Ir(III)-Catalyzed Thioether Directed Arene C−H Alkenylation

Chen Li,[a] Xian Chen,[a,‡] Rui-Peng Bao,[b,‡] Dong-Li Li,[a,*] Kun Zhang,[a] Dong-Hui Wang [b,*]

[a] School of Biotechnology & Health Sciences, Wuyi University, 22 Dongcheng Vill., Jiangmen, Guangdong 529020, China

[b] CAS Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules; Center for Excellence in Molecular Synthesis; University of Chinese Academy of Sciences; Shanghai Institute of Organic Chemistry, CAS. 345 Lingling Rd., Shanghai 200032, China.

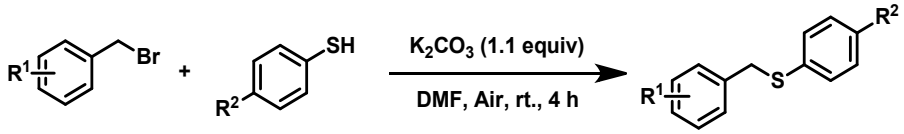
Contents

1, General Information:

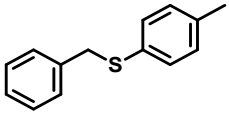
$[Cp^*IrCl_2]_2$ was purchased from Strem. The commercially available reagents were used as received without further purification. All solvents are chemical pure grade reagents, and were used without further purification. Unless stated otherwise, all reactions were performed under air atmosphere. Flash column chromatography were performanced on Silica Gel 300-400 mesh. TLC plates were monitored first with UV-254 nm, and then stained with KMnO4 aq. solution. ^1H NMR spectra were recorded at Varian AM400 400 MHz. ^{19}F NMR were recorded on a 376 MHz or 282 MHz spectrometer. ^{13}C NMR spectra were recorded on a Varian AM400 spectrometer (^{13}C:100 MHz) and Agilent 400 (^{13}C:100 MHz). ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. High resolution mass spectra were recorded at Center for Mass Spectrometry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

2, Preparation and characterization of $ArCH_2SAr$:

The arylthioethers were prepared according to reported procedures [1].

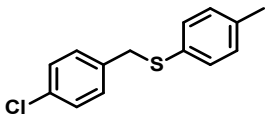


To a 100 mL round-bottomed flask that equipped with a magnetic stir bar, was charge with benzyl bromides (10.0 mmol), thiophenols (10.0 mmol) and K_2CO_3 (11.0 mmol, 1.52 g) in DMF (10.00 mL) under air atmosphere at room temperature for 4 h. And then 15 mL of water was added to the reaction mixture. The resulting mixture was transferred to a separated funnel, ethyl acetate (200 mL) was added, the aqueous layer was sperated, the organic layer was washed in turn with water (20 mL*3) and brine (20 mL *2). The resulting organic layer was dried over anhydrous sodium sulfate. The solvent was removed on a rotavap under reduced pressure, the residue was subjected to flash column chromatography to obtain the desired products.



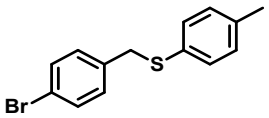
benzyl *p*-tolyl sulfane (1a),[2] the title compound was achieved as a white solid, 2.1 g, 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.32−7.21 (m, 7H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.09 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.6, 132.5, 130.7, 129.7, 128.9, 128.5, 127.139.8, 21.1.



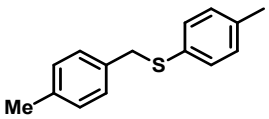
4-chlorobenzyl *p*-tolyl sulfane (1b),[3] the title compound was achieved as a white solid, 2.4 g, 97% yield.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.26−7.17 (m, 4H), 7.16 (d, *J* =8.4 Hz, 2H), 7.06 (d, *J* =8.4 Hz, 2H), 4.00 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 136.5, 132.9, 131.8, 131.2, 130.2, 129.8, 128.6, 39.3, 21.2.



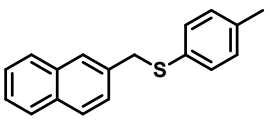
4-bromobenzyl *p*-tolyl sulfane (1c),[4] the title compound was achieved as a white solid, 2.9 g, 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.39 (d, *J* =8.4 Hz, 2H), 7.20 (d, *J* =8.0 Hz, 2H), 7.11 (d, *J* =8.0 Hz, 2H), 7.07 (d, *J* =8.0 Hz, 2H), 3.99 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 137.0, 131.8, 131.6, 131.2, 130.6, 129.8, 121.0, 39.3, 21.2.



4-methylbenzyl *p*-tolyl sulfane (1d),[3] the title compound was achieved as a white solid, 2.2 g, 99% yield.

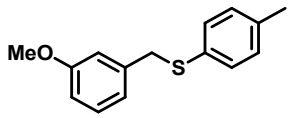
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24 (d, *J* =8.4 Hz, 2H), 7.18 (d, *J* =8.0 Hz, 2H), 7.11 (d, *J* =7.2 Hz, 2H), 7.08 (d, *J* =8.0 Hz, 2H), 4.06 (s, 2H), 2.33 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.4, 134.7, 132.8, 130.5, 129.7, 129.2, 128.8, 39.4, 21.2, 21.1.



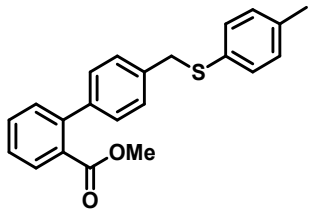
naphthalen-2-ylmethyl *p*-tolyl sulfane (1e),[4] the title compound was achieved as a white solid, 2.5 g, 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.83-7.74 (m, 3H), 7.66 (s, 1H), 7.48-7.43 (m, 3H),

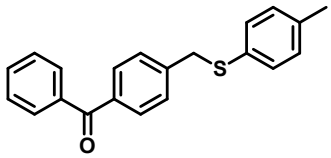
7.24 (d, J =8.4 Hz, 2H), 7.06 (d, J =8.0 Hz, 2H), 4.24 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 135.3, 133.3, 132.6, 132.4, 130.9, 129.7, 128.3, 127.8, 127.7, 127.4, 127.1, 126.1, 125.8, 40.2, 21.1.



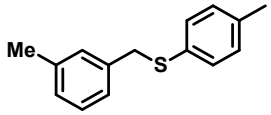
3-methoxybenzyl *p*-tolyl sulfane (1f),[5] the title compound was achieved as a colorless liquid, 2.5 g, 99% yield.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.28-7.21 (m, 3H), 7.11 (d, J =8.0 Hz, 2H), 6.91 (d, J =7.6 Hz, 1H), 6.87 (t, J =2.0 Hz, 1H), 6.82 (dd, J_1 =8.0 Hz, J_2 =2.0 Hz, 1H), 4.09 (s, 2H), 3.79 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 139.4, 136.6, 132.6, 130.7, 129.7, 129.5, 121.3, 114.2, 112.9, 55.2, 39.8, 21.2.



(4(2'-methoxycarbonyl)phenyl)benzyl *p*-tolyl sulfane (1g), the title compound was achieved as a colorless oil, 3.4 g, 99% yield.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (dd, J_1 =7.6 Hz, J_2 =1.2 Hz, 1H), 7.52 (td, J_1 =7.6 Hz, J_2 =1.2 Hz, 1H), 7.40 (td, J_1 =7.6 Hz, J_2 =1.2 Hz, 1H), 7.37 (dd, J_1 =7.6 Hz, J_2 =1.2 Hz, 1H), 7.30 (d, J =8.0 Hz, 2H), 7.26-7.21 (m, 4H), 7.08 (d, J =8.0 Hz, 2H), 4.12 (s, 2H), 3.60 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 142.1, 140.1, 136.9, 136.7, 132.4, 131.3, 130.9, 130.8, 130.7, 129.8, 129.7, 128.7, 128.4, 127.2, 52.0, 39.6, 21.1. IR (neat): ν =2948, 1718, 1491, 1447, 1281, 1244, 1124, 1088 cm^{-1}. HRMS (ESI): m/z: $[M+H]^+$ Calculated for $C_{22}H_{21}O_2S$: 349.1262, found 349.1257.

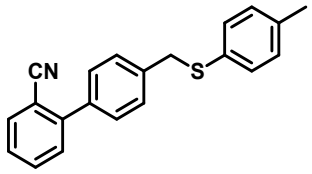


4-phenylcarbonylbenzyl *p*-tolyl sulfane (1h), the title compound was achieved as a white solid, mp. 74-75 ^{o}C, 3.2 g, 99% yield.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.78 (dd, J_1 =8.0 Hz, J_2 =1.2 Hz, 2H), 7.72 (dt, J_1 =8.4 Hz, J_2 =1.6 Hz, 2H), 7.58 (tt, J_1 =7.2 Hz, J_2 =1.2 Hz, 1H), 7.47 (t, J =7.6 Hz, 2H), 7.34 (d, J =8.4 Hz, 2H), 7.22 (d, J =8.0 Hz, 2H), 7.07 (d, J =8.0 Hz, 2H), 4.10 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 143.0, 137.7, 137.2, 136.3, 132.5, 131.6, 131.3, 130.4, 130.1, 129.8, 128.8, 128.3, 39.8, 21.2. IR (neat): ν = 2920, 1645, 1560, 1488, 1410, 1277, 1177, 1088 cm^{-1}. HRMS (ESI): m/z: $[M+H]^+$ Calculated for $C_{21}H_{19}OS$: 319.1157, found 319.1150.



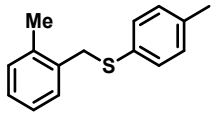
3-methylbenzyl *p*-tolyl sulfane (1i),[5] the title compound was achieved as a colorless liquid, 2.0 g, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34 (dd, J_1 =8.0 Hz, J_2 =1.2 Hz, 2H), 7.28 (t, J =7.6 Hz, 1H), 7.22 (s, 1H), 7.17 (q, J=8.0 Hz, 4H), 4.15 (s, 2H), 2.42 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.7, 136.5, 133.9, 130.6, 129.8, 128.5, 128.1, 126.1, 39.8, 21.6, 21.2.



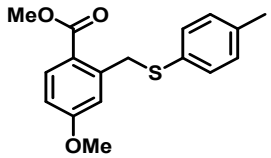
(4(2'-cyano)phenyl)benzyl *p*-tolyl sulfane (1j), the title compound was achieved as a white solid, mp. 79-80 ^{o}C, 3.0 g, 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.76 (dd, J_1 =8.0 Hz, J_2 =1.2 Hz, 1H), 7.63 (tt, J_1 =8.0 Hz, J_2 =1.2 Hz, 1H), 7.49 (tt, J_1 =8.0 Hz, J_2 =1.6 Hz, 3H), 7.43 (td, J_1 =7.6 Hz, J_2 =1.2 Hz, 1H), 7.38 (d, J =8.4 Hz, 2H), 7.25 (d, J =8.8 Hz, 2H), 7.09 (d, J =8.0 Hz, 2H), 4.12 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 138.6, 136.9, 136.9, 133.8, 132.9, 131.0, 130.1, 129.8, 129.3, 128.9, 127.6, 118.8, 111.2, 39.6, 21.2. IR (neat): ν = 2223, 1598, 1489, 1480, 1443, 1268, 1088, 1008 cm^{-1}. HRMS (ESI): m/z: $[M+H]^+$ Calculated for $C_{21}H_{18}NS$: 316.1160, found 316.1154.



2-methylbenzyl *p*-tolyl sulfane (1k),[5] the title compound was achieved as a colorless liquid, 2.3 g, 99% yield.

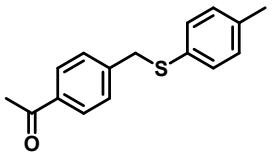
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.27 (t, J =8.0 Hz, 2H), 7.20 (q, 2H), 7.17-7.10 (m, 4H), 4.10 (s, 2H), 2.43 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.8, 135.5, 132.8, 131.1, 130.5, 129.9, 129.7, 127.5, 126.0, 38.2, 21.2, 19.3.



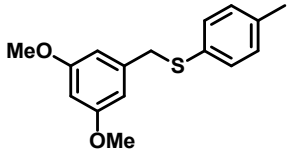
2-methoxycarbonyl-5-methoxybenzyl *p*-tolyl sulfane (1l), the title compound was achieved as a yellow oil, 1.2 g, 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.94 (d, J =8.8 Hz, 1H), 7.21 (d, J =8.4 Hz, 2H), 7.05 (d, J =8.0 Hz, 2H), 6.77 (dd, J_1 =8.8 Hz, J_2 =2.8 Hz, 1H), 6.61 (d, J =2.4 Hz, 1H), 4.46 (s, 2H), 3.85 (s, 3H), 3.71 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 162.1, 142.8, 137.0, 133.4, 132.2, 132.1, 129.6, 121.0, 116.0, 112.6, 55.3, 51.9, 39.1, 21.1. IR

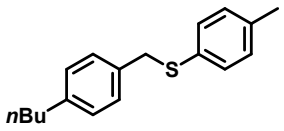
(neat): ν = 2950, 1699, 1598, 1491, 1434, 1326, 1235, 1130 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{17}H_{19}O_3S$: 303.1055, found 303.1049.



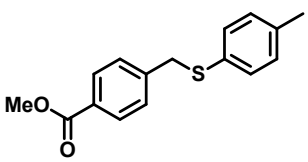
4-methylcarbonylbenzyl *p*-tolyl sulfane (1n), the title compound was achieved as a white solid, mp. 75-77 °C, 1.1 g, 97% yield.
^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.85 (d, *J* =8.4 Hz, 2H), 7.31 (d, *J* =8.4 Hz, 2H), 7.18 (d, *J* =8.4 Hz, 2H), 7.05 (d, *J* =8.0 Hz, 2H), 4.06 (s, 2H), 2.57 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 143.7, 137.2, 135.9, 131.5, 131.3, 129.8, 129.0, 128.6, 39.7, 26.7, 21.1. IR (neat): ν = 2918, 1678, 1602, 1490, 1412, 1357, 1263, 1090 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{16}H_{17}OS$: 257.1000, found 257.0994.



3,5-dimethoxybenzyl *p*-tolyl sulfane (1m),[4] the title compound was achieved as a colorless liquid, 2.3 g, 86% yield.
^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.25 (d, *J* =8.4 Hz, 2H), 7.09 (d, *J* =7.6 Hz, 2H), 6.45 (d, *J* =2.4 Hz, 2H), 6.35 (t, *J* =2.0 Hz, 1H), 4.02 (s, 2H), 3.75 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 140.1, 136.6, 132.6, 130.7, 129.7, 106.7, 99.4, 55.3, 40.1, 21.1.

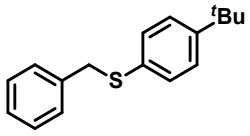


4-butylbenzyl *p*-tolyl sulfane (1o), the title compound was achieved as a white liquid, 1.1 g, 93% yield.
^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.22 (d, *J* =8.4 Hz, 2H), 7.18 (d, *J* =8.0 Hz, 2H), 7.09 (d, *J* =8.4 Hz, 2H), 7.07 (d, *J* =8.8 Hz, 2H), 4.05 (s, 2H), 2.58 (t, *J* =7.6 Hz, 2H), 2.31 (s, 3H), 1.61-1.54 (m, 2H), 1.39-1.26 (m, 2H), 0.92 (t, *J* =7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 136.4, 134.8, 132.8, 130.5, 129.6, 128.8, 128.6, 39.5, 35.3, 33.7, 22.4, 21.1, 14.0. IR (neat): ν = 2949, 2926, 1509, 1491, 1467, 1119, 1091, 1018 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{18}H_{23}S$: 271.1520, found 271.1514.

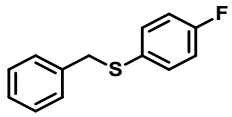


4-methoxycarbonylbenzyl *p*-tolyl sulfane (1p),[6] the title compound was achieved as a

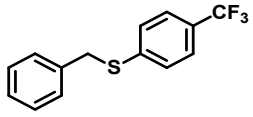
white solid, 3.1 g, 97% yield.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.93 (d, *J* =8.0 Hz, 2H), 7.28 (d, *J* =8.4 Hz, 2H), 7.17 (d, *J* =8.0 Hz, 2H), 7.05 (d, *J* =8.0 Hz, 2H), 4.06 (s, 2H), 3.89 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 143.4, 137.2, 131.5, 131.4, 129.8, 128.9, 52.1, 39.8, 21.1.



benzyl(4-(*tert*-butyl)phenyl) sulfane (1q),[2] the title compound was achieved as a colorless liquid, 2.4 g, 95% yield.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.39-7.26 (m, 9H), 4.17 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 137.8, 133.1, 129.9, 129.0, 128.6, 127.2, 126.0, 39.5, 34.6, 31.4.

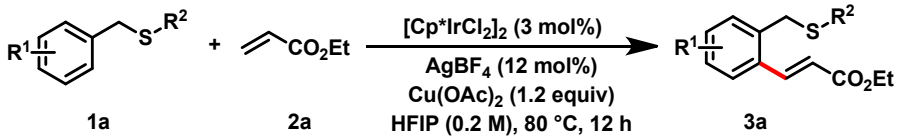


benzyl(4-fluorophenyl) sulfane (1r),[2] the title compound was achieved as a white solid, 1.9 g, 91% yield.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.31-7.26 (m, 5H), 7.24-7.21 (m, 2H), 6.95 (tt, J_1 =8.8 Hz, J_2 =2.0 Hz, 2H), 4.04 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.4 Hz, C-F), 137.6, 133.5 (d, *J* = 8.1 Hz), 130.8 (d, *J* = 3.2 Hz), 128.9, 128.5, 127.3, 116.0 (d, *J* = 21.6 Hz), 40.5.



benzyl(4-(trifluoromethyl)phenyl) sulfane (1s),[7] the title compound was achieved as a white solid, 2.4 g, 93% yield.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.49 (d, *J* =8.4 Hz, 2H), 7.37-7.26 (m, 7H), 4.19 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 136.4, 128.8, 128.8, 127.9, 127.6, 127.6, 125.7 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 270.4 Hz), 37.7.

3, General procedure for thioether directed mono-alkenylation

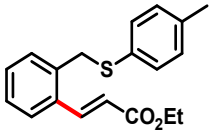


1a 2a 3a

To a 35 mL screw-top sealed tube equipped with stir bar, was added benzyl *p*-tolyl thioethers **1a** (0.4 mmol), ethyl acrylate **2a** (1.1 mmol), $[Cp^*IrCl_2]_2$ (3 mol%), $AgBF_4$ (12

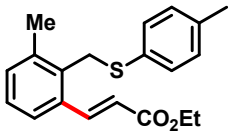
mol%) and $Cu(OAc)_2$ (87 mg, 0.48 mmol, 1.2equiv), HFIP (2 mL) was added *via* a syringe. The tube was then tightly capped. The reaction mixture was placed in a preheated oil-bath, and stirred at 80 °C for 12 h. The reaction mixture was allowed to cool to room temperature, then was quenched with water (10 mL) and extracted with ethyl acetate (3 x 20 mL). The organic layers were combined, and concentrated by rotary evaporation. The residue was subjected to flash column chromatography on silica gel, eluted with ethyl acetate/petroleum ether = 1/20, v/v) to afford the desired products **3a**.

4, Characterization data for mono-alkenylation products



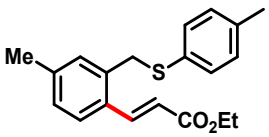
Ethyl 2-((*p*-tolylthio)methyl)cinnamate (3a),[8] the title compound was achieved as a pale yellow oil, 104 mg, 80% yield, eluted with petroleum ether/EtOAc = 20/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.00 (d, *J* = 15.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.29−7.19 (m, 5H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.33 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.15 (s, 2H), 2.31 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 141.2, 137.3, 136.7, 133.6, 132.2, 131.4, 130.6, 129.8, 129.6, 127.7, 126.7, 119.9, 60.4, 37.9, 21.0, 14.3.



Ethyl 3-methyl-2-((*p*-tolylthio)methyl)cinnamate (3b),[1] the title compound was achieved as a pale yellow oil, 91 mg, 70% yield, eluted with petroleum ether/EtOAc = 20/1.

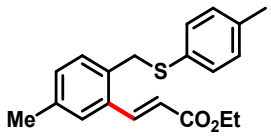
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.94 (d, *J* = 16.0 Hz, 1H), 7.36 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 1H), 7.29−7.26 (m, 2H), 7.21-7.15 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.22 (d, *J* = 15.6 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.15 (s, 2H), 2.41 (s, 3H), 2.33 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 142.1, 137.9, 137.5, 134.5, 134.4, 132.5, 132.0, 131.7, 129.7, 127.5, 124.7, 120.2, 60.4, 34.6, 21.1, 19.7, 14.3.



Ethyl 4-methyl-2-((*p*-tolylthio)methyl)cinnamate (3c),[8] the title compound was achieved as a pale yellow oil, 100 mg, 77% yield, eluted with petroleum ether/EtOAc = 20/1.

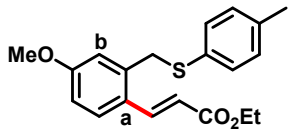
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (d, *J* = 15.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H),

7.27−7.24 (t, 2H), 7.08 (d, J = 8.0 Hz, 3H), 7.03 (s, 1H), 6.30 (d, J = 16 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 4.12 (s, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 141.2, 140.2, 137.3, 136.6, 132.1, 131.7, 131.4, 130.8, 129.6, 128.6, 126.7, 118.9, 60.4, 38.0, 21.2, 21.1, 14.3.



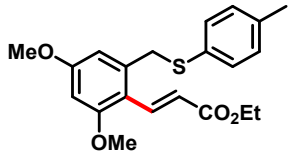
Ethyl 5-methyl-2-((*p*-tolylthio)methyl)cinnamate (3d),[8] the title compound was achieved as a pale yellow oil, 110 mg, 84% yield, eluted with petroleum ether/EtOAc = 20/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.98 (d, J = 16 Hz, 1H), 7.37 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.12−7.06 (m, 4H), 6.34 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 4.13 (s, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 141.4, 137.4, 137.1, 133.7, 133.3, 131.9, 131.7, 130.7, 130.5, 129.6, 127.2, 119.6, 60.4, 37.6, 21.1, 21.0, 14.3.



Ethyl 4-methoxy-2-((*p*-tolylthio)methyl)cinnamate (3e), the title compound was achieved as a pale yellow oil, 90 mg, 66% yield, eluted with petroleum ether/EtOAc = 20/1. The isolated products are inseparable mixture on Silica Gel, the ratio is a: b = 3: 1.

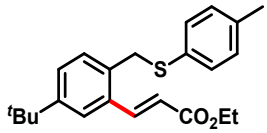
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.94 (d, J = 16.4 Hz, 1H), 7.93 (d, J = 15.6 Hz, 3H), 7.53 (d, J = 8.4 Hz, 3H), 7.29-7.24 (m, 8H), 7.20 (t, J = 8.0 Hz, 1H), 7.10-7.07 (m, 8H), 6.87-6.79 (m, 5H), 6.74-6.70 (m, 4H), 6.24 (d, J = 16 Hz, 3H), 4.26 (q, J = 7.2 Hz, 2H), 4.25 (q, J = 7.2 Hz, 6H), 4.15 (s, 2H), 4.13 (s, 6H), 3.87 (s, 3H), 3.75 (s, 9H), 2.32 (s, 3H), 2.32 (s, 9H), 1.33 (t, J = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.0, 160.7, 158.9, 140.7, 138.6, 138.3, 137.9, 137.4, 137.1, 132.2, 131.9, 131.8, 131.4, 129.9, 129.6, 128.2, 125.9, 123.1, 122.9, 122.5, 117.4, 115.2, 114.0, 110.0, 60.3, 55.5, 55.2, 38.7, 38.1, 21.0, 14.3. IR (neat): ν = 2978, 1707, 1630, 1602, 1493, 1365, 1175, 1160 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{20}H_{23}O_3S$: 343.1368, found 343.1364.



Ethyl 4,6-dimethoxy-2-((*p*-tolylthio)methyl)cinnamate (3f), the title compound was achieved as a pale yellow oil, 113 mg, 76% yield, eluted with petroleum ether/EtOAc = 20/1.

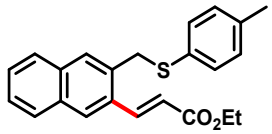
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.90 (d, J = 16 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 1H), 6.66 (d, J = 16 Hz, 1H), 6.38 (s, 1H), 6.35 (s, 1H), 4.25 (q, J =

7.2 Hz, 2H), 4.14 (s, 2H), 3.85 (s, 3H), 3.73 (s, 3H),2.32 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 160.9, 160.8, 139.9, 137.5, 137.2, 132.0, 131.8, 129.6, 120.4, 115.3, 107.0, 97.9, 60.1, 55.5, 55.2, 39.1, 21.0, 14.3. IR (neat): ν = 2976, 1694, 1621, 1596, 1450, 1305, 1171, 1158 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{21}H_{25}O_4S$: 373.1474, found 373.1469.



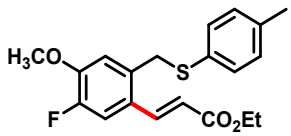
Ethyl 5-(tert-butyl)-2-((*p*-tolylthio)methyl)cinnamate (3g), the title compound was achieved as a pale yellow oil, 105 mg, 71% yield, eluted with petroleum ether/EtOAc = 20/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.04 (d, J = 16 Hz, 1H), 7.58 (s, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 6.38 (d, J = 16 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 4.16 (s, 2H), 2.33 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 150.7, 141.9, 137.1, 133.7, 133.0, 132.0, 131.7, 130.4, 129.6, 127.2, 123.5, 119.6, 60.4, 37.6, 34.6, 31.2, 21.0, 14.3. IR (neat): ν = 2966, 1709, 1634, 1492, 1365, 1301, 1174, 1036 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{23}H_{29}O_2S$: 369.1888, found 369.1884.



(*E*)-ethyl 3-(3-((*p*-tolylthio)methyl)naphthalen-2-yl)acrylate (3h), the title compound was achieved as a pale yellow oil, 136 mg, 93% yield, eluted with petroleum ether/EtOAc = 20/1.

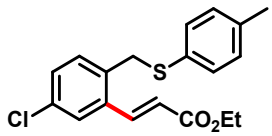
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.18 (d, J = 15.6 Hz, 1H), 8.07 (s, 1H), 7.83-7.80 (m, 1H), 7.71-7.67 (m, 1H), 7.59 (s, 1H), 7.48-7.44 (m, 2H), 7.27-7.24 (m, 3H), 7.05 (d, J = 8.0 Hz, 2H), 6.51 (d, J = 15.6 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 4.29 (s, 2H), 2.31 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 141.9, 137.4, 133.7, 133.5, 132.5, 132.2, 132.1, 131.6, 129.7, 129.2, 128.1, 127.4, 127.1, 126.9, 126.4, 120.6, 60.5, 38.8, 21.1, 14.4. IR (neat): ν = 2972, 1698, 1617, 1493, 1441, 1367, 1093, 1047 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{23}H_{23}O_2S$: 363.1419, found 363.1415.



Ethyl 5-fluoro-4-methoxy-2-((*p*-tolylthio)methyl)cinnamate (3i), the title compound was achieved as a pale yellow solid, mp. 74-75 °C, 95 mg, 66% yield, eluted with petroleum ether/EtOAc = 20/1.

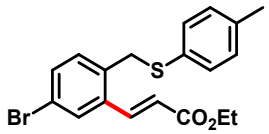
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (dd, J_1 = 16 Hz, J_2 = 1.6 Hz, 1H), 7.25 (d, J =

12 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.65 (d, J = 8.8 Hz, 1H), 6.18 (d, J = 15.6 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 4.08 (s, 2H), 3.77 (s, 3H), 2.31 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.1 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 151.4 (d, J = 245.6 Hz, C-F), 148.6 (d, J = 10.9 Hz), 139.6 (d, J = 2.0 Hz), 137.8, 133.8 (d, J = 3.3 Hz), 132.8, 130.8, 129.7, 126.0 (d, J = 6.3 Hz), 118.5, 114.9 (d, J = 2.1 Hz), 113.7 (d, J = 18.9 Hz), 60.5, 55.9, 37.6, 21.0, 14.3. IR (neat): ν = 3008, 2984, 1703, 1628, 1509, 1441, 1363, 1293, 1170, 1140 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{20}H_{22}FO_3S$: 361.1274, found 361.1270.



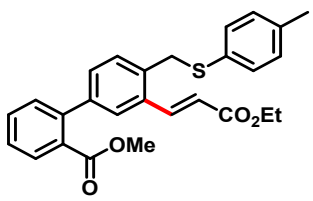
Ethyl 5-chloro-2-((*p*-tolylthio)methyl)cinnamate (3j),[8] the title compound was achieved as a pale yellow oil, 81 mg, 58% yield, eluted with petroleum ether/EtOAc = 20/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.86 (d, J = 16 Hz, 1H), 7.49 (d, J = 2 Hz, 1H), 7.22−7.19 (m, 3H), 7.09-7.04 (m, 3H), 6.29 (d, J = 15.6 Hz, 1H), 4.26 (q, J = 6.8 Hz, 2H), 4.07 (s, 2H), 2.31 (s, 3H), 1.34 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 139.9, 137.7, 135.3, 135.2, 133.5, 132.6, 131.9, 130.7, 129.7, 129.6, 126.6, 121.1, 60.6, 37.5, 21.1, 14.3.



Ethyl 5-bromo-2-((*p*-tolylthio)methyl)cinnamate (3k), the title compound was achieved as a pale yellow solid, mp. 69-71 °C, 93 mg, 60% yield, eluted with petroleum ether/EtOAc = 20/1.

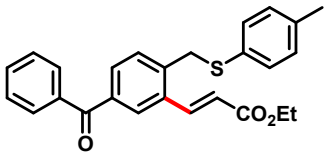
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.85 (d, J = 15.6 Hz, 1H), 7.65 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.07-7.02 (m, 3H), 6.28 (d, J = 15.6 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 4.06 (s, 2H), 2.31 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 139.8, 137.7, 135.8, 135.5, 132.6, 132.5, 132.1, 130.7, 129.7, 129.5, 121.5, 121.2, 60.6, 37.6, 21.1, 14.3. IR (neat): ν = 2982, 1712, 1634, 1562, 1489, 1312, 1183, 1090 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{19}H_{20}BrO_2S$: 391.0367, found 391.0363.



Ethyl 5-(2'-(methoxycarbonyl)phenyl)-2-((*p*-tolylthio)methyl)cinnamate (3l), the title compound was achieved as a pale yellow oil, 128 mg, 72% yield, eluted with petroleum

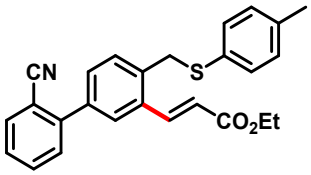
ether/EtOAc = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (d, J = 16 Hz, 1H), 7.55 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.54 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H),7.50 (d, J = 1.2 Hz, 1H), 7.43 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.35 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.28-7.24 (m, 2H), 7.25-7.19 (m, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.33 (d, J = 16 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 4.18 (s, 2H), 3.63(s, 3H), 2.32 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 166.6, 141.5, 141.1, 140.8, 137.4, 135.7, 133.4, 132.3, 131.4, 131.3, 130.6, 130.5, 130.4, 129.9, 129.8, 129.7, 127.5, 126.6, 120.2, 60.5, 51.9, 37.8, 21.0, 14.3. IR (neat): ν = 2924, 1713, 1635, 1492, 1447, 1365, 1176, 1126 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{27}H_{27}O_4S$: 447.1630, found 447.1626.



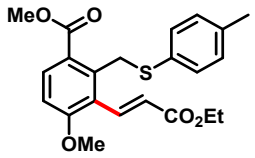
Ethyl 5-benzoyl-2-((*p*-tolylthio)methyl)cinnamate (3n), the title compound was achieved as a pale yellow oil, 100 mg, 60% yield, eluted with petroleum ether/EtOAc = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (d, J = 15.6 Hz, 1H), 7.95 (d, J = 3.6 Hz 1H), 7.78-7.76 (m, 2H), 7.67-7.59 (m, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.27-7.22 (m, 3H), 7.06 (d, J = 8.0 Hz, 2H), 6.32 (d, J = 16 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 4.17 (s, 2H), 2.31 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 166.4, 141.2, 140.3, 137.9, 137.2, 136.8, 133.8, 132.7, 132.6, 131.0, 130.6, 130.0, 129.8, 128.4, 121.3, 60.6, 38.0, 21.1, 14.3. IR (neat): ν = 2982, 1709, 1658, 1492, 1448, 1369, 1264, 1177, 1091 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{26}H_{25}O_3S$: 417.1524, found 417.1520.



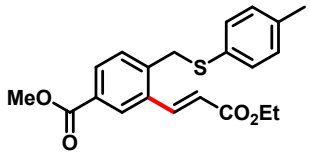
Ethyl 5-(2'-(cyano)phenyl)-2-((*p*-tolylthio)methyl)cinnamate (3m), the title compound was achieved as a pale yellow oil, 154 mg, 75% yield, eluted with petroleum ether/EtOAc = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99 (d, J = 15.6 Hz, 1H), 7.76 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.70 (d, J = 1.6 Hz, 1H), 7.64 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.52-7.45 (m, 3H), 7.31 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.39 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 4.18 (s, 2H), 2.32 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 144.3, 140.7, 137.6, 137.4, 137.2, 134.1, 133.7, 132.8, 132.5, 131.0, 130.9, 129.8, 129.7, 129.6, 127.8, 127.1, 120.9, 118.4, 111.2, 60.5, 37.8, 21.0, 14.3. IR (neat): ν = 2919, 2226, 1716, 1634, 1494, 1482, 1310, 1185, 1173 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{26}H_{24}NO_2S$: 414.1528, found 414.1521.



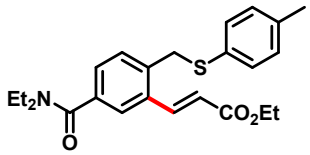
Ethyl 6-methoxy-3-methoxycarbonyl-2-((*p*-tolylthio)methyl)cinnamate (3o), the title compound was achieved as a pale yellow solid, mp. 58-60 ^{o}C, 129 mg, 81% yield, eluted with petroleum ether/EtOAc = 20/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.88 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 16 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.40 (d, *J* = 16.4 Hz, 1H), 4.61 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 2.30 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 166.9, 160.5, 140.2, 137.7, 137.4, 133.2, 132.7, 131.6, 129.5, 124.9, 124.6, 122.9, 108.9, 60.4, 55.7, 52.0, 34.7, 21.0, 14.2. IR (neat): ν = 2950, 1711, 1581, 1494, 1478, 1433, 1263, 1177, 1159 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{22}H_{25}O_5S$: 401.1423, found 401.1418.



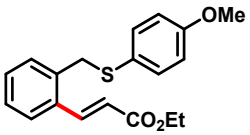
Ethyl 5-methoxycarbonyl-2-((*p*-tolylthio)methyl)cinnamate (3p), the title compound was achieved as a pale yellow oil, 88 mg, 60% yield, eluted with petroleum ether/EtOAc = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.20 (d, *J* = 1.6 Hz, 1H), 7.92 (d, *J* = 16 Hz, 1H), 7.87 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.21-7.17 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 16 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.12 (s, 2H), 3.91 (s, 3H), 2.30 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.3, 141.8, 140.2, 137.9, 133.8, 132.8, 130.7, 130.5, 130.4, 129.7, 129.5, 128.0, 121.2, 60.6, 52.2, 37.9, 21.1, 14.3. IR (neat): ν = 2988, 1709, 1637, 1488, 1436, 1371, 1176, 1145 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{21}H_{23}O_4S$: 371.1317, found 371.1313.

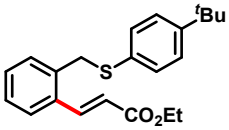


Ethyl 5-diethylcarbamoyl-2-((*p*-tolylthio)methyl)cinnamate (3q), the title compound was achieved as a colorless oil, 107 mg, 65% yield, eluted with petroleum ether/EtOAc = 5/1.

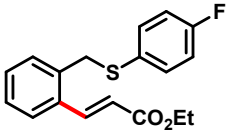
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.94 (d, *J* = 16 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.25-7.17 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.31 (d, *J* = 16 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 4.13 (s, 2H), 3.53 (s, 2H), 3.23 (s, 2H), 2.30 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 166.5, 140.5, 137.7, 137.6, 136.6, 133.9, 132.6, 130.9, 130.7 129.7, 127.4, 124.8, 120.9, 60.6, 43.3, 39.4 37.9, 21.1, 14.3, 14.2, 12.9. IR (neat): ν = 2976, 1710, 1628, 1428, 1385, 1311, 1175, 1095 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{24}H_{30}NO_3S$: 412.1946, found 412.1943.



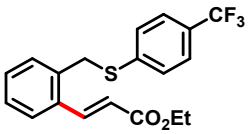
Ethyl 2-((4-methoxyphenyl)thio)cinnamate (3r), the title compound was achieved as a colorless oil, 92 mg, 70% yield, eluted with petroleum ether/EtOAc = 20/1.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (d, *J* = 16 Hz, 1H), 7.56-7.53 (m, 1H), 7.28-7.24 (m, 4H), 7.13-7.10 (m, 1H), 6.80-6.76 (m, 2H), 6.32 (d, *J* = 16 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.09 (s, 2H), 3.79 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 159.6, 141.2, 137.1, 135.3, 133.5, 130.7, 129.7, 127.6, 126.6, 125.0, 119.7, 114.4, 60.4, 55.2, 39.0, 14.3. IR (neat): ν = 2982, 1707, 1633, 1589, 1493, 1314, 1172, 1031 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{19}H_{21}O_3S$: 329.1211, found 329.1207.



Ethyl 2-((4-(*tert*-butyl)phenyl)thio)cinnamate (3s), the title compound was achieved as a pale yellow oil, 99 mg, 70% yield, eluted with petroleum ether/EtOAc = 20/1.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (d, *J* = 16 Hz, 1H), 7.57-7.53 (m, 1H), 7.29-7.23 (m, 7H), 6.35 (d, *J* = 16 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.17 (s, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 150.5, 141.4, 136.7, 133.7, 131.9, 131.5, 130.8, 130.0, 127.9, 126.8, 126.0, 120.1, 60.6, 37.7, 34.6, 31.3, 14.4. IR (neat): ν = 2962, 1709, 1634, 1488, 1365, 1313, 1175, 1119 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{22}H_{27}O_2S$: 355.1732, found 355.1729.



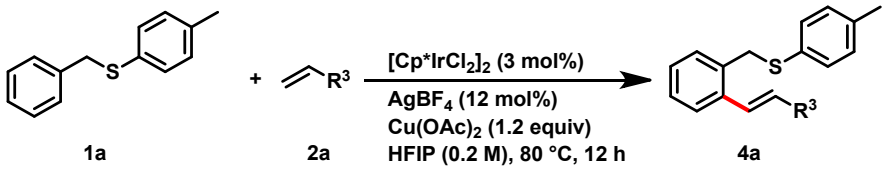
Ethyl 2-((4-fluorophenyl)thio)cinnamate (3t), the title compound was achieved as a pale yellow oil, 105 mg, 83% yield, eluted with petroleum ether/EtOAc = 20/1.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.95 (d, *J* = 15.6 Hz, 1H), 7.56-7.52 (m, 1H), 7.31-7.22 (m, 4H), 7.13-7.09 (m, 1H), 6.96-6.90 (m, 2H), 6.32 (d, *J* = 16 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.11 (s, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) -114.5 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 162.6 (d, *J* = 246.6 Hz, C-F), 141.2, 136.5, 134.9 (d, *J* = 8.2 Hz), 133.5, 130.7, 129.8, 129.7 (d, *J* = 3.3 Hz), 127.8, 126.7, 120.0, 115.9 (d, *J* = 21.7 Hz), 60.6, 38.5, 14.4. IR (neat): ν = 2982, 1707, 1634, 1589, 1489, 1313, 1216, 1176, 1155 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{18}H_{18}FO_2S$: 317.1012, found 317.1008.



Ethyl 2-((4-(trifluoromethyl)phenyl)thio)cinnamate (3u), the title compound was achieved as a white solid, mp. 59-61 °C 126 mg, 86% yield, eluted with petroleum ether/EtOAc = 20/1.

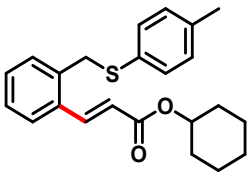
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.01 (d, *J* = 15.6 Hz, 1H), 7.58-7.56 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.30-7.26 (m, 3H), 6.38 (d, *J* = 15.6 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 4.26 (s, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 141.1, 140.8, 135.2, 133.7, 130.6, 130.2, 129.3, 128.6, 128.3, 127.0, 125.7 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 270.5 Hz), 120.6, 60.7, 36.0, 14.3. IR (neat): ν = 2980, 1704, 1603, 1482, 1371, 1324, 1158, 1106 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{19}H_{18}F_3O_2S$: 367.0980, found 367.0975.

