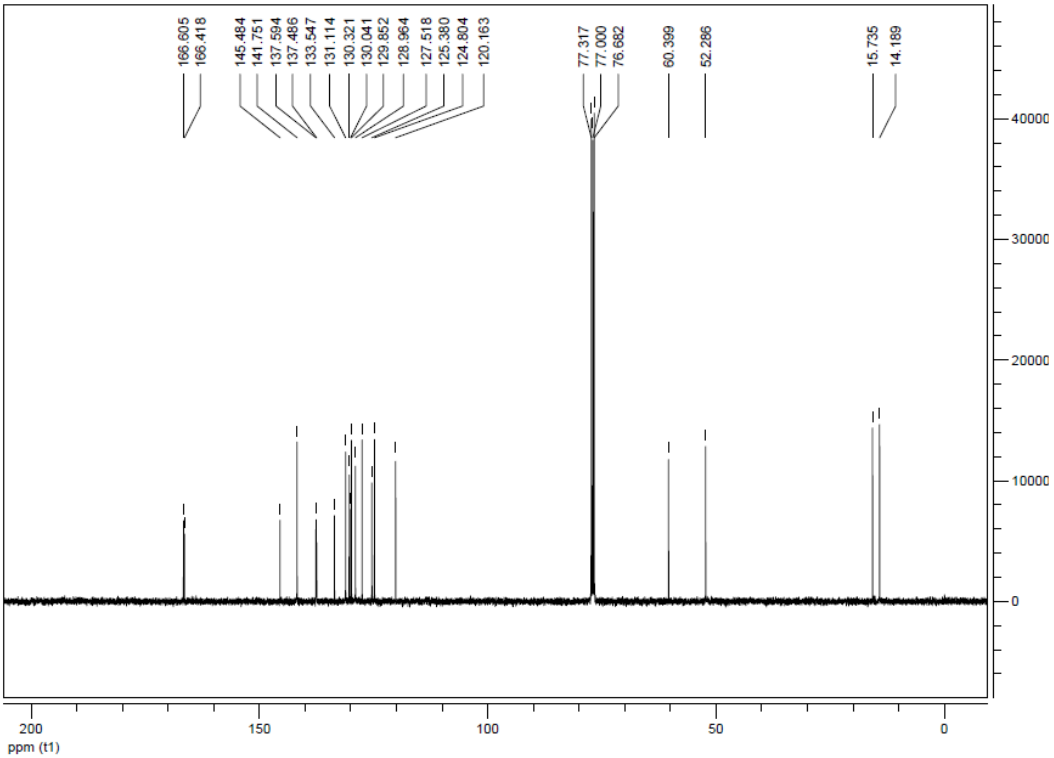
3.20
50000
40000
30000
20000
10000
0
10.0
5.0
0.0
ppm (t1)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137.486
133.547
131.114
130.321
130.041
129.852
128.964
127.518
125.380
124.804
120.163
77.317
77.000
76.682
60.399
52.286
15.735
14.189
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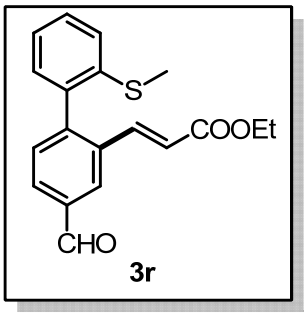
30000
20000
10000
0
200
150
100
50
0
ppm (t1)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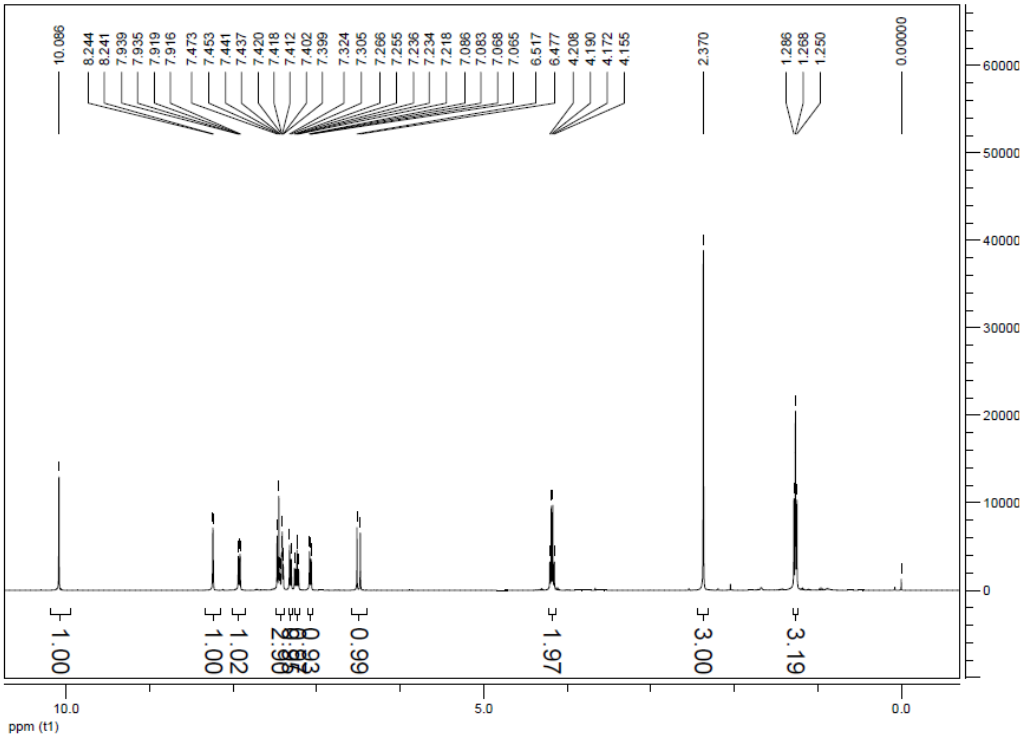
COOEt
CHO

3r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7.437
7.420
7.418
7.412
7.402
7.399
7.324
7.305
7.266
7.255
7.236
7.234
7.218
7.086
7.083
7.068
7.065
6.517
6.477
4.208
4.190
4.172
4.155
2.370
1.286
1.268
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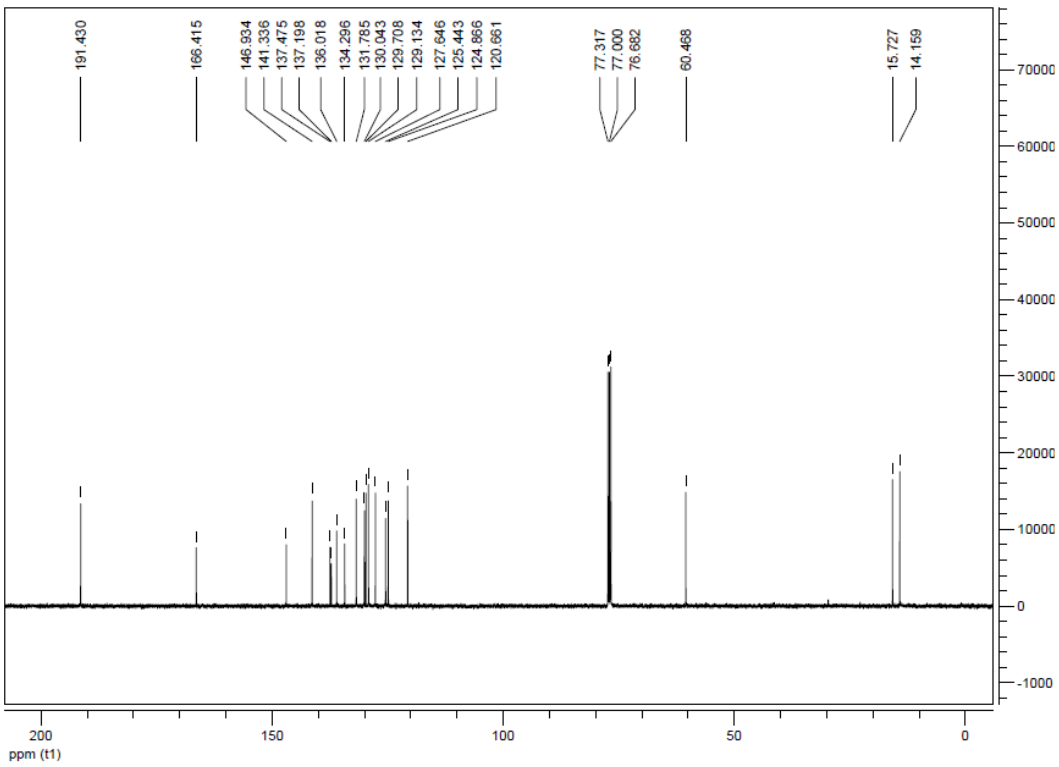
1.00
1.00
1.02
7.00
0.99
1.97
3.00
3.19
ppm (t1)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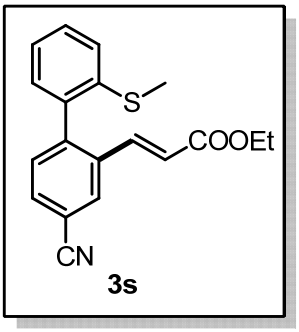
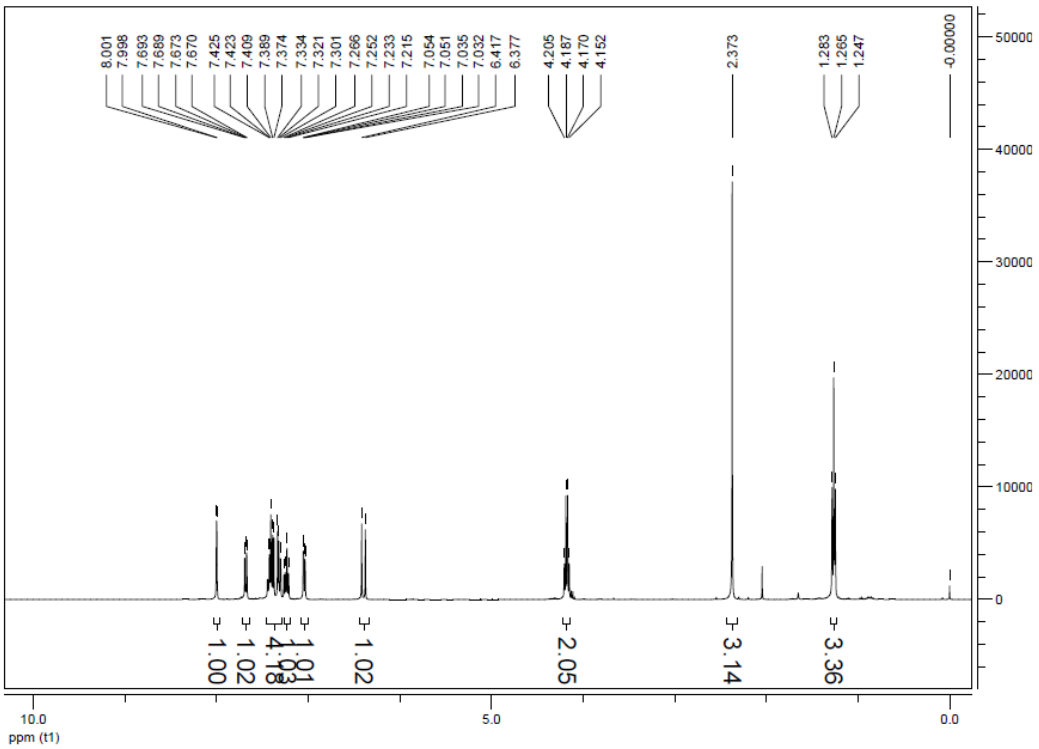
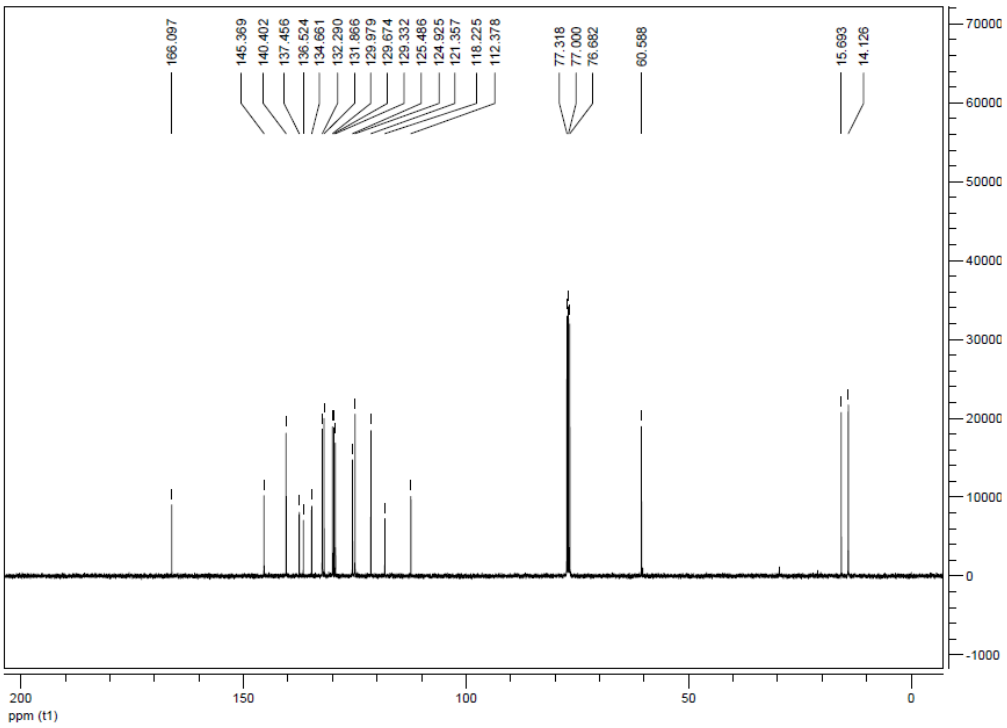
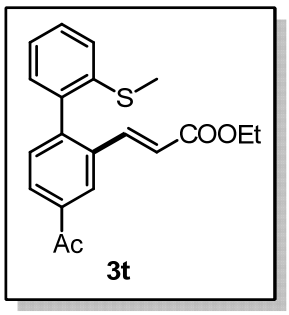
137.198
136.018
134.296
131.785
130.043
129.708
129.134
127.646
125.443
124.866
120.661
77.317
77.000
76.682
60.468
15.727
14.159
ppm (t1)


S
COOEt
CN

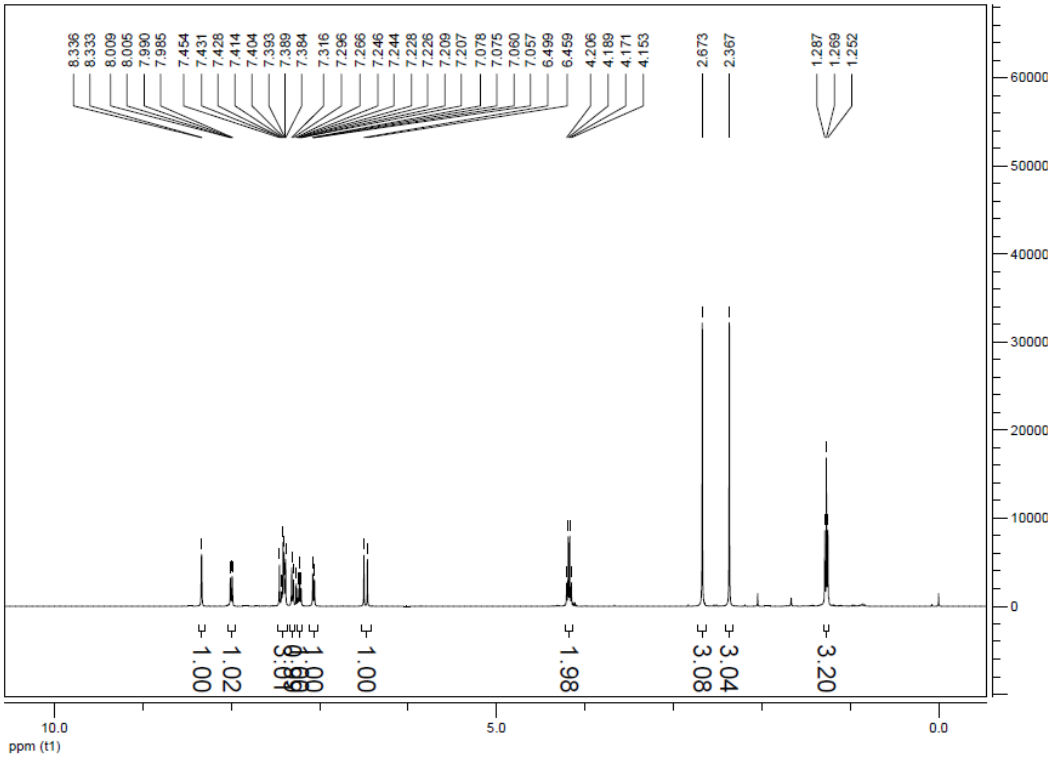
3s

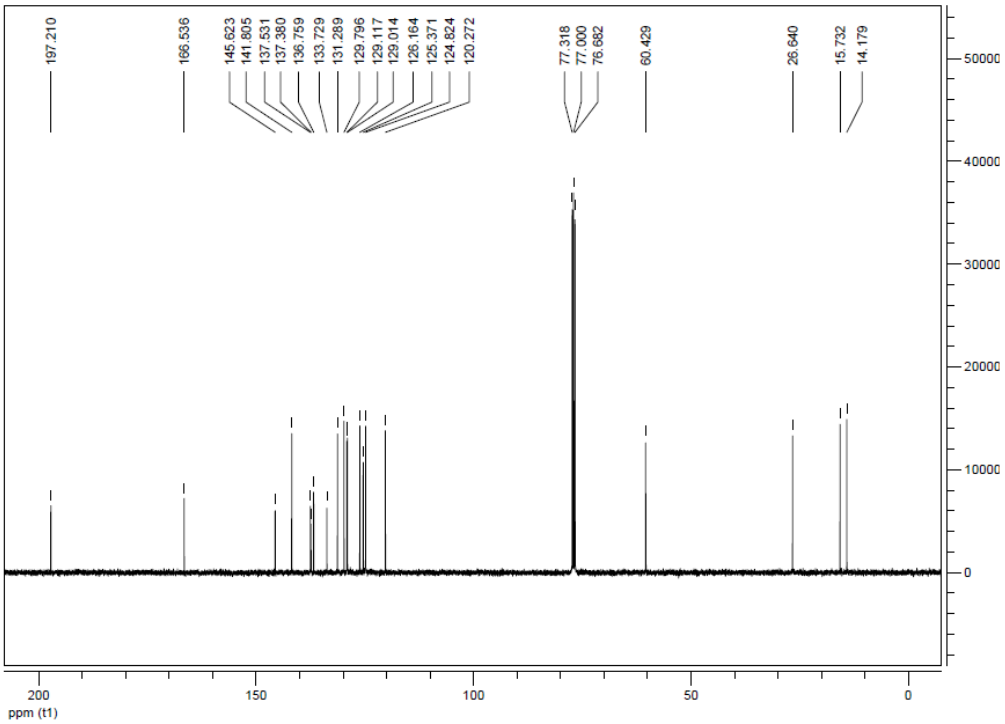

8.001
7.998
7.693
7.689
7.673
7.670
7.425
7.423
7.409
7.389
7.374
7.334
7.321
7.301
7.266
7.252
7.233
7.215
7.054
7.051
7.035
7.032
6.417
6.377
4.205
4.187
4.170
4.152
2.373
1.283
1.265
1.247
-0.00000
1.00
1.02
1.03
1.01
4.18
1.02
2.05
3.14
3.36
10.0
5.0
0.0
ppm (t1)