5, General procedure for thioether directed mono-alkenylation of various olefins



To a 35 mL screw-top sealed tube equipped with stir bar, was added sulfur ethers **1a** (0.4 mmol), alkene **2a** (0.44 mmol), $[Cp^*IrCl_2]_2$ (3 mol%), $AgBF_4$ (12 mol%) and $Cu(OAc)_2$ (87 mg, 0.48 mmol, 1.2 equiv), HFIP (2 mL) was added *via* a syringe. The tube was then tightly capped. The reaction mixture was placed in a preheated oil-bath, and stirred at 80 °C for 12 h. The reaction mixture was allowed to cool to room temperature, w ter (10 mL) was added and extracted with ethyl acetate (20 mL*3). The organic layers were combined and dried over anhydrous Na_2SO_4. After removing solvent by rotary evaporation, the residue was subjected to flash column chromatography on silica gel to afford the desired products **4a**.

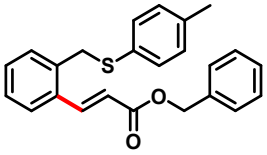
6, Characterization data for mono-alkenylation products of various olefins



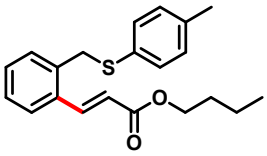
Cyclohexyl 2-((*p*-tolylthio)methyl)cinnamate (4a), the title compound was achieved as a colorless oil, 95 mg, 65% yield, eluted with petroleum ether/EtOAc = 20/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99 (d, *J* = 16 Hz, 1H), 7.56-7.52 (m, 1H), 7.27-7.18 (m, 5H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.31 (d, *J* = 16 Hz, 1H), 4.93-4.86 (m, 1H), 4.14 (s,

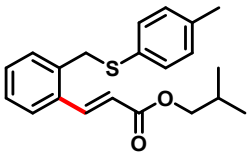
2H), 2.31 (s, 3H), 1.94-1.89 (m, 2H), 1.78-1.74 (m, 2H), 1.59-1.25 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 141.0, 137.3, 136.6, 133.7, 132.1, 131.5, 130.6, 129.7, 129.6, 127.7, 126.7, 120.6, 72.6, 38.0, 31.7, 25.4, 23.7, 21.0. IR (neat): ν = 2937, 1704, 1634, 1492, 1450, 1321, 1177, 1122 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{23}H_{27}O_2S$: 367.1732, found 367.1728.



Benzyl 2-((*p*-tolylthio)methyl)cinnamate (4b), the title compound was achieved as a pale yellow oil, 97 mg, 65% yield, eluted with petroleum ether/EtOAc = 20/1.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05 (d, *J* = 16 Hz, 1H), 7.55-7.51 (m, 1H), 7.42-7.30 (m, 5H), 7.26-7.22 (m, 2H), 7.21-7.16 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.24 (s, 2H), 4.13 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 141.8, 137.3, 136.8, 136.0, 133.5, 132.2, 131.3, 130.7, 130.0, 129.6, 128.5, 128.2, 127.7, 126.7, 119.5, 66.3, 37.9, 21.0. IR (neat): ν = 2925, 1710, 1632, 1492, 1454, 1312, 1159, 1091 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{24}H_{23}O_2S$: 375.1419, found 375.1415.

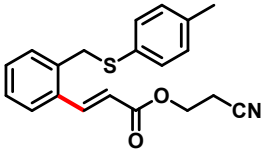


Butyl 2-((*p*-tolylthio)methyl)cinnamate (4c), the title compound was achieved as a colorless oil, 106 mg, 78% yield, eluted with petroleum ether/EtOAc = 20/1.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.01 (d, *J* = 16 Hz, 1H), 7.56-7.52 (m, 1H), 7.27-7.23 (m, 3H), 7.21-7.17 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.34 (d, *J* = 16 Hz, 1H), 4.22 (t, *J* = 6.8 Hz, 2H), 4.15 (s, 2H), 2.32 (s, 3H), 1.72-1.62 (m, 2H), 1.48-1.39 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 141.2, 137.3, 136.7, 133.5, 132.1, 131.4, 130.6, 129.8 129.6, 127.7, 126.7, 129.9, 64.3, 37.9, 30.7, 21.0, 19.1, 13.7. IR (neat): ν = 2971, 1713, 1634, 1492, 1454, 1315, 1088, 1046 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{21}H_{25}O_2S$: 341.1575, found 341.1571.

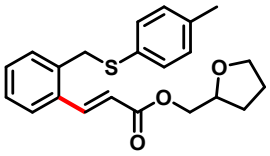


Isobutyl 2-((*p*-tolylthio)methyl)cinnamate (4d), the title compound was achieved as a pale yellow oil, 96 mg, 71% yield, eluted with petroleum ether/EtOAc = 20/1.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (d, *J* = 15.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.27-7.17 (m, 5H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 4.15 (s, 2H), 4.00 (d, *J* = 6.4 Hz, 2H), 2.31 (s, 3H), 2.06-1.94 (m, 1H), 1.00 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 141.3, 137.3, 136.7, 133.6, 132.1, 131.5, 130.6, 129.8, 129.6, 127.7,

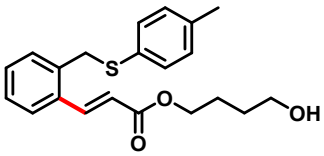
126.7, 119.9, 70.6, 37.8, 27.8, 21.0, 19.1. IR (neat): ν = 2962, 1708, 1633, 1492, 1379, 1314, 1169, 1016 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{21}H_{25}O_2S$: 341.1575, found 341.1571.



Cyanoethyl 2-((*p*-tolylthio)methyl)cinnamate (4e), the title compound was achieved as a pale yellow oil, 108 mg, 80% yield, eluted with petroleum ether/EtOAc = 5/1.
^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.06 (d, *J* = 16 Hz, 1H), 7.57-7.53 (m, 1H), 7.29-7.25 (m, 2H), 7.23-7.16 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.35 (d, *J* = 16 Hz, 1H), 4.41 (t, *J* = 6.4 Hz, 2H), 4.14 (s, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 142.9, 137.4, 137.0, 133.1, 132.2, 131.3, 130.8, 129.6, 127.8, 126.8, 118.3, 116.8, 58.7, 37.9, 21.0, 18.1. IR (neat): ν = 2962, 2258, 1716, 1633, 1492, 1314, 1266, 1214, 1166 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{20}H_{20}NO_2S$: 338.1215, found 338.1211.

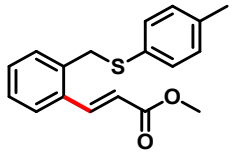


(Tetrahydrofuran-2-yl)methyl 2-((*p*-tolylthio)methyl)cinnamate (4f), the title compound was achieved as a pale yellow oil, 105 mg, 71% yield, eluted with petroleum ether/EtOAc = 20/1.
^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.03 (d, *J* = 15.6 Hz, 1H), 7.56-7.52 (m, 1H), 7.27-7.16 (m, 5H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 16 Hz, 1H), 4.29 (dd, J_1 = 10.8 Hz, J_2 = 3.2 Hz, 1H), 4.23-4.12 (m, 2H), 4.13 (s, 2H), 3.94-3.89 (m, 1H), 3.84-3.78 (s, 1H), 2.30 (s, 3H), 2.07-1.98 (m, 1H), 1.97-1.84 (m, 2H), 1.71-1.63 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 141.7, 137.3, 136.7, 133.5, 132.0, 131.4, 130.6, 129.9, 129.6, 127.7, 126.7, 119.5, 76.5, 68.4, 66.5, 37.9, 28.0, 25.7, 21.0. IR (neat): ν = 2982, 1710, 1634, 1492, 1452, 1313, 1171, 1088 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{22}H_{25}O_3S$: 369.1524, found 369.1521.

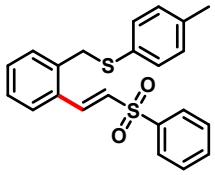


Hydroxybutyl 2-((*p*-tolylthio)methyl)cinnamate (4g), the title compound was achieved as a pale yellow oil, 102 mg, 72% yield, eluted with petroleum ether/EtOAc = 5/1.
^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.01 (d, *J* = 15.6 Hz, 1H), 7.56-7.52 (m, 1H), 7.27-7.16 (m, 5H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.33 (d, *J* = 16 Hz, 1H), 4.24 (t, *J* = 6.4 Hz, 2H), 4.13 (s, 2H), 3.69 (t, *J* = 6.4 Hz, 2H), 2.30 (s, 3H), 1.86 (s, 1H), 1.82-1.77 (m, 2H), 1.71-1.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 141.5, 137.4, 136.8, 133.6, 132.1,

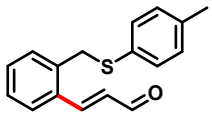
131.5, 130.8, 130.0, 129.7, 127.9, 126.8, 119.8, 64.4, 62.4, 38.0, 29.2, 25.2, 21.1. IR (neat): ν = 3417, 2948, 1706, 1633, 1492, 1452, 1314, 1171, 1040 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{21}H_{25}O_3S$: 357.1524, found 357.1521.



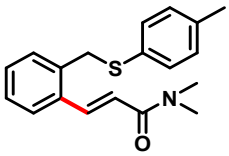
Methyl 2-((*p*-tolylthio)methyl)cinnamate (4h),[1] the title compound was achieved as a colorless oil, 80 mg, 67% yield, eluted with petroleum ether/EtOAc = 20/1.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99 (d, *J* = 16 Hz, 1H), 7.56-7.52 (m, 1H), 7.28-7.16 (m, 5H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.33 (d, *J* = 16 Hz, 1H), 4.14 (s, 2H), 3.81 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 141.6, 137.5, 136.9, 133.6, 132.3, 131.5, 130.8, 130.0, 129.7, 127.8, 126.8, 119.6, 51.7, 38.0, 21.1.



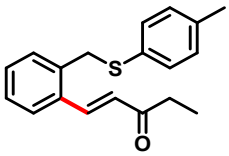
(*E*)-2-(2-(phenylsulfonyl)vinyl)benzyl *p*-tolyl sulfane (4i), the title compound was achieved as a white solid, mp. 65.4-66.3 °C, 106 mg, 70% yield, eluted with petroleum ether/EtOAc = 5/1..
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.03 (d, *J* = 15.6 Hz, 1H), 7.97-7.95 (m, 2H), 7.61 (tt, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 7.53 (tt, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 7.44 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.29-7.17 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 15.2 Hz, 1H), 4.14 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 139.7, 137.6, 137.3, 133.3, 132.1, 131.6, 131.1, 130.9, 130.7, 129.8, 129.3, 128.9, 127.9, 127.7, 127.2, 38.1, 21.1. IR (neat): ν = 2919, 1608, 1493, 1447, 1316, 1304, 1142, 1083 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{22}H_{21}O_2S_2$: 381.0983, found 381.0983.



2-((*p*-tolylthio)methyl)cinnamaldehyde (4j), the title compound was achieved as a pale yellow oil, 71 mg, 66% yield, eluted with petroleum ether/EtOAc = 20/1.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.57 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 15.6 Hz, 1H), 7.59-7.56 (m, 1H), 7.34-7.28 (m, 2H), 7.24-7.18 (m, 3H), 7.06 (d, *J* = 8.0, 2H), 6.58 (dd, J_1 = 15.6 Hz, J_2 = 7.6 Hz, 1H), 4.14 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 149.1, 137.9, 137.3, 132.9, 132.4, 131.1, 131.0, 130.9, 129.8, 129.7, 128.0, 126.9, 38.0, 21.0. IR (neat): ν = 2921, 1674, 1620, 1490, 1413, 1323, 1126, 1085 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{17}H_{17}OS$: 269.1000, found 269.0995.

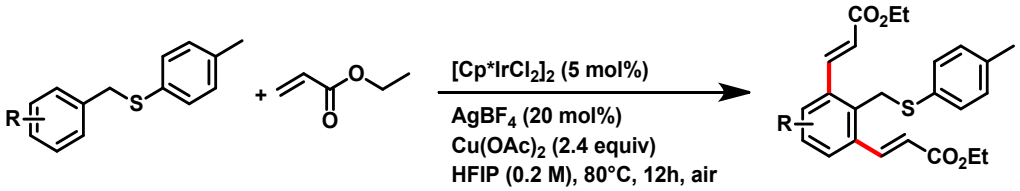


N,N-dimethyl-2-((*p*-tolylthio)methyl)cinnamamide (4k), the title compound was achieved as a pale yellow oil, 95 mg, 71% yield, eluted with petroleum ether/EtOAc = 5/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99 (d, *J* = 15.2 Hz, 1H), 7.54-7.51 (m, 1H), 7.26-7.18 (m, 5H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 15.2 Hz, 1H), 4.17 (s, 2H), 3.14 (s, 3H), 3.06 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 139.2, 136.9, 136.2, 134.7, 131.9, 131.4, 130.6, 129.6, 129.1, 127.6, 126.9, 119.9, 37.7, 37.4, 35.8, 21.0. IR (neat): ν = 2927, 1648, 1608, 1491, 1454, 1394, 1212, 1139 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{19}H_{22}NOS$: 312.1422, found 312.1418.



(*E*)-2-(3-oxopent-1-en-1-yl)benzyl *p*-tolyl sulfane (4l), the title compound was achieved as a pale yellow oil, 92 mg, 77% yield, eluted with petroleum ether/EtOAc = 20/1.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.85 (d, *J* = 16.4 Hz, 1H), 7.59-7.54 (m, 1H), 7.29-7.25 (m, 2H), 7.23-7.17 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 16 Hz, 1H), 4.14 (s, 2H), 2.65 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 139.0, 137.4, 137.0, 133.7, 132.0, 131.5, 130.7, 129.9, 129.6, 127.8, 127.8, 126.6, 38.1, 33.7, 21.0, 8.1. IR (neat): ν = 2976, 1639, 1611, 1492, 1454, 1265, 1192, 1120 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{19}H_{21}OS$: 297.1313, found 297.1309.

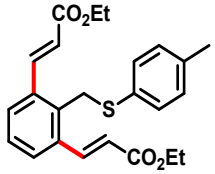
7, General procedure for thioether directed di-alkenylation



1a (0.4 mmol) **2a (4.0 equiv)** **5a**

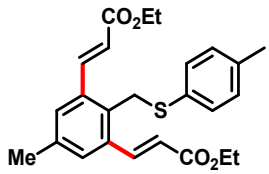
To a 35 mL screw-top sealed tube equipped with stir bar, was added sulfur ethers **1a** (0.4 mmol), ethyl acrylate **2a** (1.6 mmol), $[Cp^*IrCl_2]_2$ (16 mg, 5 mol%), $AgBF_4$ (15.8 mg, 20 mol%) and $Cu(OAc)_2$ (173.7 mg, 2.4 equiv) in HFIP (2 mL) *via* a syringe. The tube was then tightly capped. The reaction mixture was placed in a preheated oil-bath, and stirred at 80 °C for 12 h. When cooled to room temperature, the reaction mixture was quenched with water (10 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layers was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under the reduced pressure, the residue was subjected to flash column chromatography on silica gel to provide the desired product **5a.**

8, Characterization data for di-alkenylation products



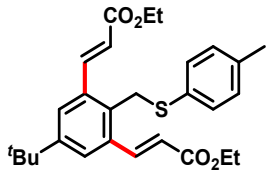
(2*E*,2'*E*)-diethyl 3,3'-(2-((*p*-tolylthio)methyl)-1,3-phenylene)diacrylate (5a),[8] the title compound was achieved as a pale yellow solid, mp. 100-101 °C, 134 mg, 82% yield, eluted with petroleum ether/EtOAc = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.93 (d, *J* = 15.6 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.22 (d, *J* = 15.6 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 4H), 4.15 (s, 2H), 2.27 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 141.5, 138.3, 135.3, 133.8, 130.7, 129.8, 128.4, 127.8, 121.5, 60.7, 34.7, 21.2, 14.4.



(2*E*,2'*E*)-diethyl 3,3'-(5-methyl-2-((*p*-tolylthio)methyl)-1,3-phenylene)diacrylate (5b),[8] the title compound was achieved as a pale yellow oil, 137 mg, 81% yield, eluted with petroleum ether/EtOAc = 5/1.

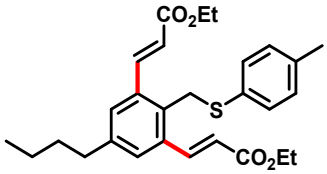
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (d, *J* = 15.6 Hz, 2H), 7.34 (s, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.27 (d, *J* = 16 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 4H), 4.17 (s, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 141.6, 137.9, 137.6, 134.9, 133.5, 132.5, 130.8, 129.8, 129.2, 121.2, 60.6, 34.5, 29.6, 21.0, 14.2.



(2*E*,2'*E*)-diethyl 3,3'-(5-(*tert*-butyl)-2-((*p*-tolylthio)methyl)-1,3-phenylene)diacrylate (5c), the title compound was achieved as a pale yellow solid, mp. 90-91 °C,148 mg, 80% yield, eluted with petroleum ether/EtOAc = 5/1.

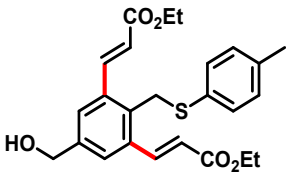
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (d, *J* = 15.6 Hz, 2H), 7.55 (s, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.31 (d, *J* = 15.6 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 4H), 4.19 (s, 2H), 2.32 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 6H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 150.9, 142.2, 138.1, 134.9, 133.3, 132.3, 131.2, 129.8, 125.7, 121.2, 60.7,

34.8, 34.6, 31.2, 21.2, 14.4. IR (neat): ν = 2964, 1706, 1634, 1466, 1364, 1316, 1173, 1095 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{28}H_{35}O_4S$: 467.2256, found 467.2252.



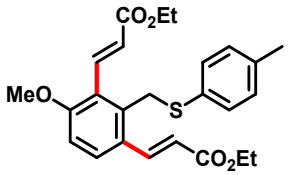
(2*E*,2'*E*)-diethyl 3,3'-(5-butyl-2-((*p*-tolylthio)methyl)-1,3-phenylene)diacrylate (5d), the title compound was achieved as a pale yellow oil, 151 mg, 80% yield, eluted with petroleum ether/EtOAc = 10/1.

^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.98 (d, *J* = 15.6 Hz, 2H), 7.34 (s, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.28 (d, *J* = 15.6 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 4H), 4.18 (s, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.63-1.55 (m, 2H), 1.38-1.30 (m, 2H), 1.34 (t, *J* = 6.8 Hz, 6H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 142.6, 141.7, 138.1, 135.1, 133.5, 132.6, 130.9, 129.8, 128.6, 121.1, 60.6, 35.3, 34.5, 33.4, 22.3, 21.2, 14.4, 13.9. IR (neat): ν = 2948, 1703, 1630, 1492, 1472, 1366, 1174, 1164 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{28}H_{35}O_4S$: 467.2256, found 467.2254.



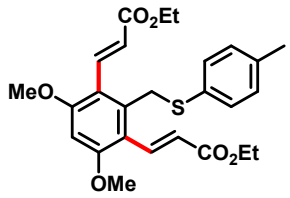
(2*E*,2'*E*)-diethyl 3,3'-(5-(hydroxymethyl)-2-((*p*-tolylthio)methyl)-1,3-phenylene) diacrylate (5e), the title compound was achieved as a pale yellow solid, mp. 110-113 °C, 126 mg, 71% yield, eluted with petroleum ether/EtOAc = 2/1.

^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (d, *J* = 15.6 Hz, 2H), 7.52 (s, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.29 (d, *J* = 16 Hz, 2H), 4.71 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 4H), 4.17 (s, 2H), 2.31 (s, 3H), 2.05 (s, 1H), 1.34 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 141.4, 140.7, 138.3, 135.4, 134.4, 133.6, 130.7, 129.8, 126.7, 121.5, 64.4, 60.7, 34.5, 21.2, 14.3. IR (neat): ν = 3397, 2956, 1706, 1630, 1492, 1447, 1363, 1181, 1037 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{25}H_{29}O_5S$: 441.1736, found 441.1731.



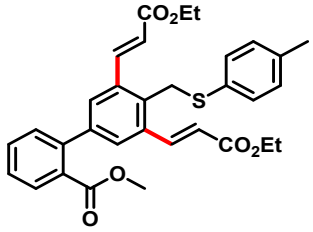
(2*E*,2'*E*)-diethyl 3,3'-(4-methoxy-2-((*p*-tolylthio)methyl)-1,3-phenylene)diacrylate (5f), the title compound was achieved as a pale yellow oil, 132 mg, 75% yield, eluted with petroleum ether/EtOAc = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (d, *J* = 15.6 Hz, 1H), 7.87 (d, *J* = 16.4 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.67 (d, *J* = 16 Hz, 1H), 6.22 (d, *J* = 15.6 Hz, 1H), 4.26 (q, *J* = 6.8 Hz, 2H), 4.25 (q, *J* = 6.8 Hz, 2H), 4.19 (s, 2H), 3.87 (s, 3H), 2.32 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.9, 159.7, 141.6, 137.9, 136.5, 133.0, 131.3, 129.9, 128.9, 127.5, 124.6, 124.1, 123.9, 118.8, 110.5, 60.5, 60.3, 55.8, 35.8, 21.2, 14.4. IR (neat): ν = 2980, 1706, 1630, 1471, 1365, 1314, 1181, 1159 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{25}H_{29}O_5S$: 441.1736, found 441.1730.



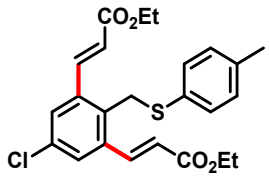
(2*E*,2'*E*)-diethyl 3,3'-(4,6-dimethoxy-2-((*p*-tolylthio)methyl)-1,3-phenylene)diacrylate (5g), the title compound was achieved as a pale yellow oil, 166 mg, 88% yield, eluted with petroleum ether/EtOAc = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.95 (d, *J* = 16 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.69 (d, *J* = 16 Hz, 2H), 6.45 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 4H), 4.20 (s, 2H), 3.90 (s, 6H), 2.33 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 160.7, 138.3, 137.9, 137.7, 132.8, 131.7, 129.9, 122.4, 116.6, 94.5, 60.3, 55.7, 36.9, 21.2, 14.4. IR (neat): ν = 2974, 1702, 1615, 1465, 1401, 1308, 1172, 1141 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{26}H_{31}O_6S$: 471.1841, found 471.1834.



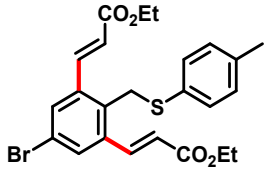
(2*E*,2'*E*)-diethyl 3,3'-(2'-(methoxycarbonyl)-4-((*p*-tolylthio)methyl)-[1,1'-biphenyl]-3,5-diyl)diacrylate (5h), the title compound was achieved as a white solid, mp. 115-117 ^{o}C, 174 mg, 80% yield, eluted with petroleum ether/EtOAc = 2/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.00 (d, *J* = 16 Hz, 2H), 7.89 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.56 (tt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.47 (s, 2H), 7.45 (tt, J_1 = 9.6 Hz, J_2 = 1.2 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.27 (d, *J* = 15.6 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 4H), 4.23 (s, 2H), 3.68 (s, 3H), 2.31 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 166.5, 141.3, 141.0, 140.9, 138.4, 134.9, 134.2, 133.9, 131.7, 130.7, 130.6, 130.4, 130.2, 129.8, 128.4, 127.9, 121.6, 60.6, 52.2, 34.6, 21.2, 14.3. IR (neat): ν = 2984, 1709, 1632, 1492, 1439, 1367, 1173, 1091 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{32}H_{33}O_6S$: 545.1998, found 545.1988.



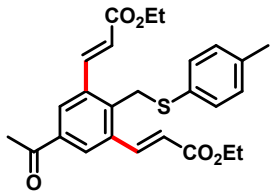
(2*E*,2'*E*)-diethyl 3,3'-(5-chloro-2-((*p*-tolylthio)methyl)-1,3-phenylene)diacrylate (5i),[8] the title compound was achieved as a white solid, mp. 96-97 °C, 121 mg, 68% yield, eluted with petroleum ether/EtOAc = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.85 (d, *J* = 16 Hz, 2H), 7.46 (s, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.23 (d, *J* = 15.6 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 4H), 4.11 (s, 2H), 2.31 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 140.2, 138.6, 136.9, 134.1, 133.9, 133.8, 130.1, 129.9, 127.9, 122.5, 60.8, 34.4, 21.2, 14.4.



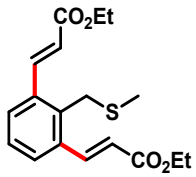
(2*E*,2'*E*)-diethyl 3,3'-(5-bromo-2-((*p*-tolylthio)methyl)-1,3-phenylene)diacrylate (5j), the title compound was achieved as a pale yellow oil, 132 mg, 68% yield, eluted with petroleum ether/EtOAc = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.84 (d, *J* = 15.6 Hz, 2H), 7.61 (s, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.23 (d, *J* = 16 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 4H), 4.10 (s, 2H), 2.30 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 140.0, 138.6, 137.2, 134.4, 134.1, 130.9, 130.1, 129.9, 122.6, 121.8, 60.8, 34.5, 21.2, 14.4. IR (neat): ν = 2924, 1713, 1635, 1493, 1365, 1309, 1176, 1081 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{24}H_{26}BrO_4S$: 489.0735, found 489.0737.



(2*E*,2'*E*)-diethyl 3,3'-(5-acetyl-2-((*p*-tolylthio)methyl)-1,3-phenylene)diacrylate (5k), the title compound was achieved as a white oil, 148 mg, 81% yield, eluted with petroleum ether/EtOAc = 2/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.04 (s, 2H), 7.90 (d, *J* = 15.6 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.31 (d, *J* = 15.6 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 4H), 4.17 (s, 2H), 2.62 (s, 3H), 2.30 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 166.2, 140.6, 140.1, 138.8, 136.2, 135.8, 134.3, 129.9, 129.7, 127.8, 122.5, 60.8, 34.7, 26.6, 21.2, 14.3. IR (neat): ν = 2974, 1702, 1682, 1629, 1488, 1429, 1366, 1174, 1038 cm^{-1}. HRMS (ESI): m/z: $[MH]^+$ Calculated for $C_{26}H_{29}O_5S$: 453.1736, found 453.1733.



(2*E*,2'*E*)-diethyl 3,3'-(2-((methylthio)methyl)-1,3-phenylene)diacrylate (5l),[8] the title compound was achieved as a pale yellow oil, 96 mg, 71% yield, eluted with petroleum ether/EtOAc = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.08 (d, *J* = 16 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 15.6 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 4H), 3.90 (s, 2H), 2.12 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 141.8, 135.8, 134.9, 128.5, 127.8, 121.6, 60.7, 31.6, 15.9, 14.3.

9, References

1. Yu, M.; Xie, Y.; Xie, C.; Zhang, Y. *Org. Lett*. **2012**, *14*, 2164.

2. Li, Y.; Pu, J.; Jiang, X. *Org. Lett*. **2014**, *16*, 2692.

3. Miyazaki, T.; Kasai, S.; Ogiwara, Y.; Sakai. N. *Eur. J. Org. Chem*. **2016**, *2016*, 1043.

4. Santoni, G.; Mba, M.; Bonchio, M.; Nugent, W. A.; Zonta, C.; Licini, G. *Chem. Eur. J*. **2010**, *16*, 645.

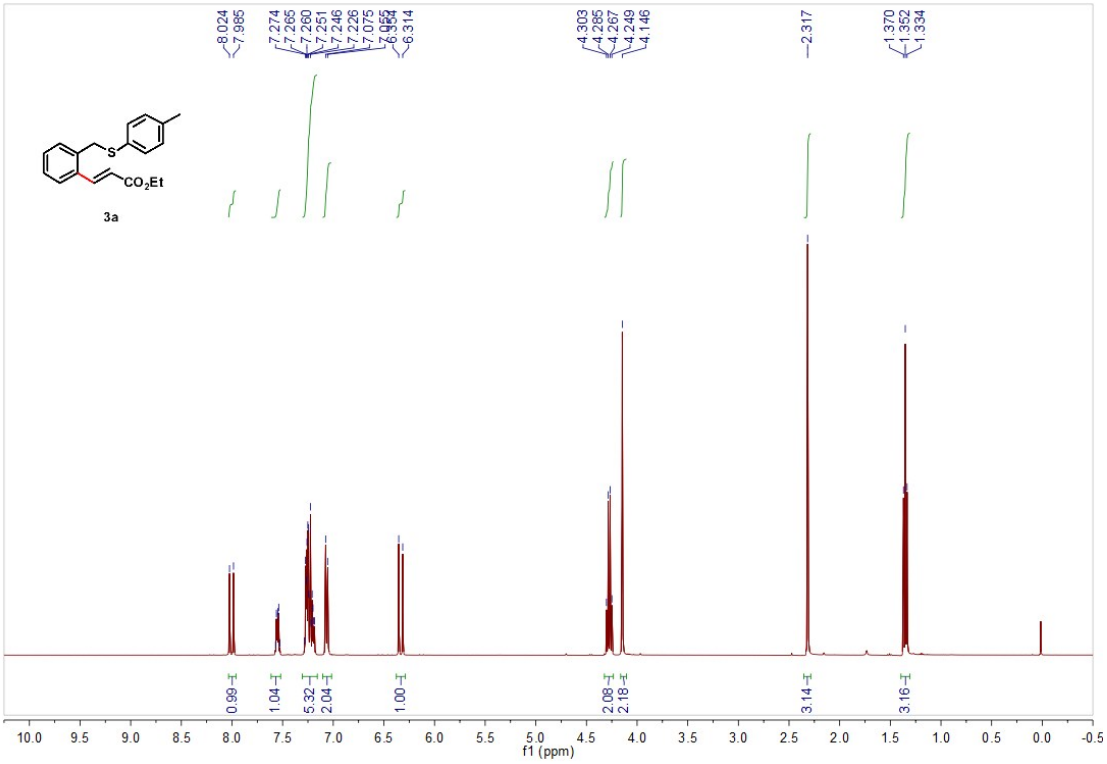
5. Yao, J.; Yu, M.; Zhang, Y. *Adv. Synth. Catal*. **2012**, *354*, 3205.

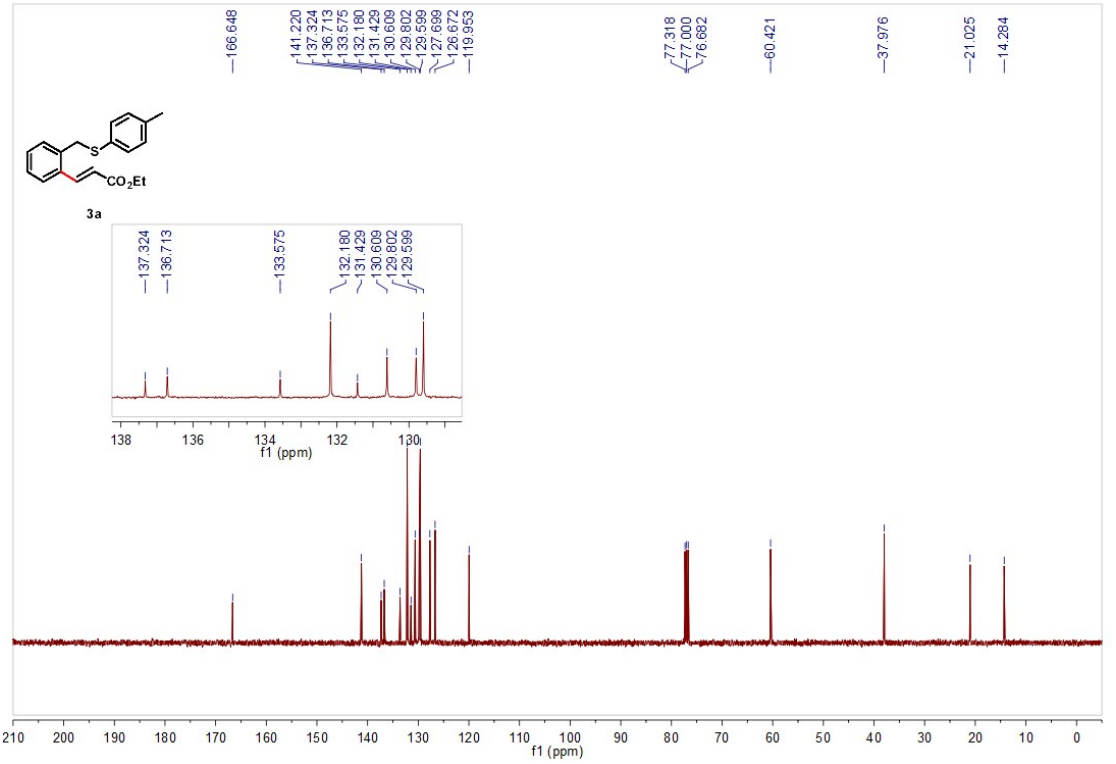
6. El-Hegazy, F. E.-Z. M.; El-Bardan, A. A.; Hamed, E. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *88*, 113.

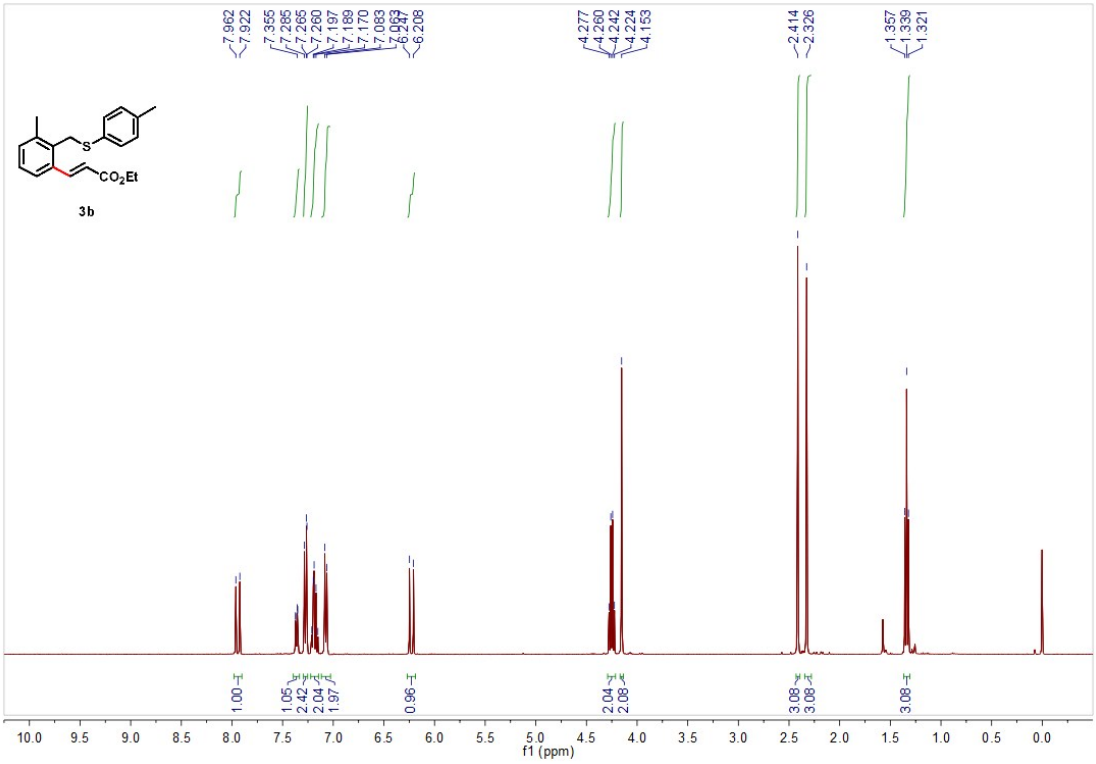
7. Huang, H.; Kang, J. Y. *Org. Lett*. **2017**, *19*, 544.

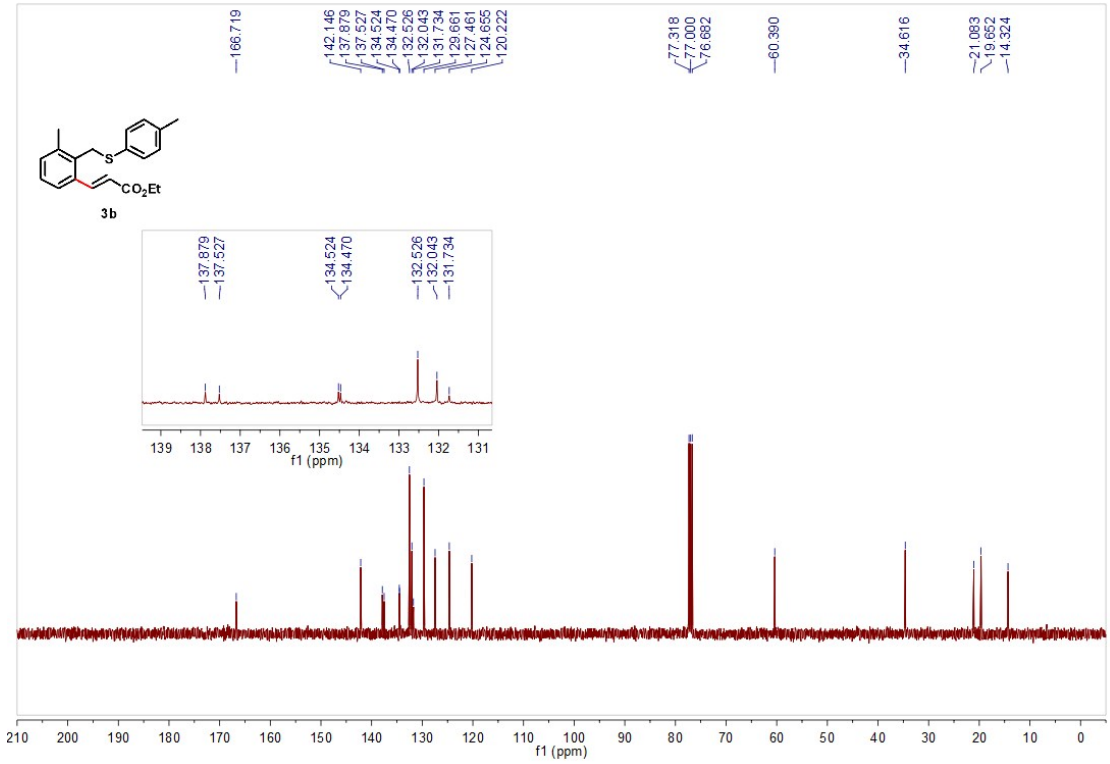
8. Zhang, X.-S.; Zhu, Q.-L.; Zhang, Y.-F.; Li, Y.-B.; Shi, Z.-J. *Chem. Eur. J*. **2013**, *19*, 11898.

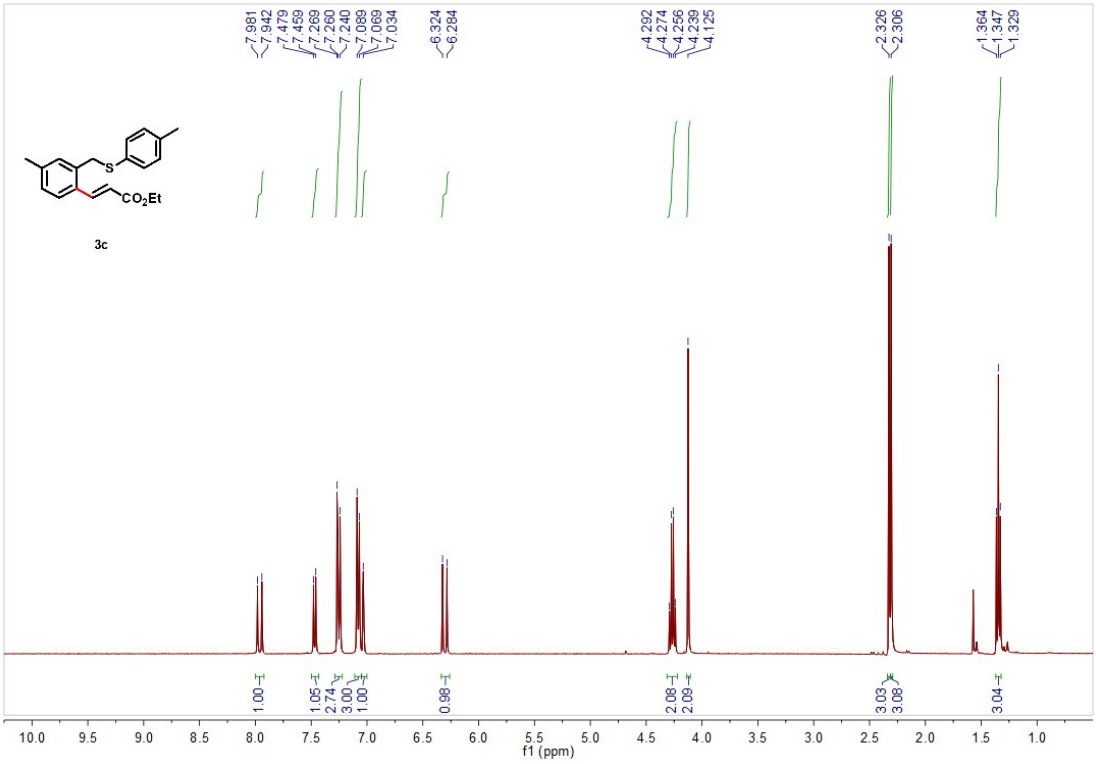
10, ^{1}H NMR, ^{13}C NMR and ^{19}F spectra

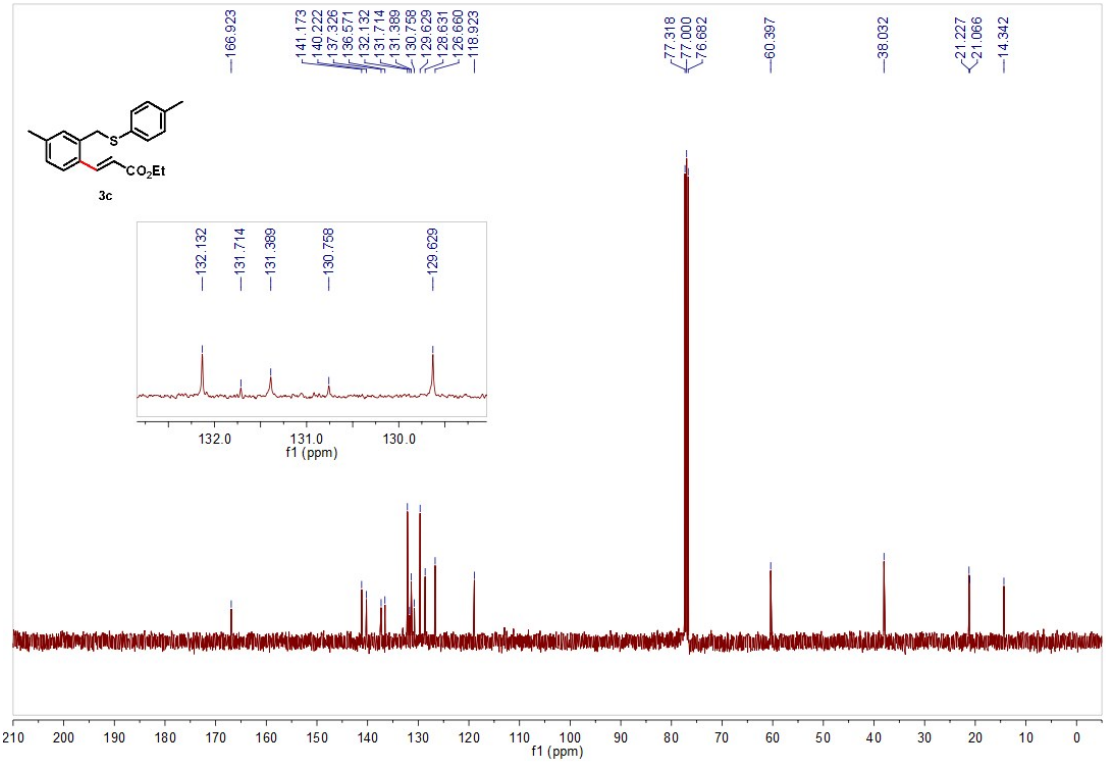


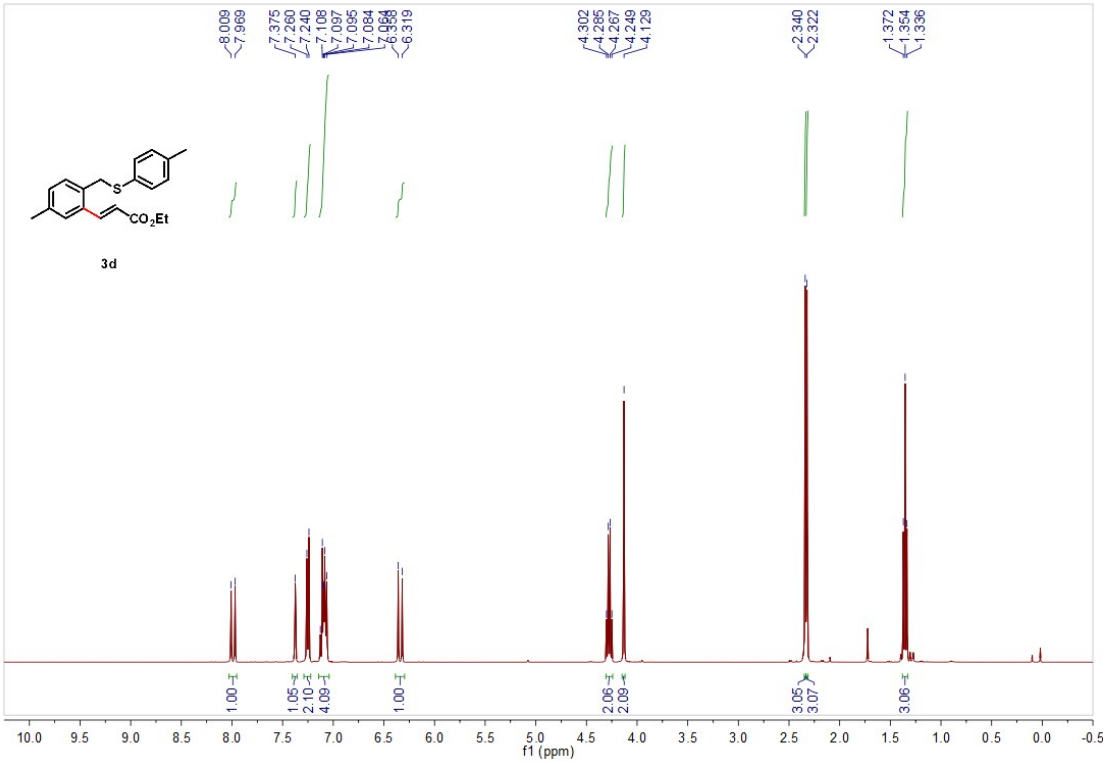


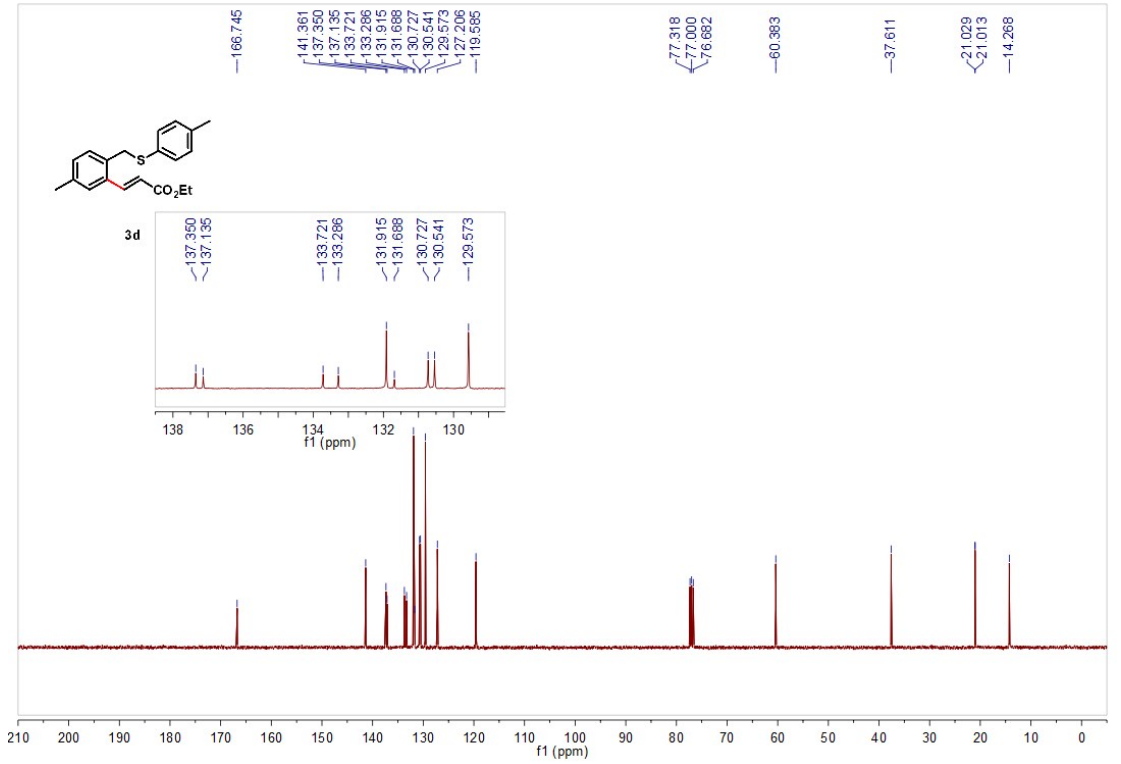

7.962
7.922
7.355
7.285
7.265
7.260
7.197
7.189
7.170
7.083
6.247
6.208
4.277
4.260
4.242
4.224
4.153
2.414
2.326
1.357
1.339
1.321
1.00
1.05
2.42
2.04
1.97
0.96
2.04
2.08
3.08
3.08
3.08
CO2Et
3b
f1 (ppm)

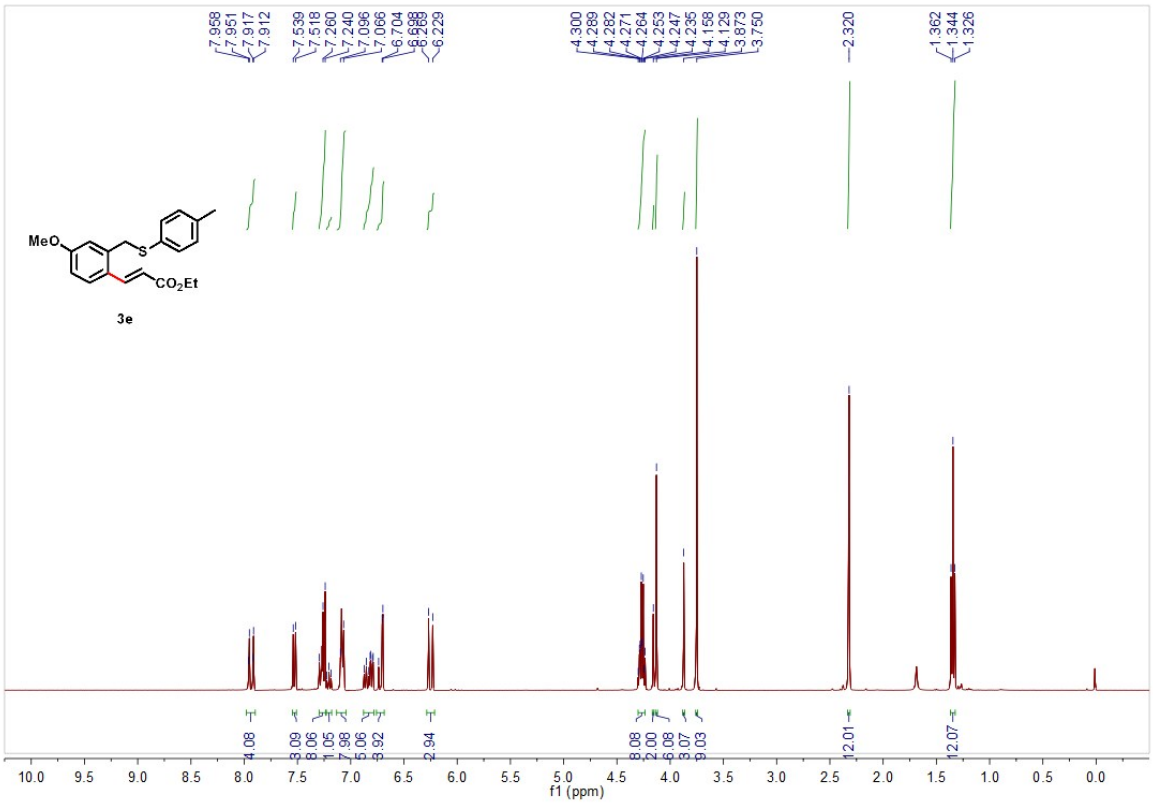

166.719
142.146
137.879
137.527
134.524
134.470
132.526
132.043
131.734
129.661
127.461
124.655
120.222
77.318
77.000
76.682
60.390
34.616
21.083
19.652
14.324
CO2Et
3b
137.879
137.527
134.524
134.470
132.526
132.043
131.734
f1 (ppm)
f1 (ppm)

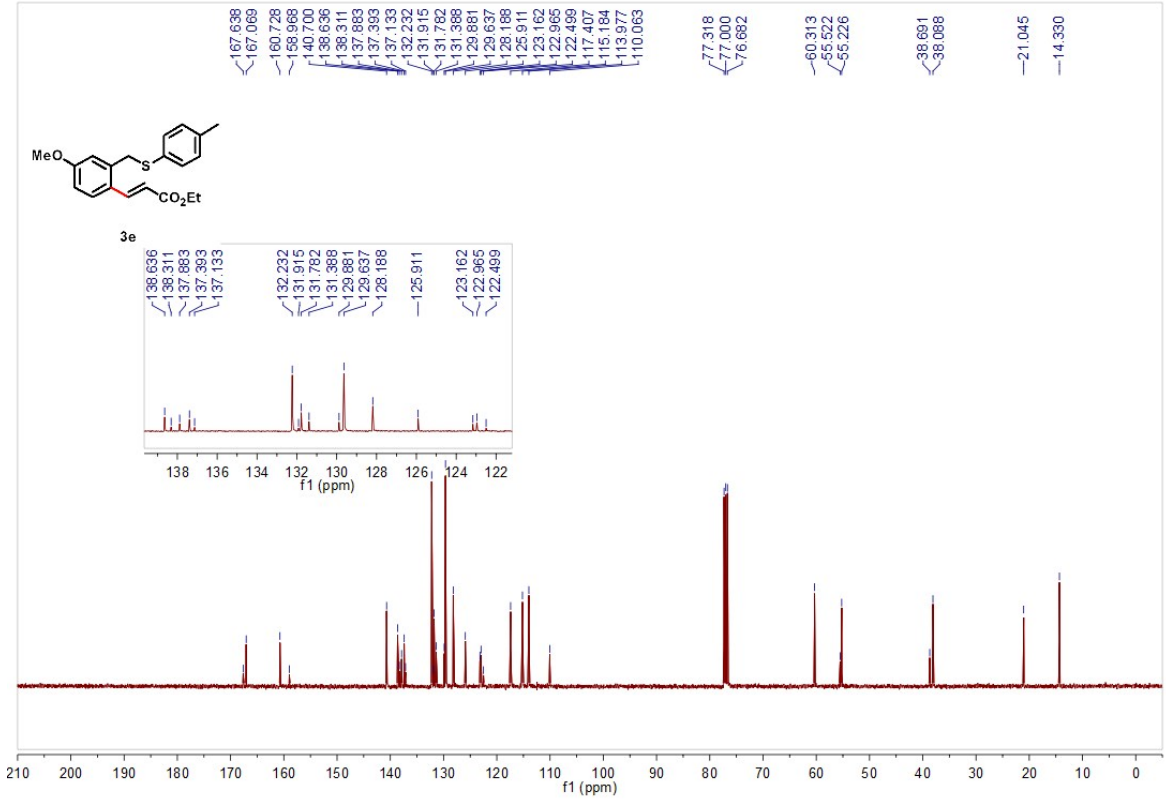

7.981
7.942
7.479
7.459
7.269
7.260
7.240
7.089
7.069
7.034
6.324
6.284
4.292
4.274
4.256
4.239
4.125
2.326
2.306
1.364
1.347
1.329
1.00
1.05
2.74
3.00
1.00
0.98
2.08
2.09
3.03
3.08
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)
CO2Et
3c

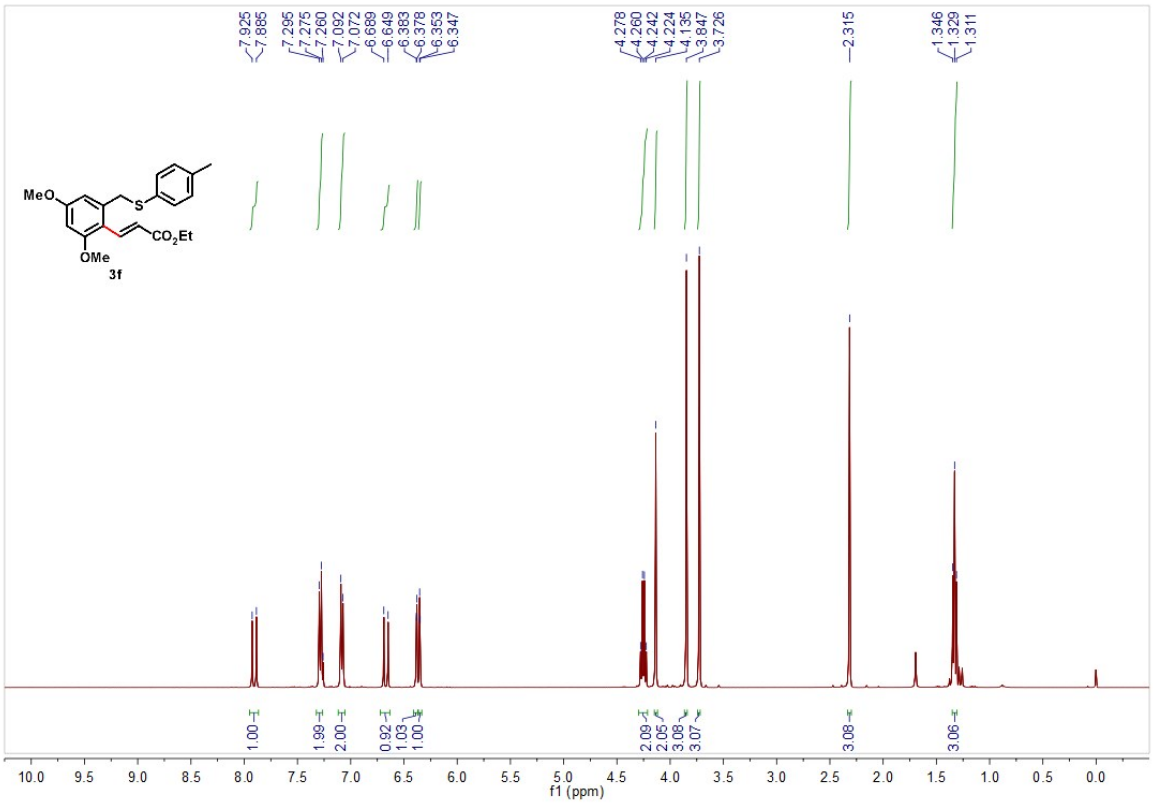

166.923
141.173
140.222
137.326
136.571
132.132
131.714
131.389
130.758
129.629
128.631
126.660
118.923
77.318
77.000
76.682
60.397
38.032
21.227
21.066
14.342
132.132
131.714
131.389
130.758
129.629
132.0
131.0
130.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
CO2Et
3c

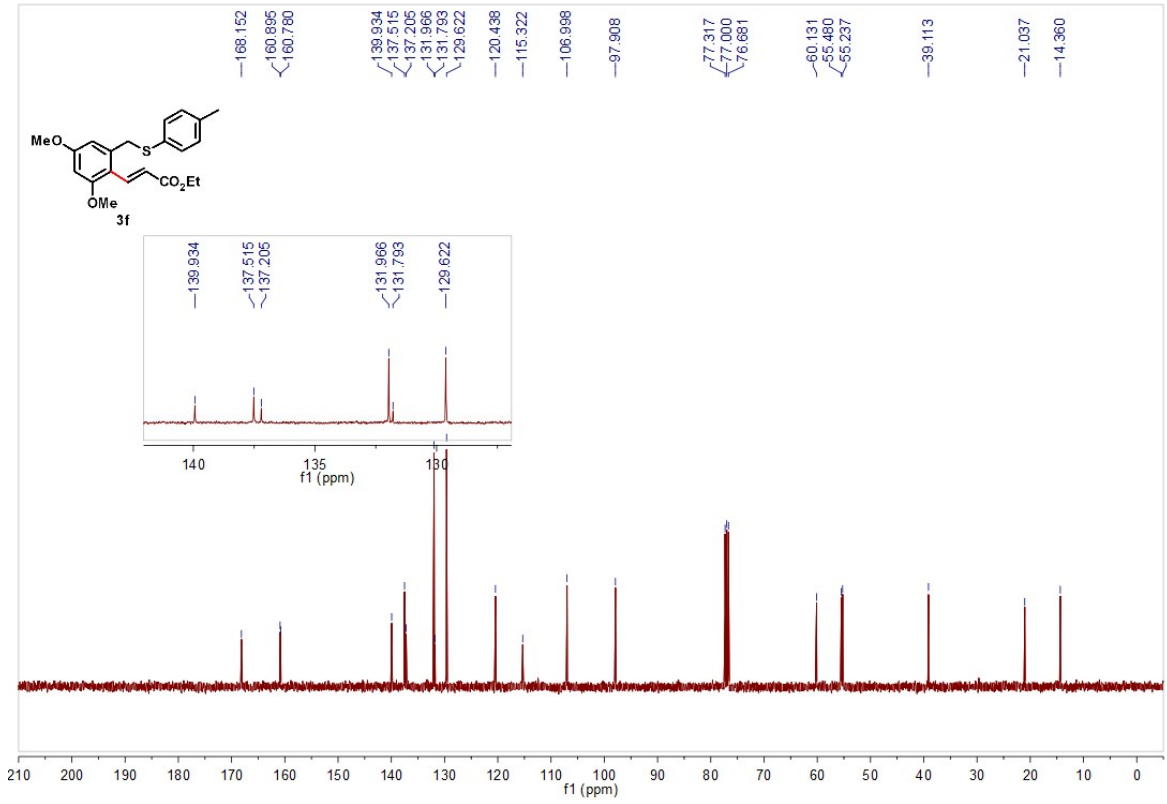

8.009
7.969
7.375
7.260
7.240
7.108
7.097
7.095
7.084
7.064
6.958
6.319
4.302
4.285
4.267
4.249
4.129
2.340
2.322
1.372
1.354
1.336
S
CO2Et
3d
1.00
1.05
2.10
4.09
1.00
2.06
2.09
3.05
3.07
3.06
f1 (ppm)

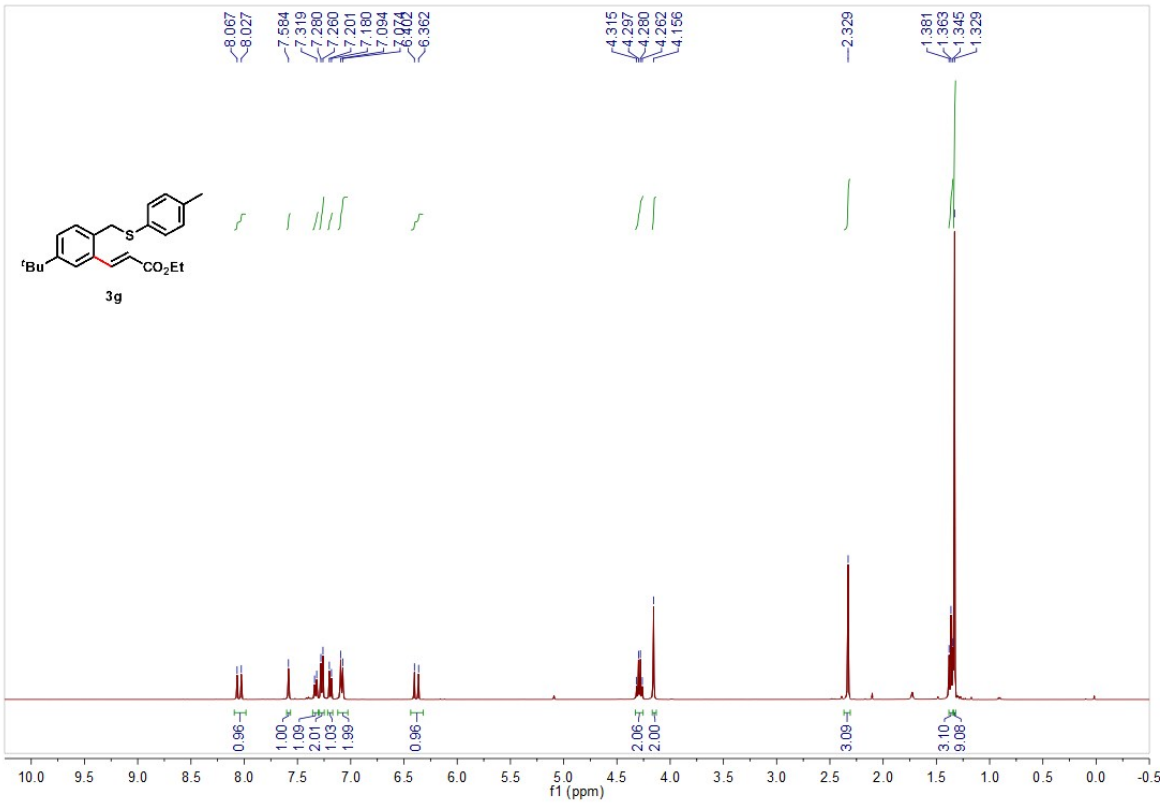

166.745
141.361
137.350
137.135
133.721
133.286
131.915
131.688
130.727
130.541
129.573
127.206
119.585
77.318
77.000
76.682
60.383
37.611
21.029
21.013
14.268
S
CO2Et
3d
137.350
137.135
133.721
133.286
131.915
131.688
130.727
130.541
129.573
138
136
134
132
130
f1 (ppm)
f1 (ppm)

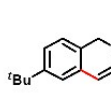

7.958
7.951
7.917
7.912
7.539
7.518
7.260
7.240
7.096
7.066
6.704
6.688
6.229
4.300
4.289
4.282
4.271
4.264
4.253
4.247
4.235
4.158
4.129
3.873
3.750
2.320
1.362
1.344
1.326
MeO
S
CO2Et
3e
4.08
3.09
8.06
1.05
7.98
5.06
8.92
2.94
8.08
2.00
6.08
8.07
9.03
12.01
12.07
f1 (ppm)


167.638
167.069
160.728
158.968
140.700
138.636
138.311
137.883
137.393
137.133
132.232
131.915
131.782
131.388
129.881
129.637
128.188
125.911
123.162
122.965
122.499
117.407
115.184
113.977
110.063
77.318
77.000
76.682
60.313
55.522
55.226
38.691
38.088
21.045
14.330
MeO
S
CO2Et
3e
f1 (ppm)


7.925
7.885
7.295
7.275
7.260
7.092
7.072
6.689
6.649
6.383
6.378
6.353
6.347
4.278
4.260
4.242
4.224
4.135
3.847
3.726
2.315
1.346
1.329
1.311
MeO
S
CO2Et
OMe
3f
1.00
1.99
2.00
0.92
1.03
1.00
2.09
2.05
3.08
3.07
3.08
3.06
f1 (ppm)

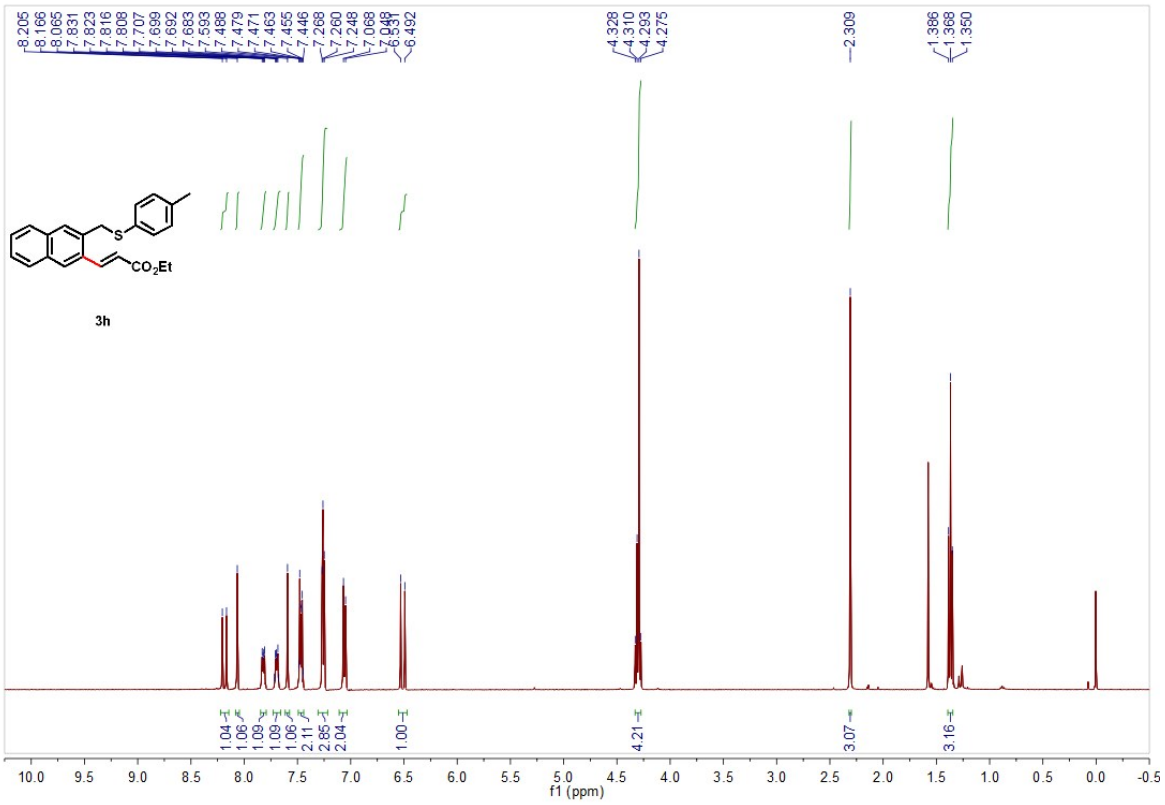

168.152
160.895
160.780
139.934
137.515
137.205
131.966
131.793
129.622
120.438
115.322
106.998
97.908
77.317
77.000
76.681
60.131
55.480
55.237
39.113
21.037
14.360
MeO
S
CO2Et
OMe
3f
f1 (ppm)

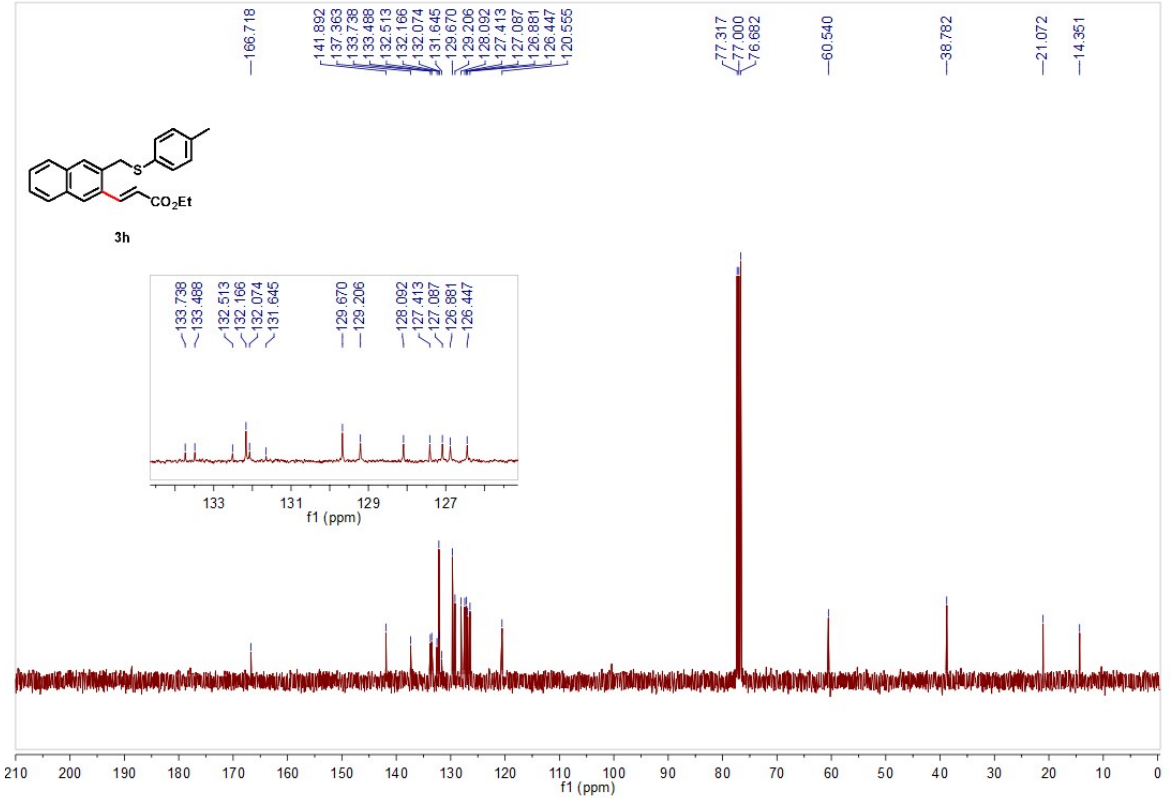

8.067
8.027
7.584
7.319
7.280
7.260
7.201
7.180
7.094
6.404
6.362
4.315
4.297
4.280
4.262
4.156
2.329
1.381
1.363
1.345
1.329
0.96
1.00
1.09
2.01
1.03
1.99
0.96
2.06
2.00
3.09
3.10
9.08
f1 (ppm)

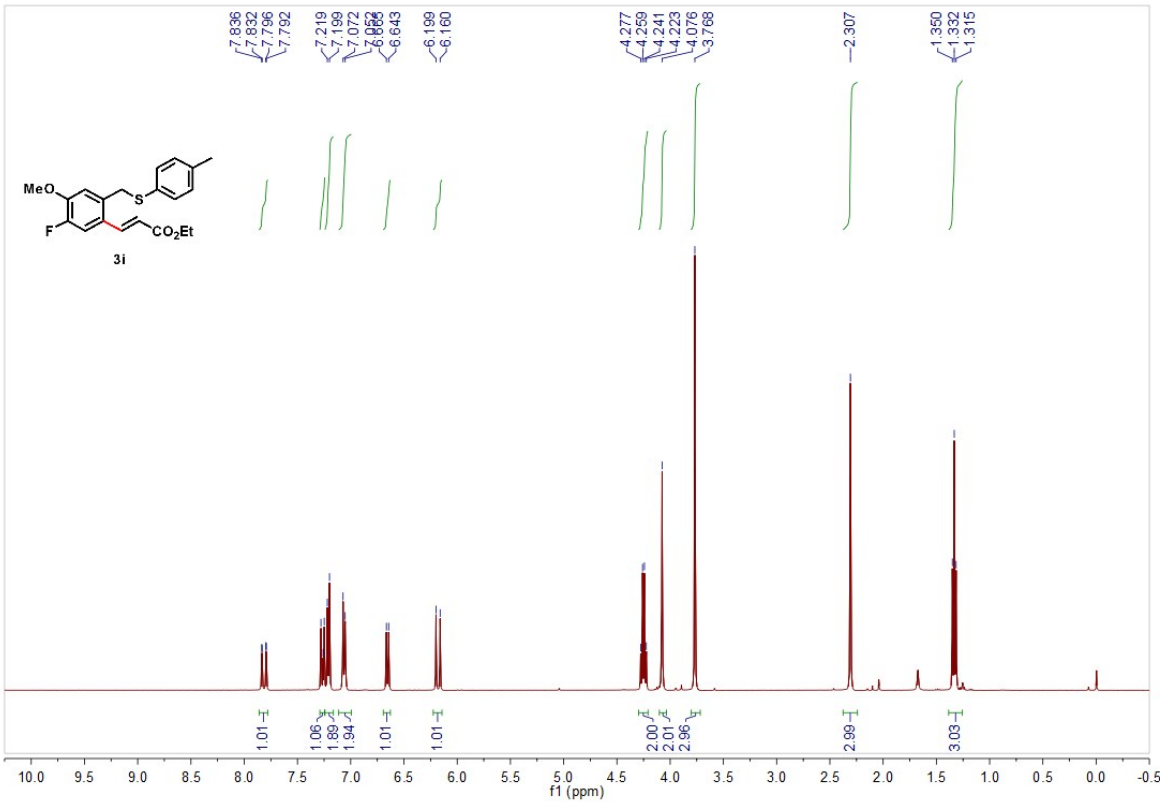

tBu
CO2Et
S

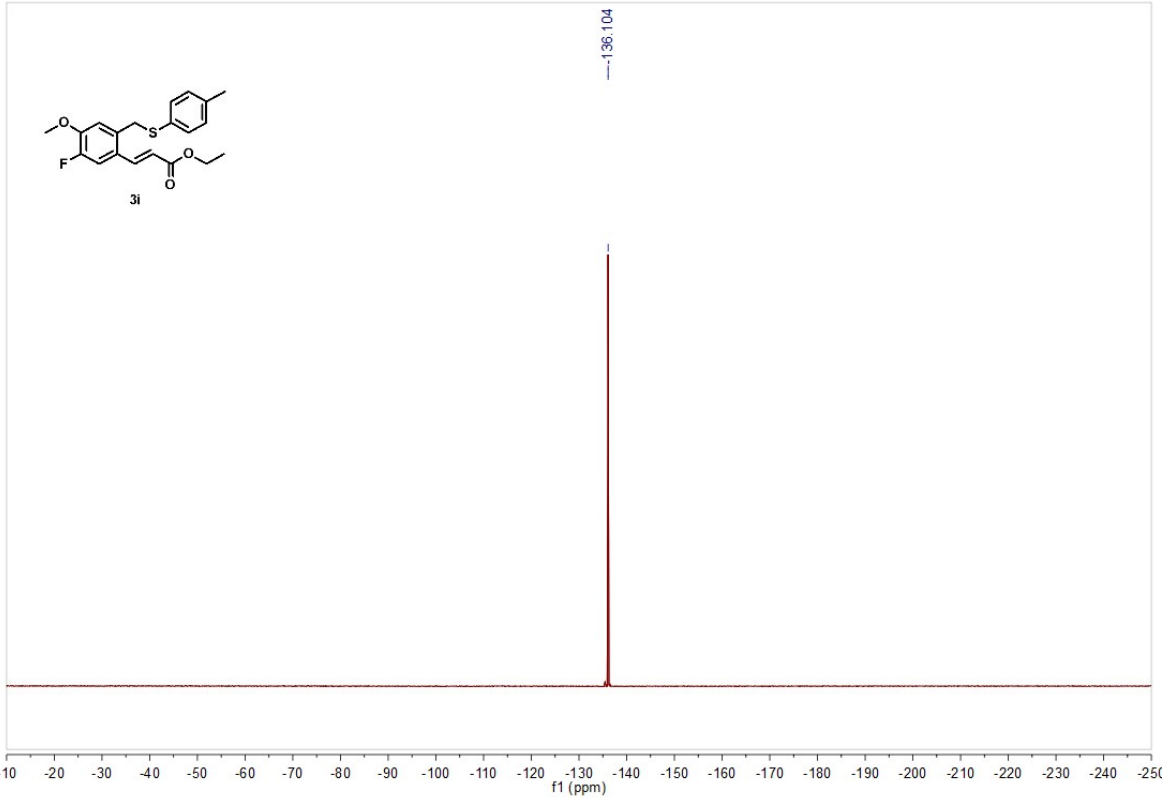
3g

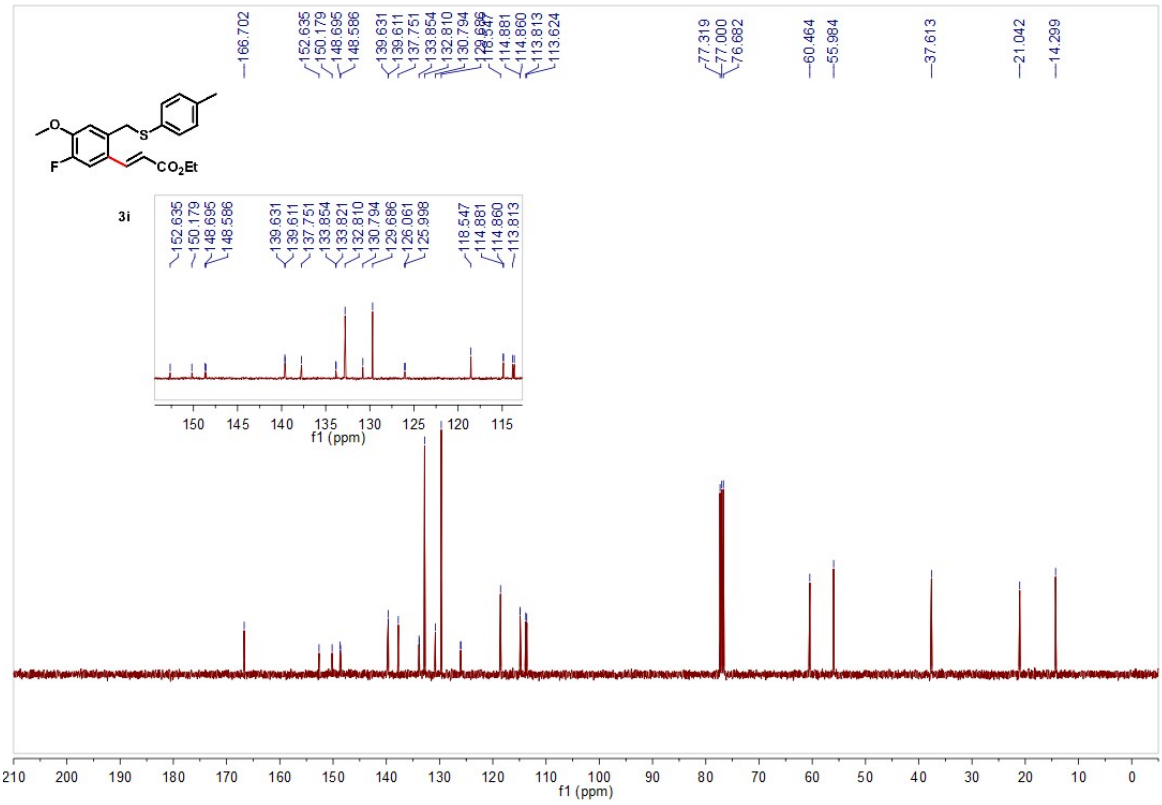
166.802
150.687
141.914
137.075
133.653
133.024
131.966
131.683
130.396
129.598
127.247
123.523
119.561
77.318
77.000
76.682
60.441
37.565
34.553
31.158
21.039
14.302
133.653
133.024
131.966
131.683
130.396
129.598
f1 (ppm)
f1 (ppm)