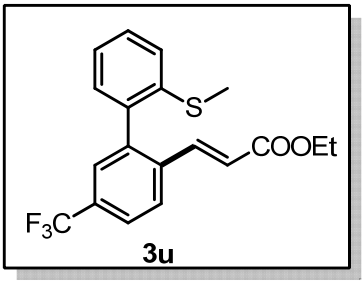

166.097
145.369
140.402
137.456
136.524
134.661
132.290
131.866
129.979
129.674
129.332
125.486
124.925
121.357
118.225
112.378
77.318
77.000
76.682
60.588
15.693
14.126
200
150
100
50
0
ppm (t1)


S
COOEt
Ac

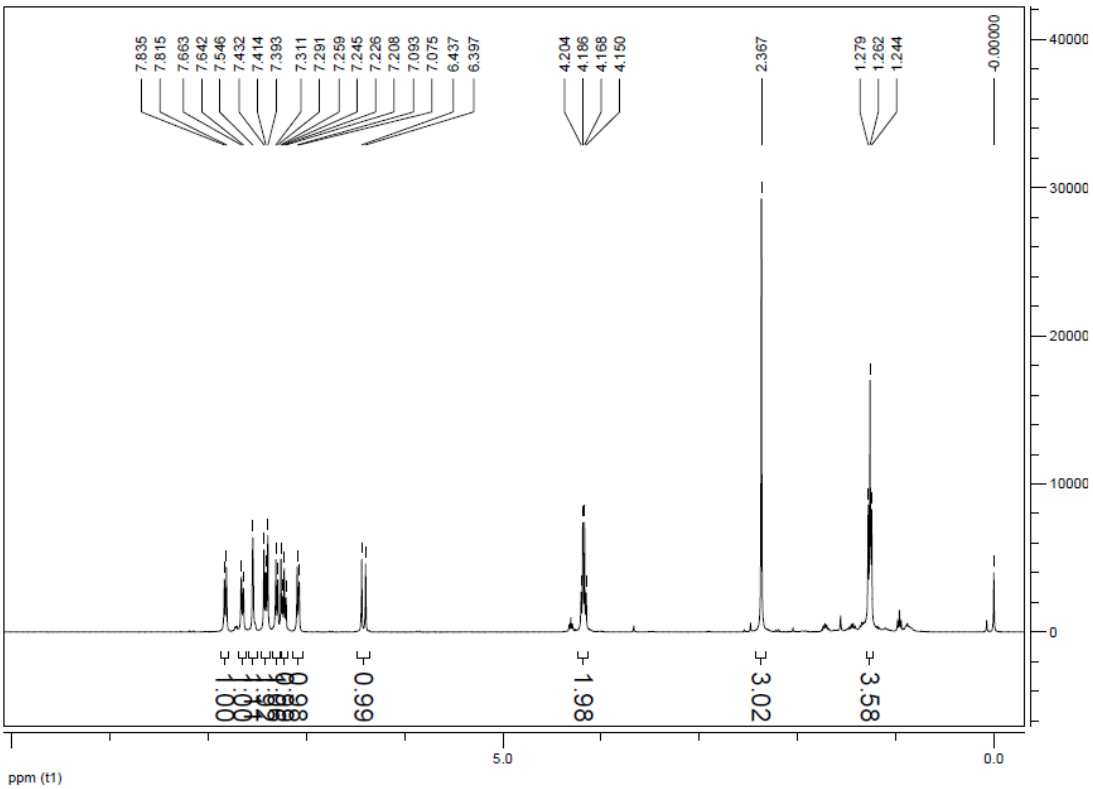
3t

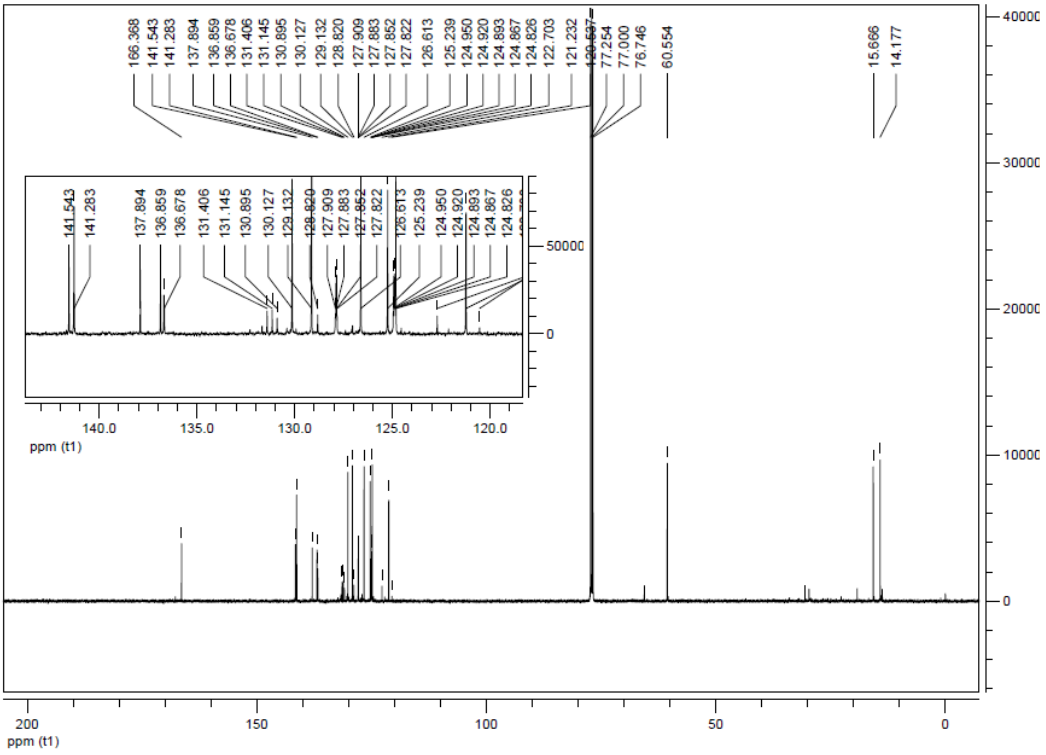

8.336
8.333
8.009
8.005
7.990
7.985
7.454
7.431
7.428
7.414
7.404
7.393
7.389
7.384
7.316
7.296
7.266
7.246
7.244
7.228
7.226
7.209
7.207
7.078
7.075
7.060
7.057
6.499
6.459
4.206
4.189
4.171
4.153
2.673
2.367
1.287
1.269
1.252
1.00
1.02
3.01
1.00
1.98
3.08
3.04
3.20
60000
50000
40000
30000
20000
10000
0
10.0
5.0
0.0
ppm (t1)

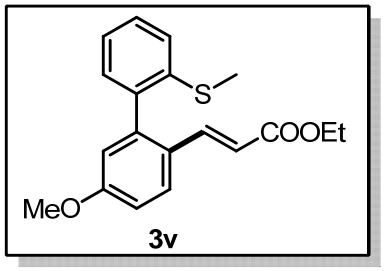

197.210
166.536
145.623
141.805
137.531
137.380
136.759
133.729
131.289
129.796
129.117
129.014
126.164
125.371
124.824
120.272
77.318
77.000
76.682
60.429
26.640
15.732
14.179
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)


S
COOEt
F3C

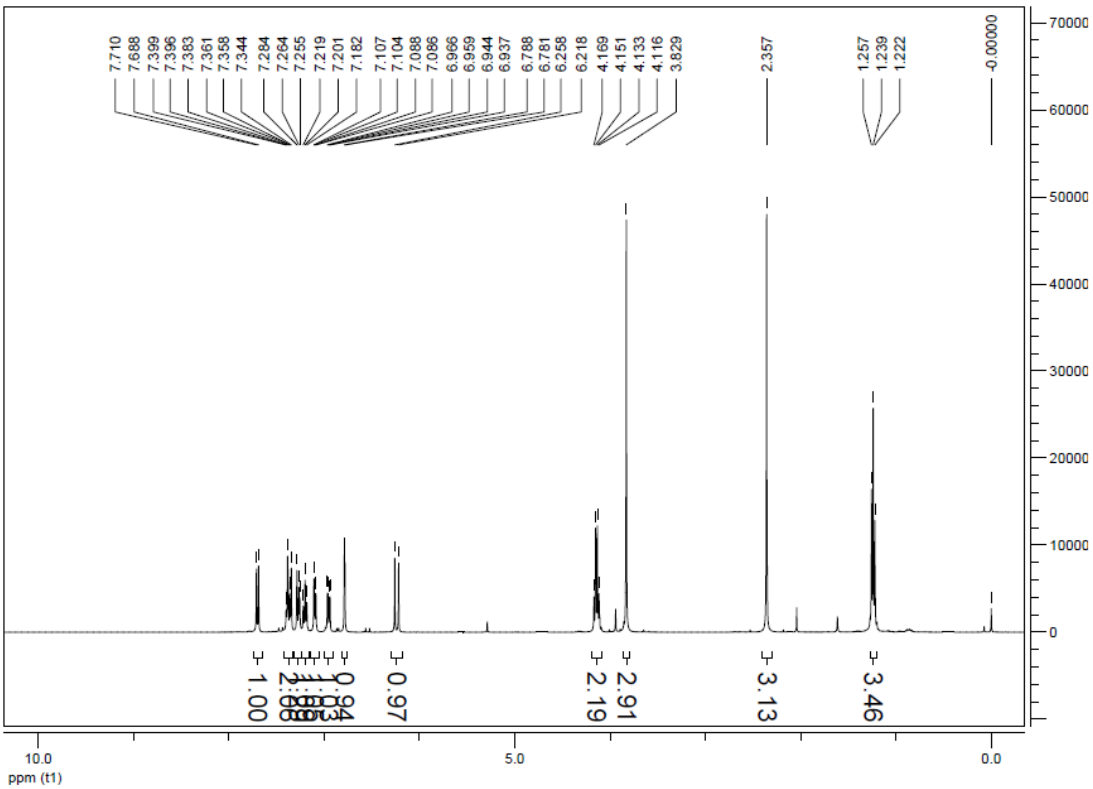
3u

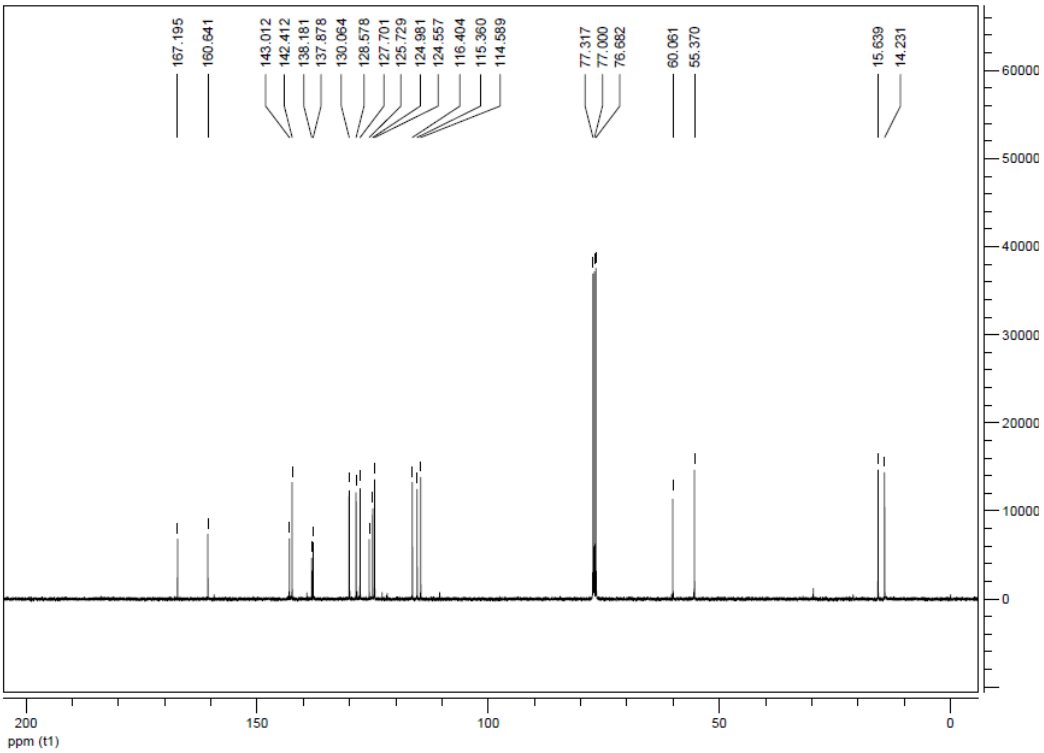

7.835
7.815
7.663
7.642
7.546
7.432
7.414
7.393
7.311
7.291
7.259
7.245
7.226
7.208
7.093
7.075
6.437
6.397
4.204
4.186
4.168
4.150
2.367
1.279
1.262
1.244
-0.00000
1.00
0.99
1.98
3.02
3.58
ppm (t1)

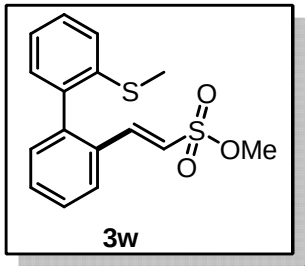

166.368
141.543
141.283
137.894
136.859
136.678
131.406
131.145
130.895
130.127
129.132
128.820
127.909
127.883
127.852
127.822
126.613
125.239
124.950
124.920
124.893
124.867
124.826
122.703
121.232
77.254
77.000
76.746
60.554
15.666
14.177
ppm (t1)


S
COOEt
MeO

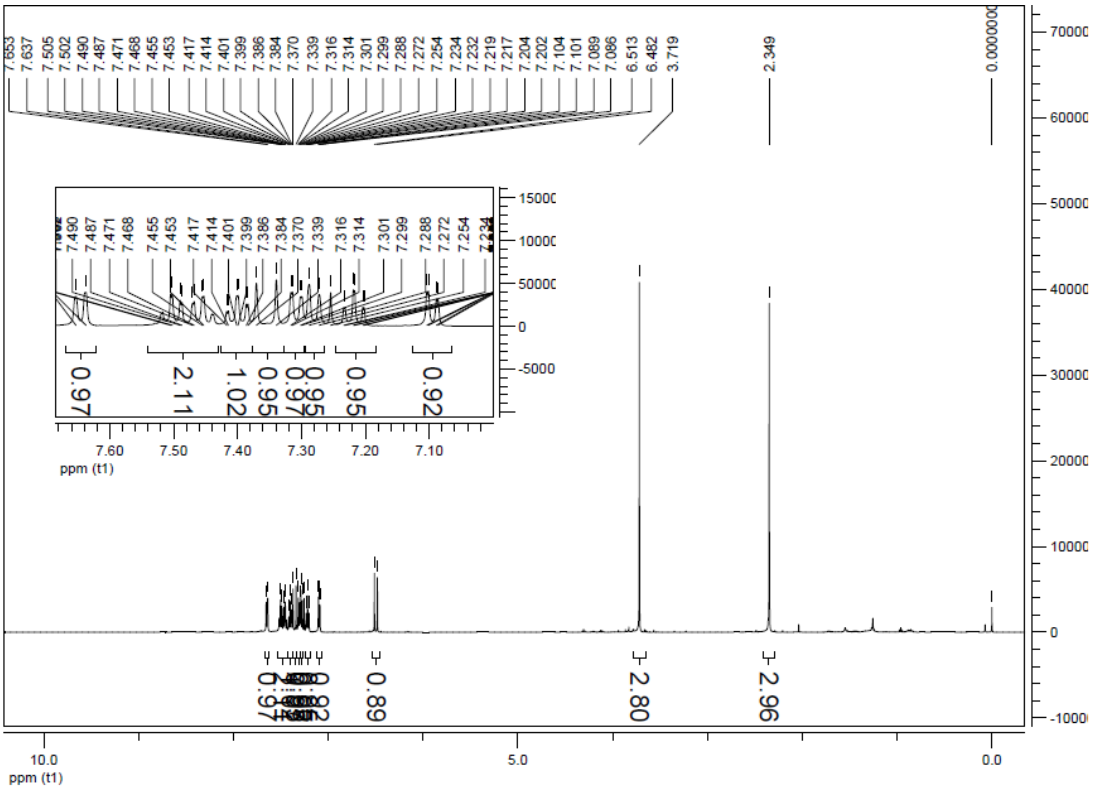
3v

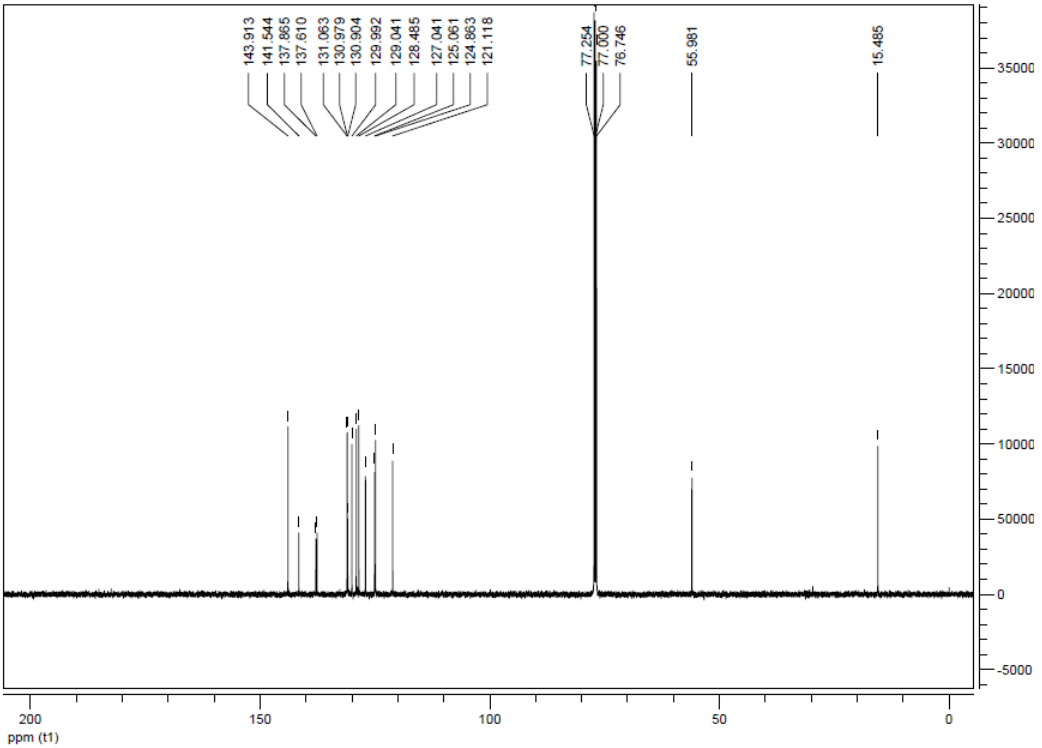

7.710
7.688
7.399
7.396
7.383
7.361
7.358
7.344
7.284
7.264
7.255
7.219
7.201
7.182
7.107
7.104
7.088
7.086
6.966
6.959
6.944
6.937
6.788
6.781
6.258
6.218
4.169
4.151
4.133
4.116
3.829
2.357
1.257
1.239
1.222
-0.00000
1.00
0.97
2.19
2.91
3.13
3.46
10.0
5.0
0.0
ppm (t1)

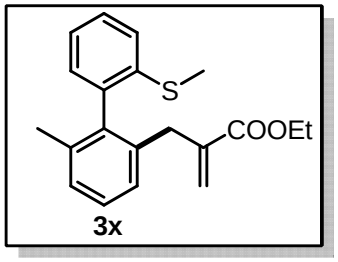

167.195
160.641
143.012
142.412
138.181
137.878
130.064
128.578
127.701
125.729
124.981
124.557
116.404
115.360
114.589
77.317
77.000
76.682
60.061
55.370
15.639
14.231
200
150
100
50
0
ppm (t1)


S
O
S
O
OMe
O

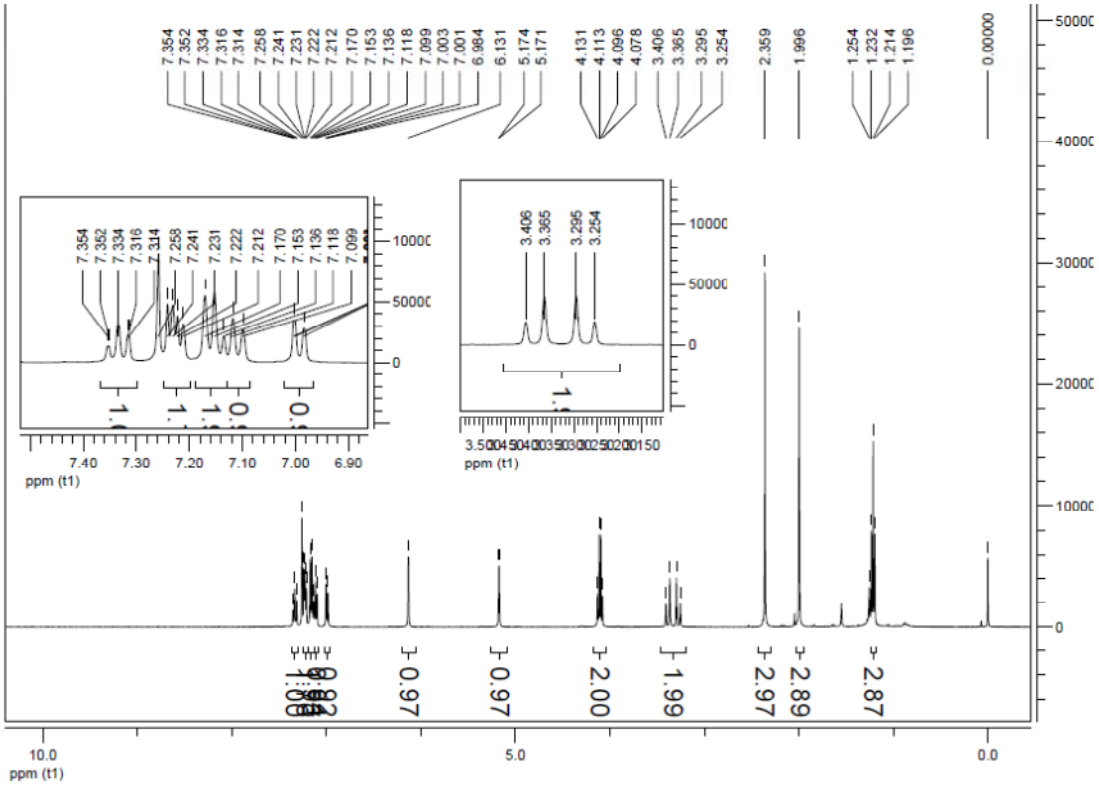
3w

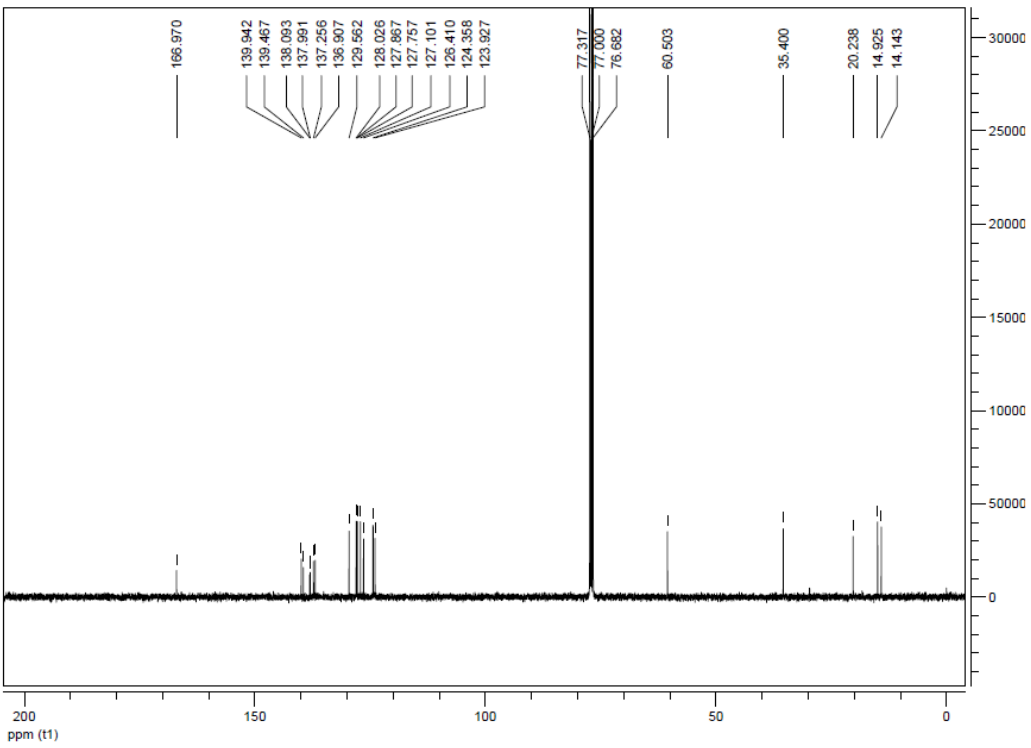

7.653
7.637
7.505
7.502
7.490
7.487
7.471
7.468
7.455
7.453
7.417
7.414
7.401
7.399
7.386
7.384
7.370
7.339
7.316
7.314
7.301
7.299
7.288
7.272
7.254
7.234
7.232
7.219
7.217
7.204
7.202
7.104
7.101
7.089
7.086
6.513
6.482
3.719
2.349
0.000000
0.97
2.11
1.02
0.95
0.89
0.95
0.92
0.89
2.80
2.96
ppm (t1)


143.913
141.544
137.865
137.610
131.063
130.979
130.904
129.992
129.041
128.485
127.041
125.061
124.863
121.118
77.254
77.000
76.746
55.981
15.485
ppm (t1)

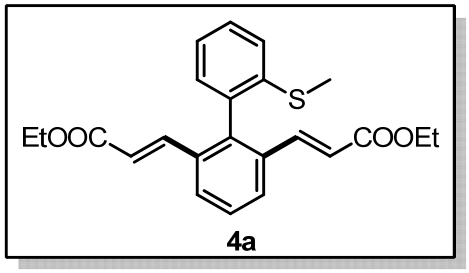

S
COOEt

3x

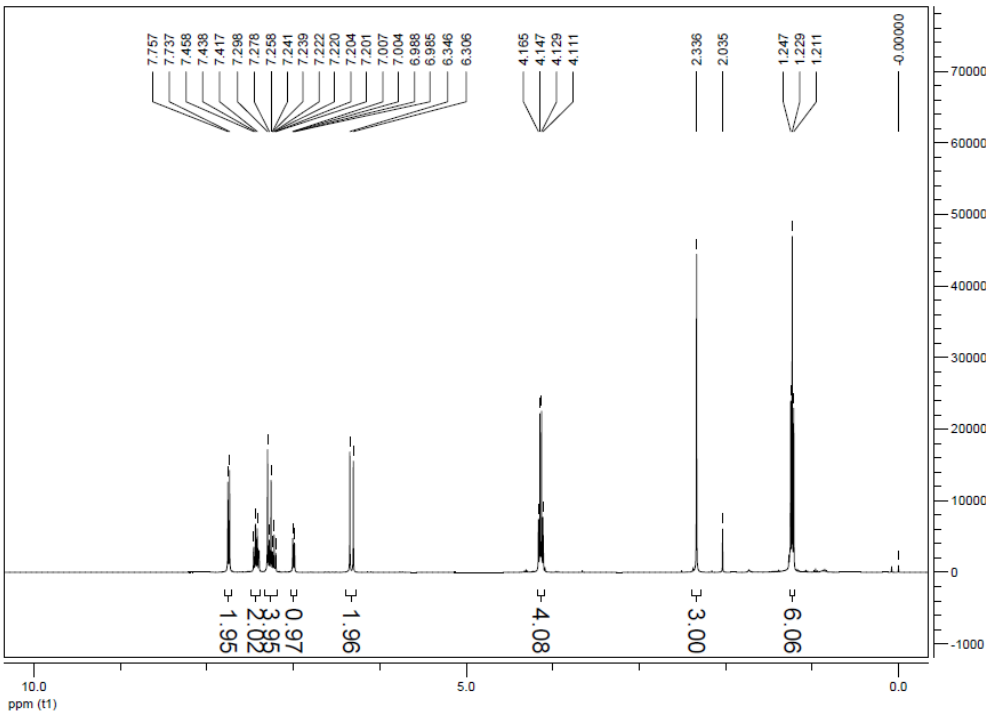

7.354
7.352
7.334
7.316
7.314
7.258
7.241
7.231
7.222
7.212
7.170
7.153
7.136
7.118
7.099
7.003
7.001
6.984
6.131
5.174
5.171
4.131
4.113
4.096
4.078
3.406
3.365
3.295
3.254
2.359
1.996
1.254
1.232
1.214
1.196
0.00000
ppm (t1)
10.0
5.0
0.0
2.87
2.89
2.97
2.00
1.99
0.97
0.97

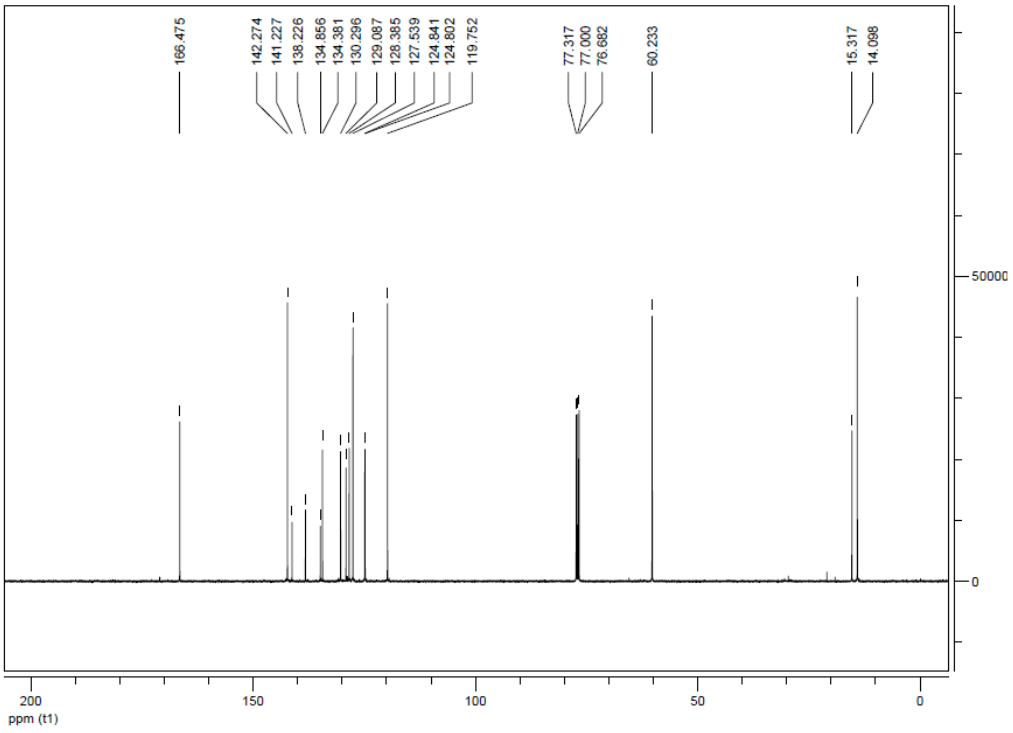

166.970
139.942
139.467
138.093
137.991
137.256
136.907
129.562
128.026
127.867
127.757
127.101
126.410
124.358
123.927
77.317
77.000
76.682
60.503
35.400
20.238
14.925
14.143
ppm (t1)
200
150
100
50
0

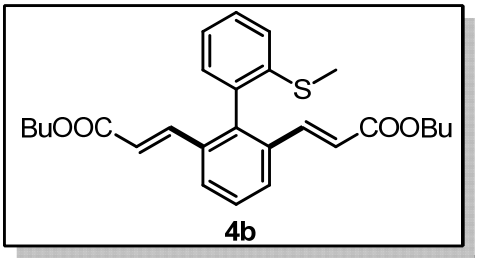
3. Characterization of di-alkenylation product 4