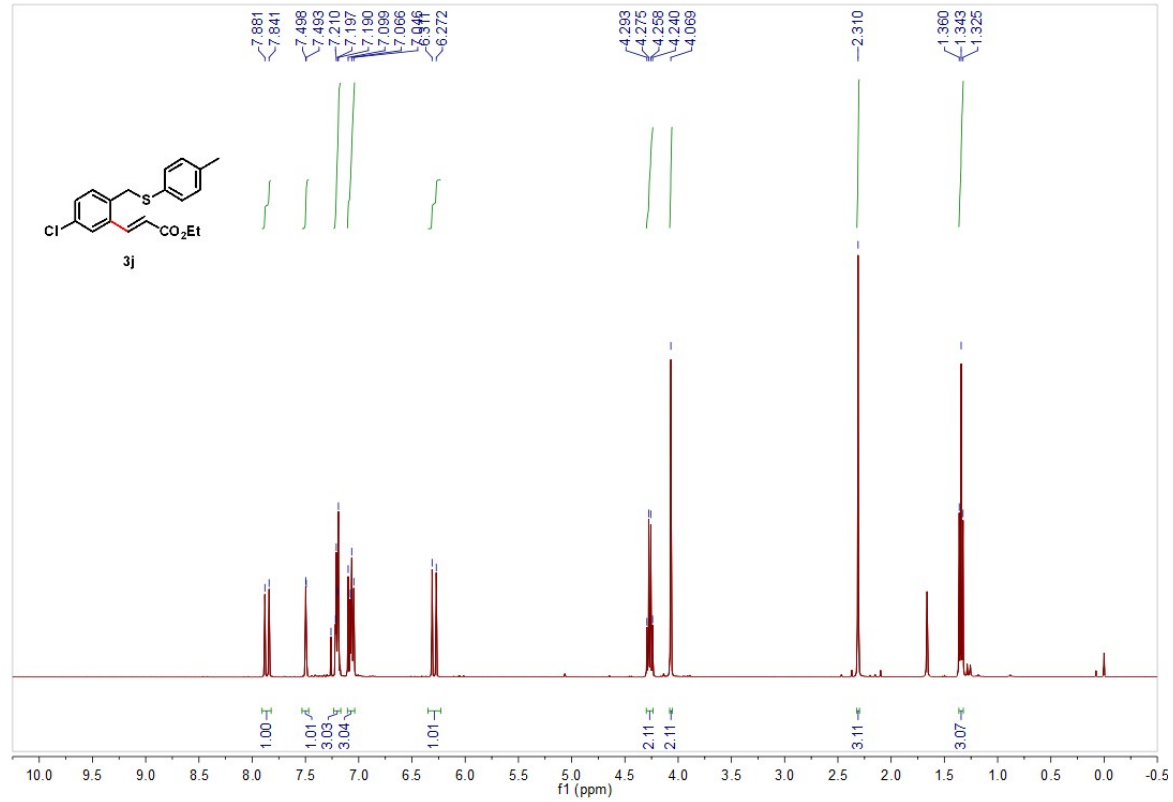

8.205
8.166
8.065
7.831
7.823
7.816
7.808
7.707
7.699
7.692
7.683
7.593
7.488
7.479
7.471
7.463
7.455
7.446
7.268
7.260
7.248
7.068
6.492
4.328
4.310
4.293
4.275
2.309
1.386
1.368
1.350
3h
1.04
1.06
1.09
1.09
1.06
2.11
2.85
2.04
1.00
4.21
3.07
3.16
f1 (ppm)

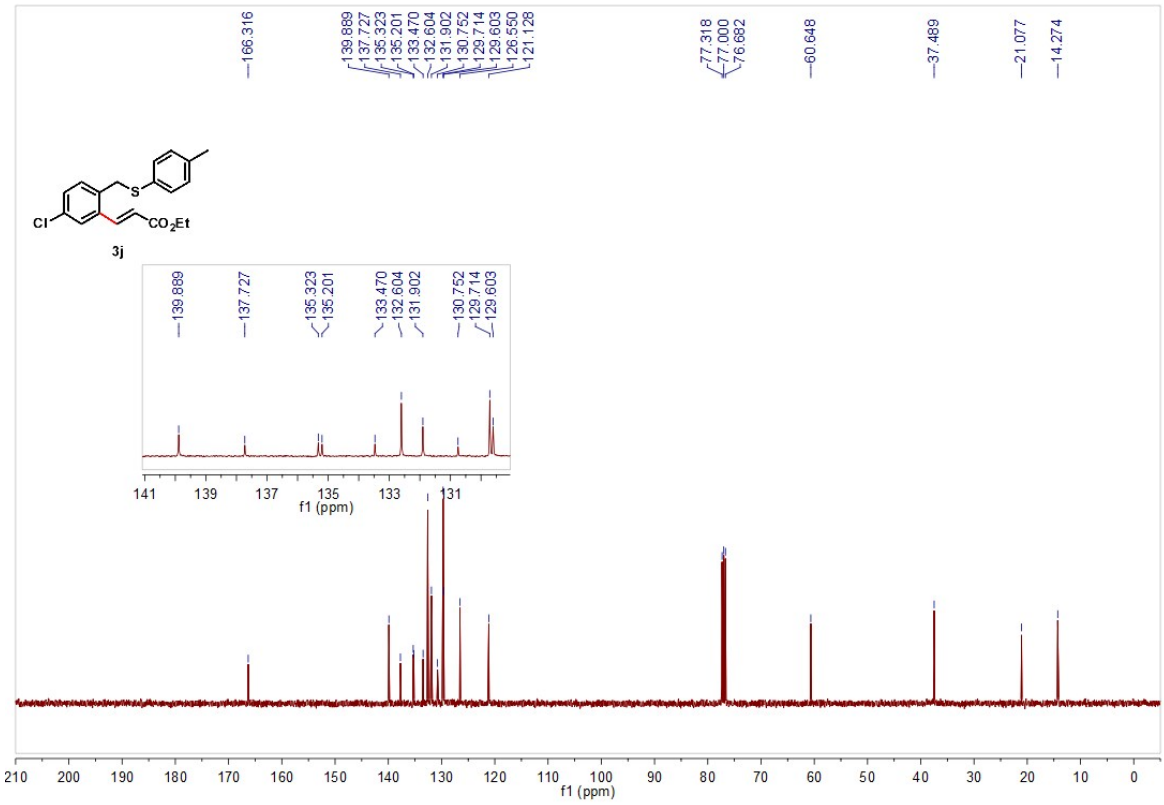

166.718
141.892
137.363
133.738
133.488
132.513
132.166
132.074
131.645
129.670
129.206
128.092
127.413
127.087
126.881
126.447
120.555
77.317
77.000
76.682
60.540
38.782
21.072
14.351
3h
f1 (ppm)

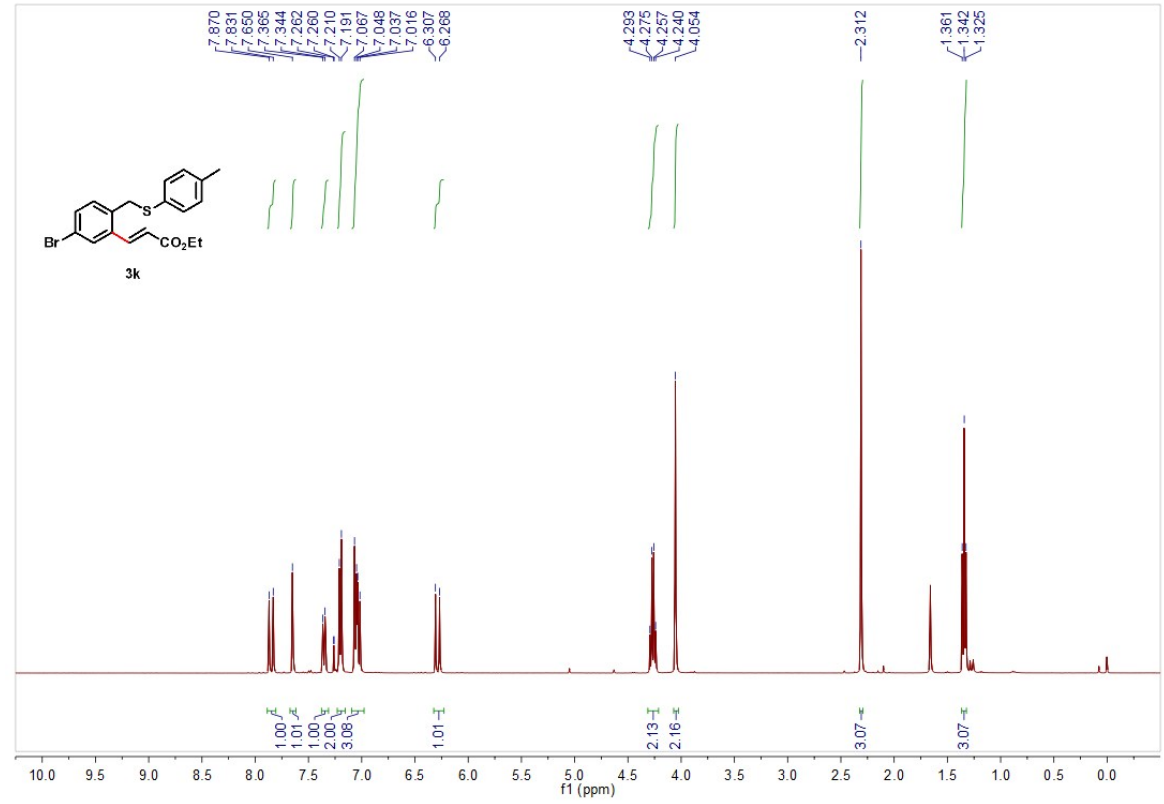

7.836
7.832
7.796
7.792
7.219
7.199
7.072
6.643
6.199
6.160
4.277
4.259
4.241
4.223
4.076
3.768
2.307
1.350
1.332
1.315
MeO
F
S
CO2Et
3i
1.01
1.06
1.89
1.94
1.01
1.01
2.00
2.01
2.96
2.99
3.03
f1 (ppm)

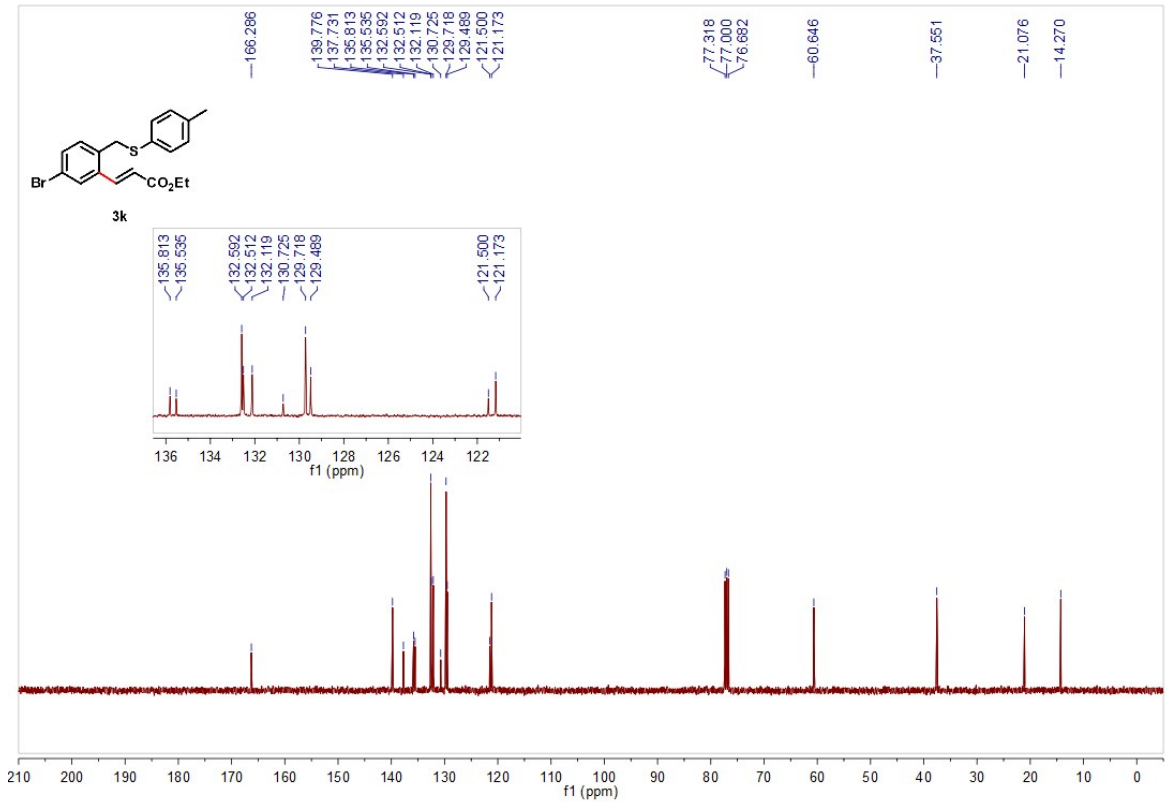

-136.104
O
F
S
O
O
3i
f1 (ppm)

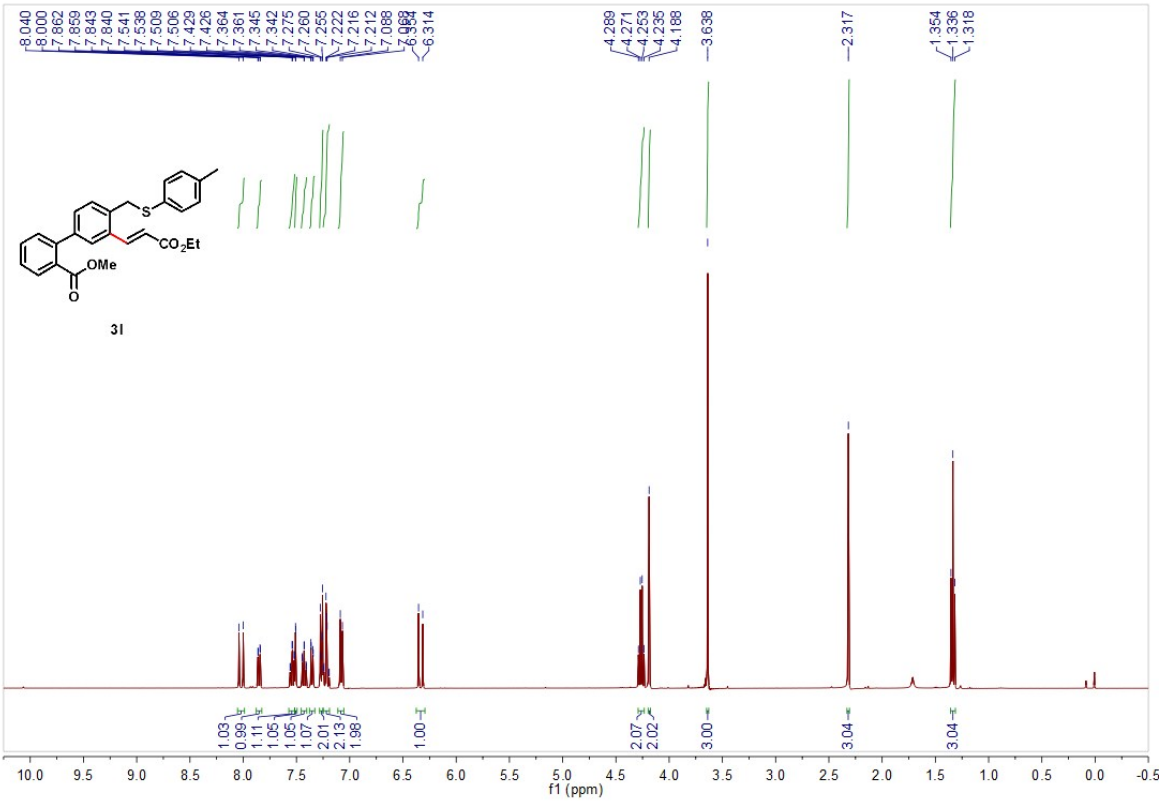

166.702
152.635
150.179
148.695
148.586
139.631
139.611
137.751
133.854
132.810
130.794
114.881
114.860
113.813
113.624
77.319
77.000
76.682
60.464
55.984
37.613
21.042
14.299
O
F
S
CO2Et
3i
f1 (ppm)

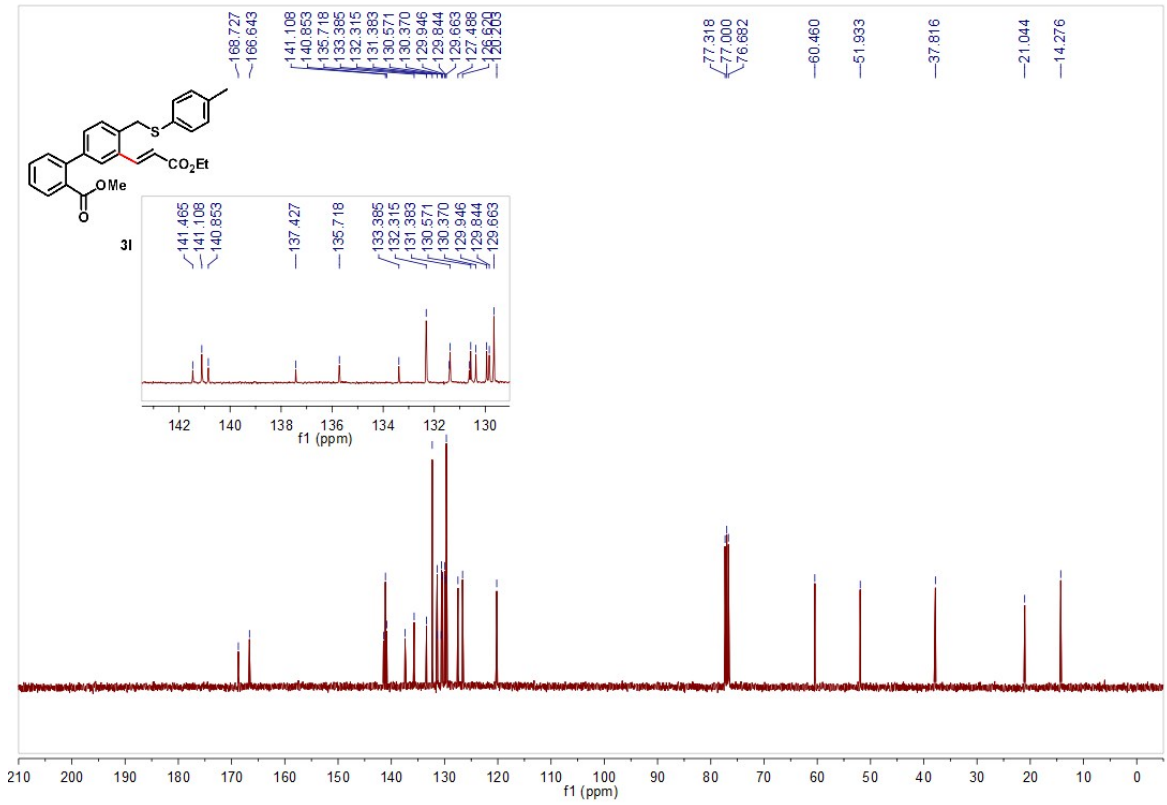

7.881
7.841
7.498
7.493
7.210
7.197
7.190
7.099
7.066
6.272
4.293
4.275
4.258
4.240
4.069
2.310
1.360
1.343
1.325
Cl
S
CO2Et
3j
1.00
1.01
3.03
3.04
1.01
2.11
2.11
3.11
3.07
f1 (ppm)

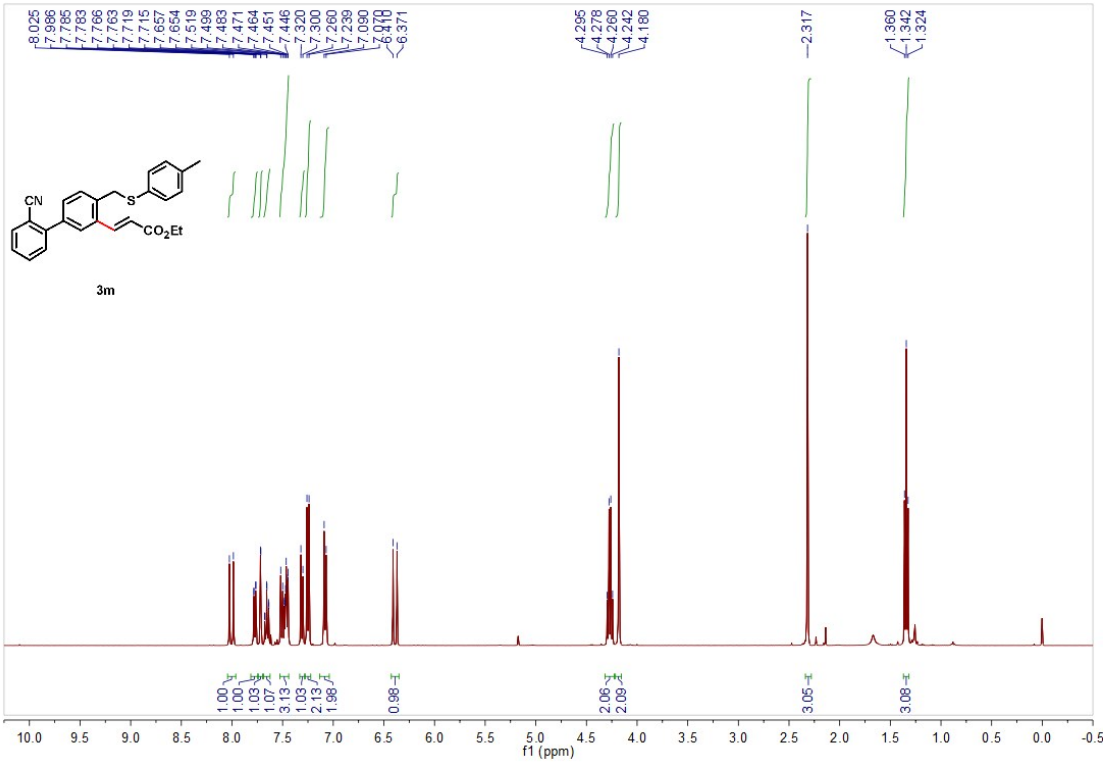

166.316
139.889
137.727
135.323
135.201
133.470
132.604
131.902
130.752
129.714
129.603
126.550
121.128
77.318
77.000
76.682
60.648
37.489
21.077
14.274
Cl
S
CO2Et
3j
f1 (ppm)

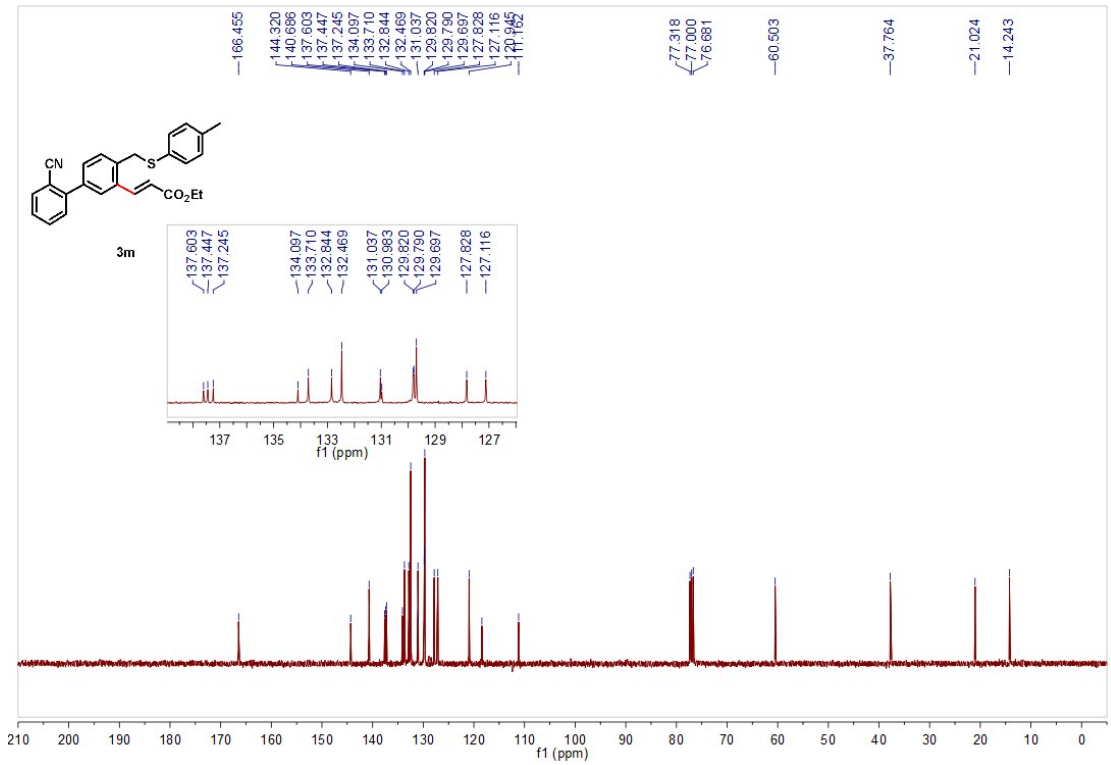

7.870
7.831
7.650
7.365
7.344
7.262
7.260
7.210
7.191
7.067
7.048
7.037
7.016
6.307
6.268
4.293
4.275
4.257
4.240
4.054
2.312
1.361
1.342
1.325
Br
S
CO2Et
3k
1.00
1.01
1.00
2.00
3.08
1.01
2.13
2.16
3.07
3.07
f1 (ppm)

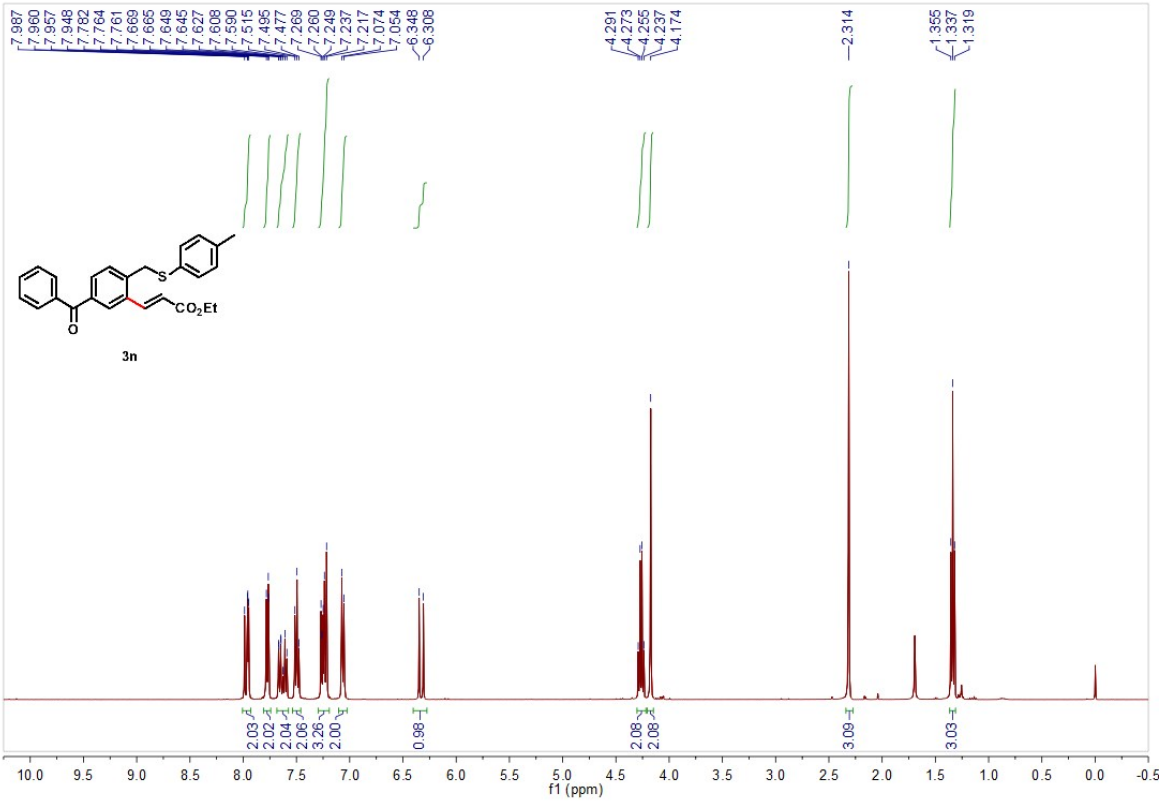

166.286
139.776
137.731
135.813
135.535
132.592
132.512
132.119
130.725
129.718
129.489
121.500
121.173
77.318
77.000
76.682
60.646
37.551
21.076
14.270
Br
S
CO2Et
3k
f1 (ppm)

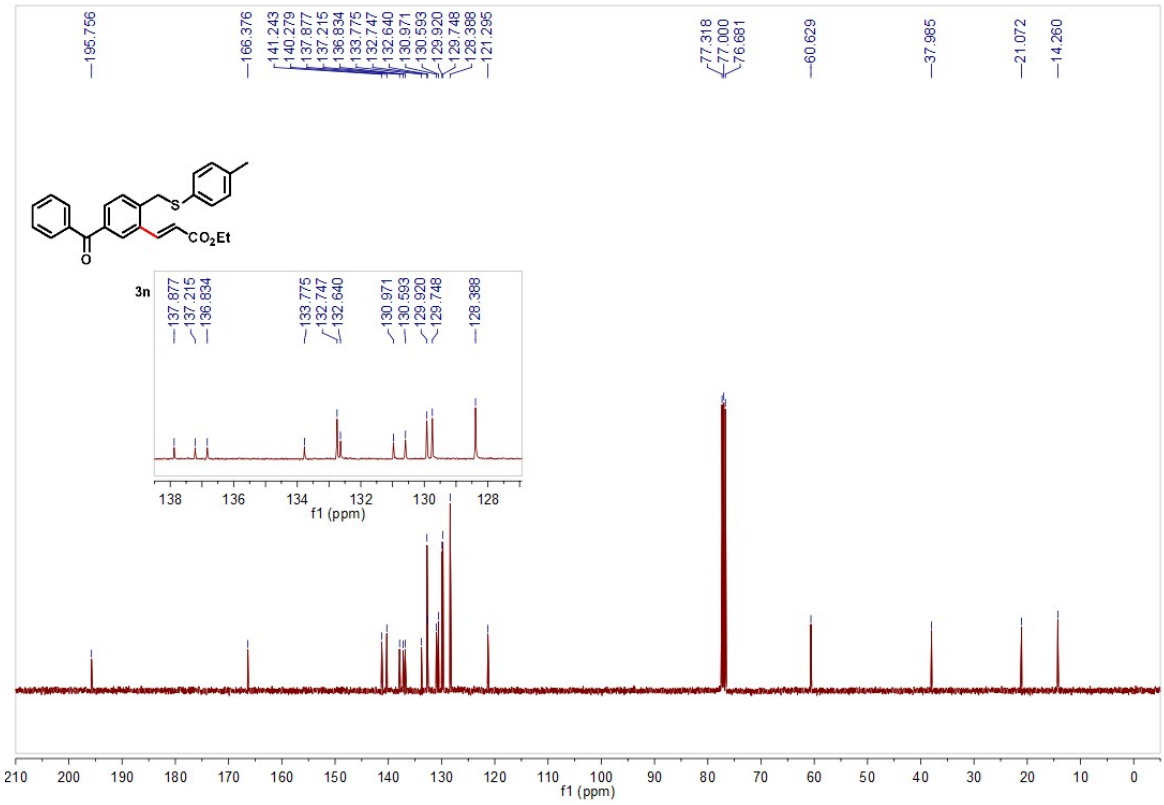

8.040
8.000
7.862
7.859
7.843
7.840
7.541
7.538
7.509
7.506
7.429
7.426
7.364
7.361
7.345
7.342
7.275
7.260
7.255
7.222
7.216
7.212
7.088
6.314
4.289
4.271
4.253
4.236
4.188
3.638
2.317
1.354
1.336
1.318
S
CO2Et
OMe
O
3l
f1 (ppm)

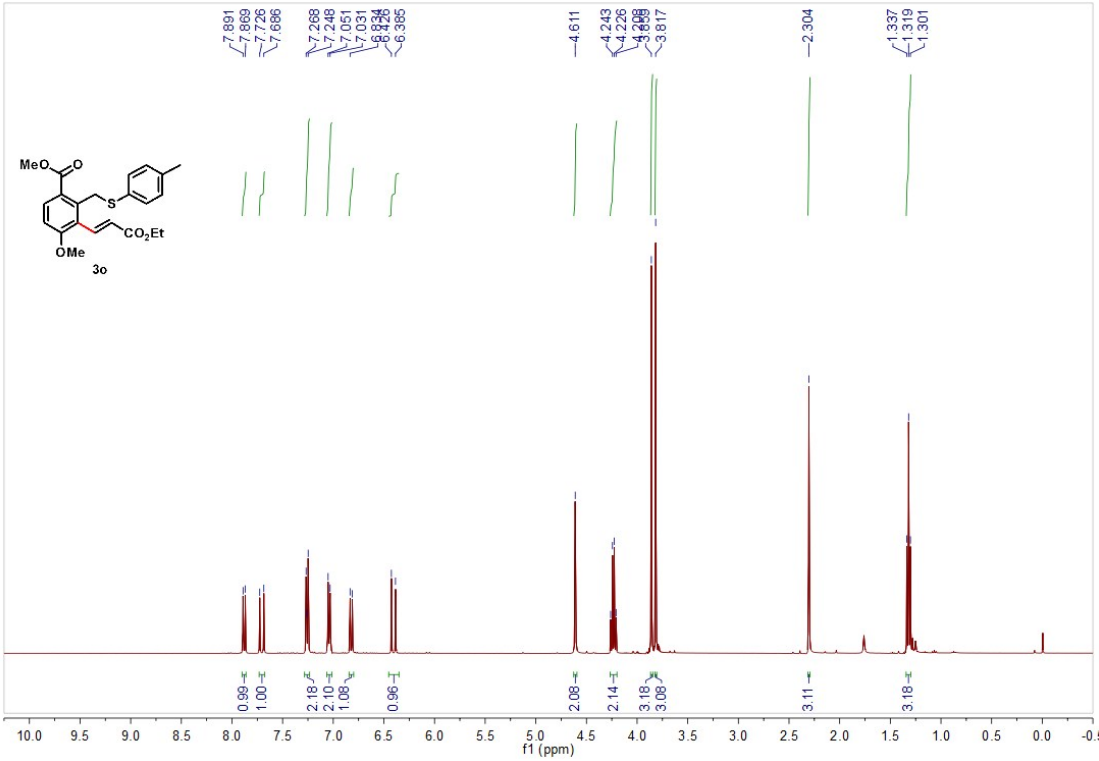

168.727
166.643
141.108
140.853
135.718
133.385
132.315
131.383
130.571
130.370
129.946
129.844
129.663
127.488
126.620
120.203
77.318
77.000
76.682
60.460
51.933
37.816
21.044
14.276
OMe
CO2Et
S
3l
141.465
141.108
140.853
137.427
135.718
133.385
132.315
131.383
130.571
130.370
129.946
129.844
129.663
142
140
138
136
134
132
130
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

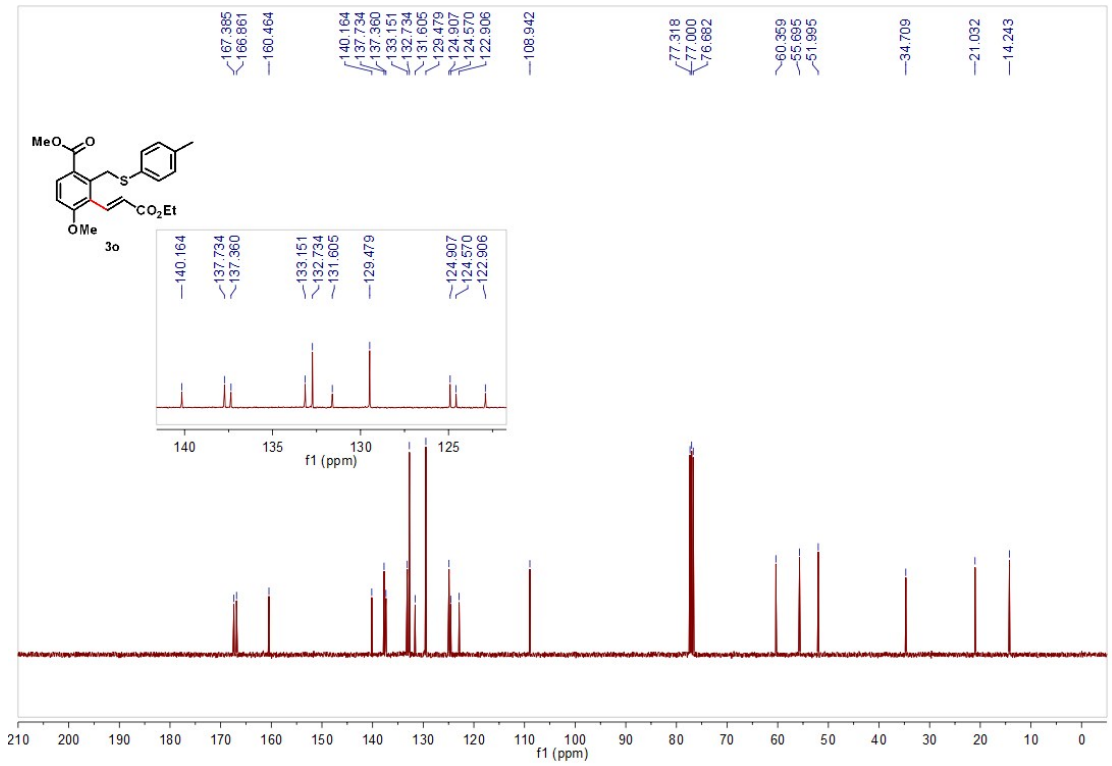

8.025
7.986
7.785
7.783
7.766
7.763
7.719
7.715
7.657
7.654
7.519
7.499
7.483
7.471
7.464
7.451
7.446
7.320
7.300
7.260
7.239
7.090
7.078
6.410
6.371
4.295
4.278
4.260
4.242
4.180
2.317
1.360
1.342
1.324
CN
CO2Et
S
3m
1.00
1.00
1.03
1.07
3.13
1.03
2.13
1.98
0.98
2.06
2.09
3.05
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

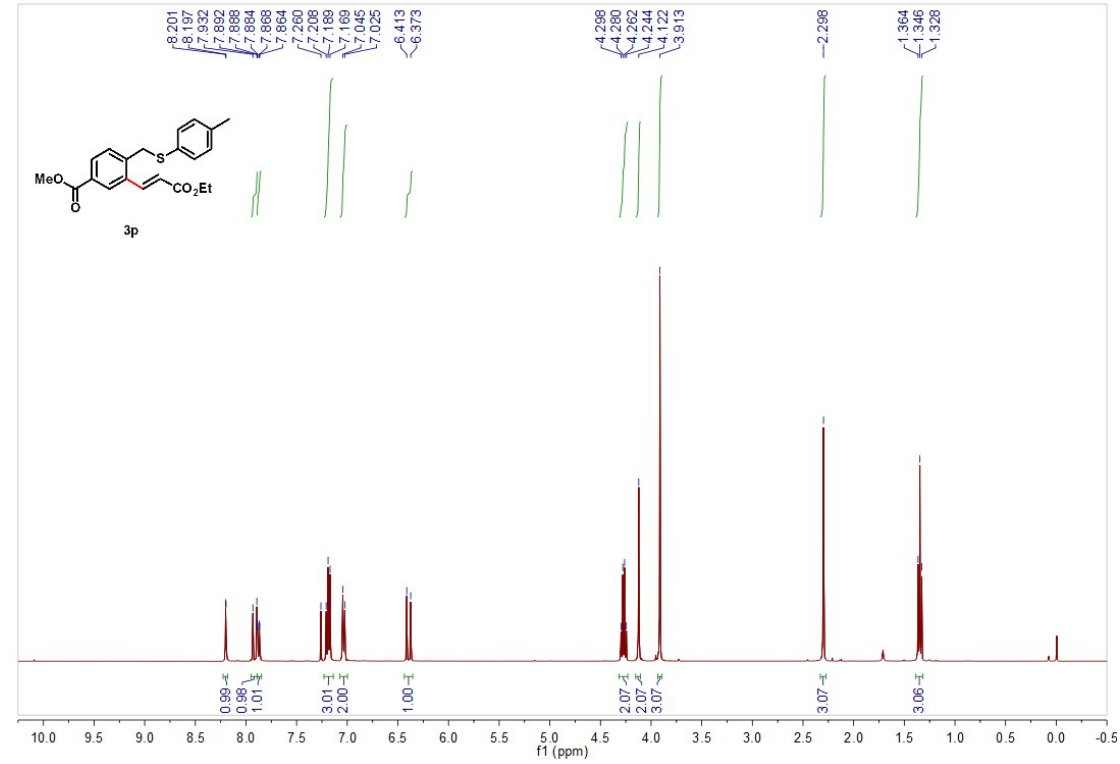

166.455
144.320
140.686
137.603
137.447
137.245
134.097
133.710
132.844
132.469
131.037
129.820
129.790
129.697
127.828
127.116
120.945
117.162
77.318
77.000
76.681
60.503
37.764
21.024
14.243
CN
S
CO2Et
3m
137.603
137.447
137.245
134.097
133.710
132.844
132.469
131.037
130.983
129.820
129.790
129.697
127.828
127.116
137
135
133
131
129
127
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