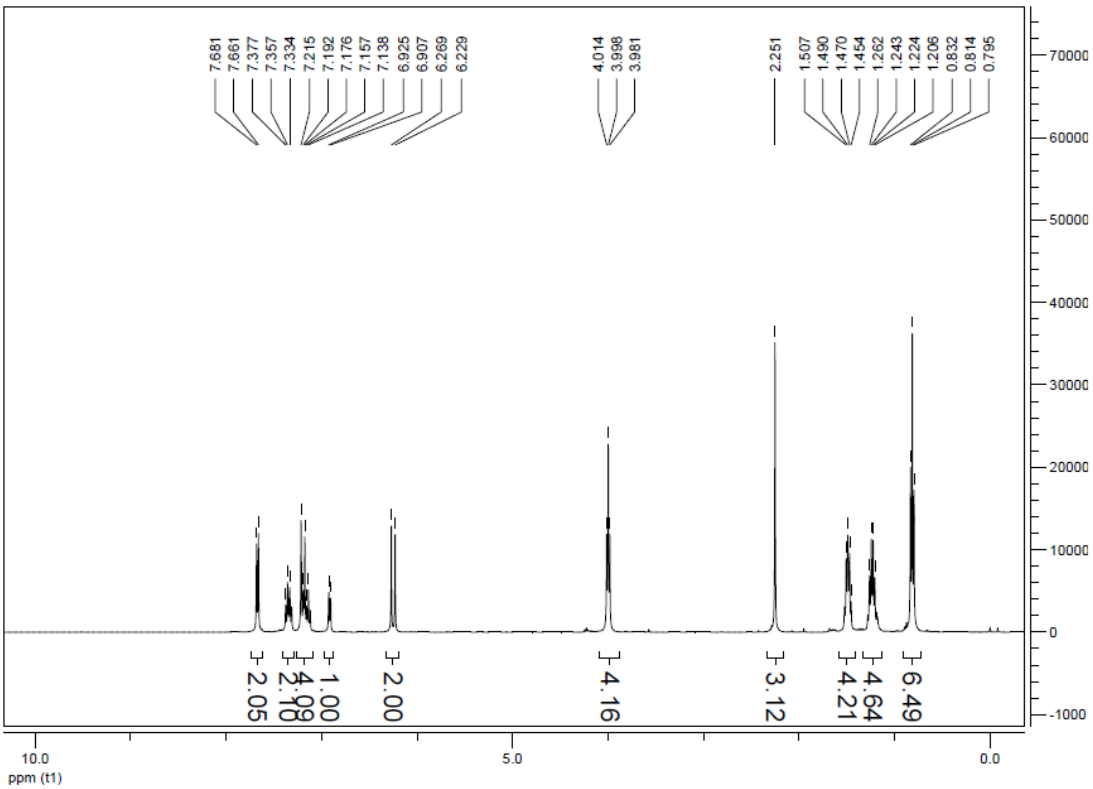
4a

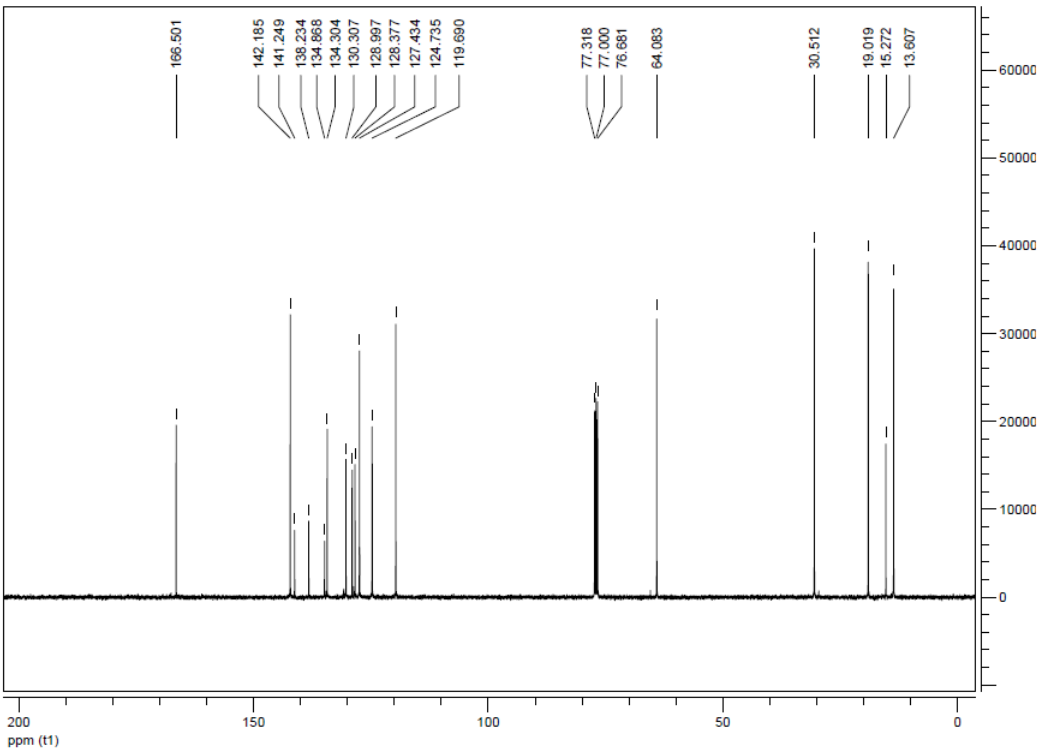


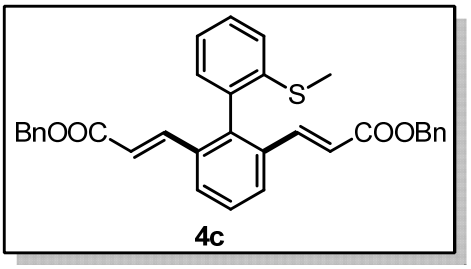



BuOOC
S
COOBu

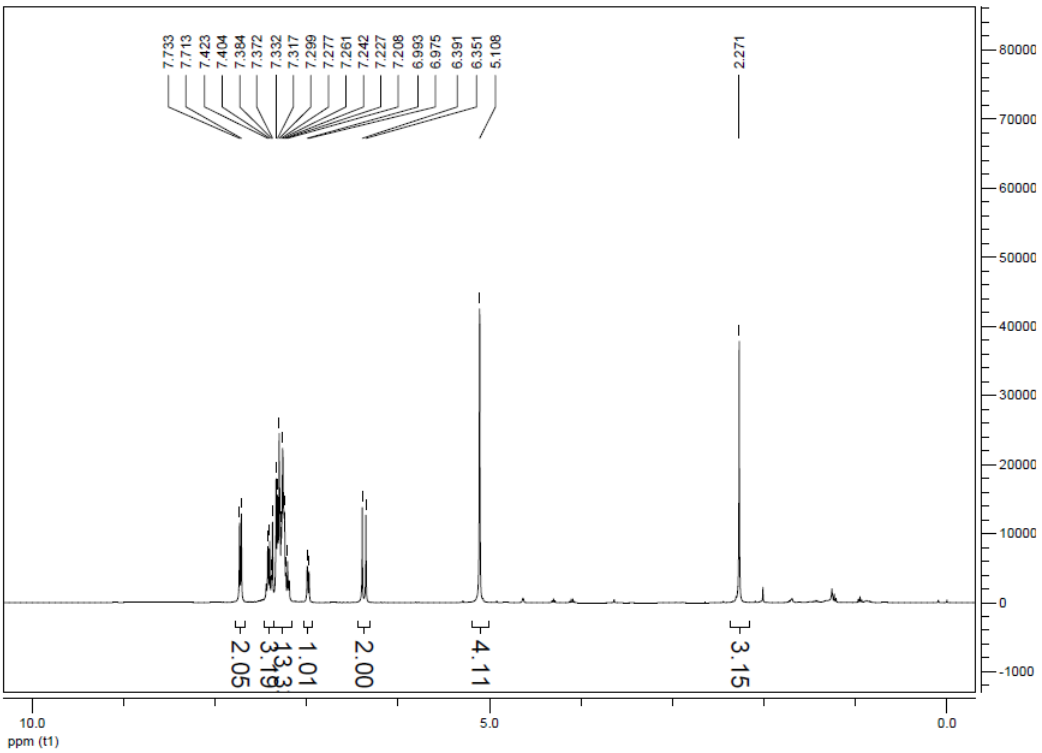
4b

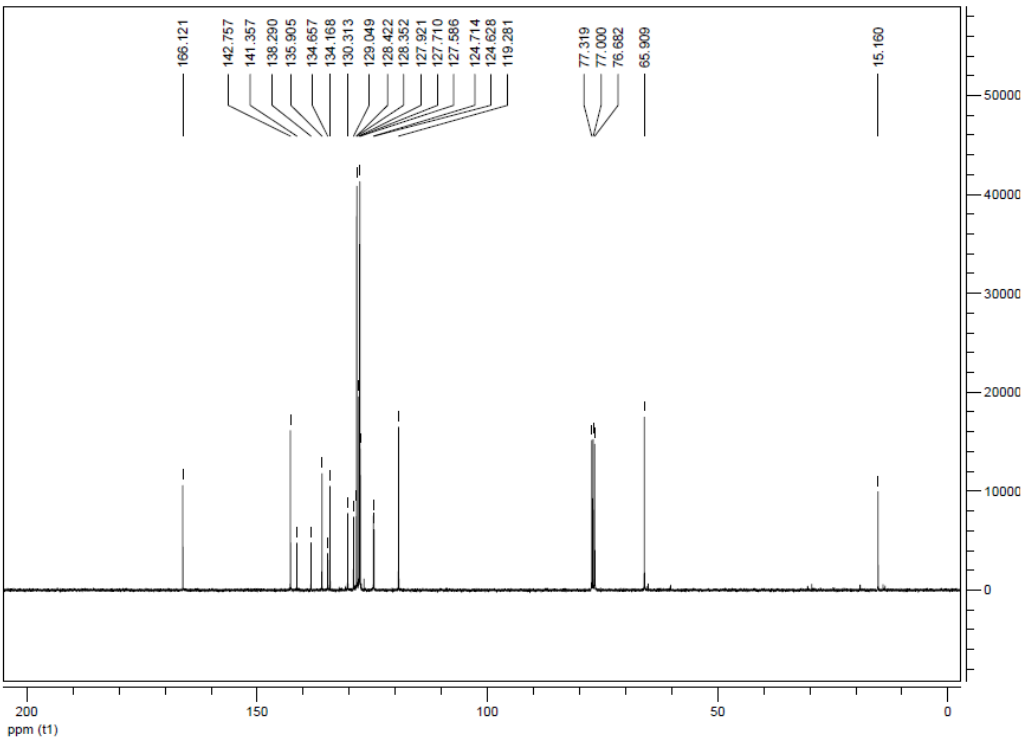

7.681
7.661
7.377
7.357
7.334
7.215
7.192
7.176
7.157
7.138
6.925
6.907
6.269
6.229
4.014
3.998
3.981
2.251
1.507
1.490
1.470
1.454
1.262
1.243
1.224
1.206
0.832
0.814
0.795
2.05
2.10
4.09
1.00
2.00
4.16
3.12
4.21
4.64
6.49
10.0
5.0
0.0
ppm (t1)

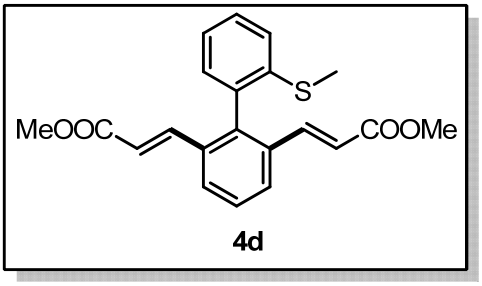

166.501
142.185
141.249
138.234
134.868
134.304
130.307
128.997
128.377
127.434
124.735
119.690
77.318
77.000
76.681
64.083
30.512
19.019
15.272
13.607
200
150
100
50
0
ppm (t1)


BnOOC
COOBn
S

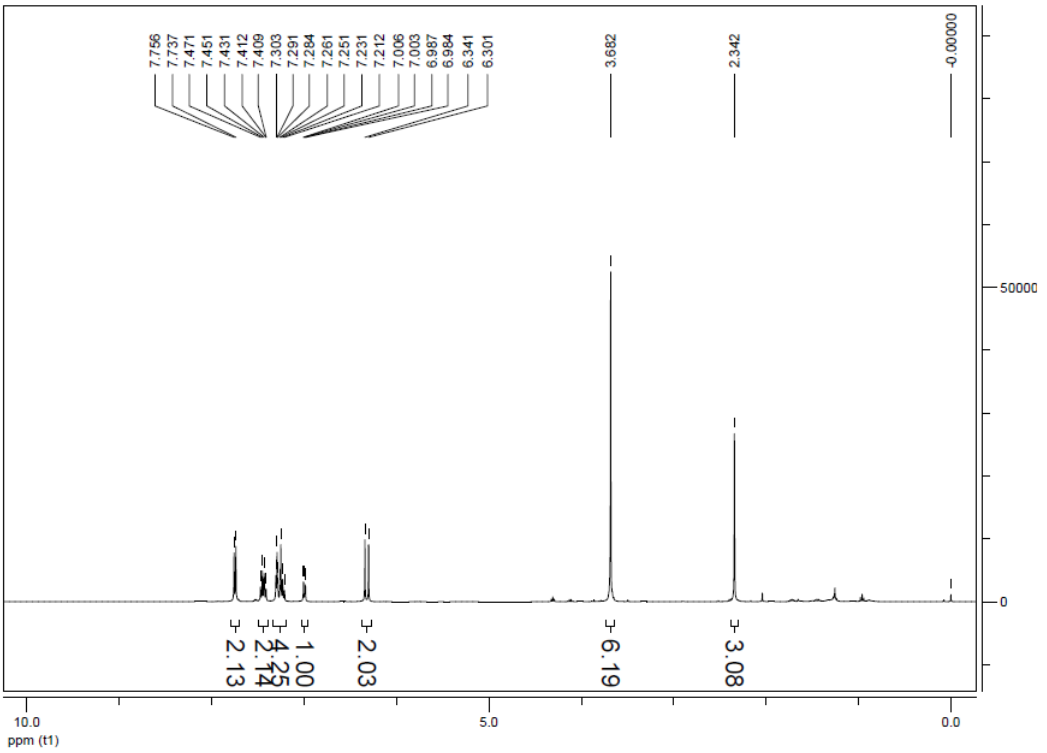
4c

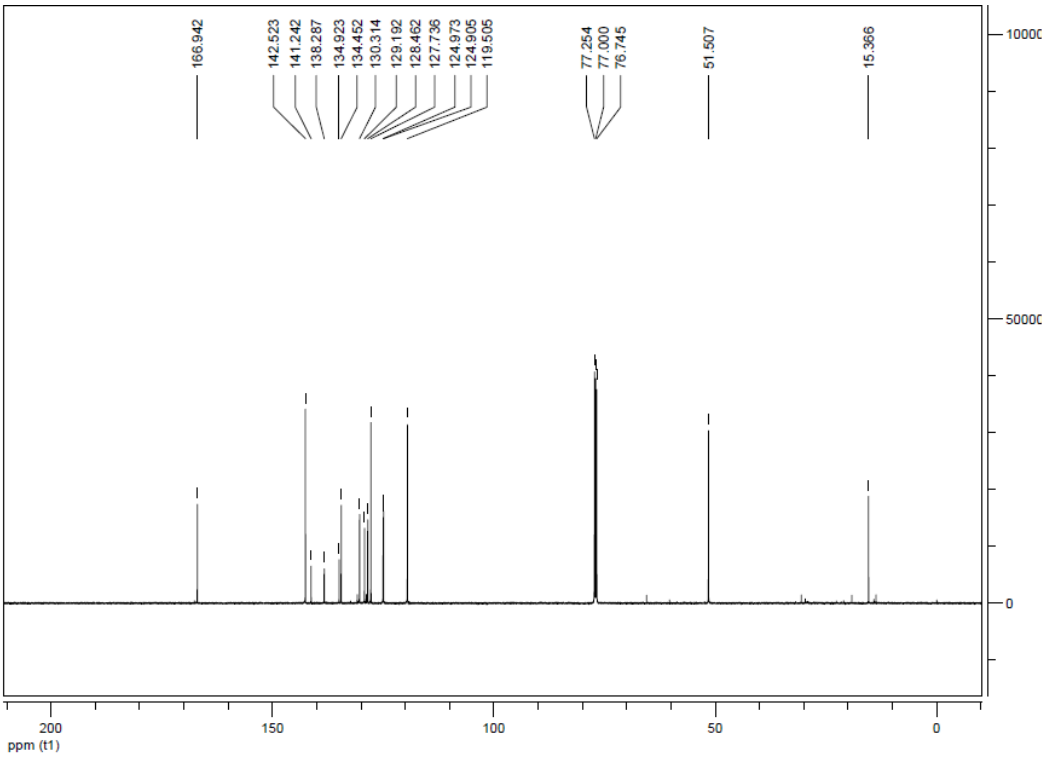

7.733
7.713
7.423
7.404
7.384
7.372
7.332
7.317
7.299
7.277
7.261
7.242
7.227
7.208
6.993
6.975
6.391
6.351
5.108
2.271
2.05
3.19
3.13
1.01
2.00
4.11
3.15
ppm (t1)

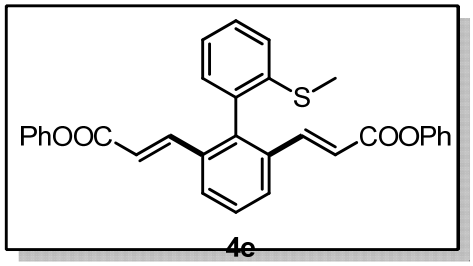

166.121
142.757
141.357
138.290
135.905
134.657
134.168
130.313
129.049
128.422
128.352
127.921
127.710
127.586
124.714
124.628
119.281
77.319
77.000
76.682
65.909
15.160
ppm (t1)


MeOOC
S
COOMe

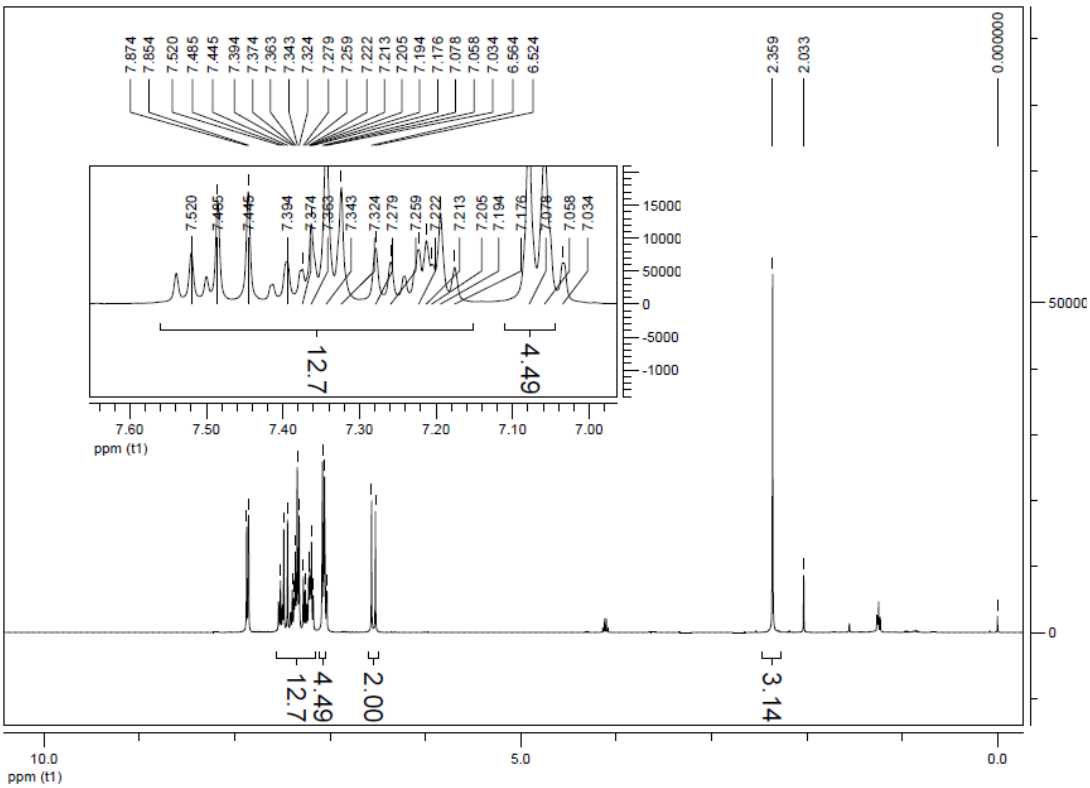
4d

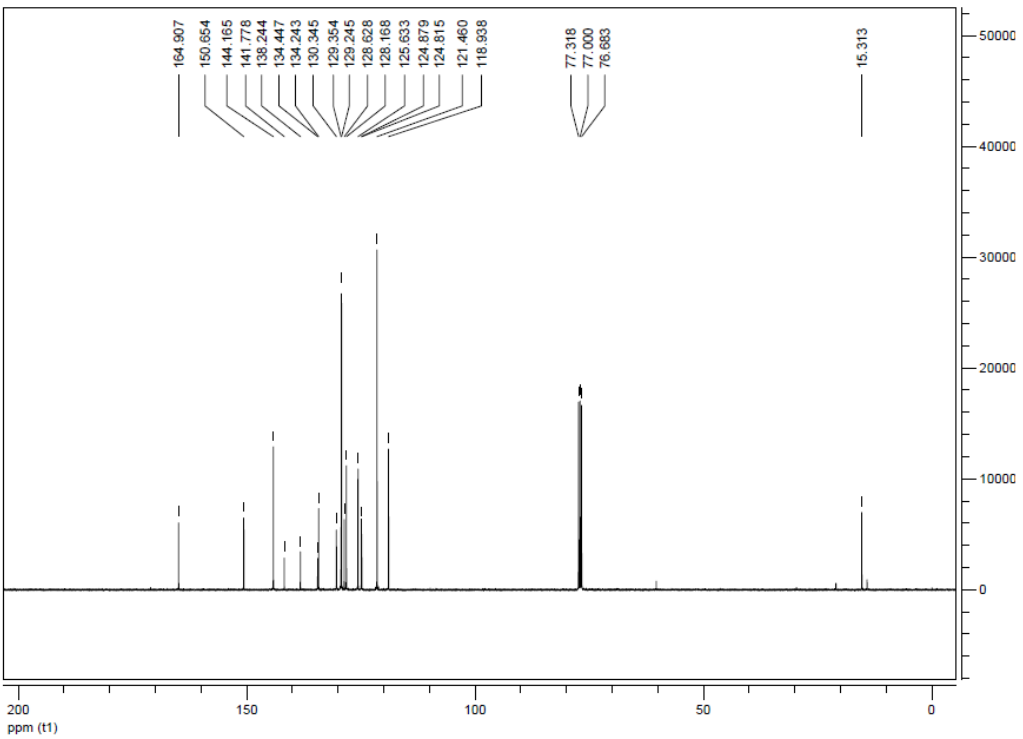

7.756
7.737
7.471
7.451
7.431
7.412
7.409
7.303
7.291
7.284
7.261
7.251
7.231
7.212
7.006
7.003
6.987
6.984
6.341
6.301
3.682
2.342
-0.00000
50000
0
2.13
2.14
4.25
1.00
2.03
6.19
3.08
10.0
5.0
0.0
ppm (t1)


166.942
142.523
141.242
138.287
134.923
134.452
130.314
129.192
128.462
127.736
124.973
124.905
119.505
77.254
77.000
76.745
51.507
15.366
100000
50000
0
200
150
100
50
0
ppm (t1)


PhOOC
S
COOPh

4e


7.874
7.854
7.520
7.485
7.445
7.394
7.374
7.363
7.343
7.324
7.279
7.259
7.222
7.213
7.205
7.194
7.176
7.078
7.058
7.034
6.564
6.524
2.359
2.033
0.000000
12.7
4.49
2.00
3.14
ppm (t1)


164.907
150.654
144.165
141.778
138.244
134.447
134.243
130.345
129.354
129.245
128.628
128.168
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124.879
124.815
121.460
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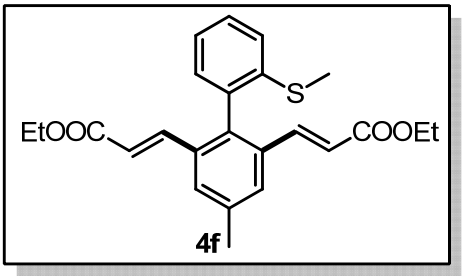
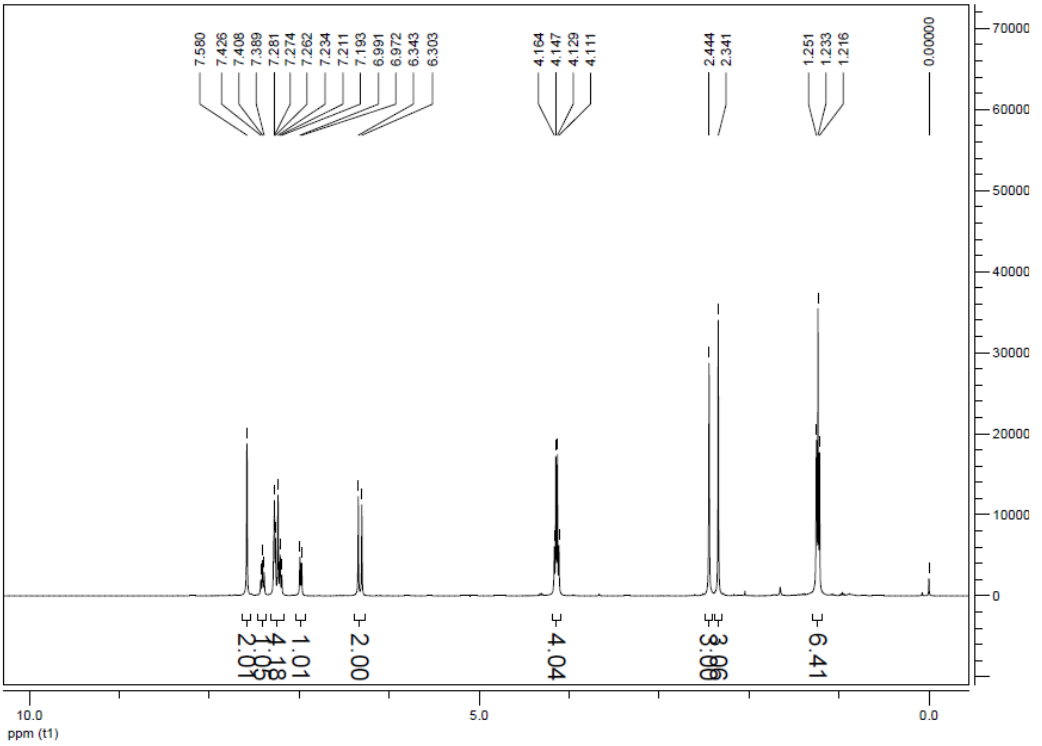
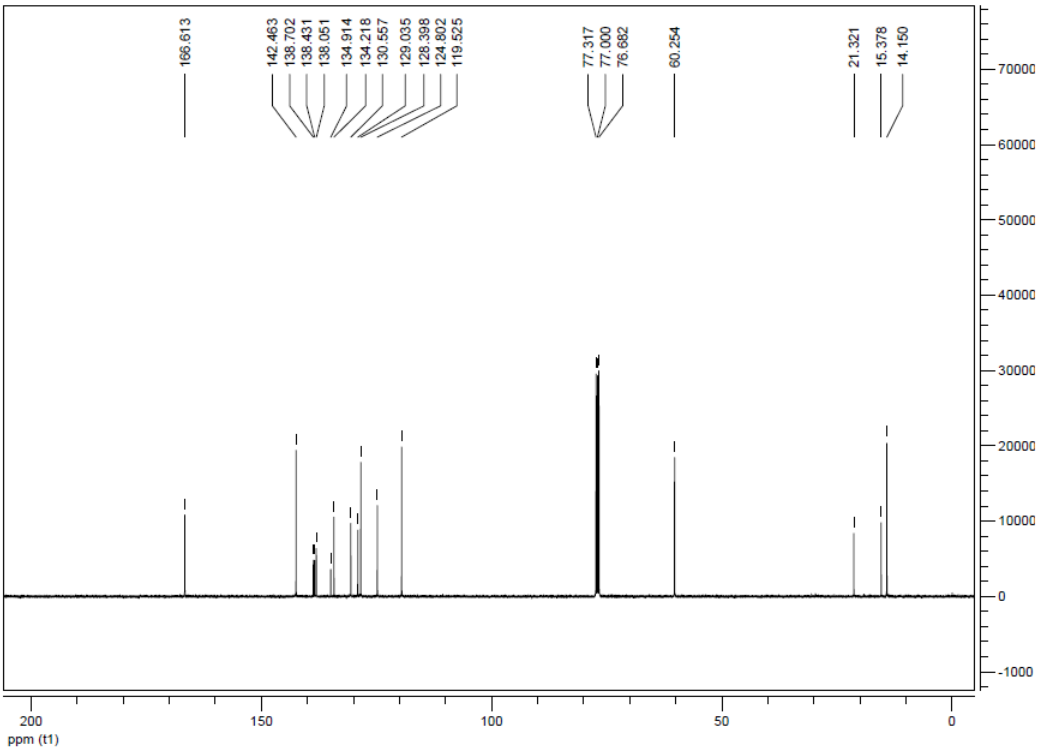
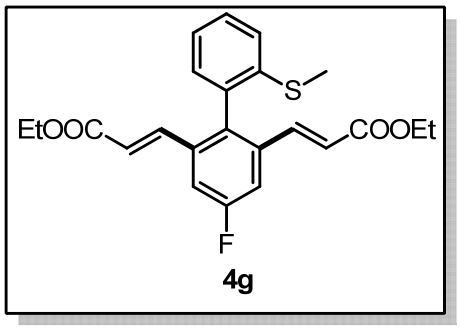
77.318
77.000
76.683
15.313
ppm (t1)

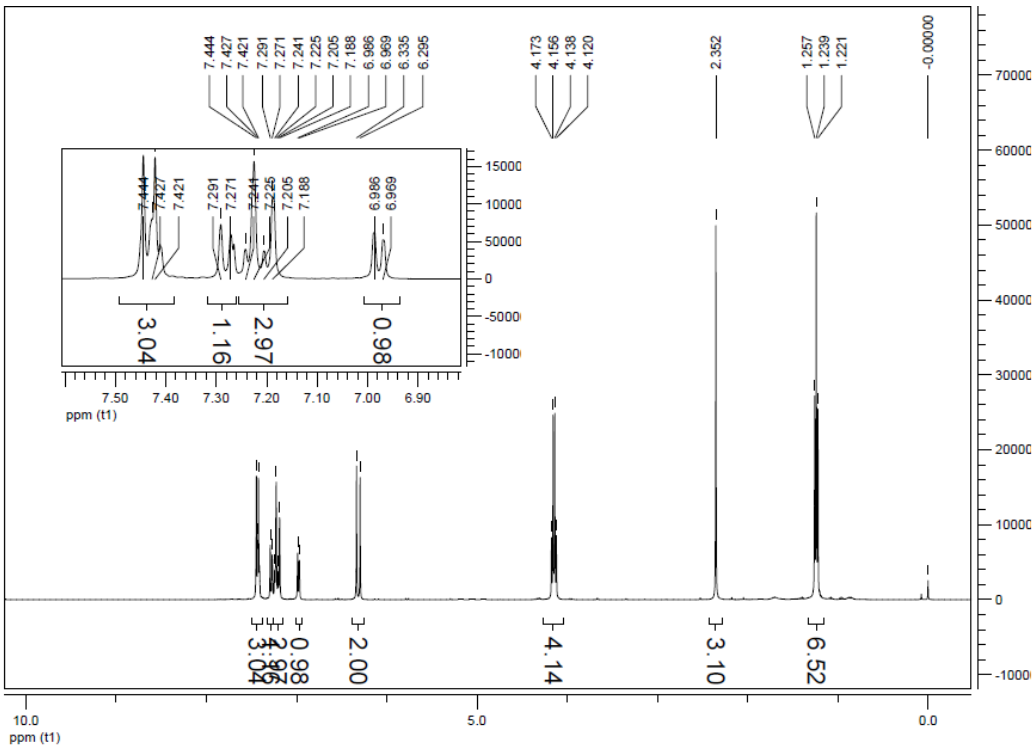

EtOOC
COOEt
S
4f

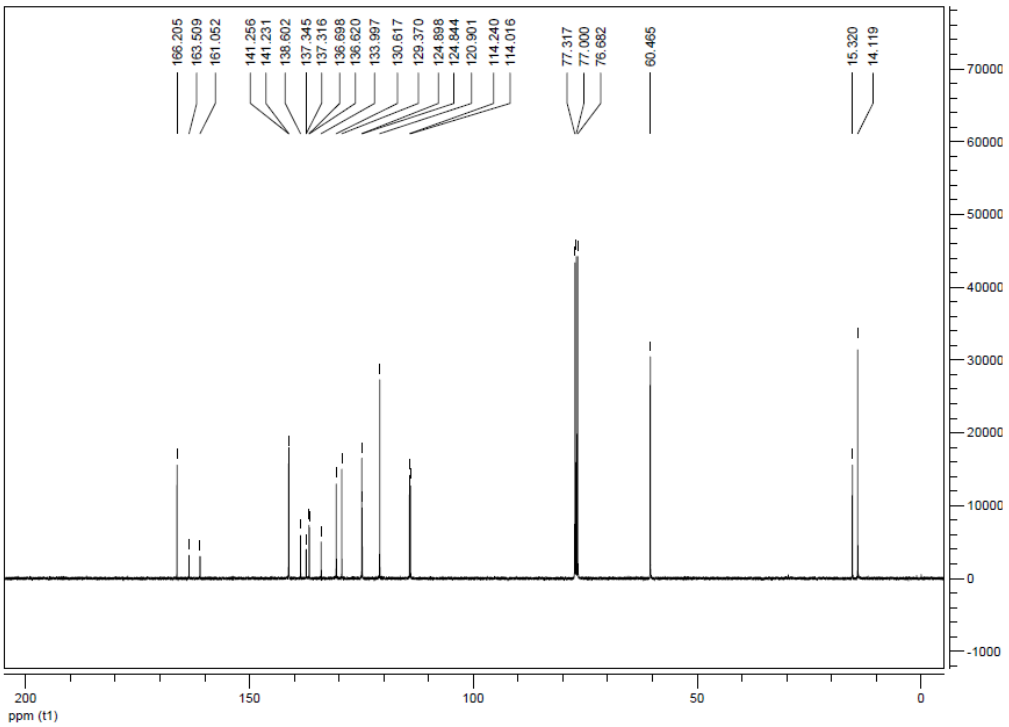

7.580
7.426
7.408
7.389
7.281
7.274
7.262
7.234
7.211
7.193
6.991
6.972
6.343
6.303
4.164
4.147
4.129
4.111
2.444
2.341
1.251
1.233
1.216
0.00000
2.07
1.05
4.18
1.01
2.00
4.04
3.06
6.41
10.0
5.0
0.0
ppm (t1)

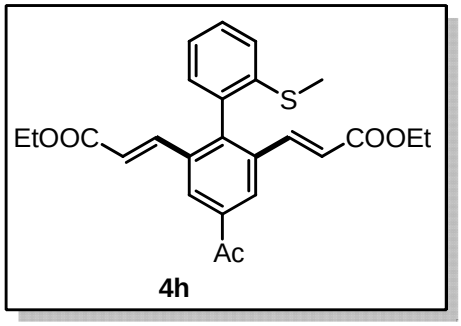

166.613
142.463
138.702
138.431
138.051
134.914
134.218
130.557
129.035
128.398
124.802
119.525
77.317
77.000
76.682
60.254
21.321
15.378
14.150
200
150
100
50
0
ppm (t1)