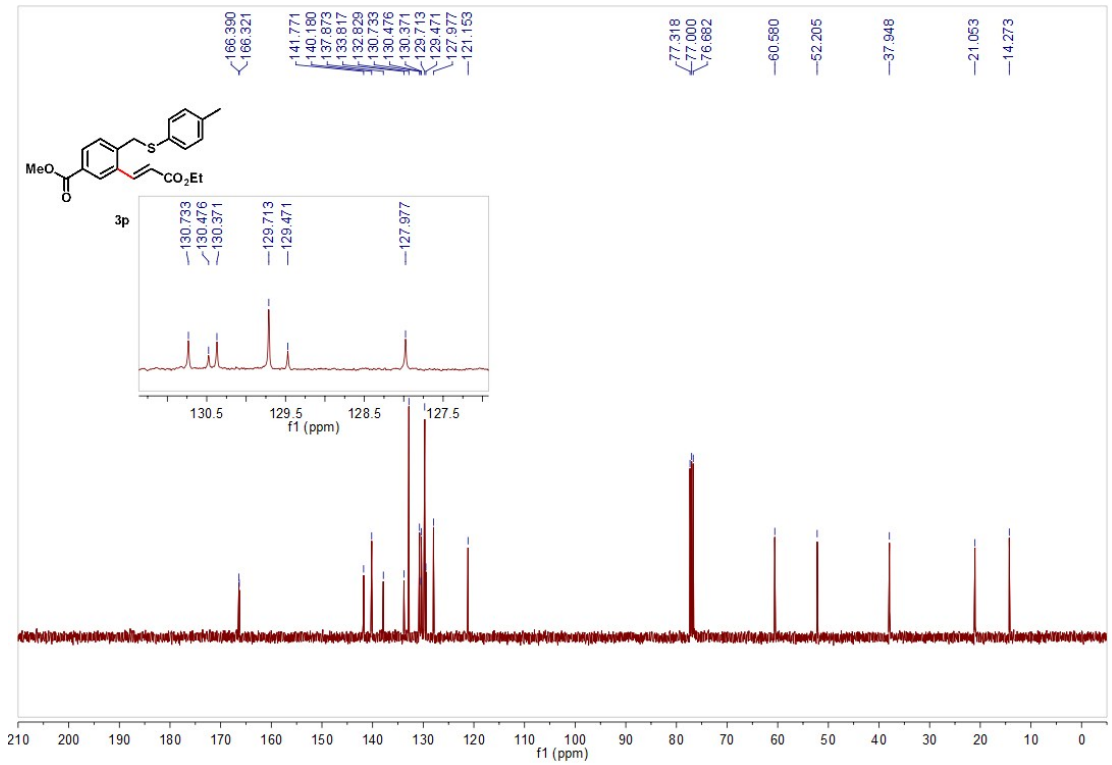

7.987
7.960
7.957
7.948
7.782
7.764
7.761
7.669
7.665
7.649
7.645
7.627
7.608
7.590
7.515
7.495
7.477
7.269
7.260
7.249
7.237
7.217
7.074
7.054
6.348
6.308
4.291
4.273
4.255
4.237
4.174
2.314
1.355
1.337
1.319
S
CO2Et
O
3n
2.03
2.02
2.04
2.06
3.26
2.00
0.98
2.08
2.08
3.09
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

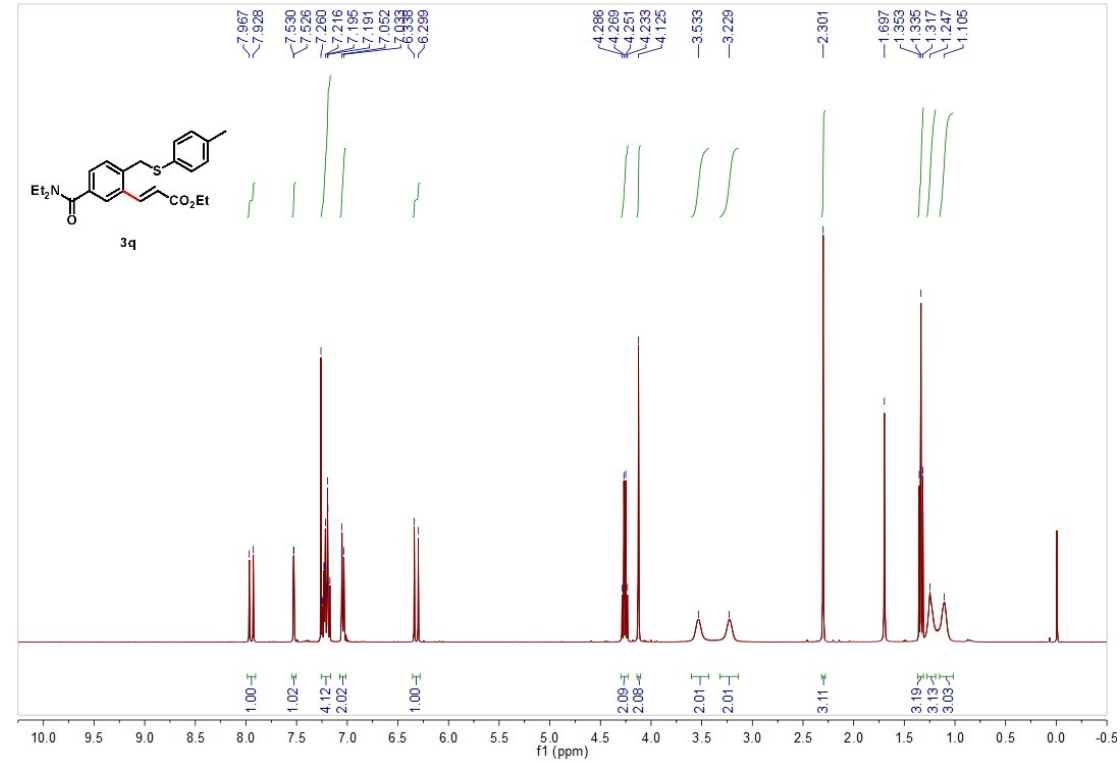

195.756
166.376
141.243
140.279
137.877
137.215
136.834
133.775
132.747
132.640
130.971
130.593
129.920
129.748
128.388
121.295
77.318
77.000
76.681
60.629
37.985
21.072
14.260
3n
137.877
137.215
136.834
133.775
132.747
132.640
130.971
130.593
129.920
129.748
128.388
f1 (ppm)
f1 (ppm)

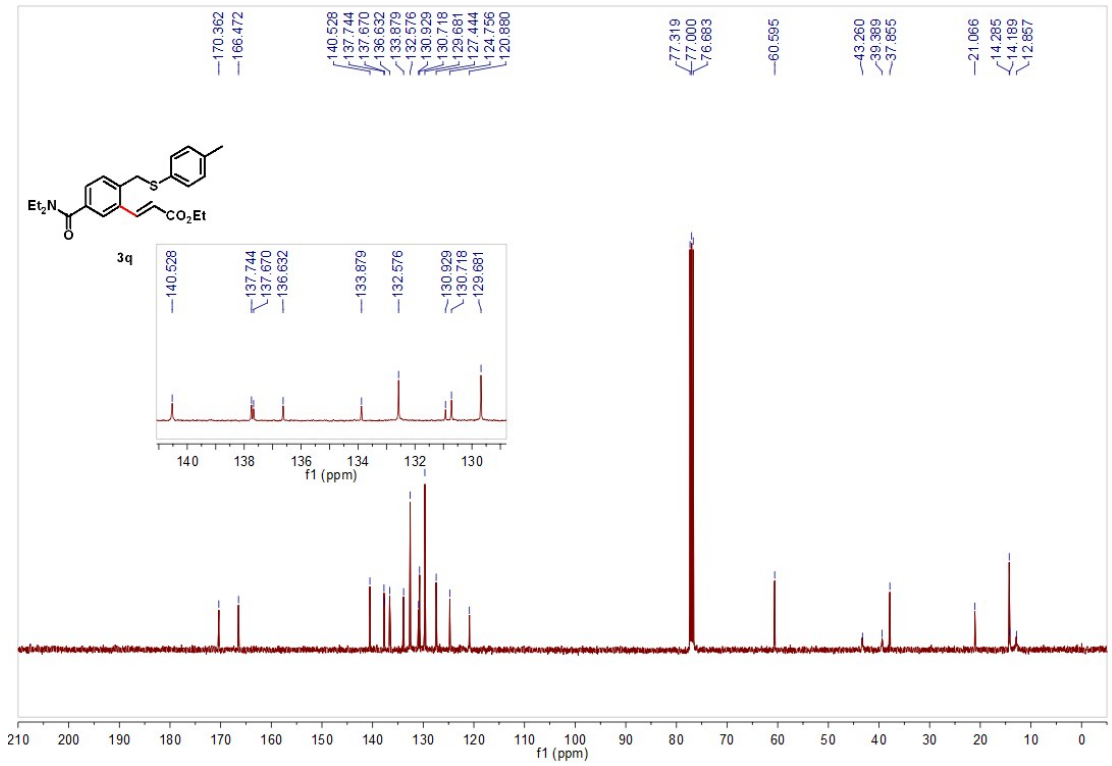

7.891
7.869
7.726
7.686
7.268
7.248
7.051
7.031
6.434
6.426
6.385
4.611
4.243
4.226
3.817
2.304
1.337
1.319
1.301
3o
0.99
1.00
2.18
2.10
1.08
0.96
2.08
2.14
3.18
3.08
3.11
3.18
f1 (ppm)

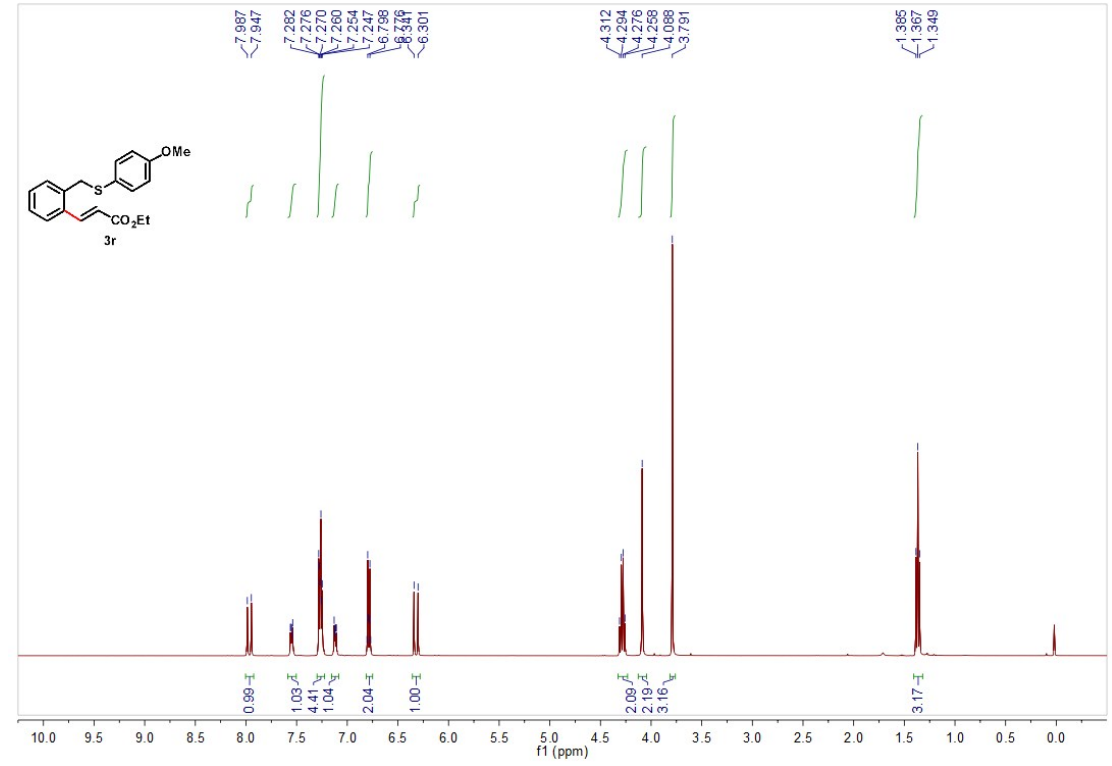

167.385
166.861
160.464
140.164
137.734
137.360
133.151
132.734
131.605
129.479
124.907
124.570
122.906
108.942
77.318
77.000
76.682
60.359
55.695
51.995
34.709
21.032
14.243
MeO
O
S
CO2Et
OMe
3o
f1 (ppm)

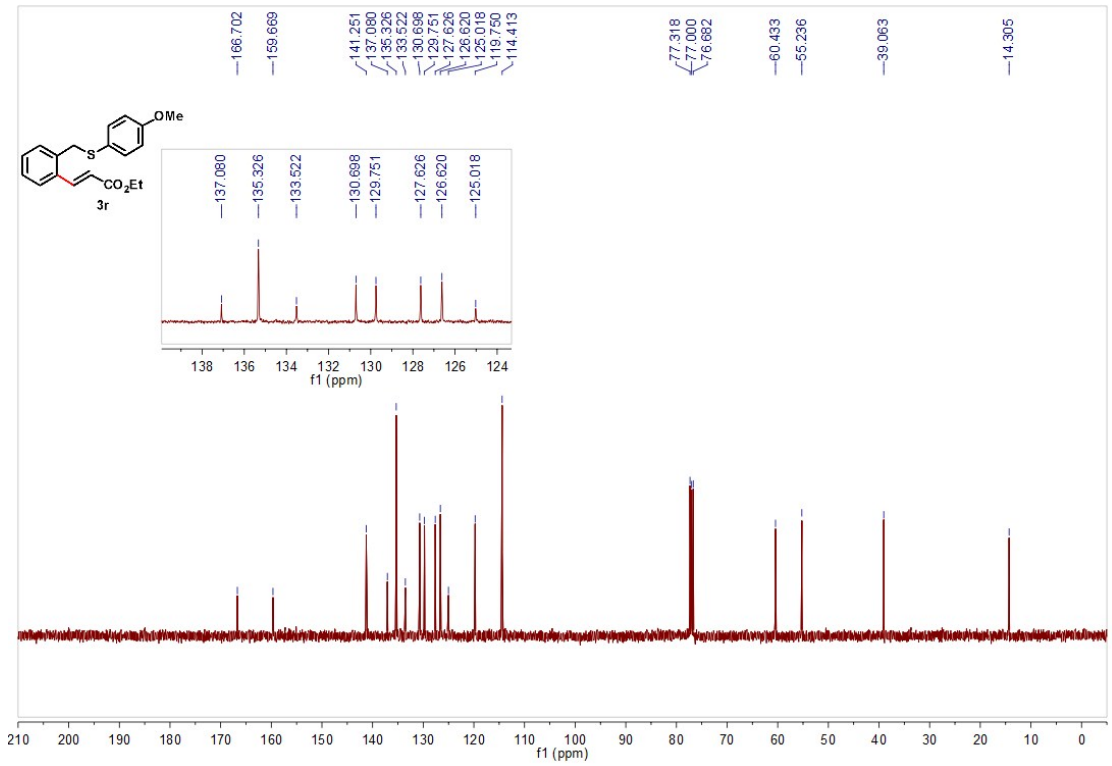

8.201
8.197
7.932
7.892
7.888
7.884
7.868
7.864
7.260
7.208
7.188
7.169
7.045
7.025
6.413
6.373
4.298
4.280
4.262
4.244
4.122
3.913
2.298
1.364
1.346
1.328
MeO
O
S
CO2Et
3p
0.99
0.98
1.01
3.01
2.00
1.00
2.07
2.07
3.07
3.07
3.06
f1 (ppm)

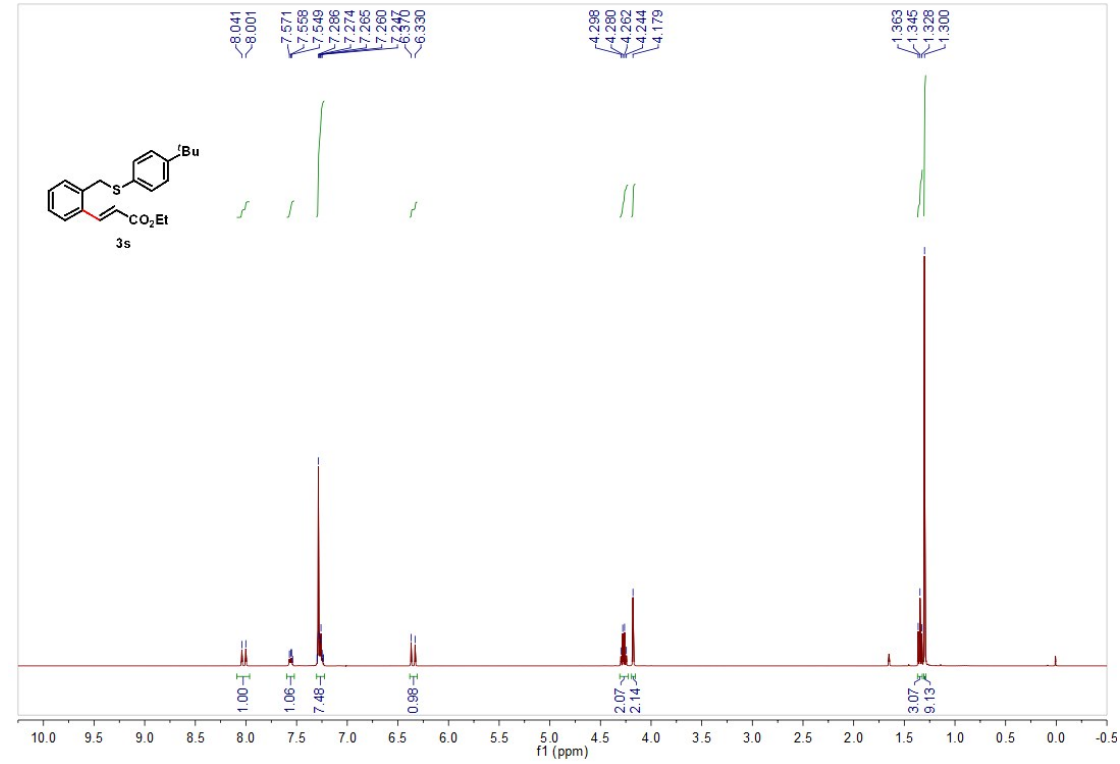

166.390
166.321
141.771
140.180
137.873
133.817
132.929
130.733
130.476
130.371
129.713
129.471
127.977
121.153
77.318
77.000
76.682
60.580
52.205
37.948
21.053
14.273
MeO
O
S
CO2Et
3p
130.733
130.476
130.371
129.713
129.471
127.977
130.5
129.5
128.5
127.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

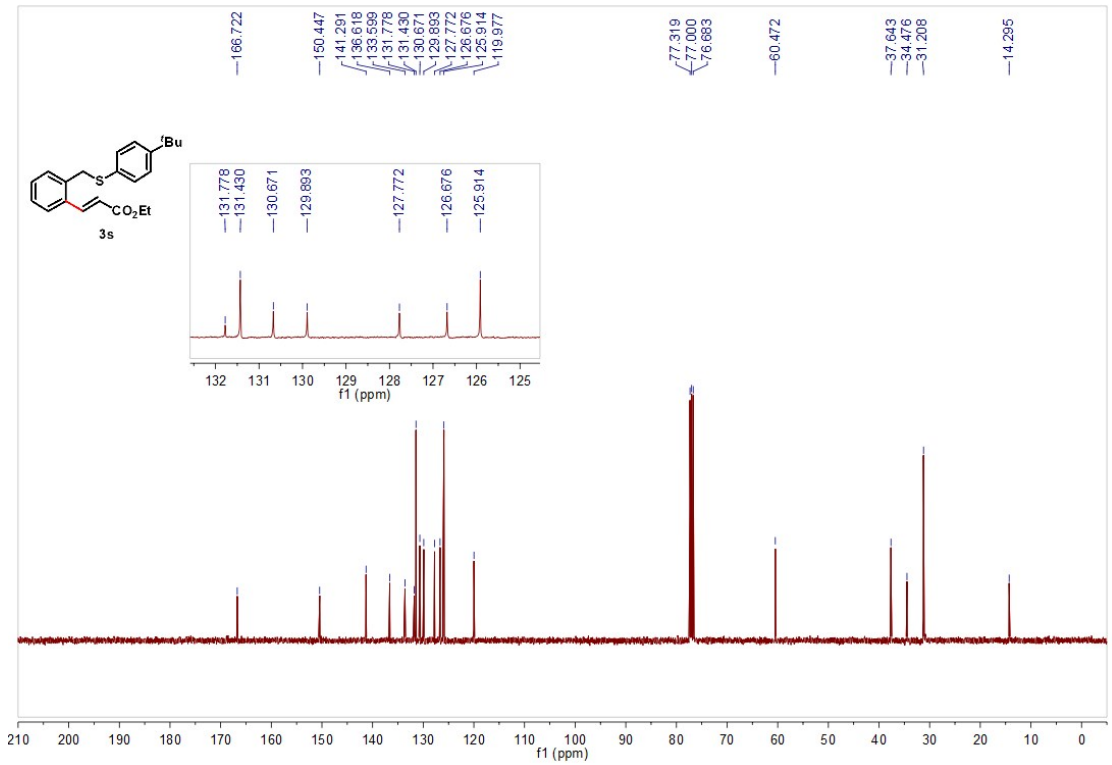

7.967
7.928
7.530
7.526
7.260
7.216
7.195
7.191
7.052
6.299
4.286
4.269
4.251
4.233
4.125
3.533
3.229
2.301
1.697
1.353
1.335
1.317
1.247
1.105
Et2N
O
S
CO2Et
3q
1.00
1.02
4.12
2.02
1.00
2.09
2.08
2.01
2.01
3.11
3.19
3.13
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

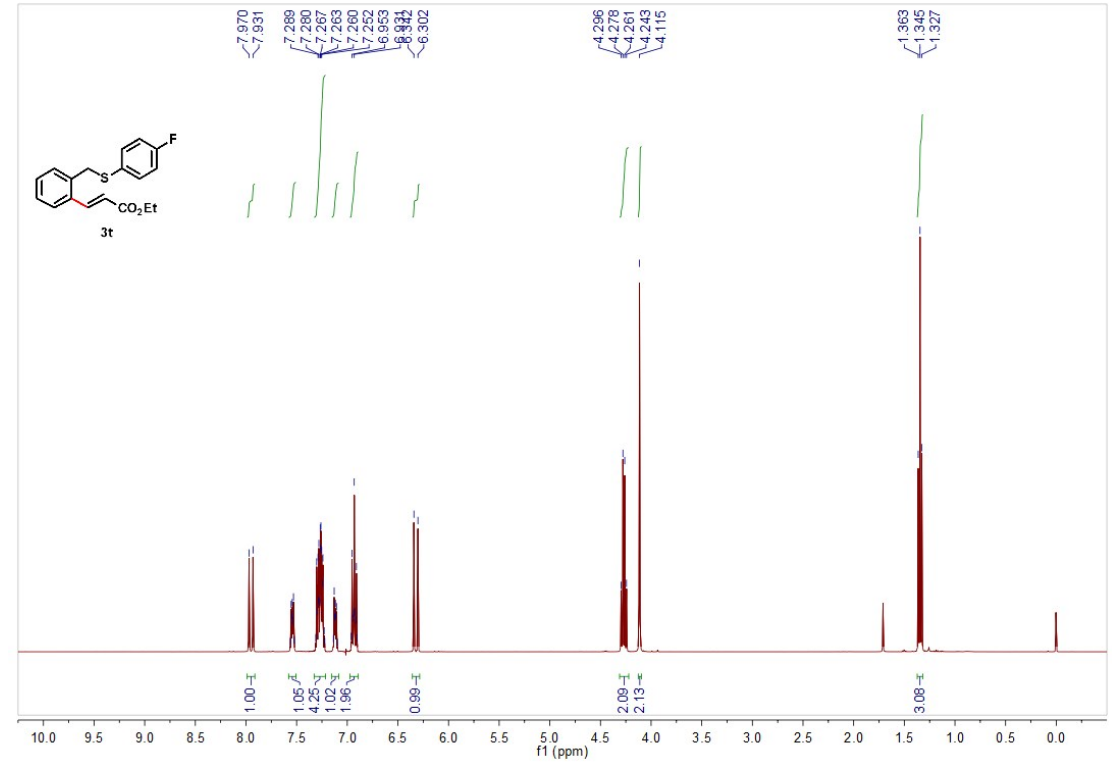

170.362
166.472
140.528
137.744
137.670
136.632
133.879
132.576
130.929
130.718
129.681
127.444
124.756
120.880
77.319
77.000
76.683
60.595
43.260
39.389
37.855
21.066
14.285
14.189
12.857
Et2N
CO2Et
3q
f1 (ppm)

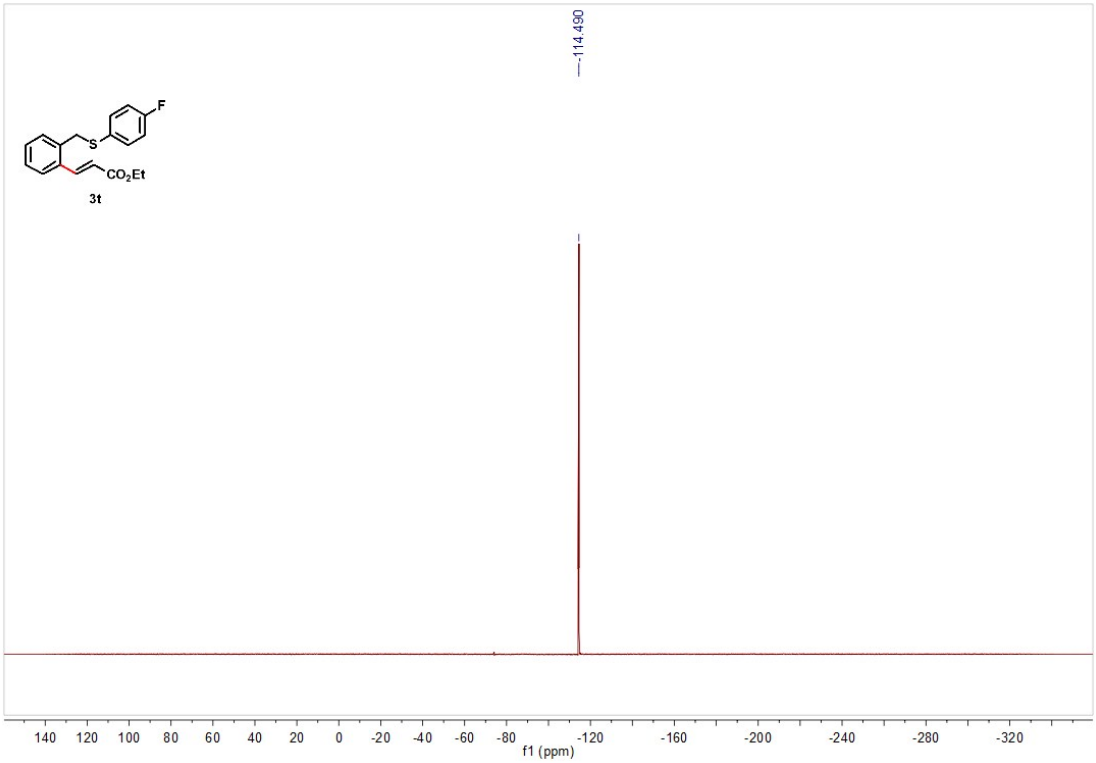

7.987
7.947
7.282
7.276
7.270
7.260
7.254
7.247
6.798
6.776
6.341
6.301
4.312
4.294
4.276
4.258
4.088
3.791
1.385
1.367
1.349
OMe
CO2Et
3r
0.99
1.03
4.41
1.04
2.04
1.00
2.09
2.19
3.16
3.17
f1 (ppm)

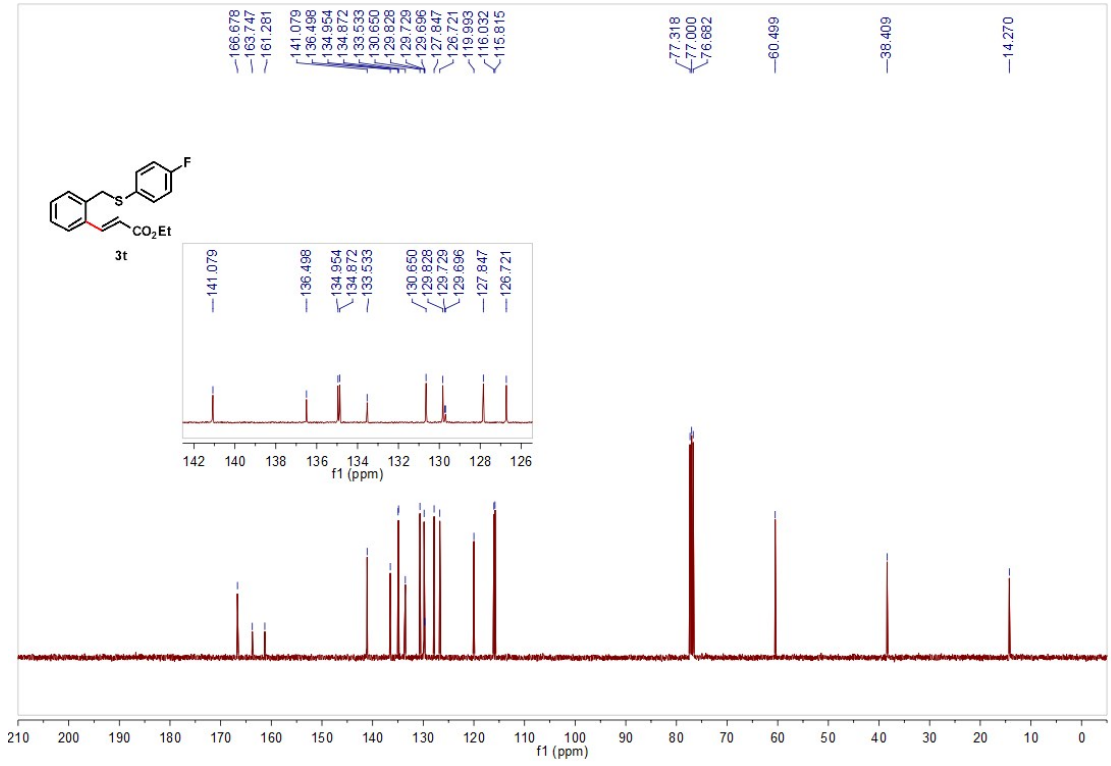

166.702
159.669
141.251
137.080
135.326
133.522
130.698
129.751
127.626
126.620
125.018
119.750
114.413
77.318
77.000
76.682
60.433
55.236
39.063
14.305
OMe
S
CO2Et
3r
f1 (ppm)
f1 (ppm)

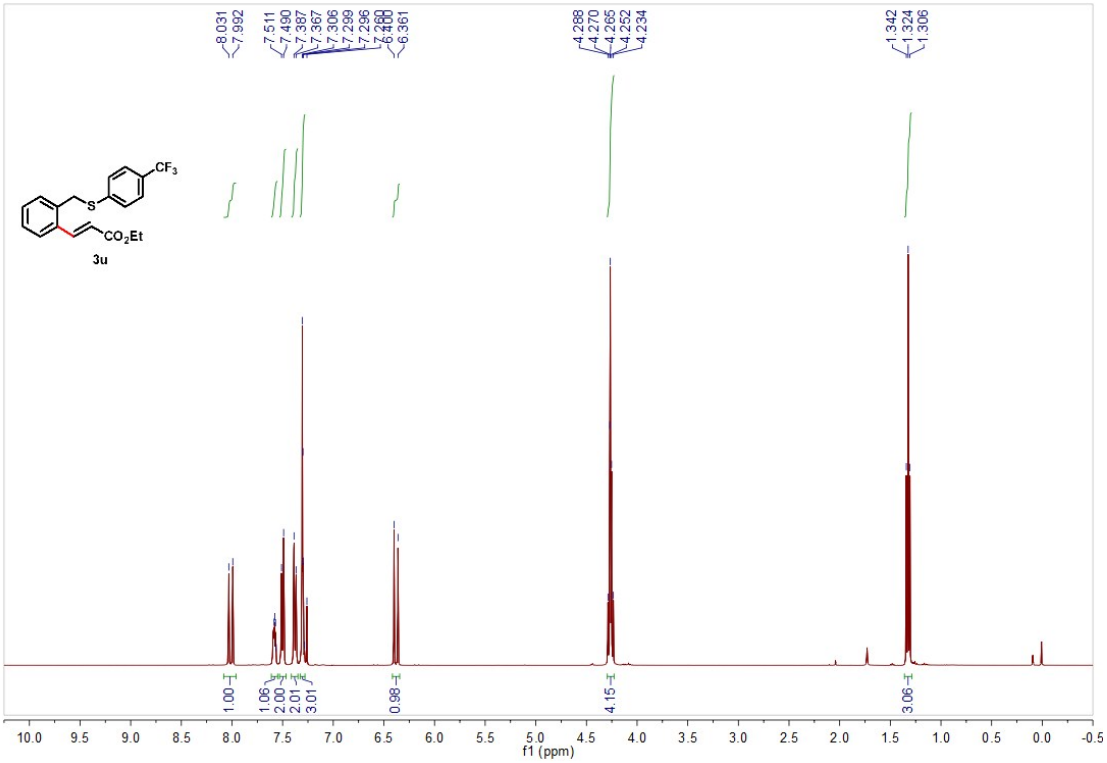

8.041
8.001
7.571
7.558
7.549
7.286
7.274
7.265
7.260
7.247
6.340
6.330
4.298
4.280
4.262
4.244
4.179
1.363
1.345
1.328
1.300
tBu
S
CO2Et
3s
1.00
1.06
7.48
0.98
2.07
2.14
3.07
9.13
f1 (ppm)

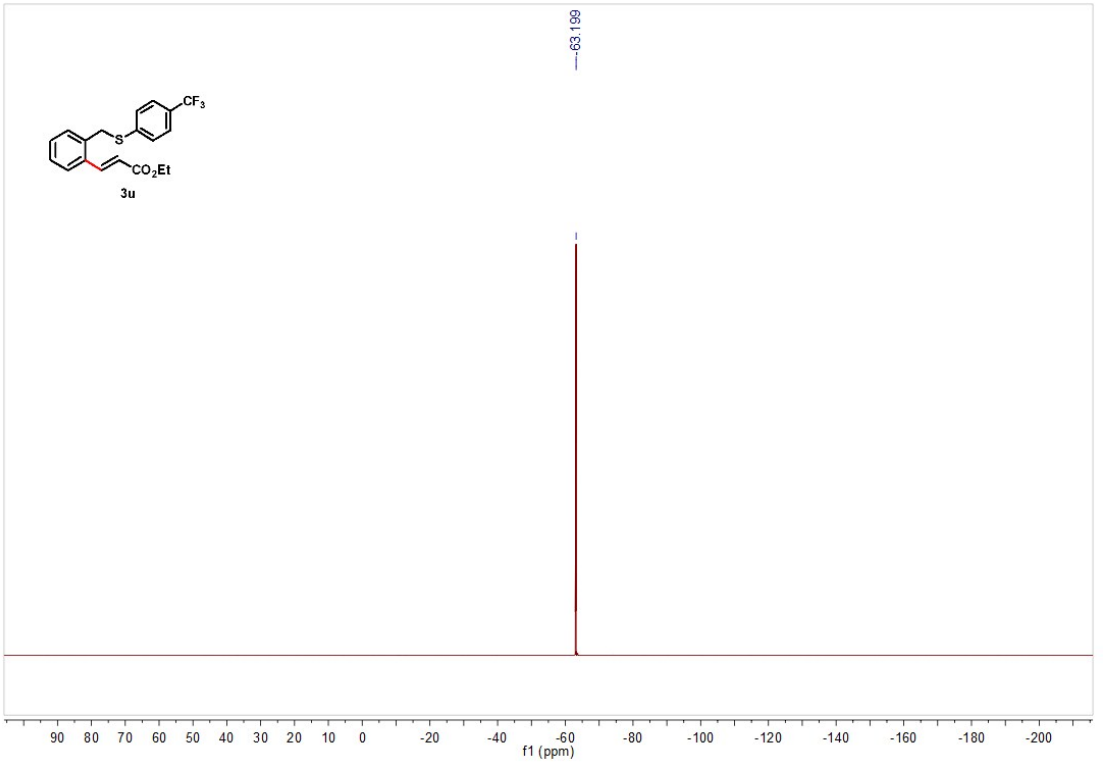

166.722
150.447
141.291
136.618
133.599
131.778
131.430
130.671
129.893
127.772
126.676
125.914
119.977
77.319
77.000
76.683
60.472
37.643
34.476
31.208
14.295
tBu
S
CO2Et
3s
f1 (ppm)

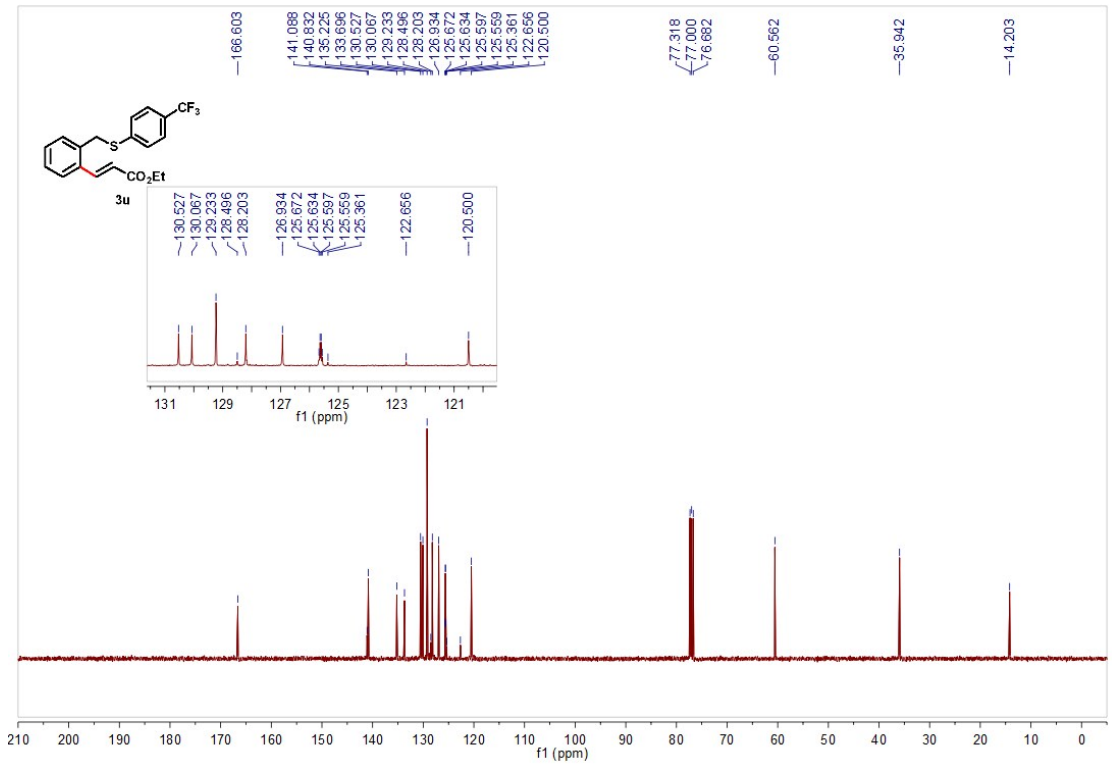

7.970
7.931
7.289
7.280
7.267
7.263
7.260
7.252
6.953
6.302
4.296
4.278
4.261
4.243
4.115
1.363
1.345
1.327
F
S
CO2Et
3t
1.00
1.05
4.25
1.02
1.96
0.99
2.09
2.13
3.08
f1 (ppm)