EtOOC
COOEt
S
F

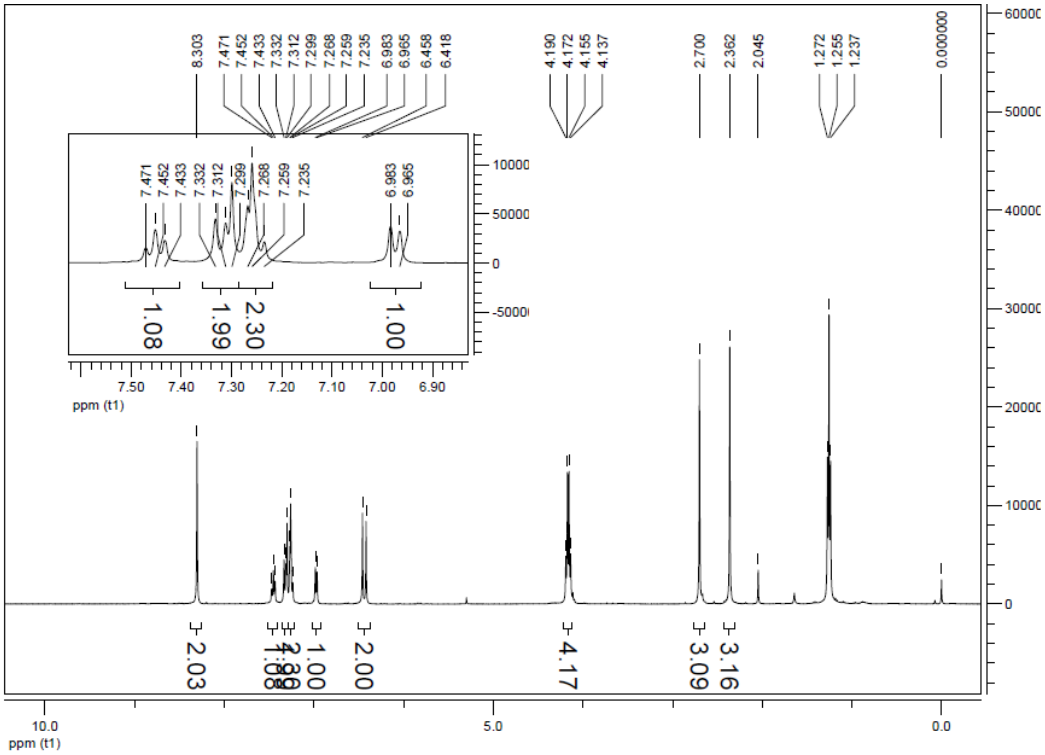
4g

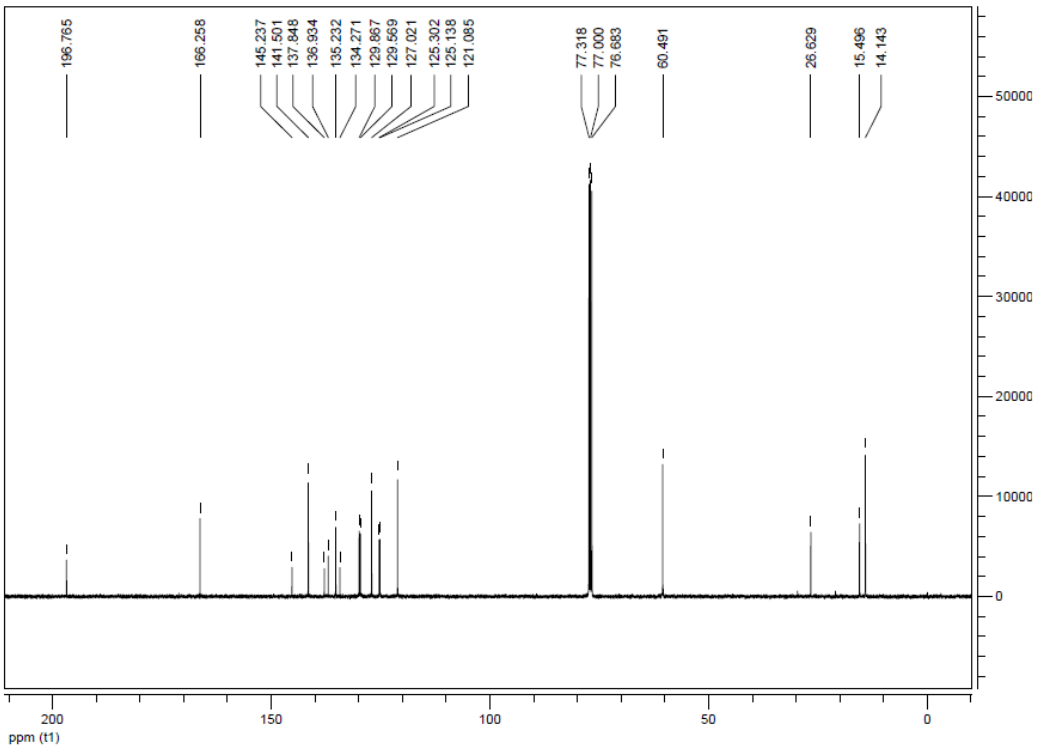

7.444
7.427
7.421
7.291
7.271
7.241
7.225
7.205
7.188
6.986
6.969
6.335
6.295
4.173
4.156
4.138
4.120
2.352
1.257
1.239
1.221
-0.00000
3.04
1.16
2.97
0.98
ppm (t1)
3.04
2.86
0.98
2.00
4.14
3.10
6.52


166.205
163.509
161.052
141.256
141.231
138.602
137.345
137.316
136.698
136.620
133.997
130.617
129.370
124.898
124.844
120.901
114.240
114.016
77.317
77.000
76.682
60.465
15.320
14.119
ppm (t1)

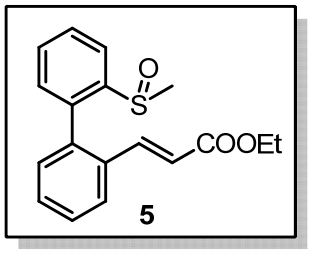

S
EtOOC
COOEt
Ac

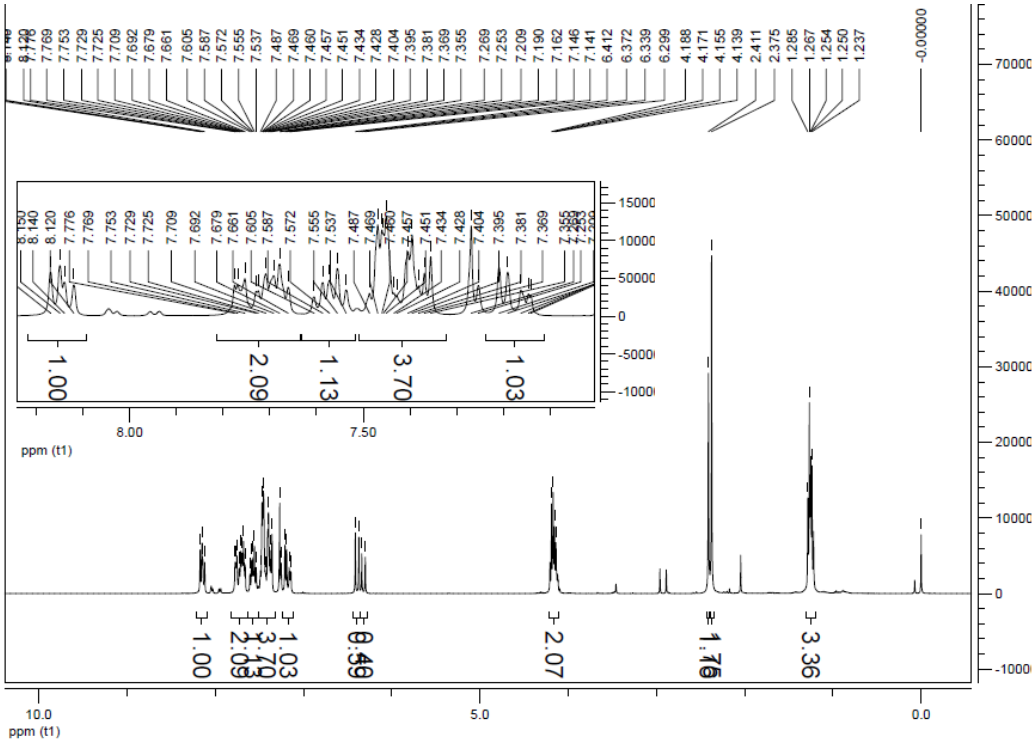
4h

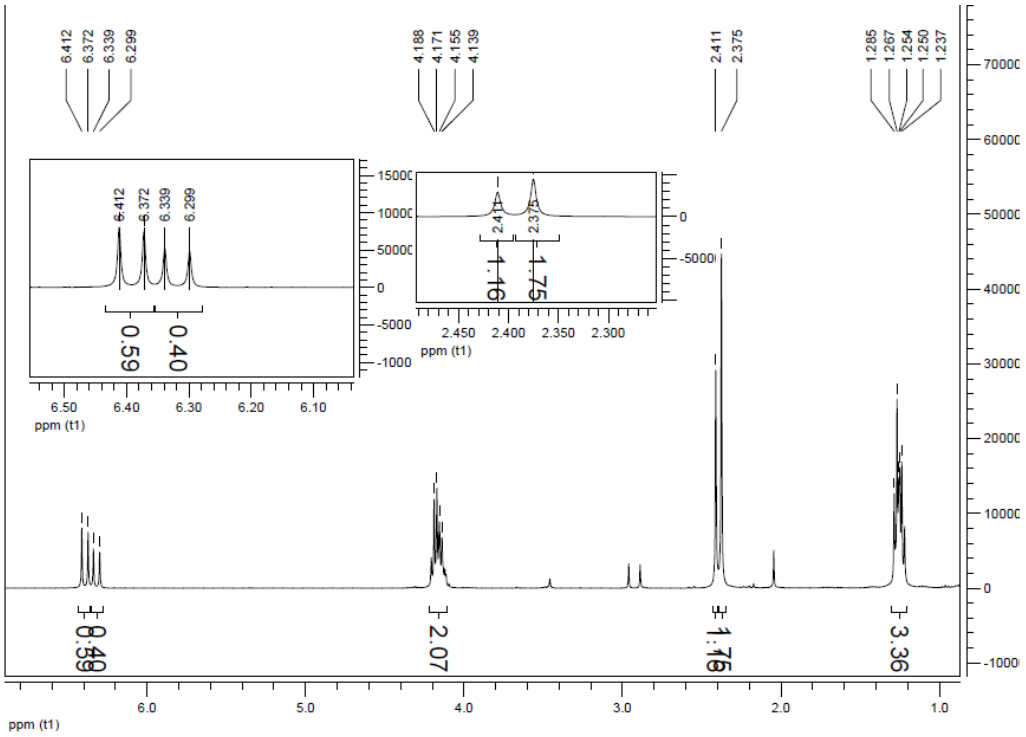

8.303
7.471
7.452
7.433
7.332
7.312
7.299
7.268
7.259
7.235
6.983
6.965
6.458
6.418
4.190
4.172
4.155
4.137
2.700
2.362
2.045
1.272
1.255
1.237
0.000000
1.08
1.99
2.30
1.00
ppm (t1)
2.03
1.00
2.00
4.17
3.09
3.16

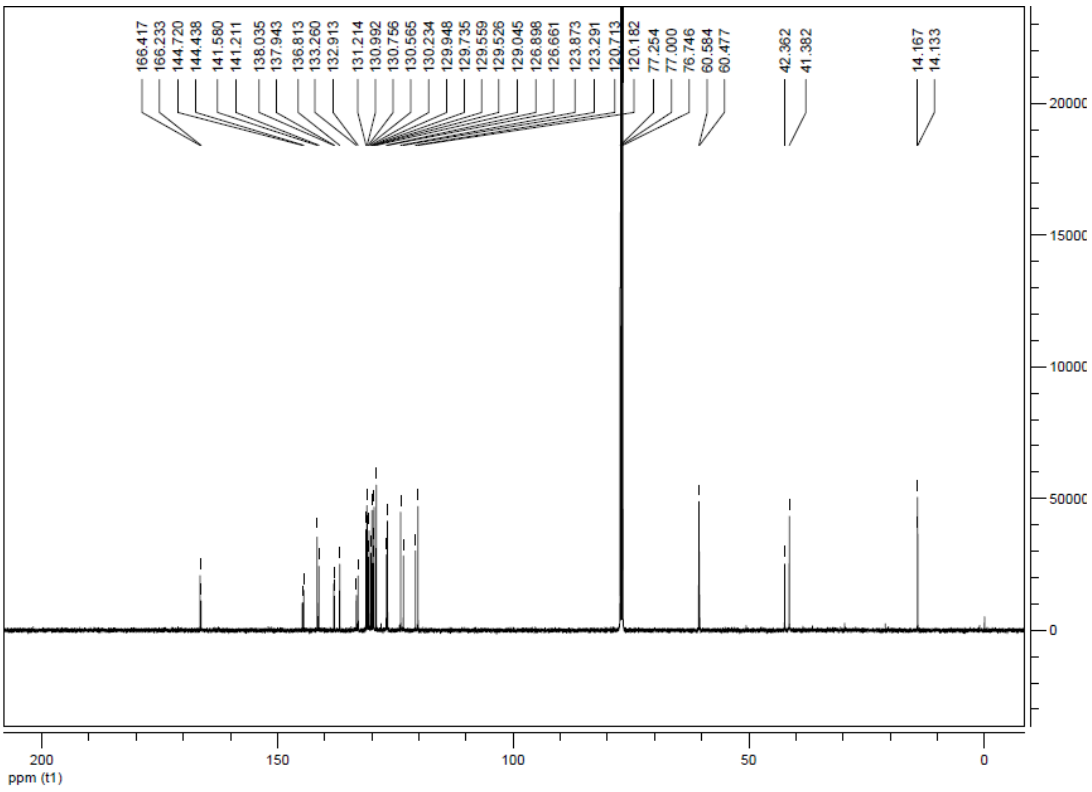

196.765
166.258
145.237
141.501
137.848
136.934
135.232
134.271
129.867
129.569
127.021
125.302
125.138
121.085
77.318
77.000
76.683
60.491
26.629
15.496
14.143
ppm (t1)

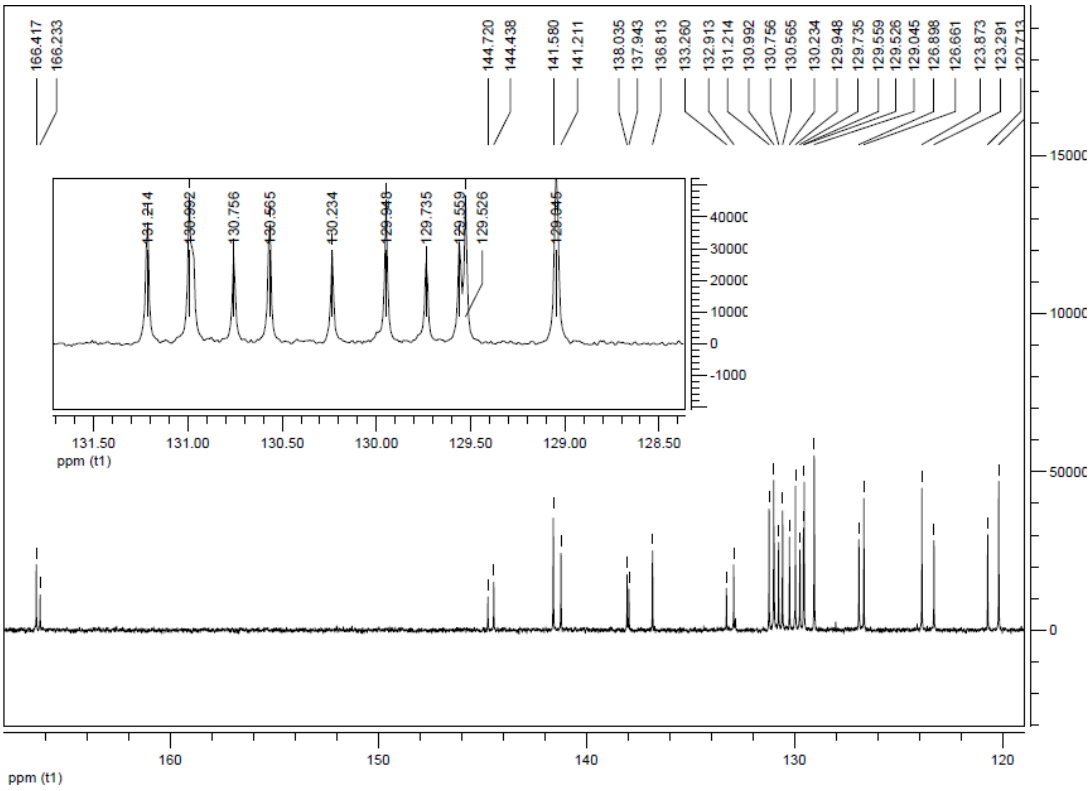
4. Characterization of transformation product 5 and ether directing groups