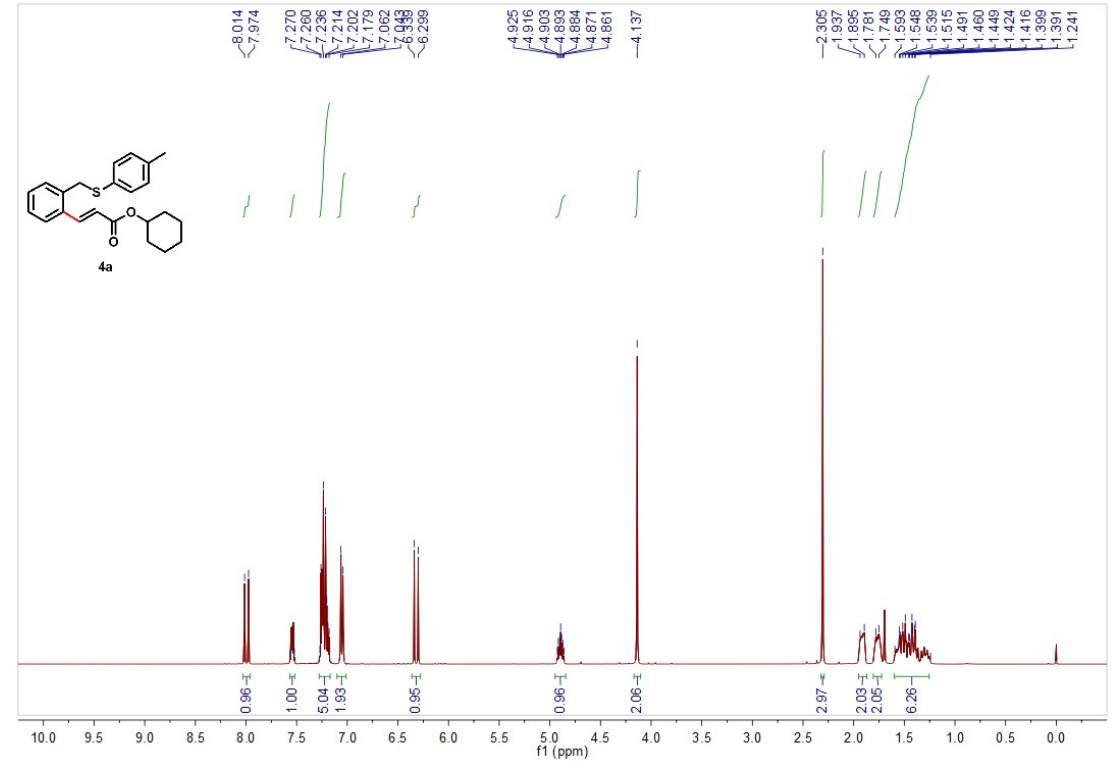

-114.490
F
S
CO2Et
3t
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280 -320
f1 (ppm)

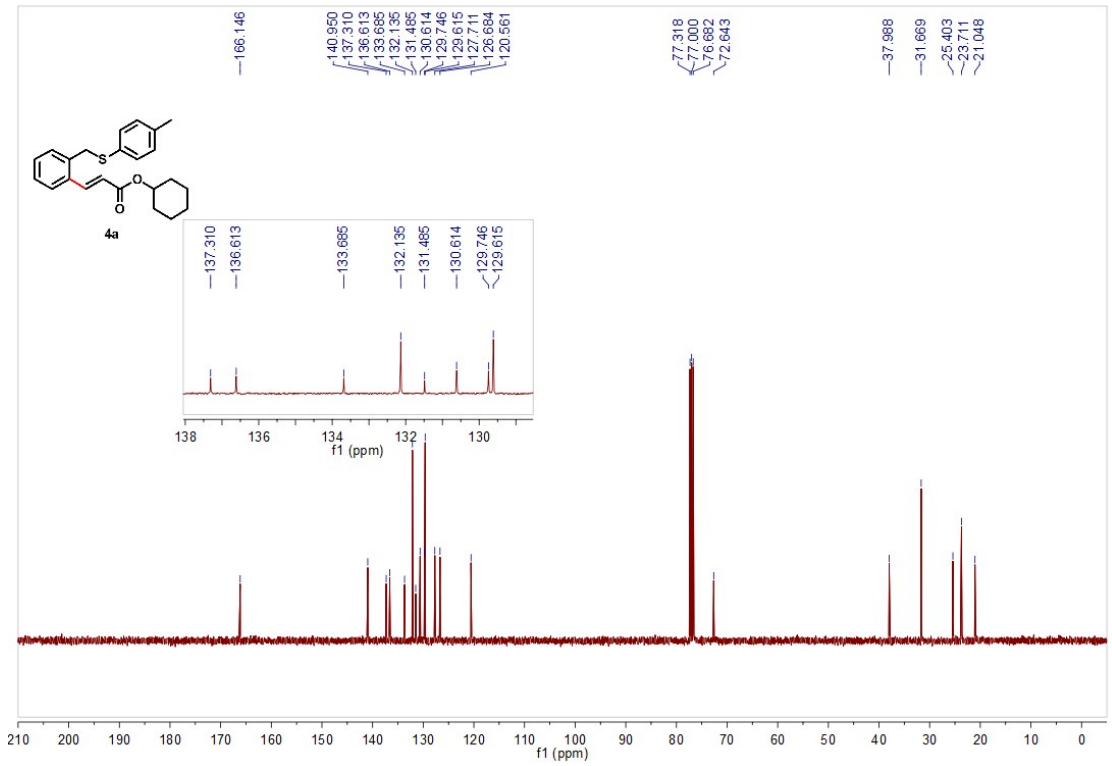

166.678
163.747
161.281
141.079
136.498
134.954
134.872
133.533
130.650
129.828
129.729
129.696
127.847
126.721
119.993
116.032
115.815
77.318
77.000
76.682
60.499
38.409
14.270
F
S
CO2Et
3t
141.079
136.498
134.954
134.872
133.533
130.650
129.828
129.729
129.696
127.847
126.721
142 140 138 136 134 132 130 128 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

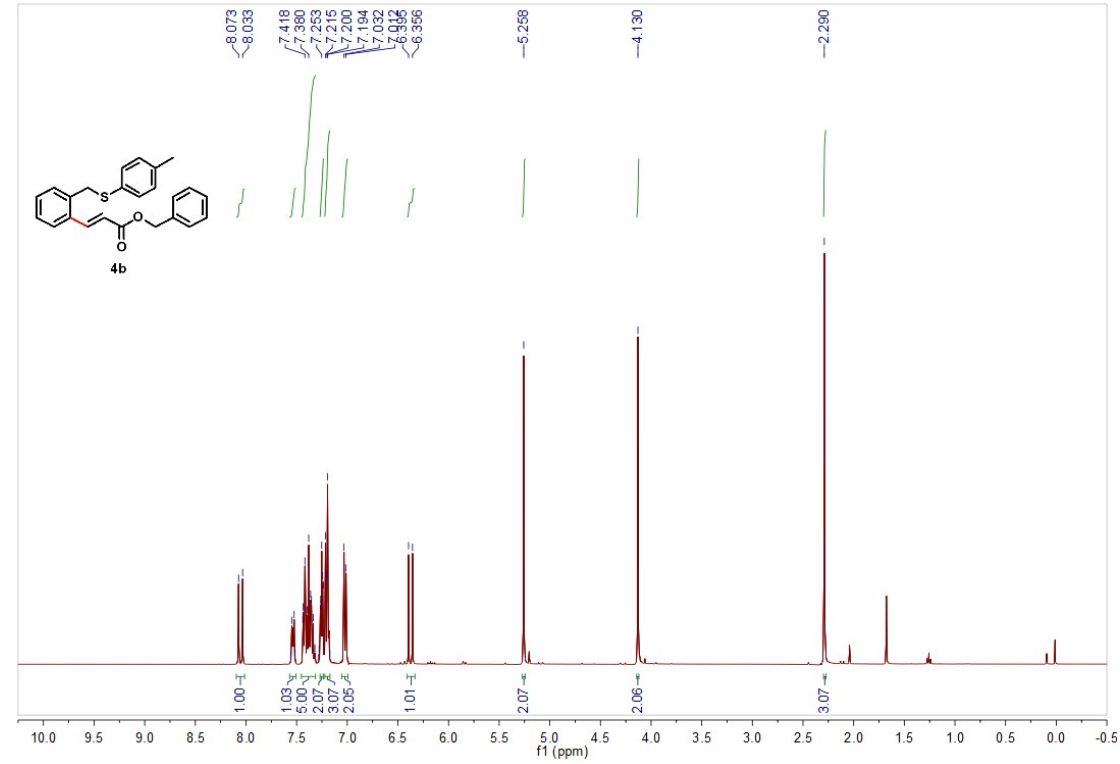

8.031
7.992
7.511
7.490
7.387
7.367
7.306
7.299
7.296
6.400
6.361
4.288
4.270
4.265
4.252
4.234
1.342
1.324
1.306
1.00
1.06
2.00
2.01
3.01
0.98
4.15
3.06
f1 (ppm)
3u

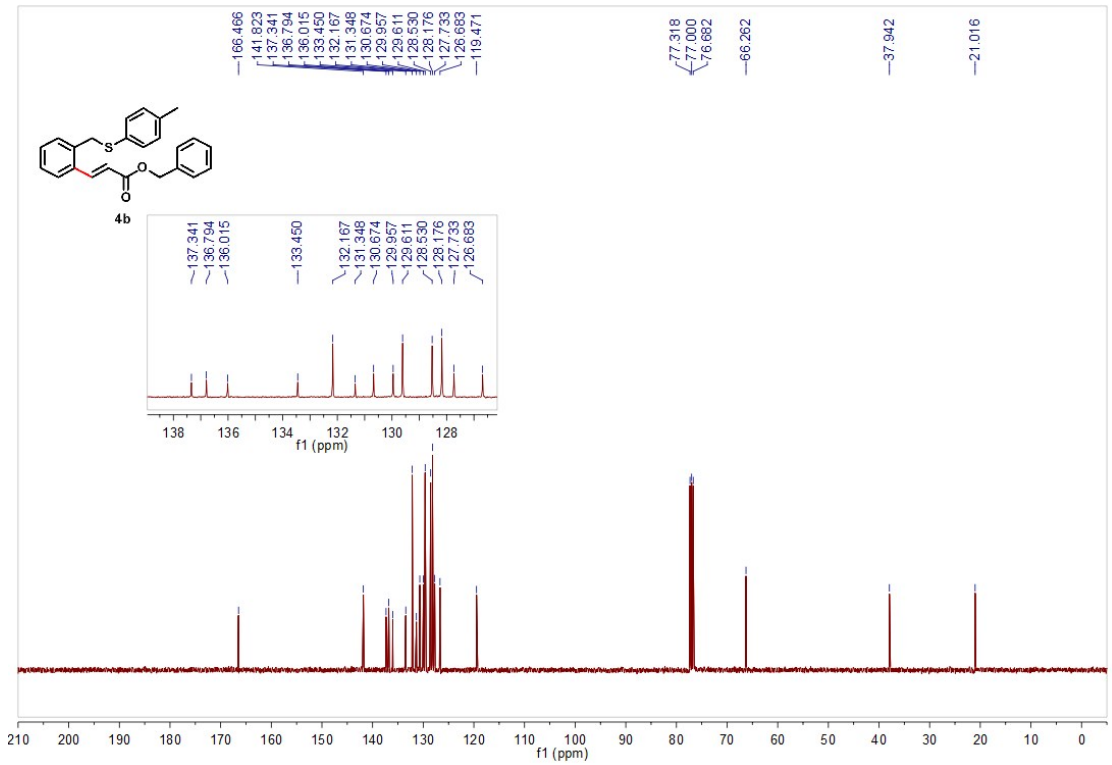

-63.199
f1 (ppm)
3u

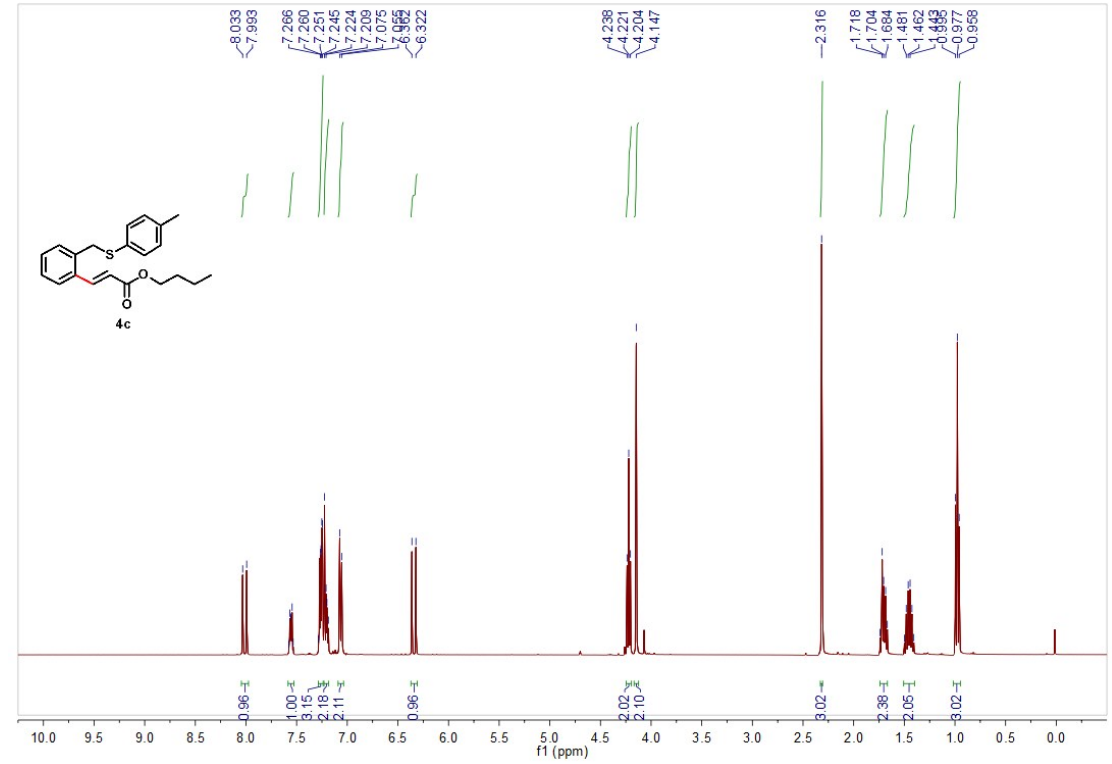

166.603
141.088
140.832
135.225
133.696
130.527
130.067
129.233
128.496
128.203
126.934
125.672
125.634
125.597
125.559
125.361
122.656
120.500
77.318
77.000
76.682
60.562
35.942
14.203
CF3
S
CO2Et
3u
f1 (ppm)
f1 (ppm)

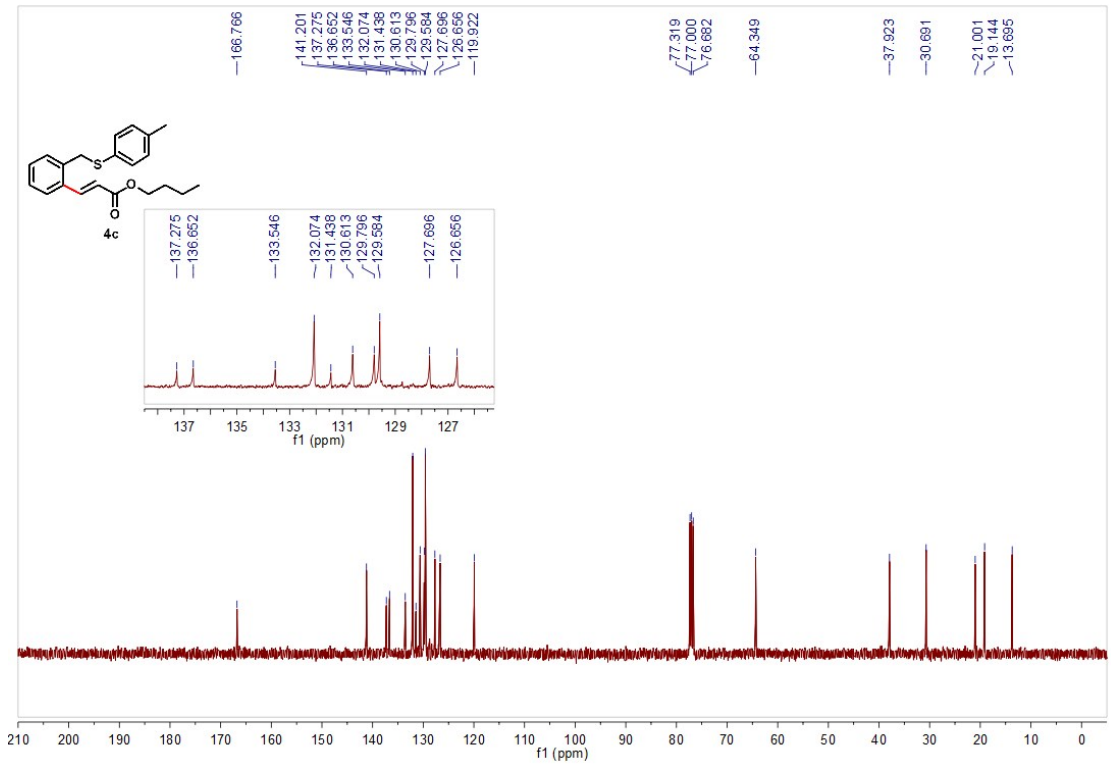

8.014
7.974
7.270
7.260
7.236
7.214
7.202
7.179
7.062
6.299
4.925
4.916
4.903
4.893
4.884
4.871
4.861
4.137
2.305
1.937
1.895
1.781
1.749
1.593
1.548
1.539
1.515
1.491
1.460
1.449
1.424
1.416
1.399
1.391
1.241
S
O
O
4a
0.96
1.00
5.04
1.93
0.95
0.96
2.06
2.97
2.03
2.05
6.26
f1 (ppm)

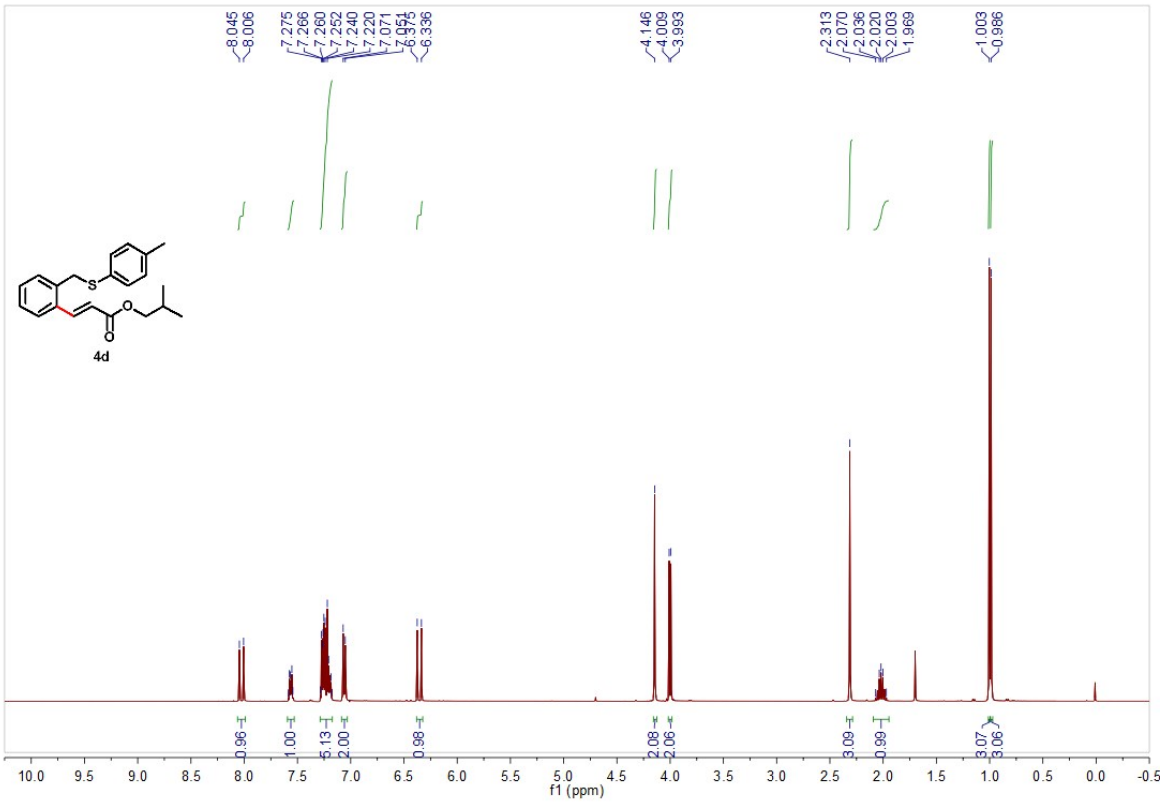

166.146
140.950
137.310
136.613
133.685
132.135
131.485
130.614
129.746
129.615
127.711
126.684
120.561
77.318
77.000
76.682
72.643
37.988
31.669
25.403
23.711
21.048
4a
f1 (ppm)
f1 (ppm)

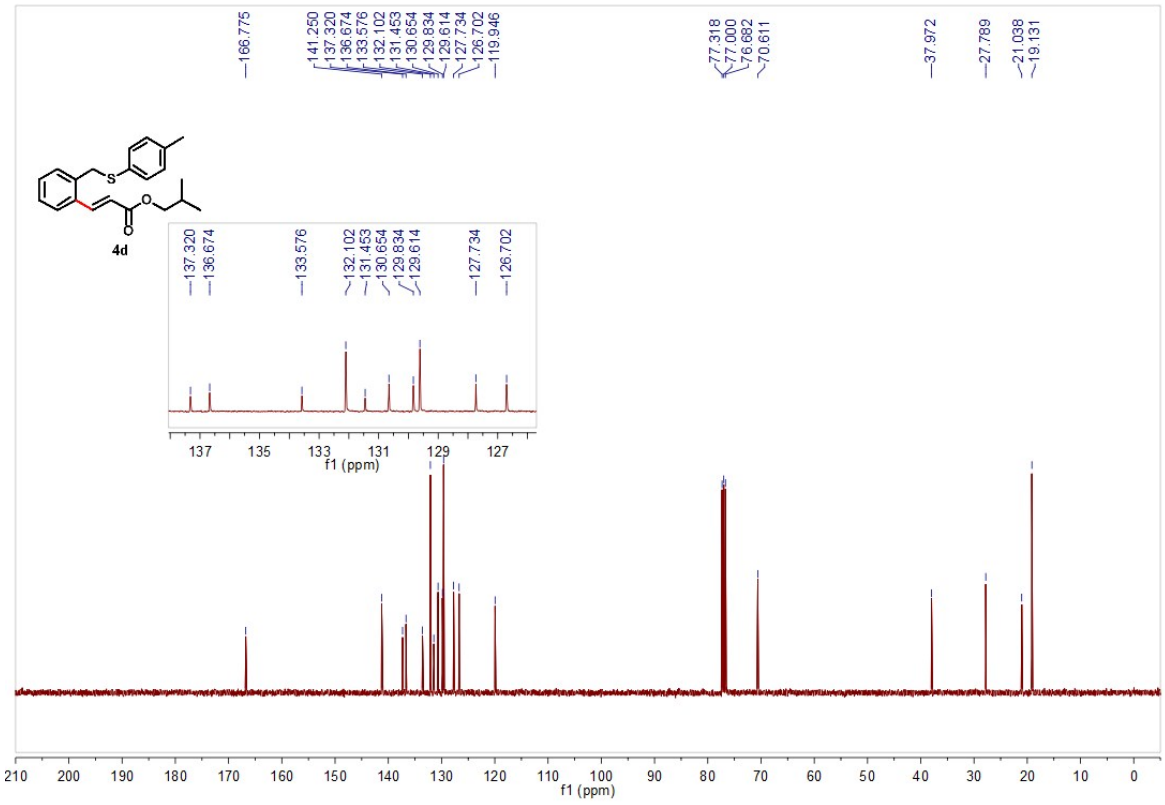

8.073
8.033
7.418
7.380
7.253
7.215
7.200
7.194
7.032
6.395
6.356
5.258
4.130
2.290
4b
1.00
1.03
5.00
2.07
3.07
2.05
1.01
2.07
2.06
3.07
f1 (ppm)

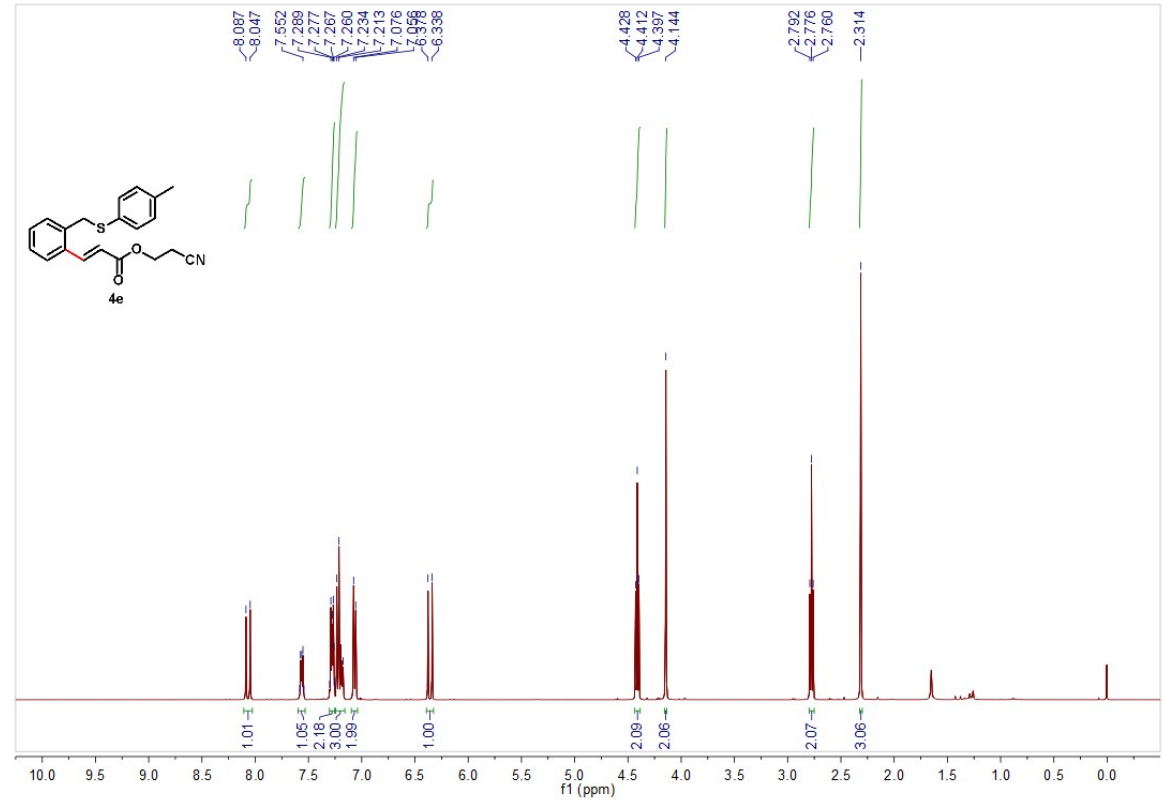

166.466
141.823
137.341
136.794
136.015
133.450
132.167
131.348
130.674
129.957
129.611
128.530
128.176
127.733
126.683
119.471
77.318
77.000
76.682
66.262
37.942
21.016
4b
f1 (ppm)

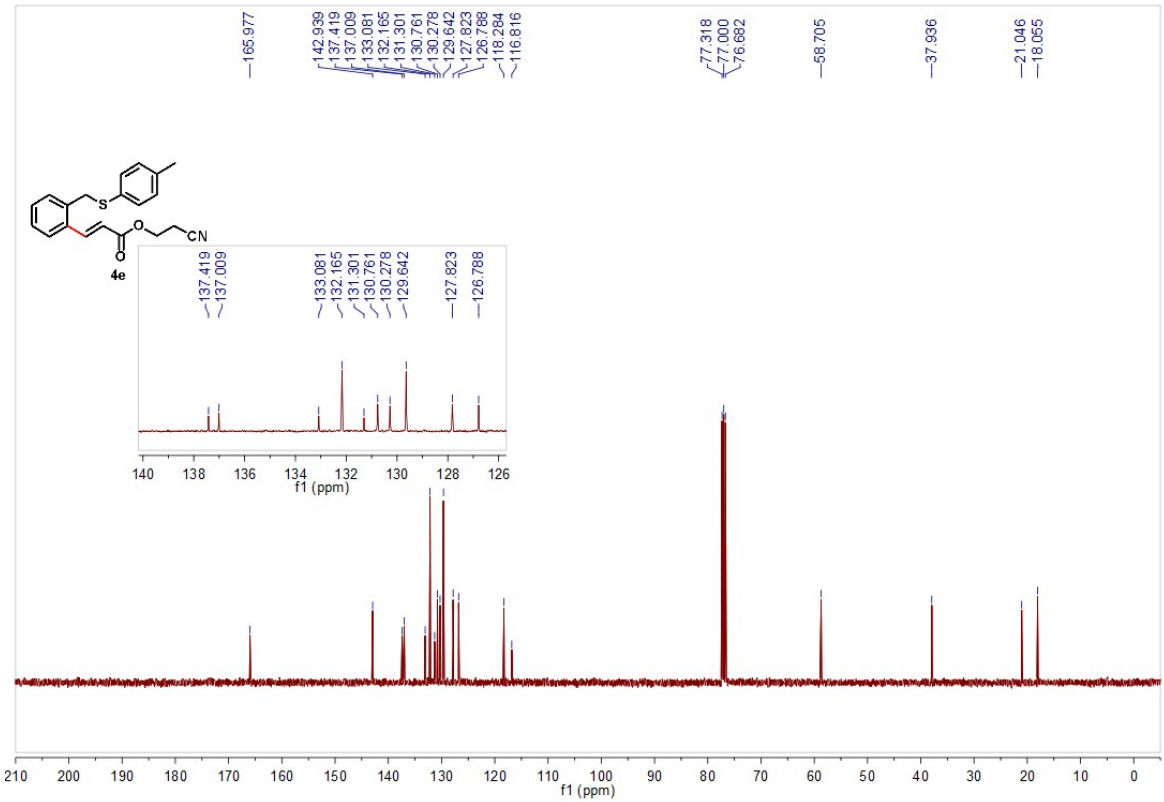

8.033
7.993
7.266
7.260
7.251
7.245
7.224
7.209
7.075
6.962
6.322
4.238
4.221
4.204
4.147
2.316
1.718
1.704
1.684
1.481
1.462
0.977
0.958
0.96
1.00
3.15
2.18
2.11
0.96
2.02
2.10
3.02
2.38
2.05
3.02
4c
f1 (ppm)

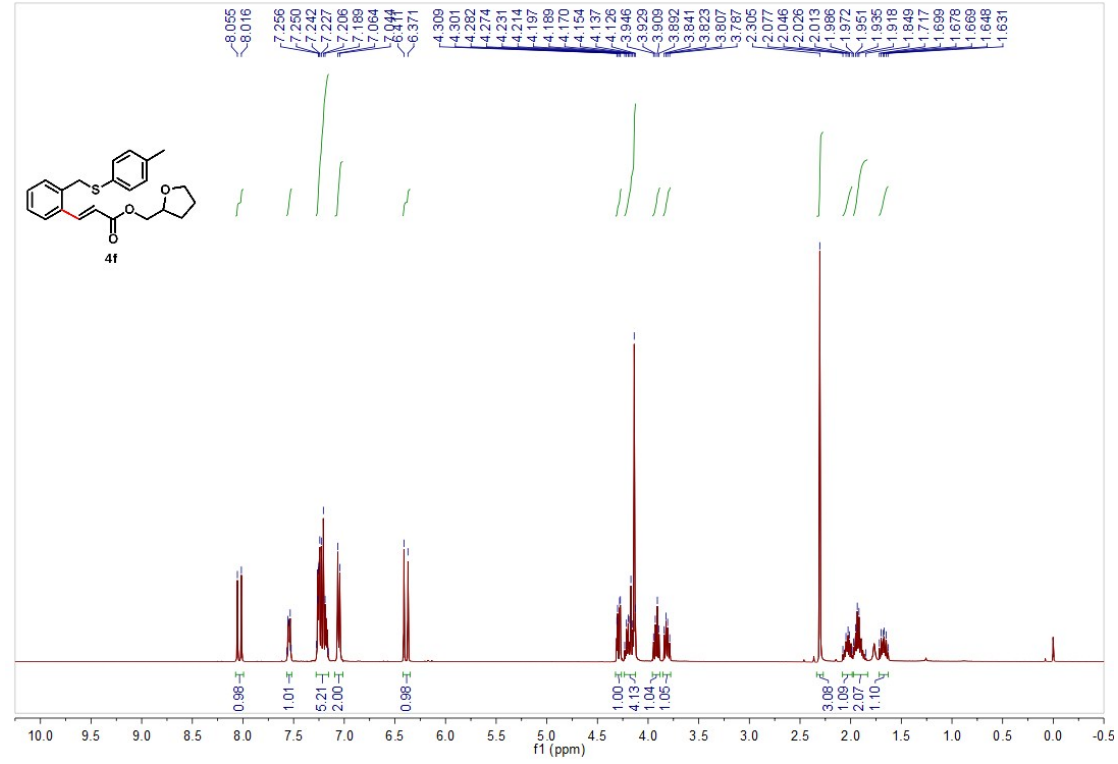

166.766
141.201
137.275
136.652
133.546
132.074
131.438
130.613
129.796
129.584
127.696
126.656
119.922
77.319
77.000
76.682
64.349
37.923
30.691
21.001
19.144
13.695
4c
f1 (ppm)

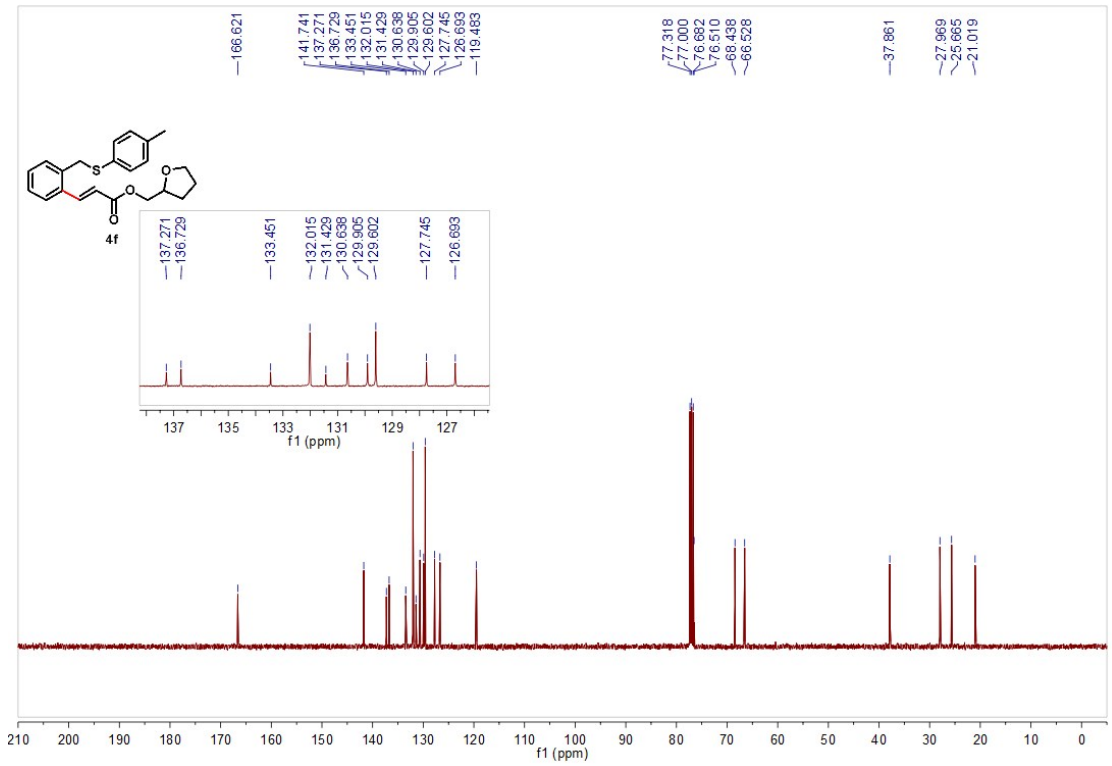

8.045
8.006
7.275
7.266
7.260
7.252
7.240
7.220
7.071
6.354
6.336
4.146
4.009
3.993
2.313
2.070
2.036
2.020
2.003
1.969
1.003
0.986
4d
f1 (ppm)

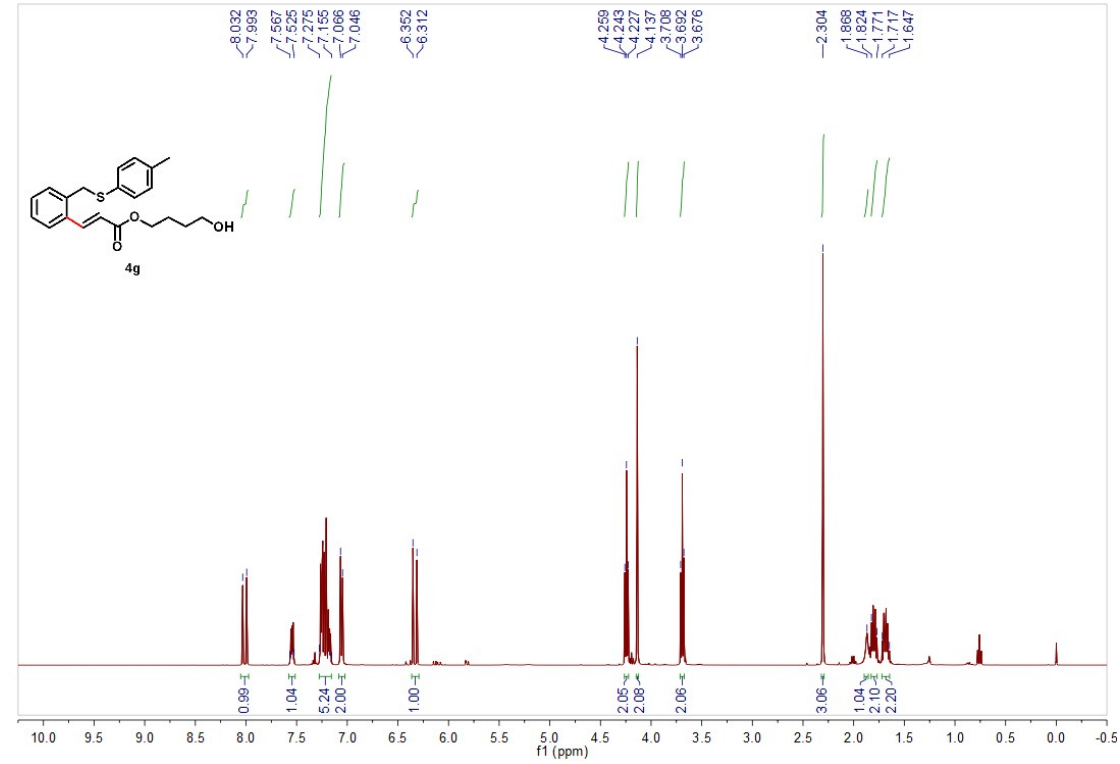

166.775
141.250
137.320
136.674
133.576
132.102
131.453
130.654
129.834
129.614
127.734
126.702
119.946
77.318
77.000
76.682
70.611
37.972
27.789
21.038
19.131
4d
137.320
136.674
133.576
132.102
131.453
130.654
129.834
129.614
127.734
126.702
137
135
133
131
129
127
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

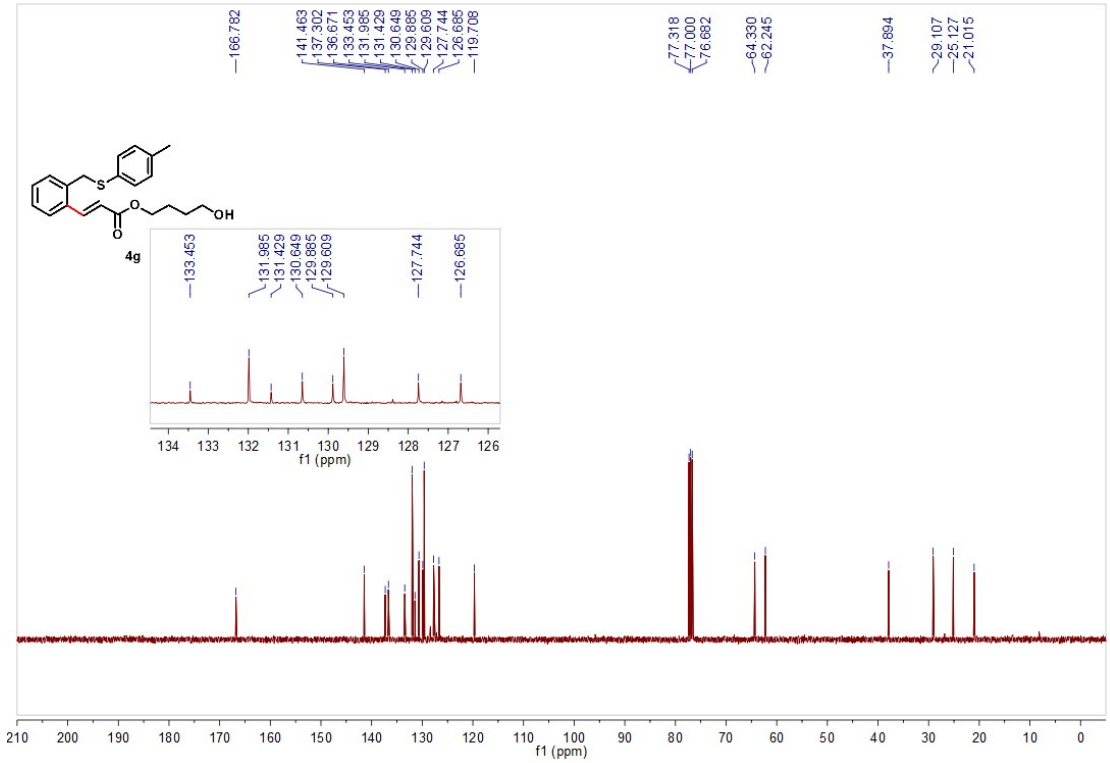

8.087
8.047
7.552
7.289
7.277
7.267
7.260
7.234
7.213
7.076
6.398
6.338
4.428
4.412
4.397
4.144
2.792
2.776
2.760
2.314
4e
CN
1.01
1.05
2.18
3.00
1.99
1.00
2.09
2.06
2.07
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

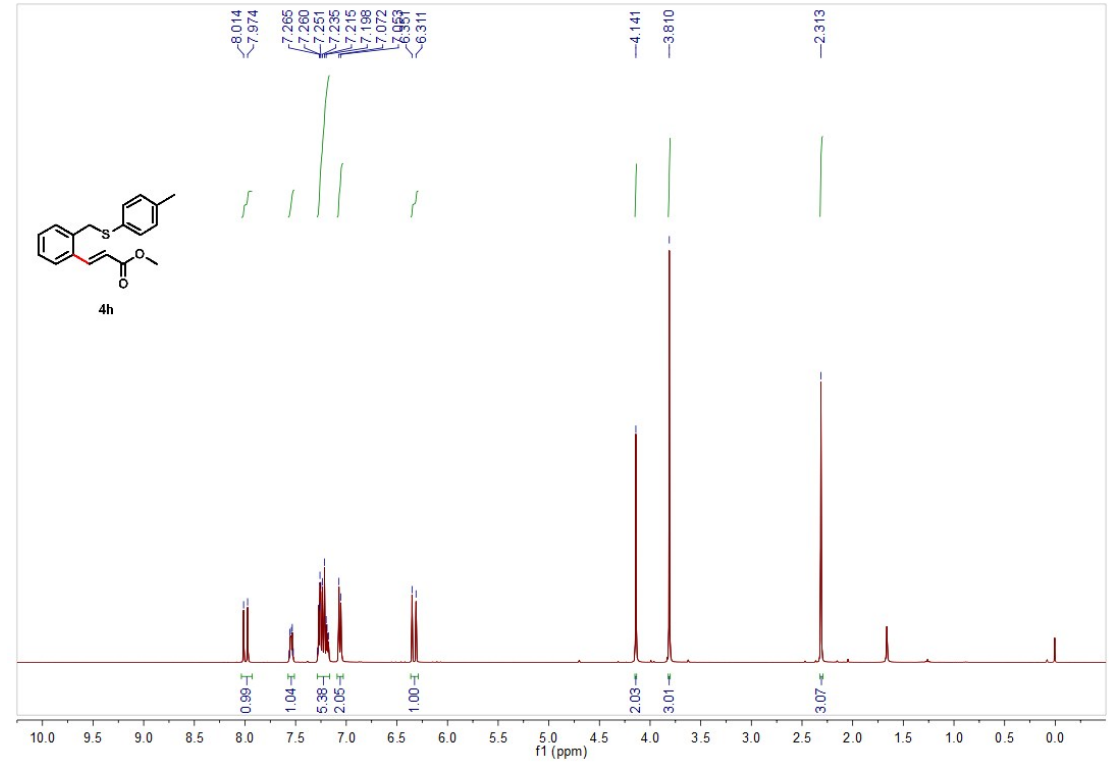

165.977
142.939
137.419
137.009
133.081
132.165
131.301
130.761
130.278
129.642
127.823
126.788
118.284
116.816
77.318
77.000
76.682
58.705
37.936
21.046
18.055
4e
f1 (ppm)

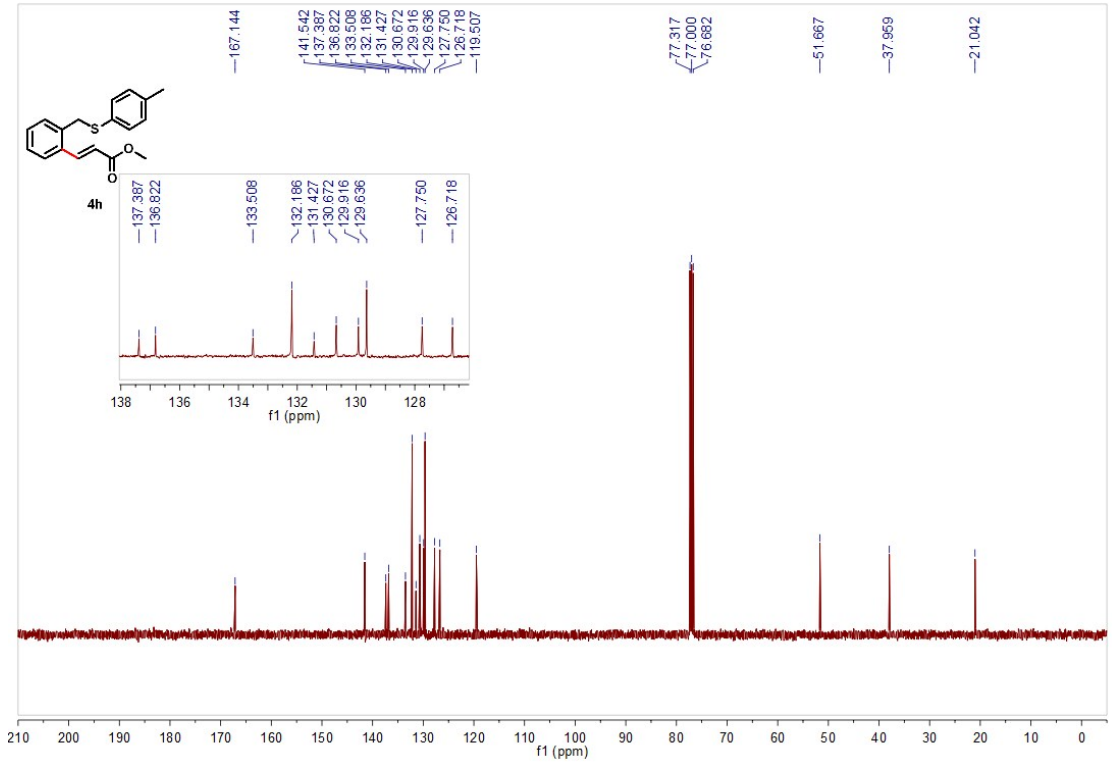

8.055
8.016
7.256
7.250
7.242
7.227
7.206
7.189
7.064
6.371
4.309
4.301
4.282
4.274
4.231
4.214
4.197
4.189
4.170
4.154
4.137
4.126
3.946
3.929
3.909
3.892
3.841
3.823
3.807
3.787
2.305
2.077
2.046
2.026
2.013
1.986
1.972
1.951
1.935
1.918
1.849
1.717
1.699
1.669
1.648
1.631
4f
f1 (ppm)

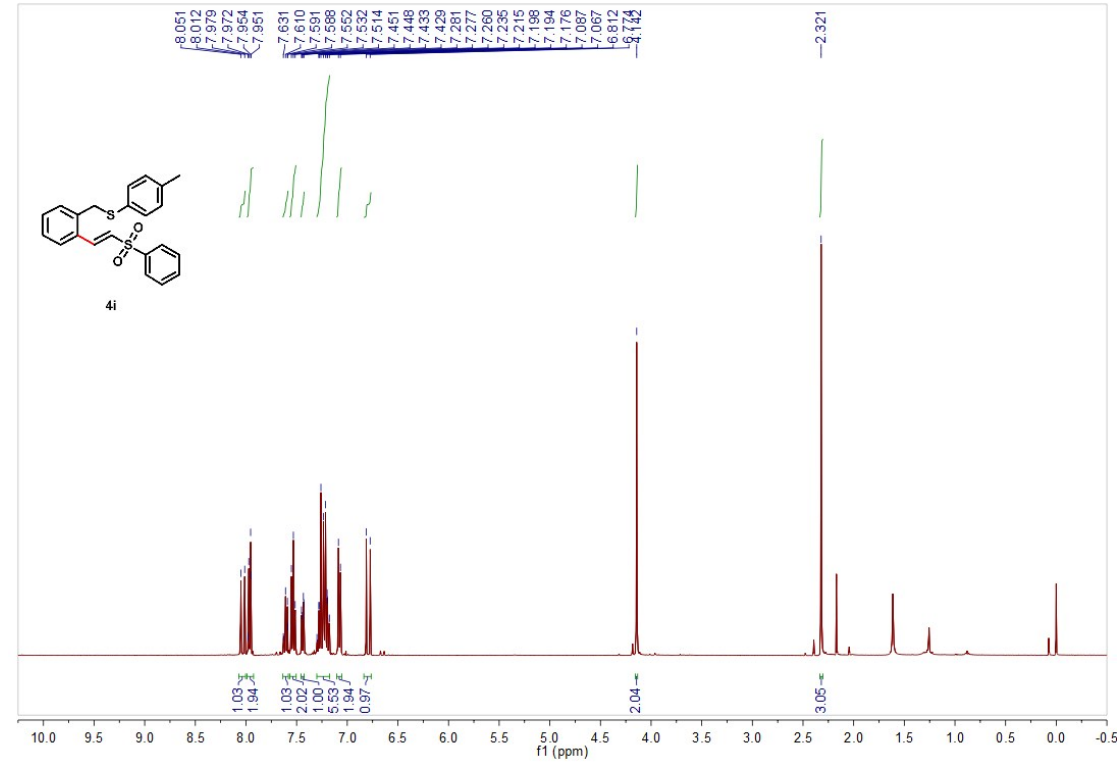

166.621
141.741
137.271
136.729
133.451
132.015
131.429
130.638
129.905
129.602
127.745
126.693
119.483
77.318
77.000
76.682
76.510
68.438
66.528
37.861
27.969
25.665
21.019
4f
137.271
136.729
133.451
132.015
131.429
130.638
129.905
129.602
127.745
126.693
137
135
133
131
129
127
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

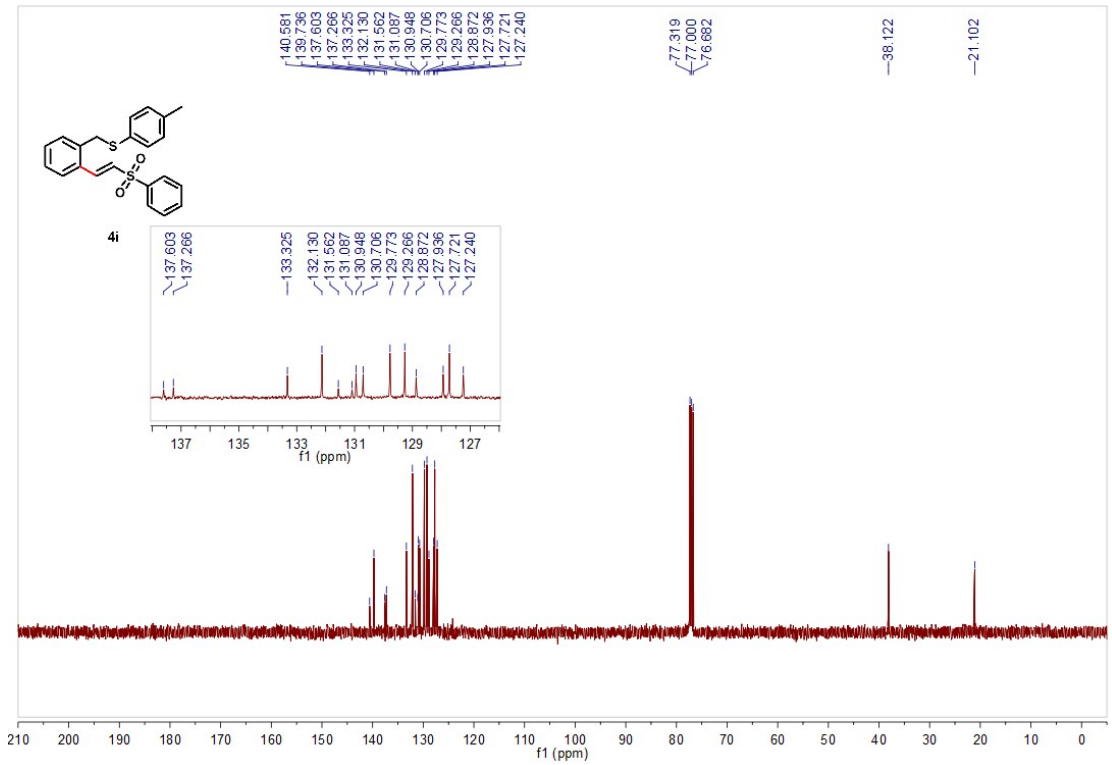

8.032
7.993
7.567
7.525
7.275
7.155
7.066
7.046
6.352
6.312
4.259
4.243
4.227
4.137
3.708
3.692
3.676
2.304
1.868
1.824
1.771
1.717
1.647
OH
4g
0.99
1.04
5.24
2.00
1.00
2.05
2.08
2.06
3.06
1.04
2.10
2.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

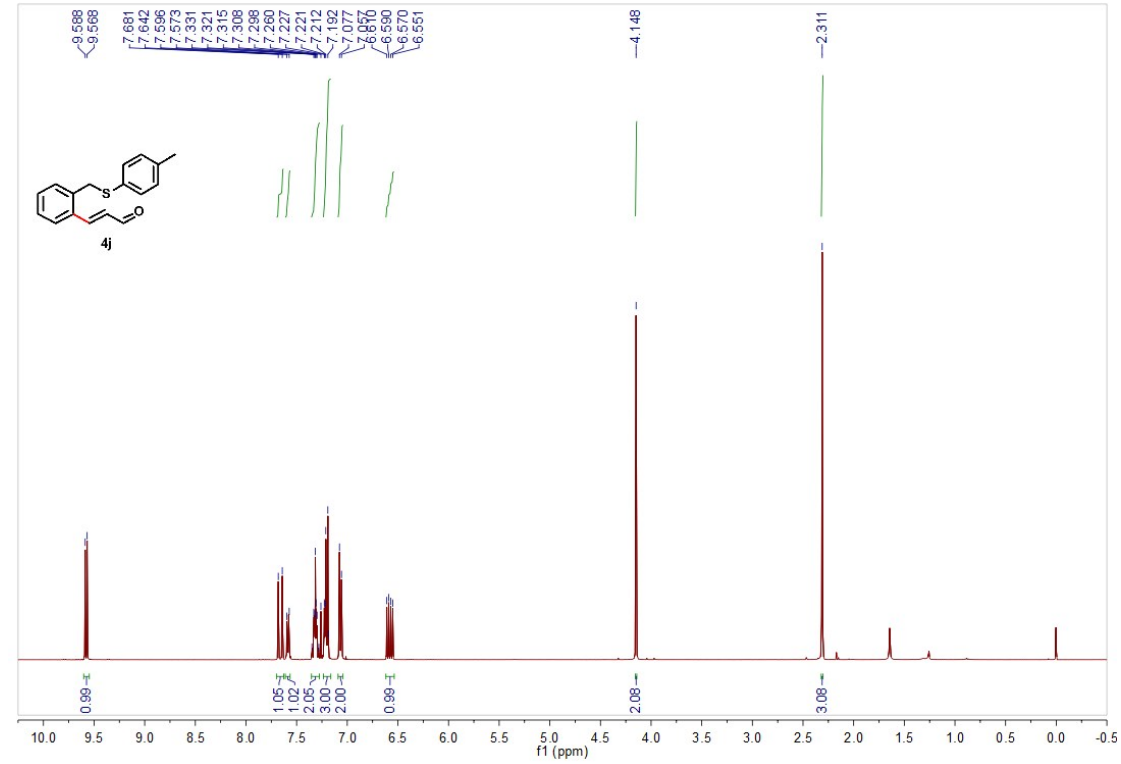

166.782
141.463
137.302
136.671
133.453
131.985
131.429
130.649
129.885
129.609
127.744
126.685
119.708
77.318
77.000
76.682
64.330
62.245
37.894
29.107
25.127
21.015
OH
4g
f1 (ppm)

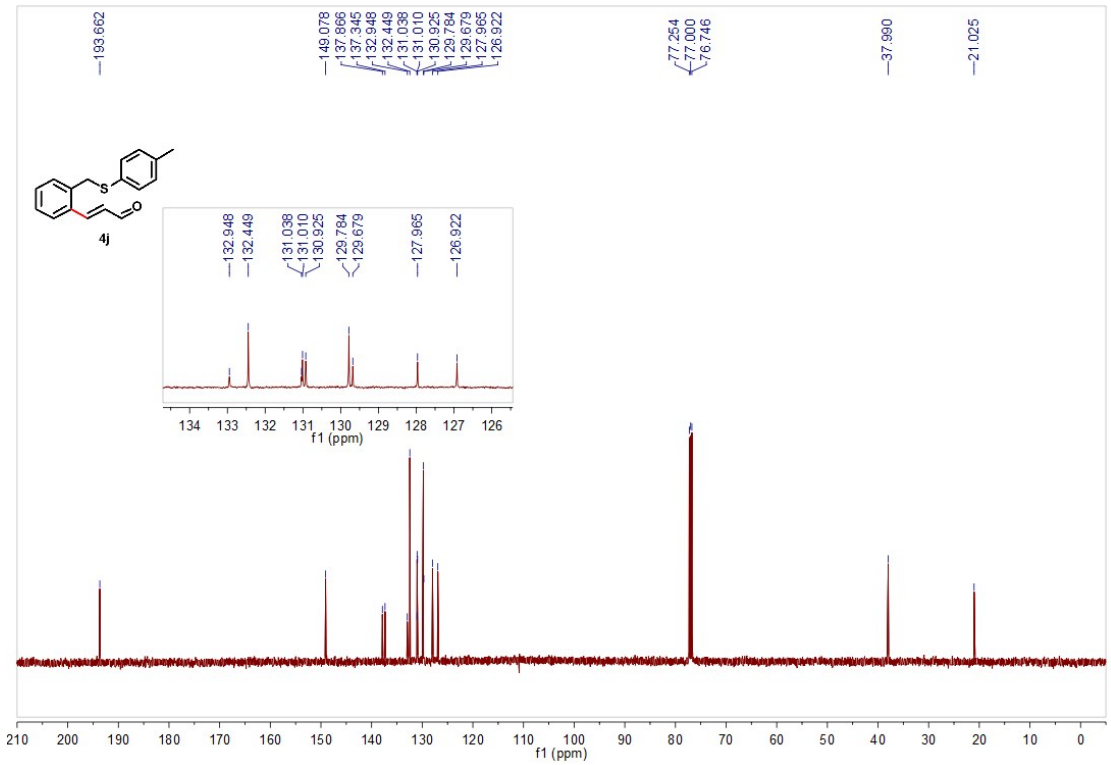

8.014
7.974
7.265
7.260
7.251
7.235
7.215
7.198
7.072
6.963
6.951
6.311
4.141
3.810
2.313
4h
0.99
1.04
5.38
2.05
1.00
2.03
3.01
3.07
f1 (ppm)

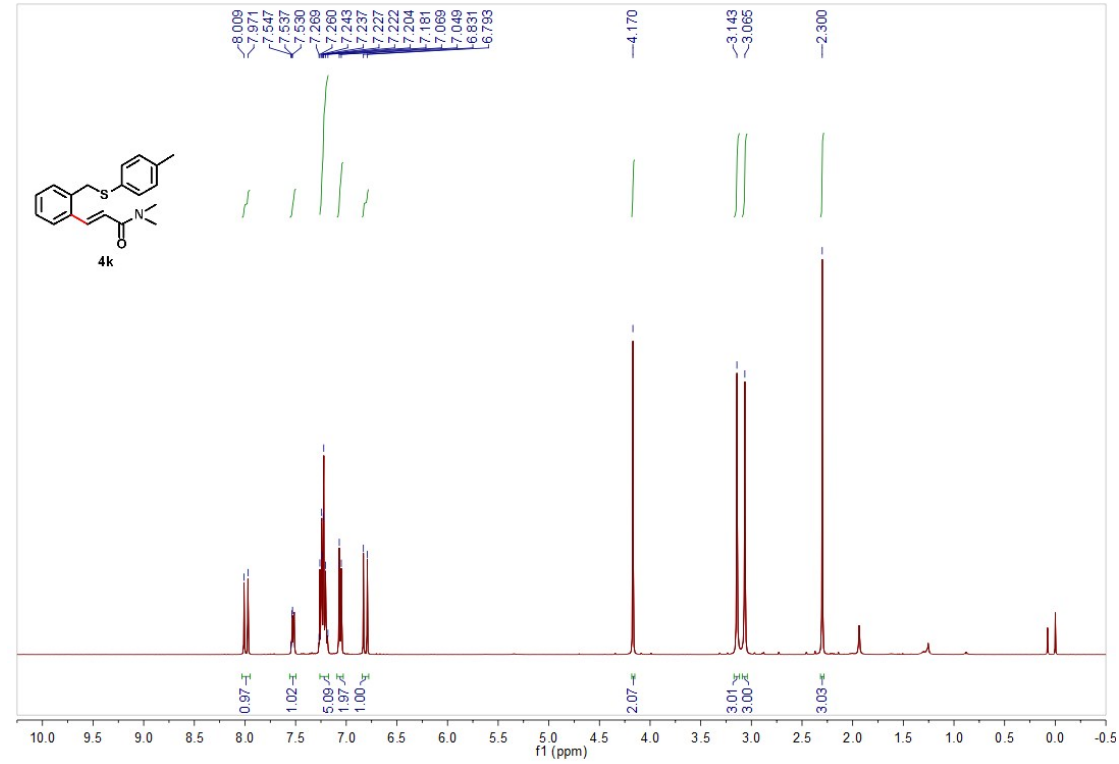

167.144
141.542
137.387
136.822
133.508
132.186
131.427
130.672
129.916
129.636
127.750
126.718
119.507
77.317
77.000
76.682
51.667
37.959
21.042
4h
f1 (ppm)

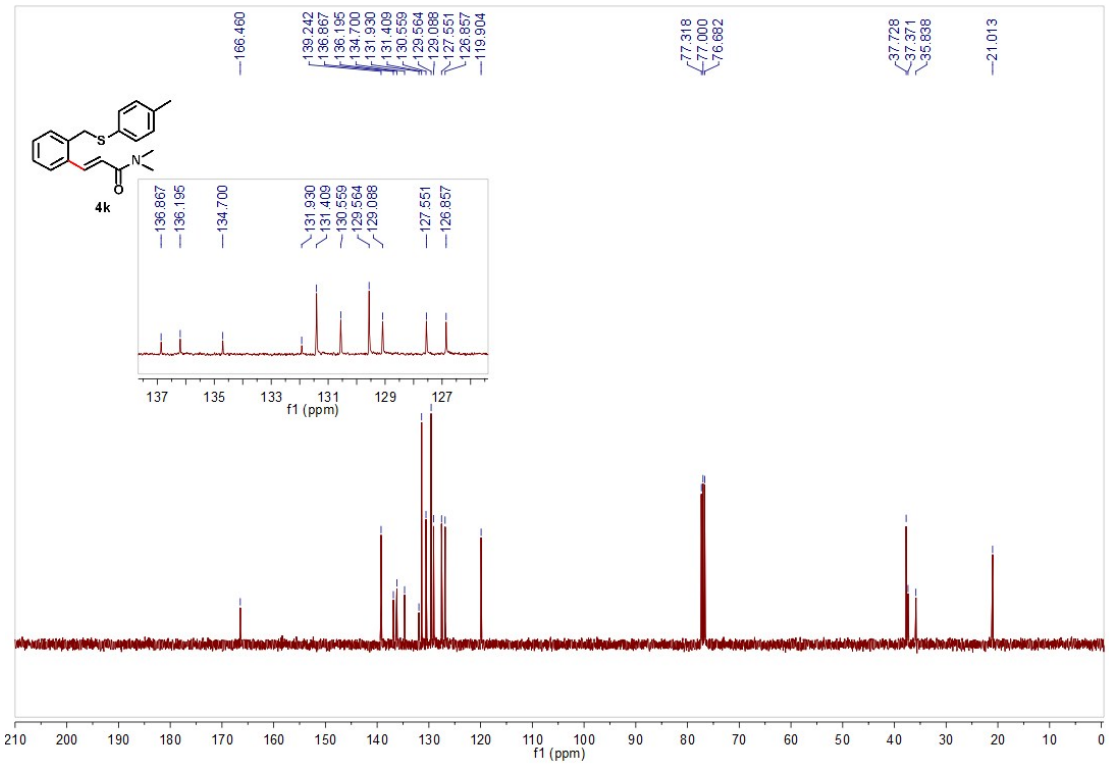

8.051
8.012
7.979
7.972
7.954
7.951
7.631
7.610
7.591
7.588
7.552
7.532
7.514
7.451
7.448
7.433
7.429
7.281
7.277
7.260
7.235
7.215
7.198
7.194
7.176
7.087
7.067
6.812
4.142
2.321
4i
1.03
1.94
1.03
2.02
1.00
5.53
1.94
0.97
2.04
3.05
f1 (ppm)

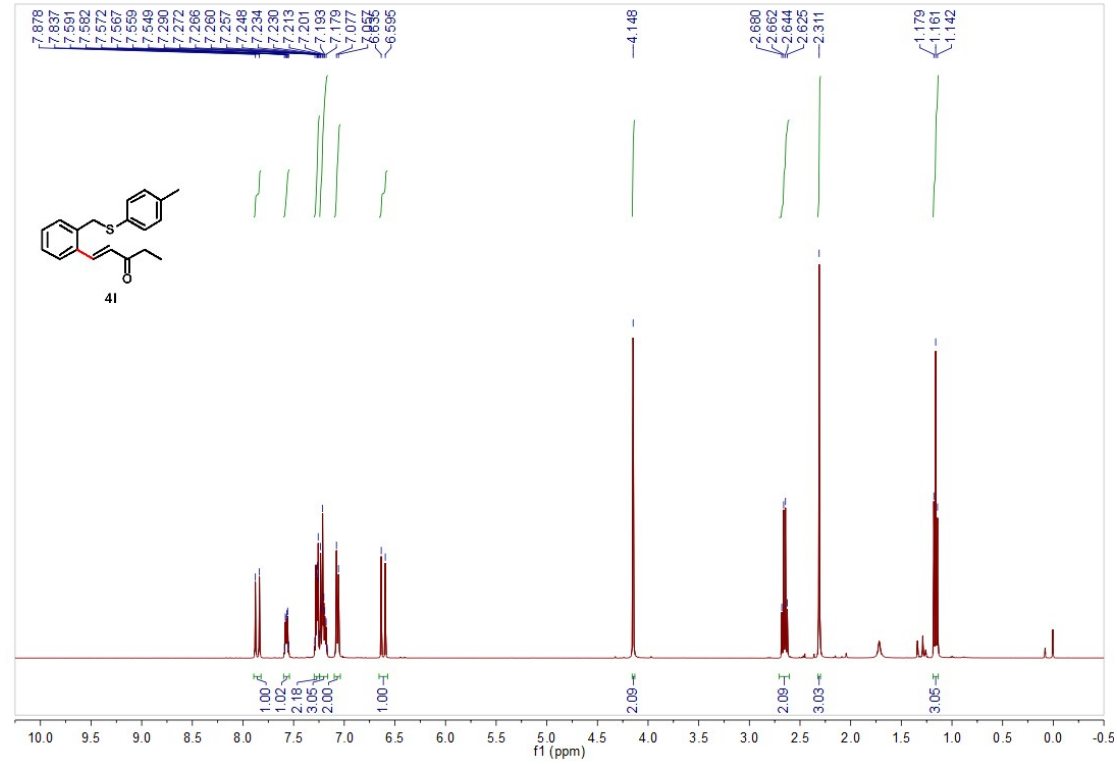

140.581
139.736
137.603
137.266
133.325
132.130
131.562
131.087
130.948
130.706
129.773
129.266
128.872
127.936
127.721
127.240
77.319
77.000
76.682
38.122
21.102
4i
137.603
137.266
133.325
132.130
131.562
131.087
130.948
130.706
129.773
129.266
128.872
127.936
127.721
127.240
137
135
133
131
129
127
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

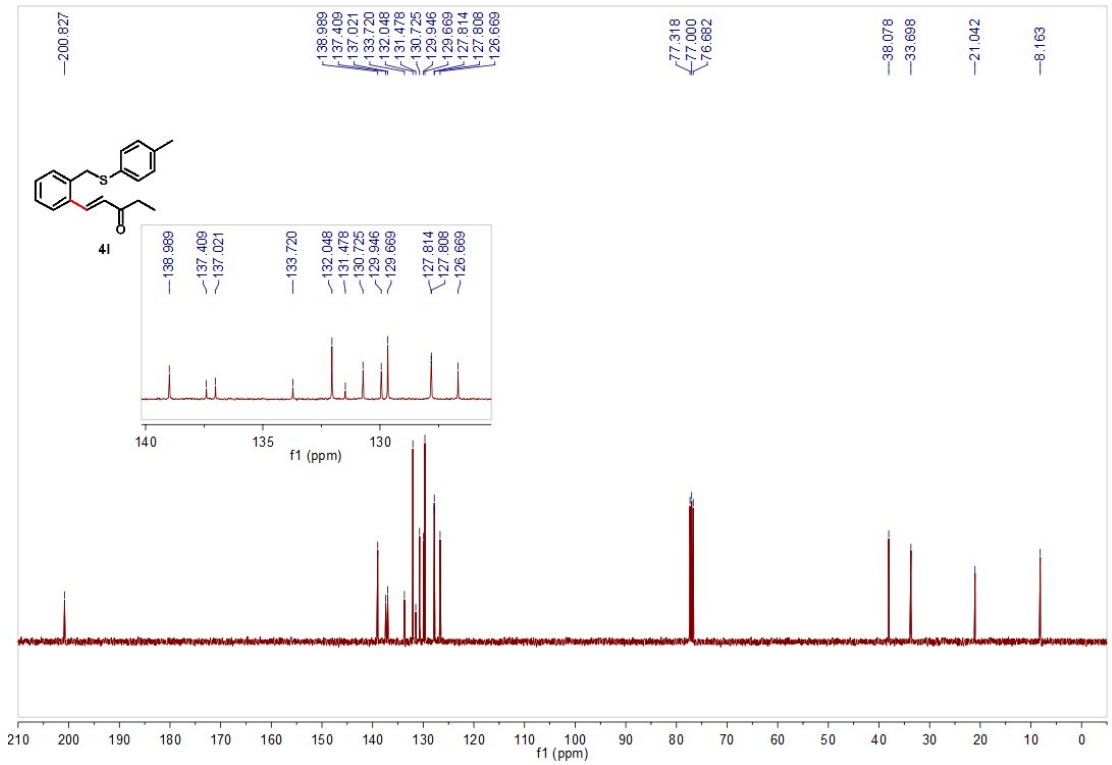

9.588
9.568
7.681
7.642
7.596
7.573
7.331
7.321
7.315
7.308
7.298
7.260
7.227
7.221
7.212
7.192
7.077
7.057
6.810
6.590
6.570
6.551
4.148
2.311
4j
0.99
1.05
1.02
2.05
3.00
2.00
0.99
2.08
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

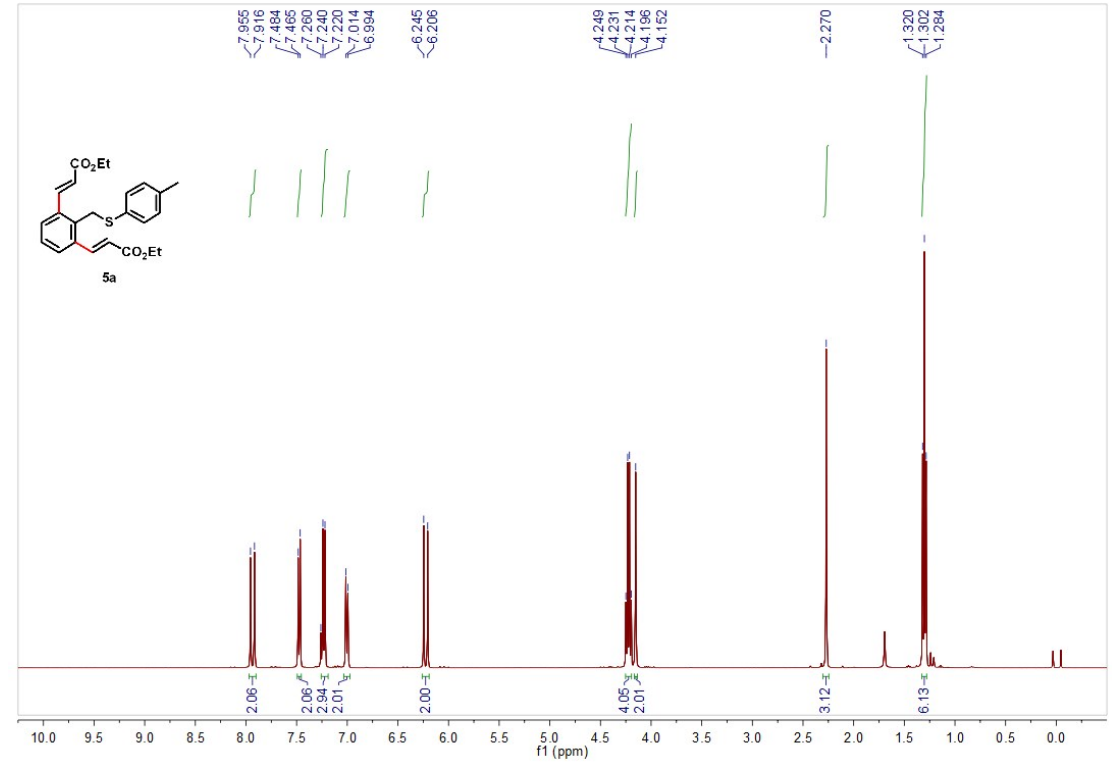

193.662
149.078
137.866
137.345
132.948
132.449
131.038
131.010
130.925
129.784
129.679
127.965
126.922
77.254
77.000
76.746
37.990
21.025
4j
f1 (ppm)
f1 (ppm)

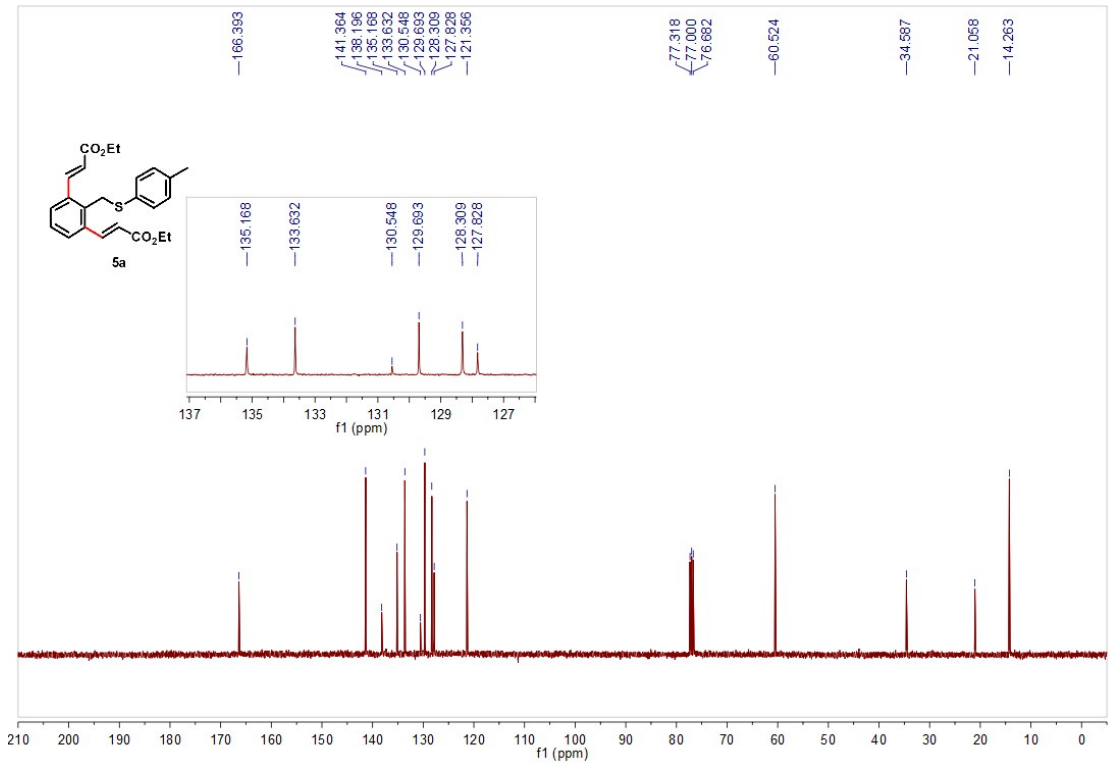

8.009
7.971
7.547
7.537
7.530
7.269
7.260
7.243
7.237
7.227
7.222
7.204
7.181
7.069
7.049
6.831
6.793
4.170
3.143
3.065
2.300
4k
0.97
1.02
5.09
1.97
1.00
2.07
3.01
3.00
3.03
f1 (ppm)

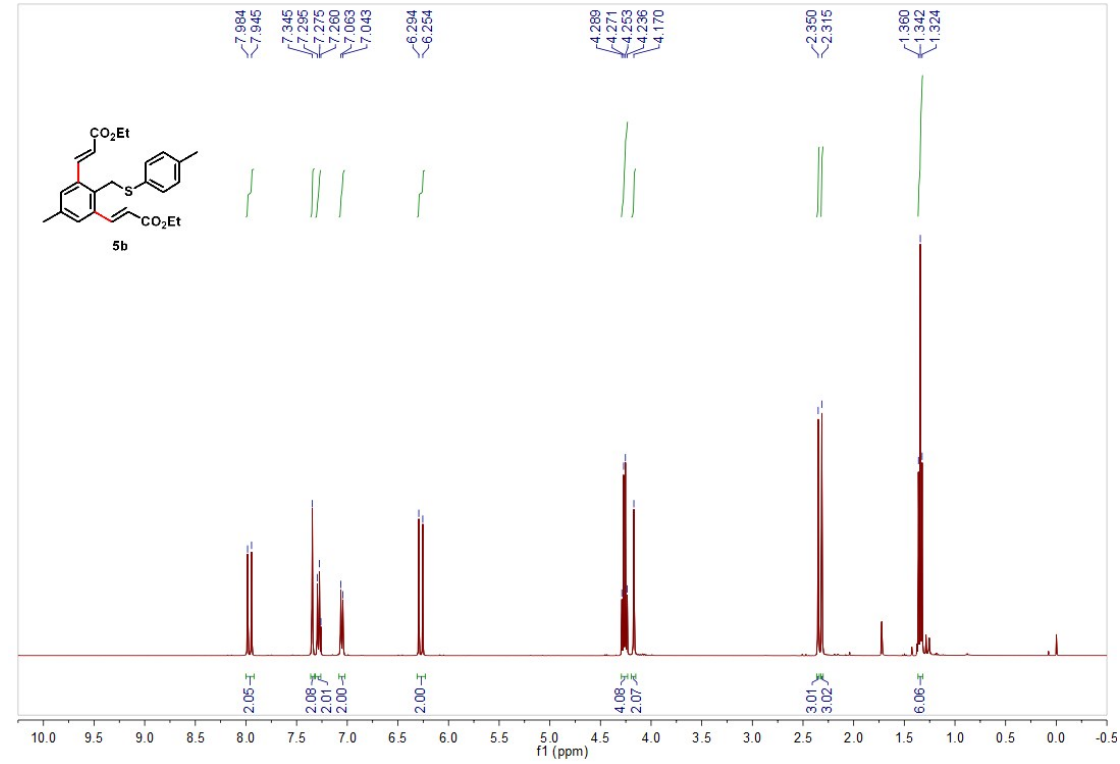

166.460
139.242
136.867
136.195
134.700
131.930
131.409
130.559
129.564
129.088
127.551
126.857
119.904
77.318
77.000
76.682
37.728
37.371
36.838
21.013
4k
f1 (ppm)