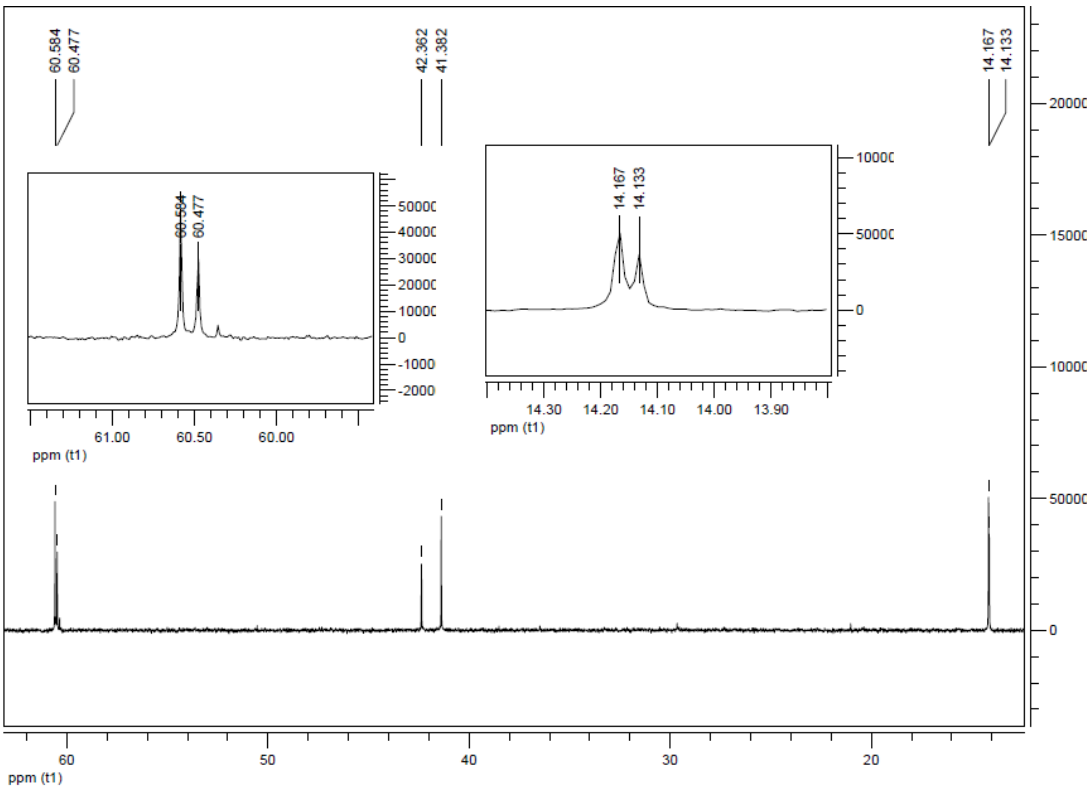


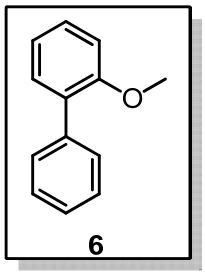


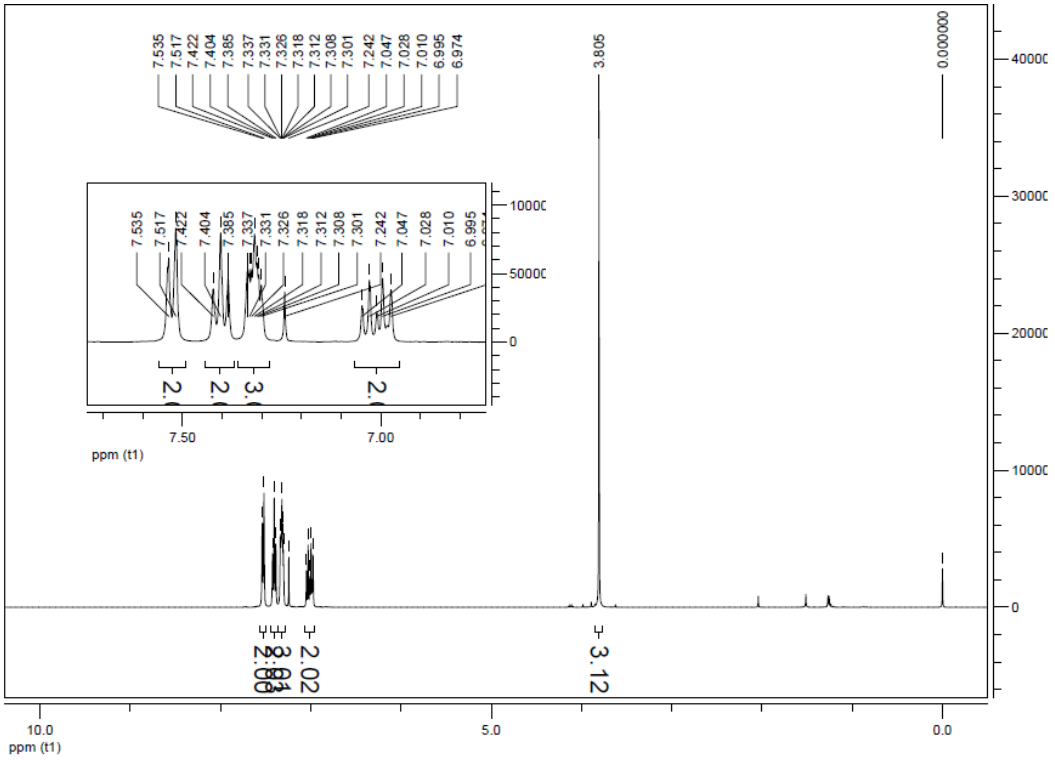


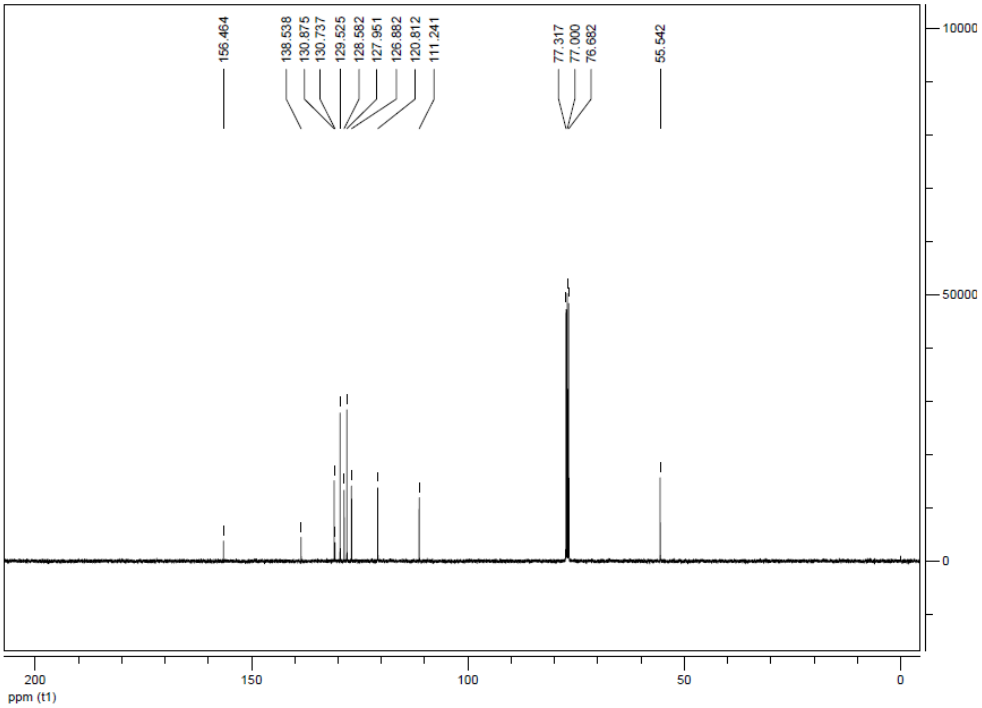

166.417
166.233
144.720
144.438
141.580
141.211
138.035
137.943
136.813
133.260
132.913
131.214
130.992
130.756
130.565
130.234
129.948
129.735
129.559
129.526
129.045
126.898
126.661
123.873
123.291
120.713
120.182
77.254
77.000
76.746
60.584
60.477
42.362
41.382
14.167
14.133
200
150
100
50
0
ppm (t1)

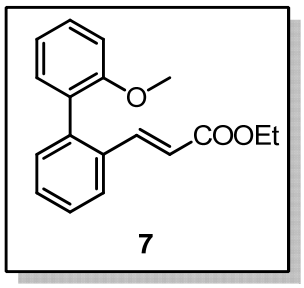

166.417
166.233
144.720
144.438
141.580
141.211
138.035
137.943
136.813
133.260
132.913
131.214
130.992
130.756
130.565
130.234
129.948
129.735
129.559
129.526
129.045
126.898
126.661
123.873
123.291
120.713
131.214
130.992
130.756
130.565
130.234
129.948
129.735
129.559
129.526
129.045
131.50
131.00
130.50
130.00
129.50
129.00
128.50
ppm (t1)
160
150
140
130
120
ppm (t1)


60.584
60.477
42.362
41.382
14.167
14.133
60.584
60.477
61.00
60.50
60.00
ppm (t1)
14.167
14.133
14.30
14.20
14.10
14.00
13.90
ppm (t1)
60
50
40
30
20
ppm (t1)

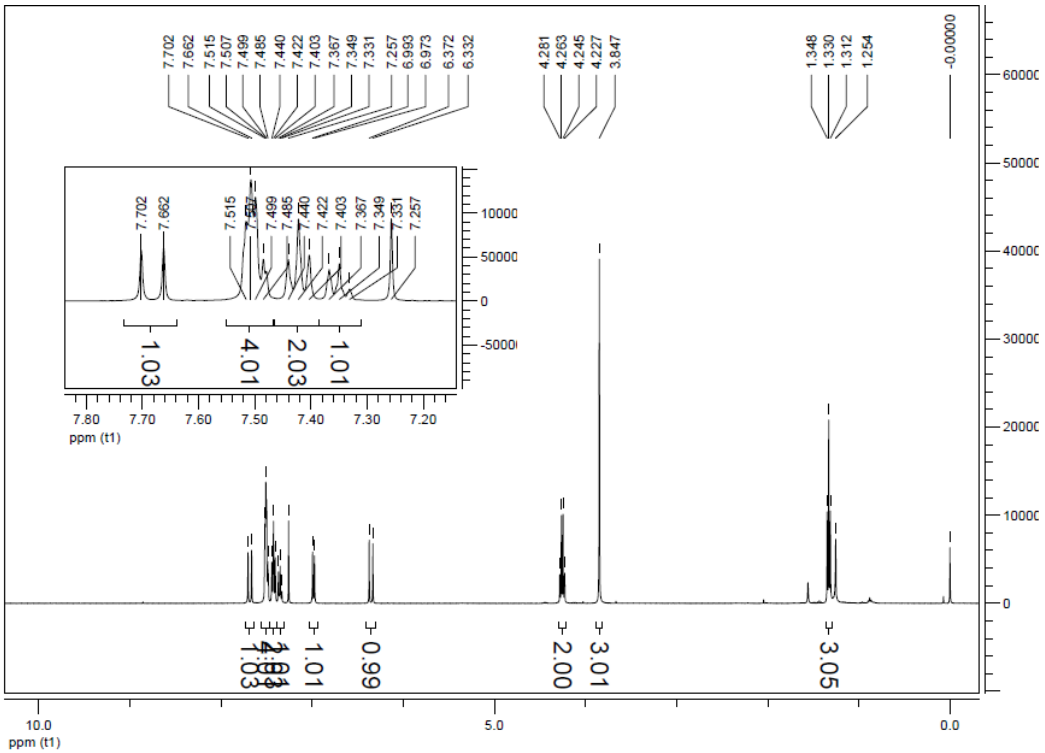

O
6

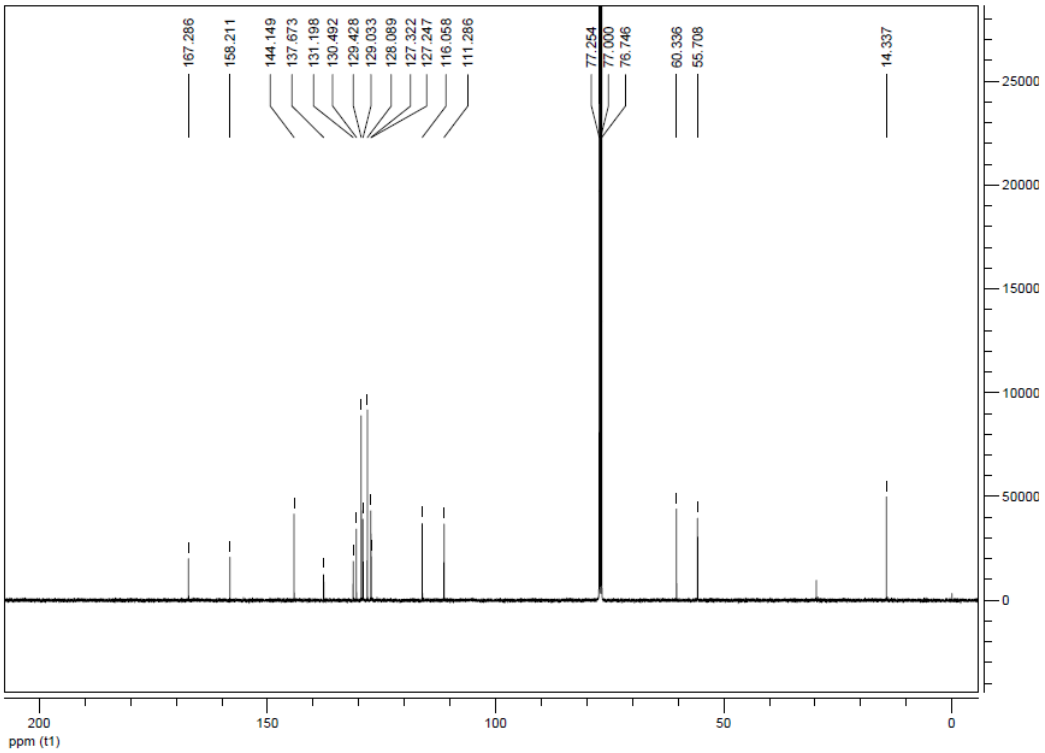

7.535
7.517
7.422
7.404
7.385
7.337
7.331
7.326
7.318
7.312
7.308
7.301
7.242
7.047
7.028
7.010
6.995
6.974
3.806
0.000000
7.50
7.00
ppm (t1)
2.00
3.01
2.02
3.12
10.0
5.0
0.0
ppm (t1)


156.464
138.538
130.875
130.737
129.525
128.582
127.951
126.882
120.812
111.241
77.317
77.000
76.682
55.542
200
150
100
50
0
ppm (t1)

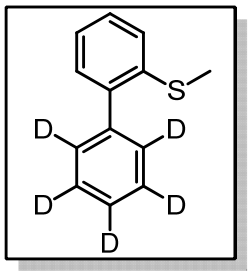

O
COOEt

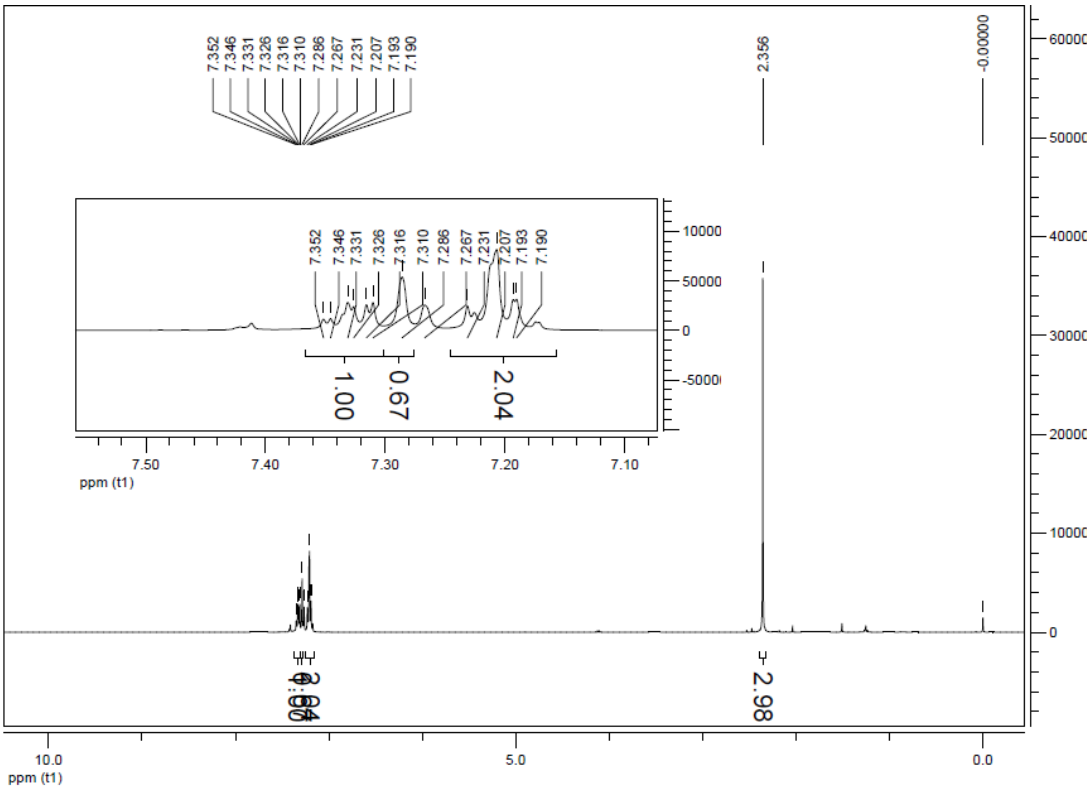
7

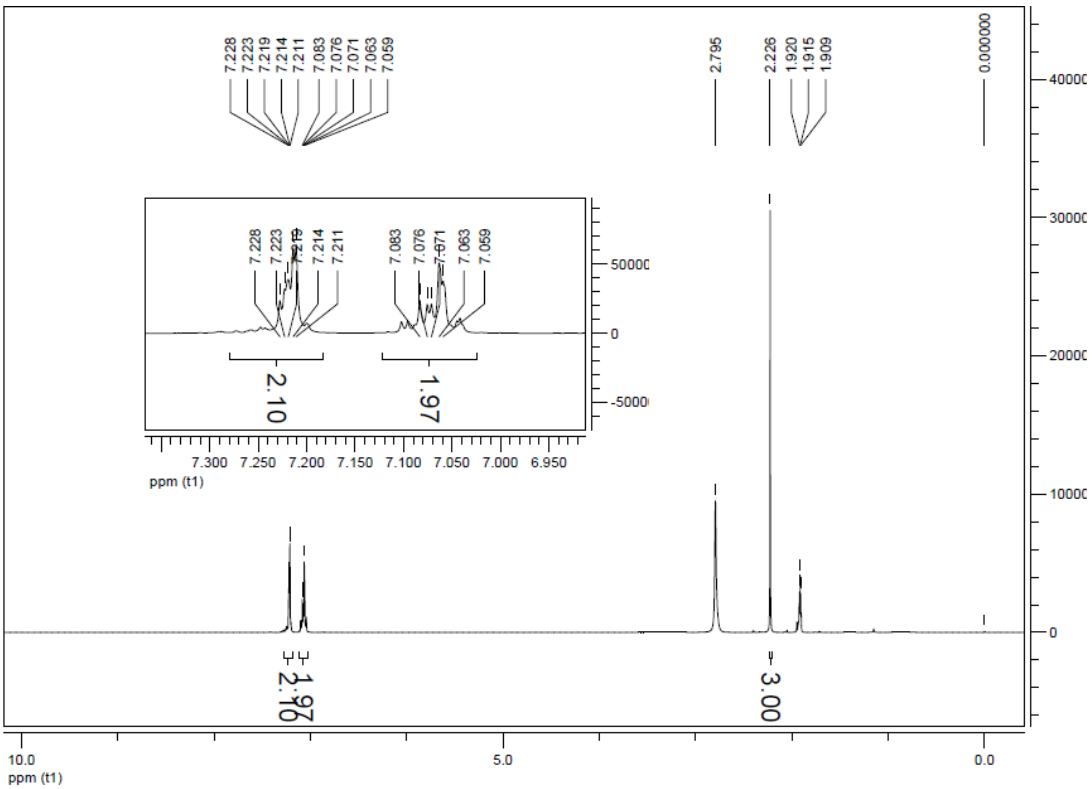

7.702
7.662
7.515
7.507
7.499
7.485
7.440
7.422
7.403
7.367
7.349
7.331
7.257
6.993
6.973
6.372
6.332
4.281
4.263
4.245
4.227
3.847
1.348
1.330
1.312
1.254
-0.00000
1.03
4.01
2.03
1.01
1.01
0.99
2.00
3.01
3.05
ppm (t1)

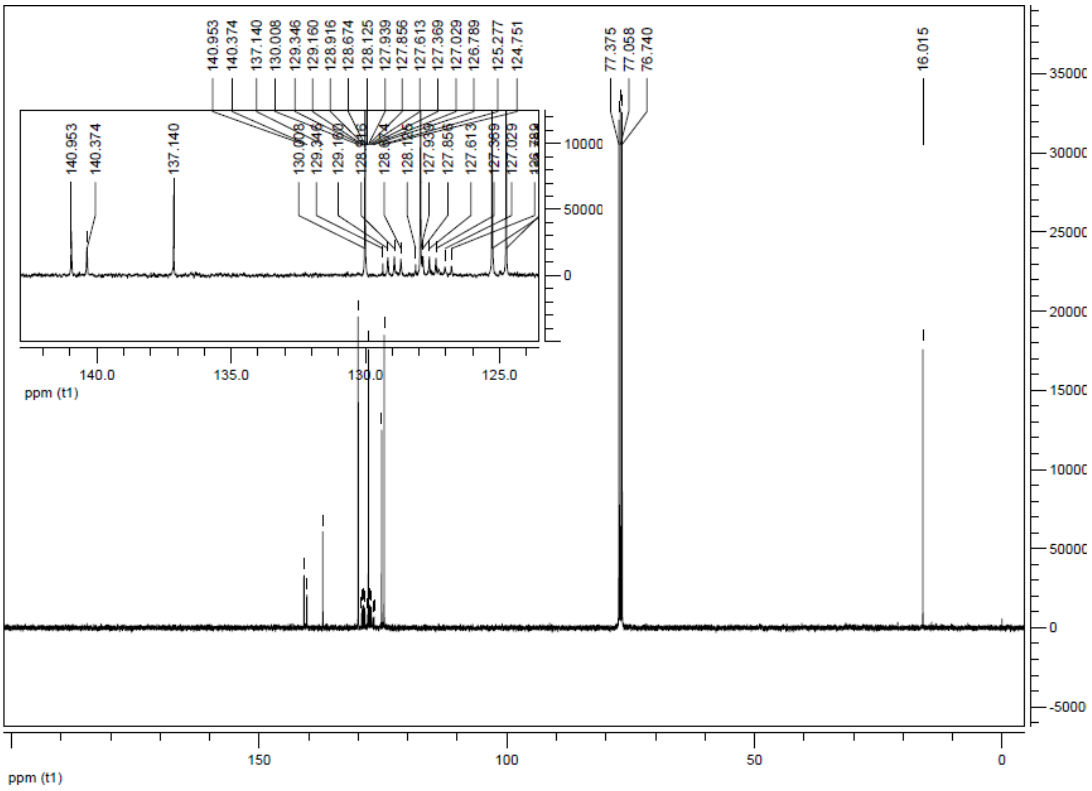

167.286
158.211
144.149
137.673
131.198
130.492
129.428
129.033
128.089
127.322
127.247
116.058
111.286
77.254
77.000
76.746
60.336
55.708
14.337
ppm (t1)

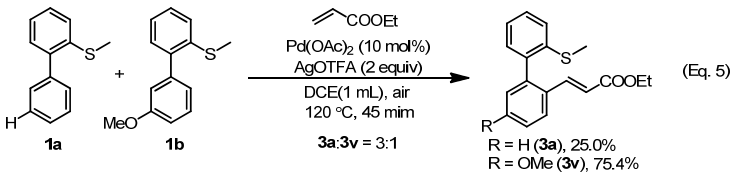
5. Characterization of mechanism study

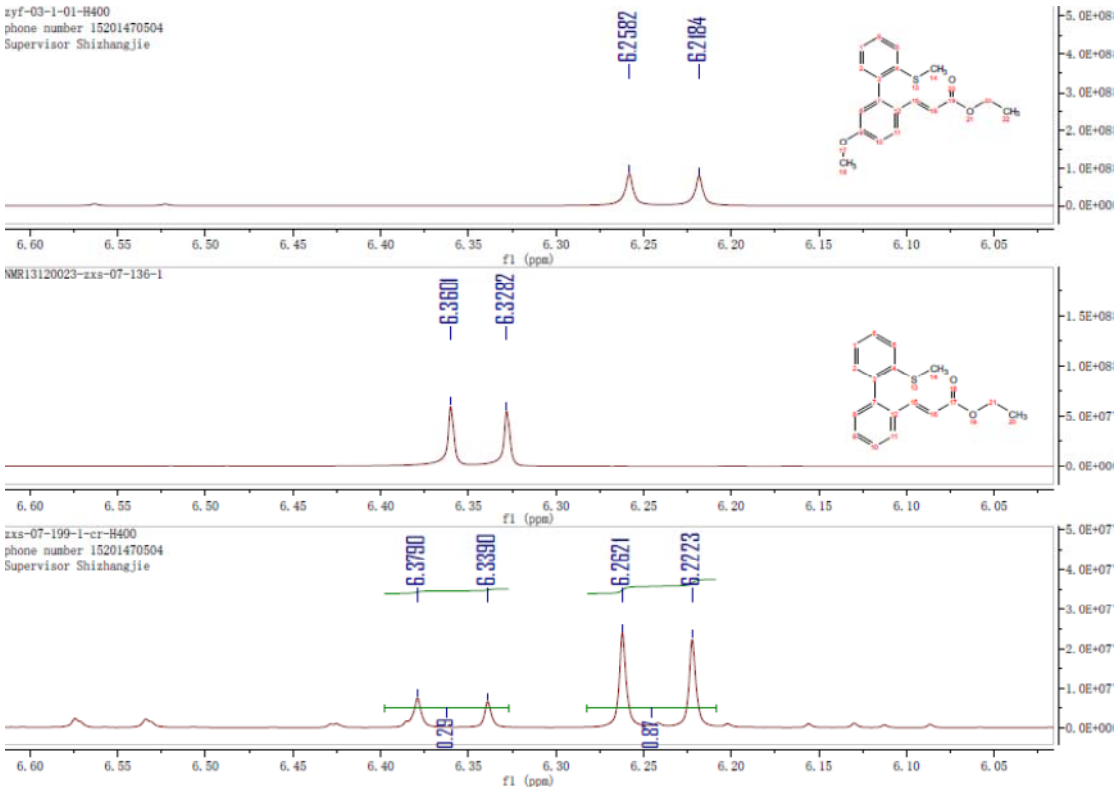


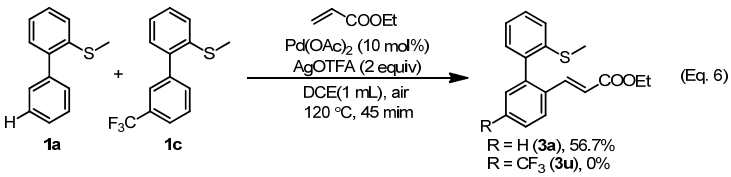



7.228
7.223
7.219
7.214
7.211
7.083
7.076
7.071
7.063
7.059
2.795
2.226
1.920
1.915
1.909
0.000000
2.10
1.97
2.16
3.00
ppm (t1)

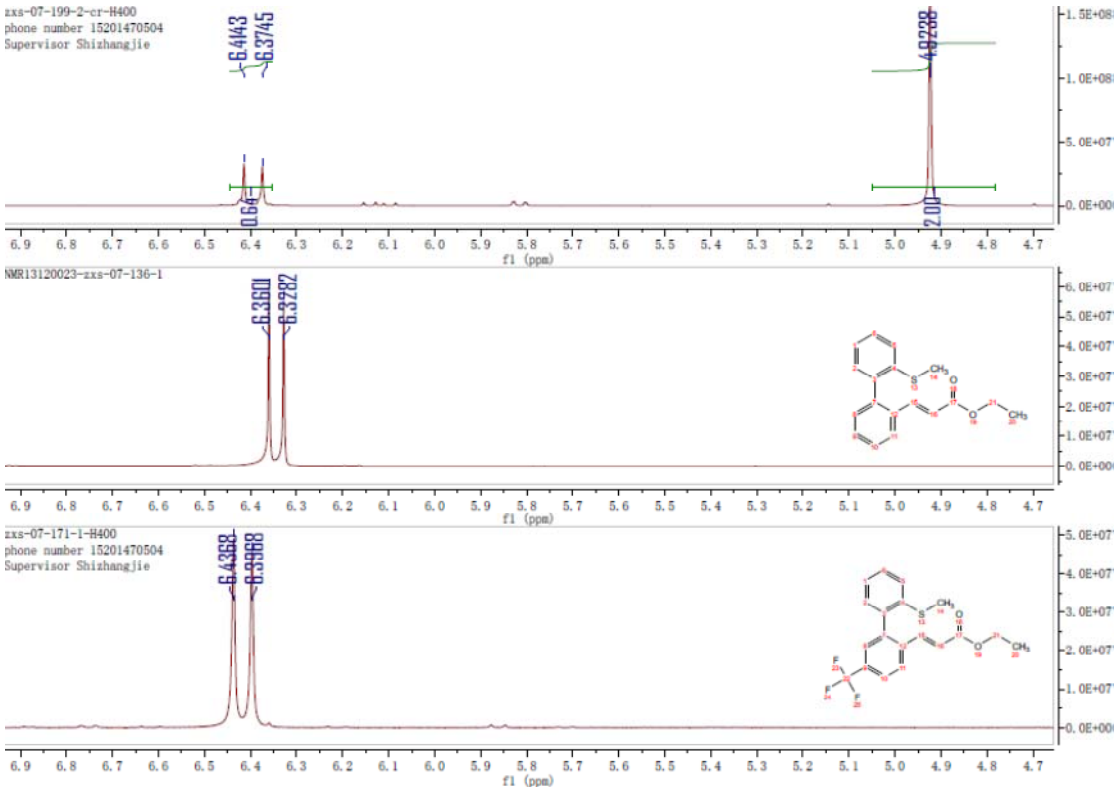

140.953
140.374
137.140
130.008
129.346
129.160
128.916
128.674
128.125
127.939
127.856
127.613
127.369
127.029
126.789
125.277
124.751
77.375
77.058
76.740
16.015
ppm (t1)

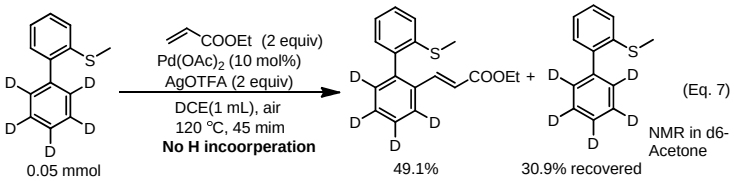

COOEt
Pd(OAc)2 (10 mol%)
AgOTFA (2 equiv)
DCE(1 mL), air
120 °C, 45 mim
3a:3v = 3:1
COOEt
(Eq. 5)
1a
1b
R = H (3a), 25.0%
R = OMe (3v), 75.4%

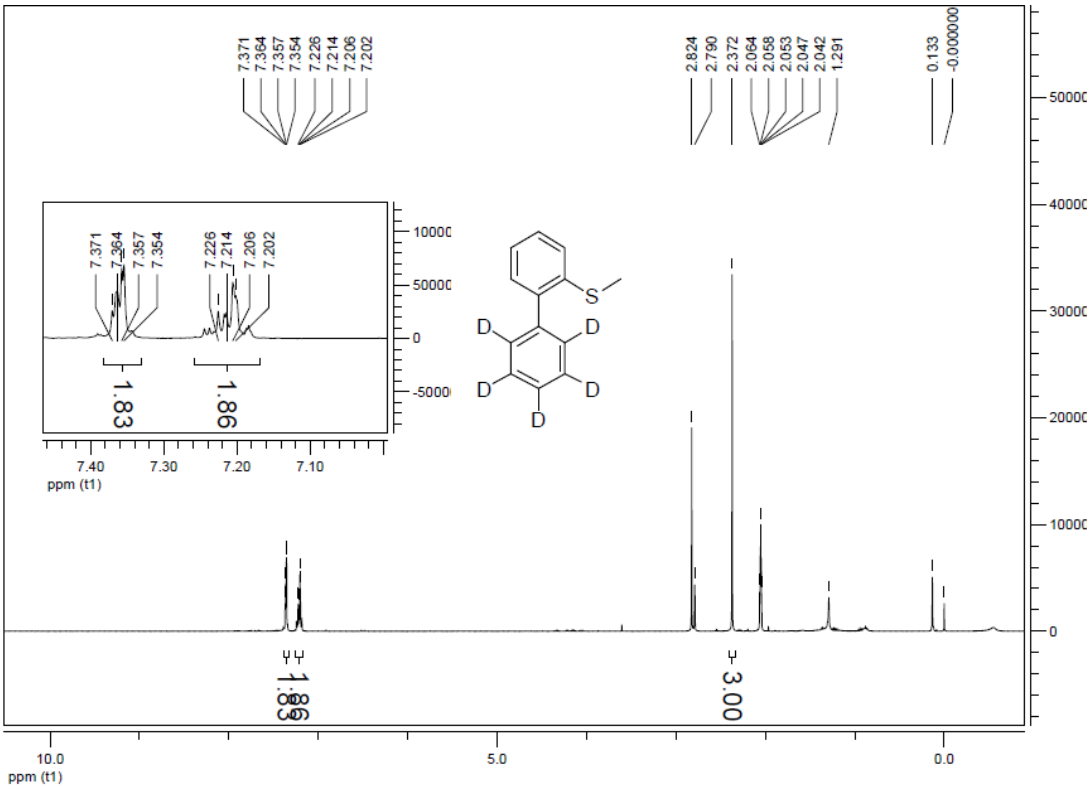

zyf-03-1-01-H400
phone number 15201470504
Supervisor Shizhangjie
6.2582
6.2184
f1 (ppm)
NMR13120023-zxs-07-136-1
6.3601
6.3282
f1 (ppm)
zxs-07-199-1-cr-H400
phone number 15201470504
Supervisor Shizhangjie
6.3780
6.3390
6.2621
6.2223
0.29
0.87
f1 (ppm)


COOEt
Pd(OAc)2 (10 mol%)
AgOTFA (2 equiv)
DCE(1 mL), air
120 °C, 45 mim
S
S
H
F3C
1a
1c
S
COOEt
R
R = H (3a), 56.7%
R = CF3 (3u), 0%

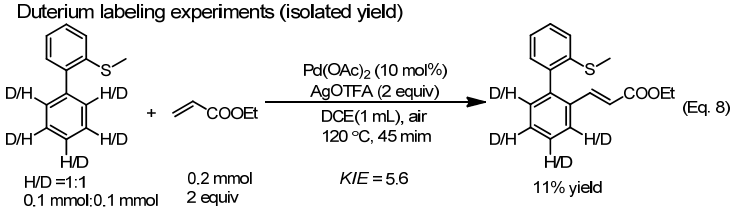
(Eq. 6)


zxs-07-199-2-cr-H400
phone number 15201470504
Supervisor Shizhangjie
6.4443
6.3745
4.9238
0.64
2.00
f1 (ppm)
NMR13120023-zxs-07-136-1
6.3601
6.3282
f1 (ppm)
zxs-07-171-1-H400
phone number 15201470504
Supervisor Shizhangjie
6.4368
6.3968
f1 (ppm)


COOEt (2 equiv)
Pd(OAc)2 (10 mol%)
AgOTFA (2 equiv)
DCE(1 mL), air
120 °C, 45 mim
No H incoorperation
0.05 mmol
49.1%
30.9% recovered
(Eq. 7)
NMR in d6-Acetone


7.371
7.364
7.357
7.354
7.226
7.214
7.206
7.202
2.824
2.790
2.372
2.064
2.058
2.053
2.047
2.042
1.291
0.133
-0.000000
1.83
1.86
3.00
ppm (t1)

Duterium labeling experiments (isolated yield)



H/D =1:1
0.1 mmol:0.1 mmol

0.2 mmol
2 equiv

KIE = 5.6

11% yield