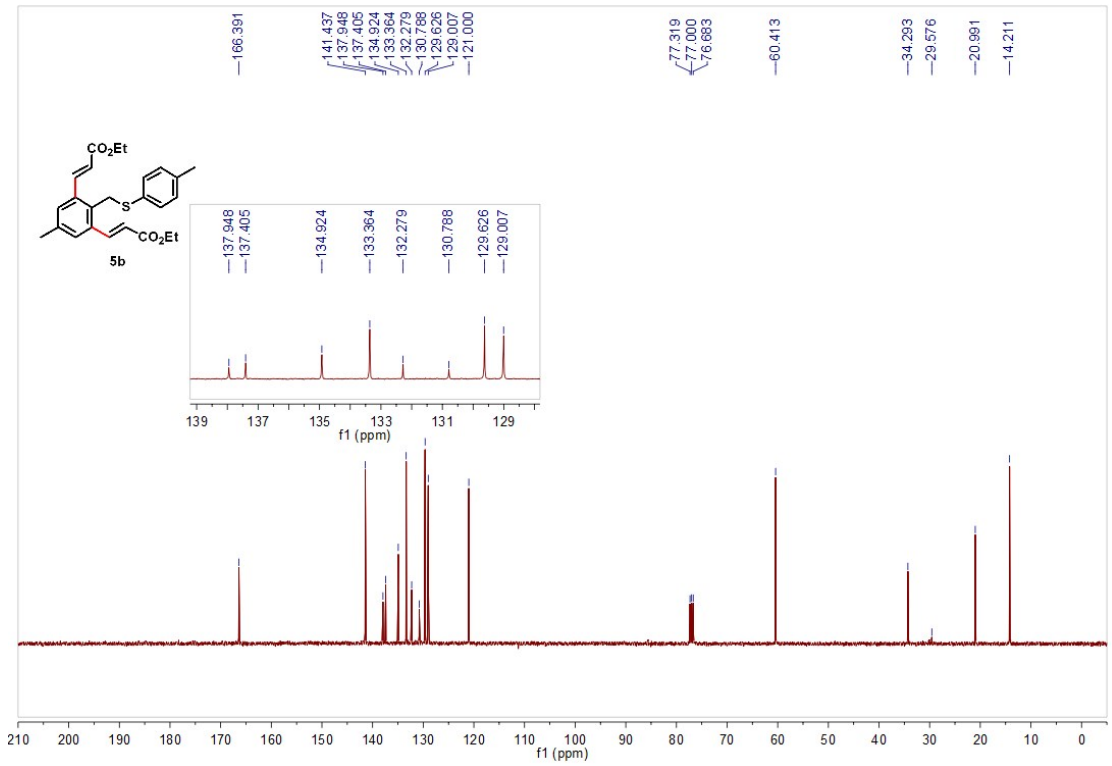

7.878
7.837
7.591
7.582
7.572
7.567
7.559
7.549
7.290
7.272
7.266
7.260
7.257
7.248
7.234
7.230
7.213
7.201
7.193
7.179
7.077
6.595
4.148
2.680
2.662
2.644
2.625
2.311
1.179
1.161
1.142
4l
1.00
1.02
2.18
3.05
2.00
1.00
2.09
2.09
3.03
3.05
f1 (ppm)

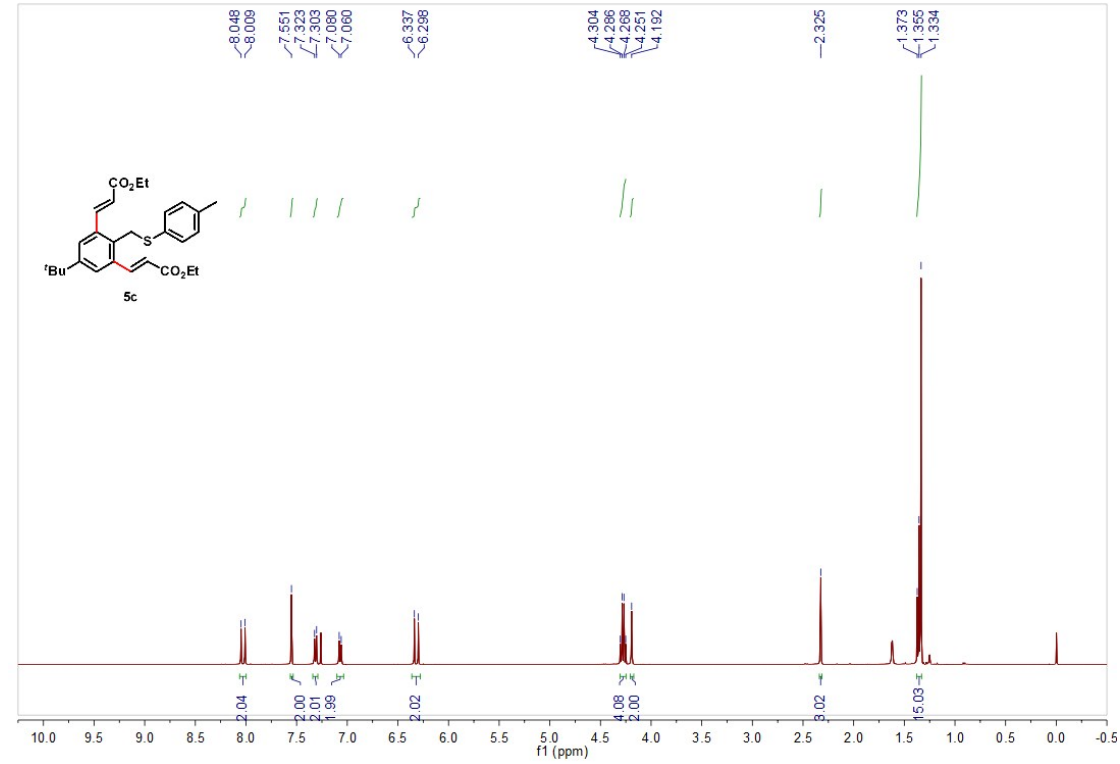

200.827
138.989
137.409
137.021
133.720
132.048
131.478
130.725
129.946
129.669
127.814
127.808
126.669
77.318
77.000
76.682
38.078
33.698
21.042
8.163
4l
f1 (ppm)

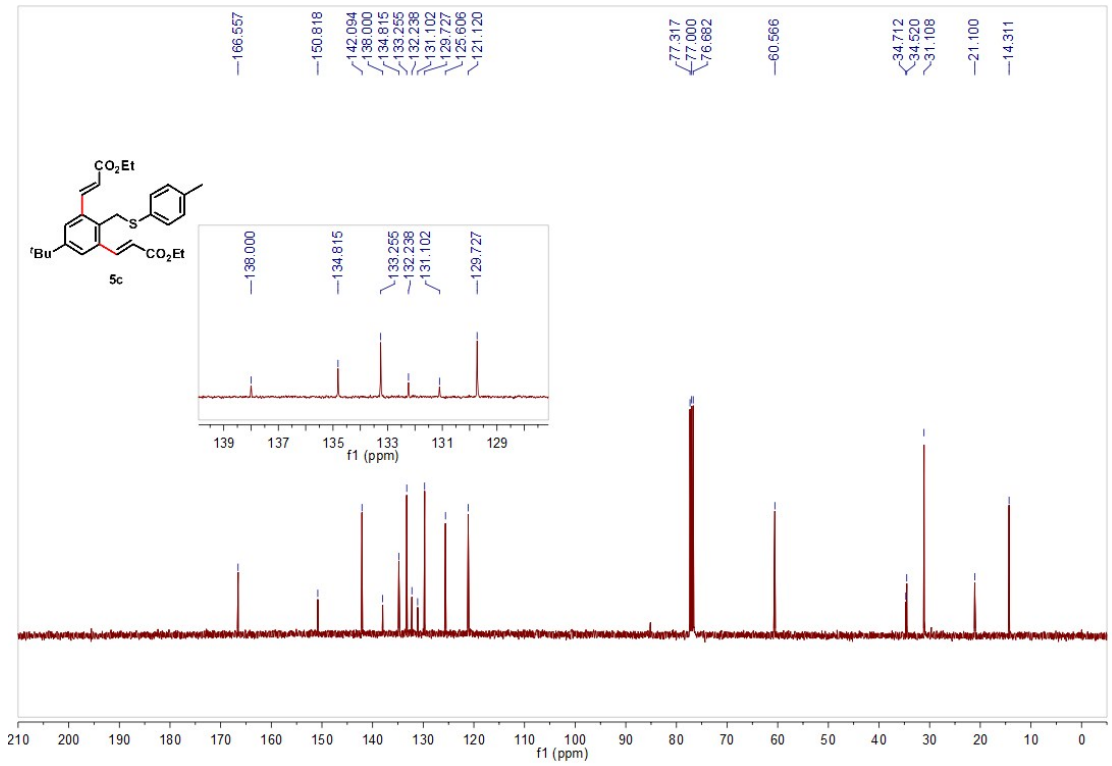

7.955
7.916
7.484
7.465
7.260
7.240
7.220
7.014
6.994
6.245
6.206
4.249
4.231
4.214
4.196
4.152
2.270
1.320
1.302
1.284
CO2Et
CO2Et
5a
2.06
2.06
2.94
2.01
2.00
4.05
2.01
3.12
6.13
f1 (ppm)

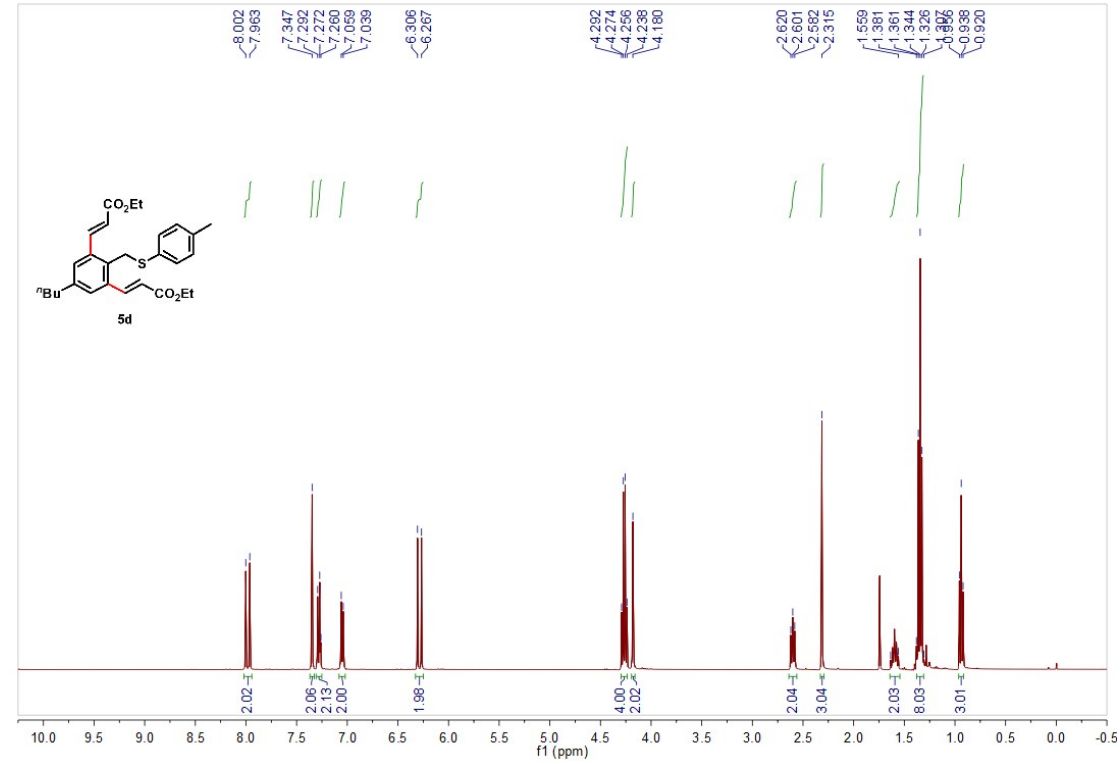

166.393
141.364
138.196
135.168
133.632
130.548
129.693
128.309
127.828
121.356
77.318
77.000
76.682
60.524
34.587
21.058
14.263
CO2Et
S
CO2Et
5a
135.168
133.632
130.548
129.693
128.309
127.828
137
135
133
131
129
127
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

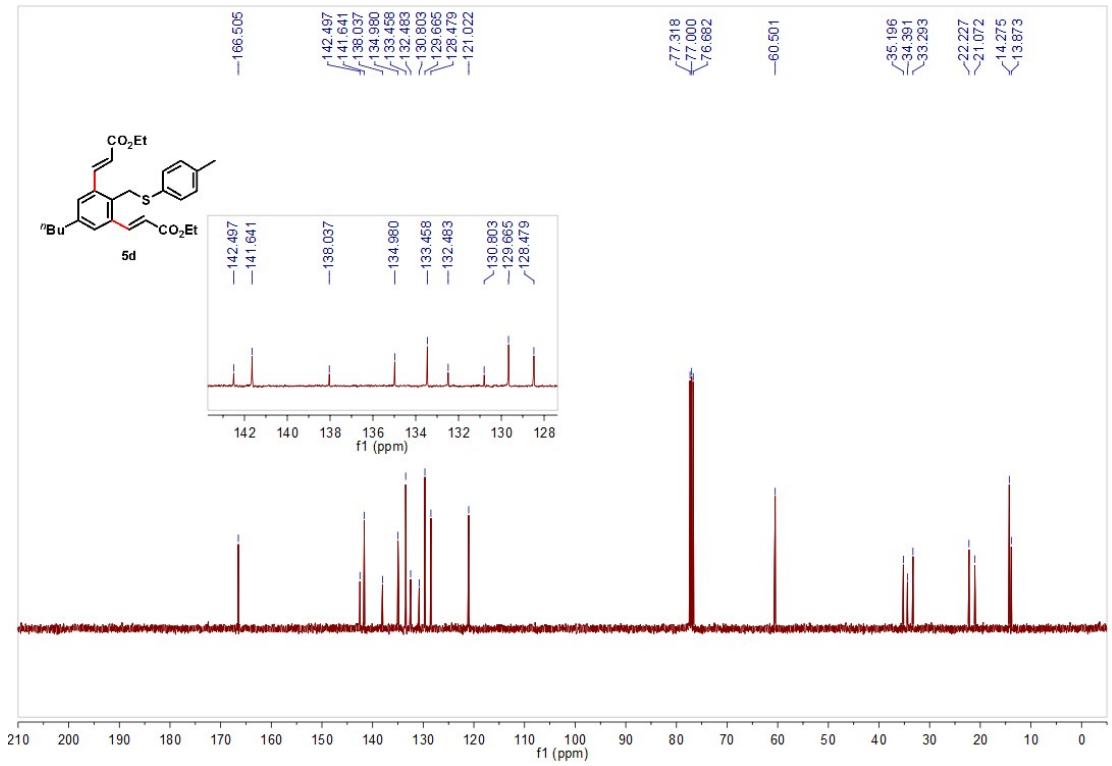

7.984
7.945
7.345
7.296
7.275
7.260
7.063
7.043
6.294
6.254
4.289
4.271
4.253
4.236
4.170
2.350
2.315
1.360
1.342
1.324
CO2Et
S
CO2Et
5b
2.05
2.08
2.01
2.00
2.00
4.08
2.07
3.01
3.02
6.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

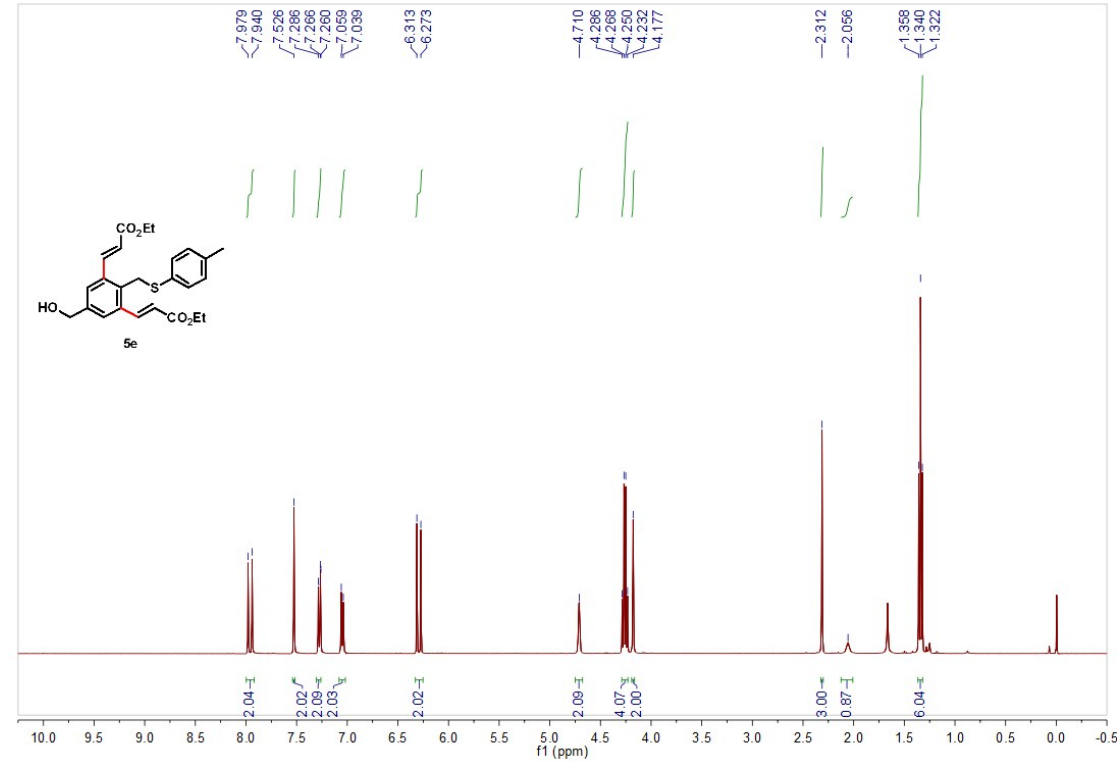

166.391
141.437
137.948
137.405
134.924
133.364
132.279
130.788
129.626
129.007
121.000
77.319
77.000
76.683
60.413
34.293
29.576
20.991
14.211
CO2Et
S
CO2Et
5b
f1 (ppm)
f1 (ppm)

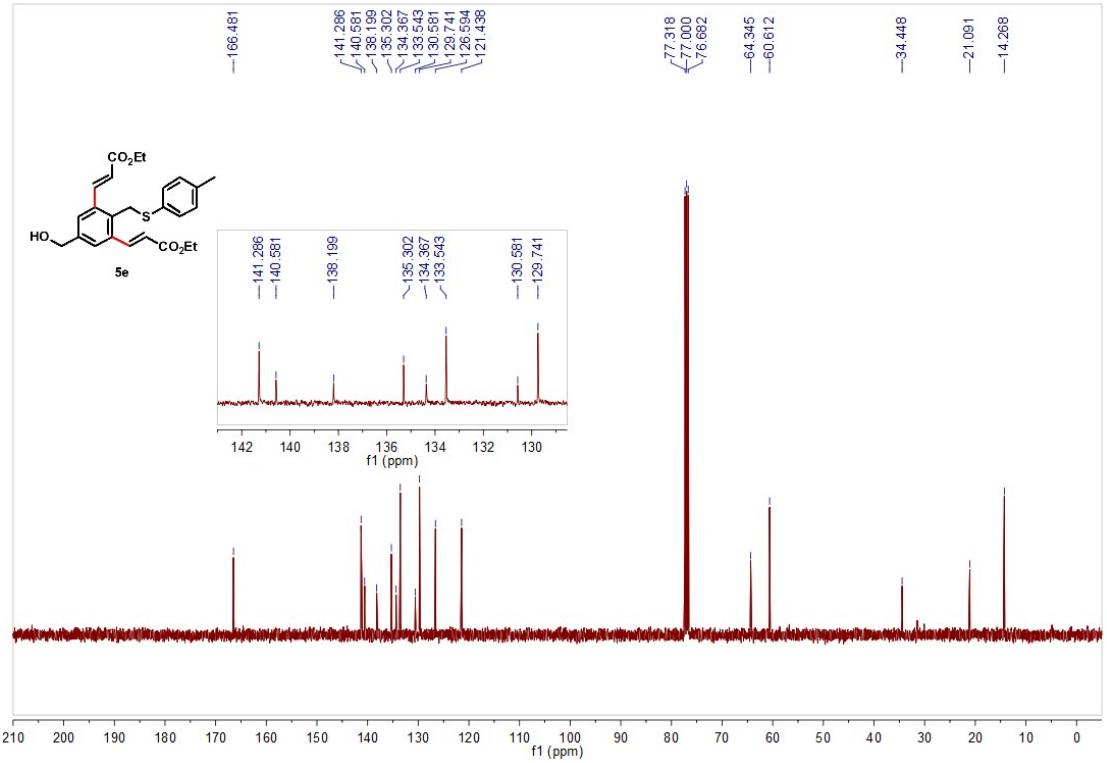

8.048
8.009
7.551
7.323
7.303
7.080
7.060
6.337
6.298
4.304
4.286
4.268
4.251
4.192
2.325
1.373
1.355
1.334
CO2Et
S
tBu
CO2Et
5c
2.04
2.00
2.01
1.99
2.02
4.08
2.00
3.02
15.03
f1 (ppm)

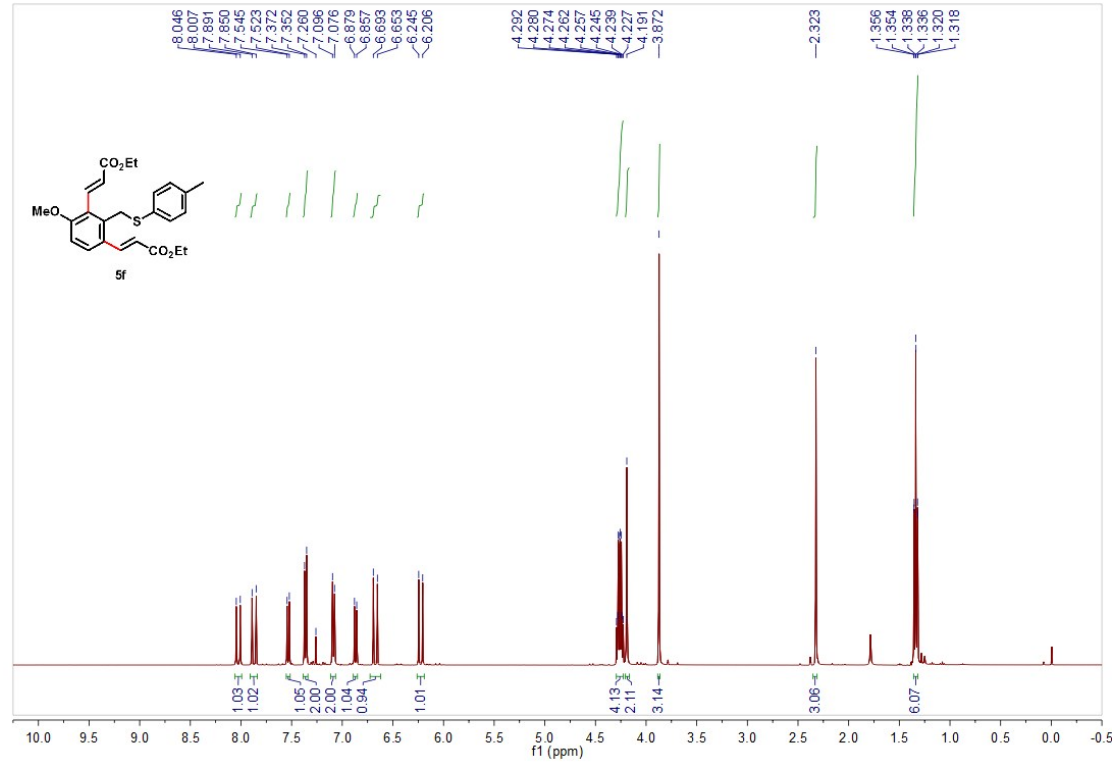

166.557
150.818
142.094
138.000
134.815
133.255
132.238
131.102
129.727
125.606
121.120
77.317
77.000
76.682
60.566
34.712
34.520
31.108
21.100
14.311
5c
f1 (ppm)

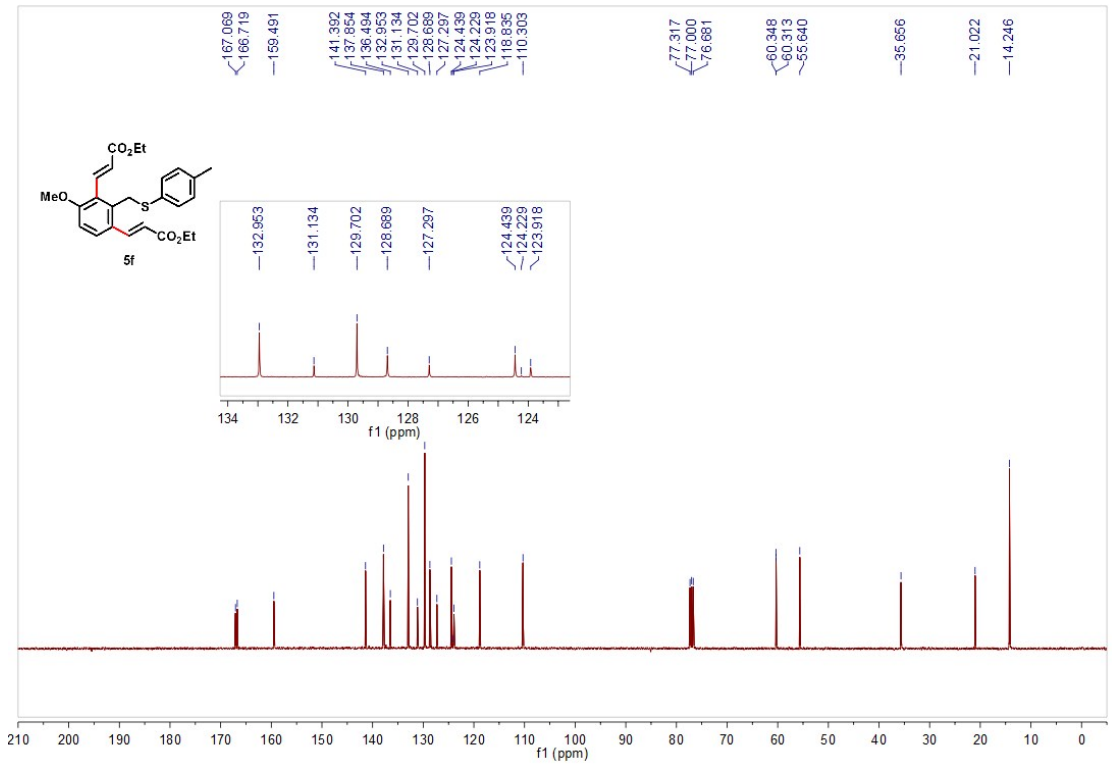

8.002
7.963
7.347
7.292
7.272
7.260
7.059
7.039
6.306
6.267
4.292
4.274
4.256
4.238
4.180
2.620
2.601
2.582
2.315
1.559
1.381
1.361
1.344
1.326
0.966
0.938
0.920
5d
2.02
2.06
2.13
2.00
1.98
4.00
2.02
2.04
3.04
2.03
8.03
3.01
f1 (ppm)

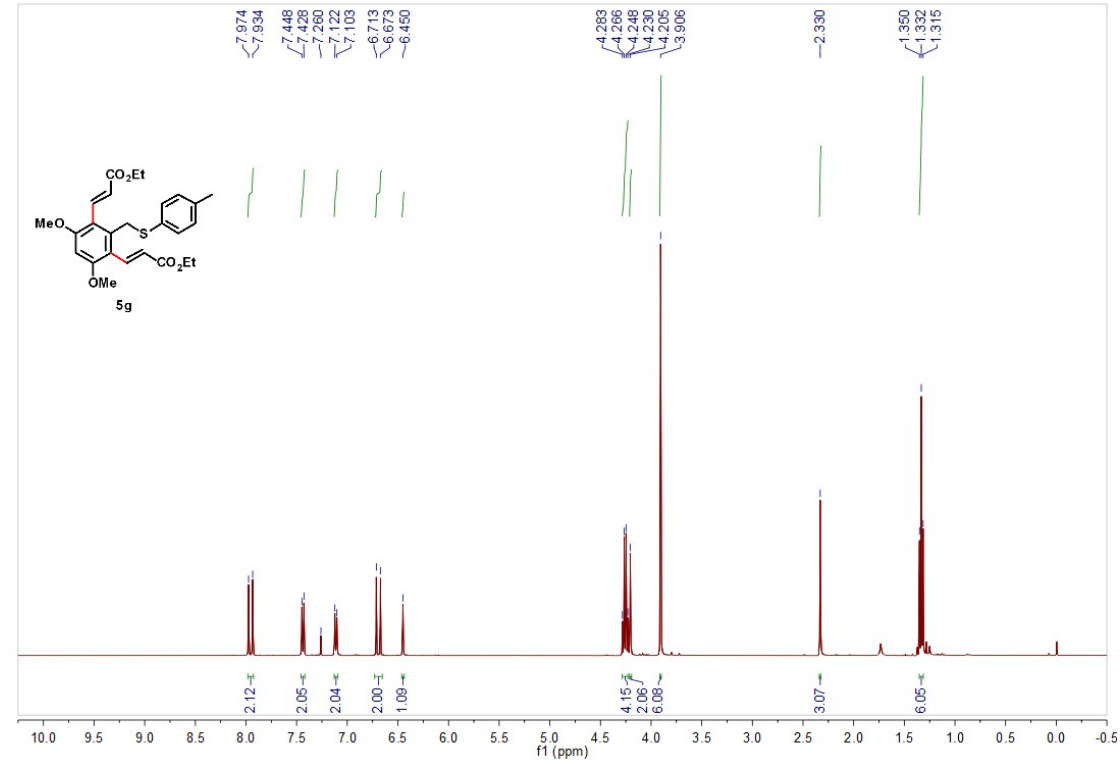

166.505
142.497
141.641
138.037
134.980
133.458
132.483
130.803
129.665
128.479
121.022
77.318
77.000
76.682
60.501
35.196
34.391
33.293
22.227
21.072
14.275
13.873
5d
f1 (ppm)

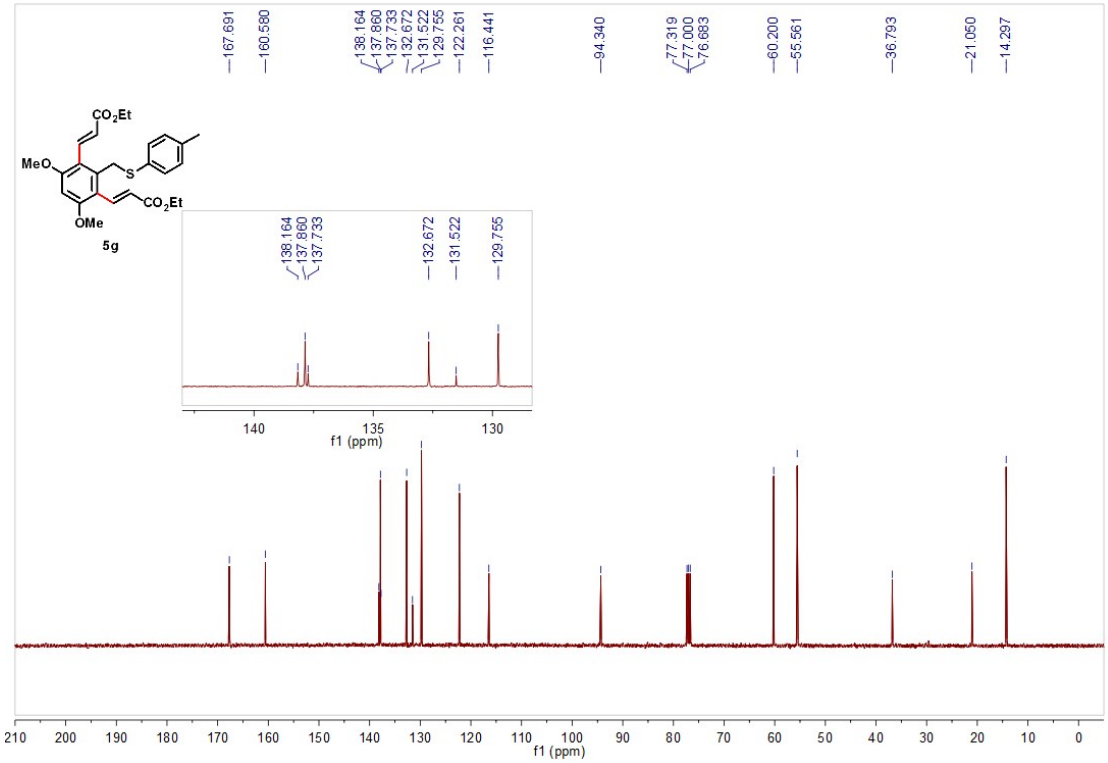

7.979
7.940
7.526
7.286
7.266
7.260
7.059
7.039
6.313
6.273
4.710
4.286
4.268
4.250
4.232
4.177
2.312
2.056
1.358
1.340
1.322
5e
2.04
2.02
2.09
2.03
2.02
2.09
4.07
2.00
3.00
0.87
6.04
f1 (ppm)

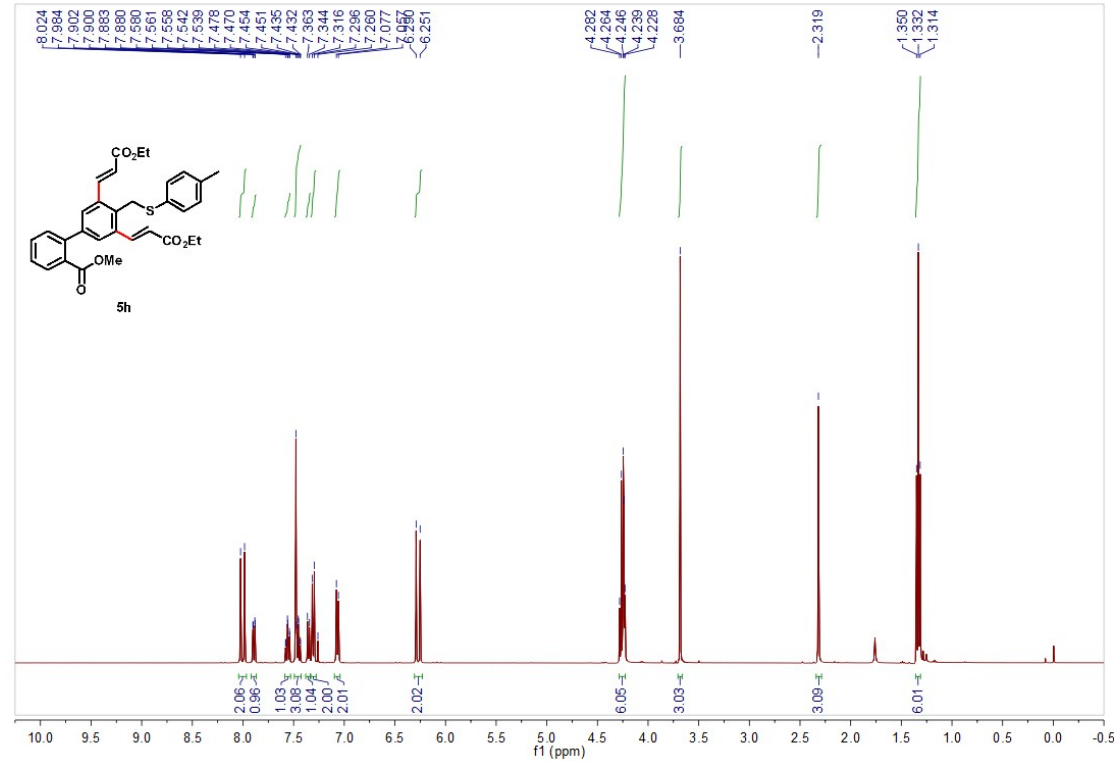

166.481
141.286
140.581
138.199
135.302
134.367
133.543
130.581
129.741
126.594
121.438
77.318
77.000
76.682
64.345
60.612
34.448
21.091
14.268
CO2Et
HO
S
CO2Et
5e
f1 (ppm)

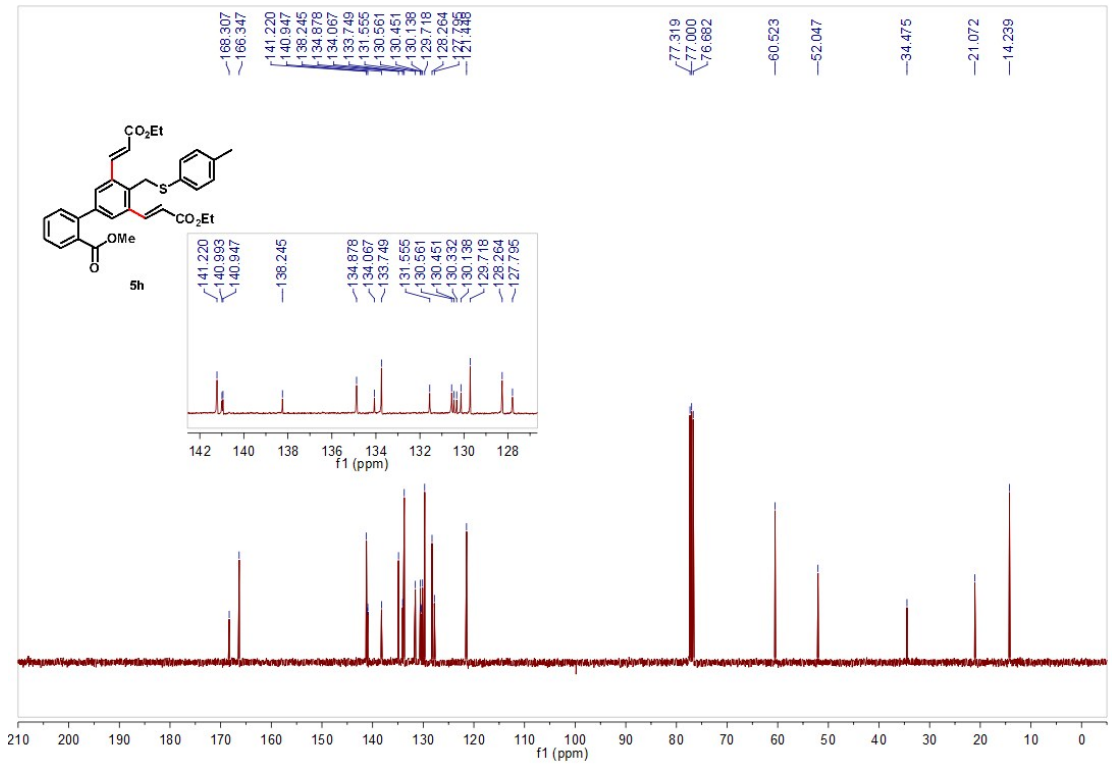

8.046
8.007
7.891
7.850
7.545
7.523
7.372
7.352
7.260
7.096
7.076
6.879
6.857
6.693
6.653
6.245
6.206
4.292
4.280
4.274
4.262
4.257
4.245
4.239
4.227
4.191
3.872
2.323
1.356
1.354
1.338
1.336
1.320
1.318
CO2Et
MeO
S
CO2Et
5f
f1 (ppm)

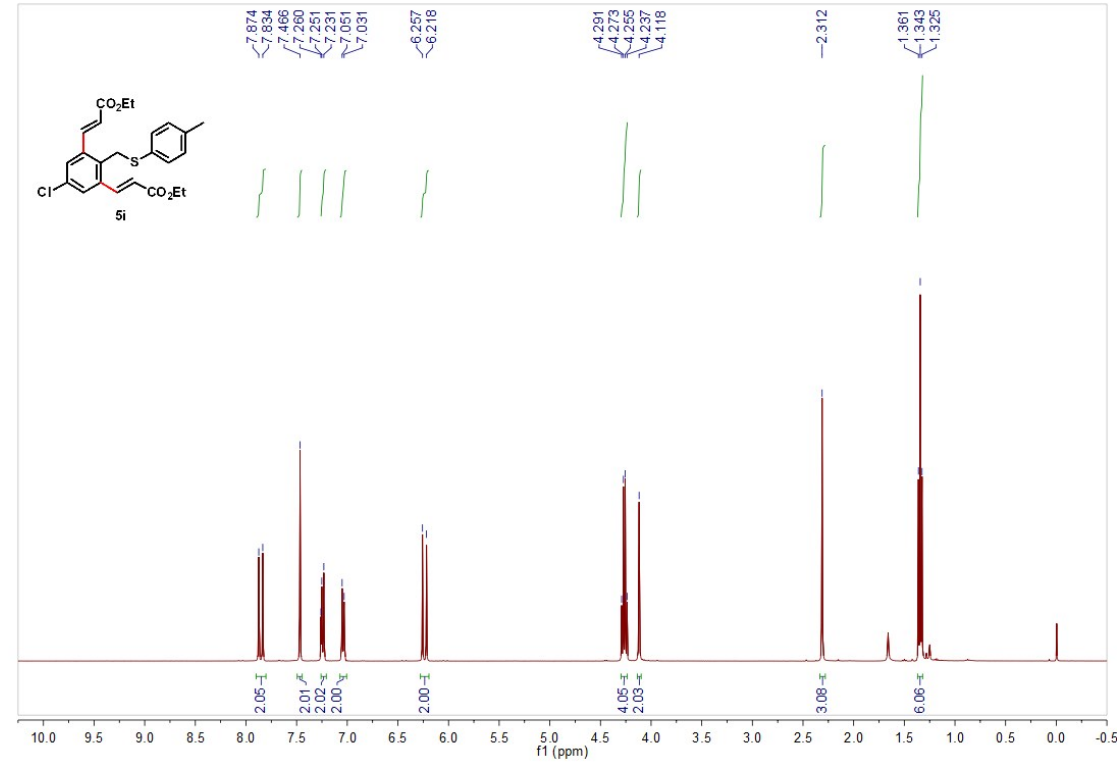

167.069
166.719
159.491
141.392
137.854
136.494
132.953
131.134
129.702
128.689
127.297
124.439
124.229
123.918
118.835
110.303
77.317
77.000
76.681
60.348
60.313
55.640
35.656
21.022
14.246
MeO
S
CO2Et
CO2Et
5f
f1 (ppm)
f1 (ppm)

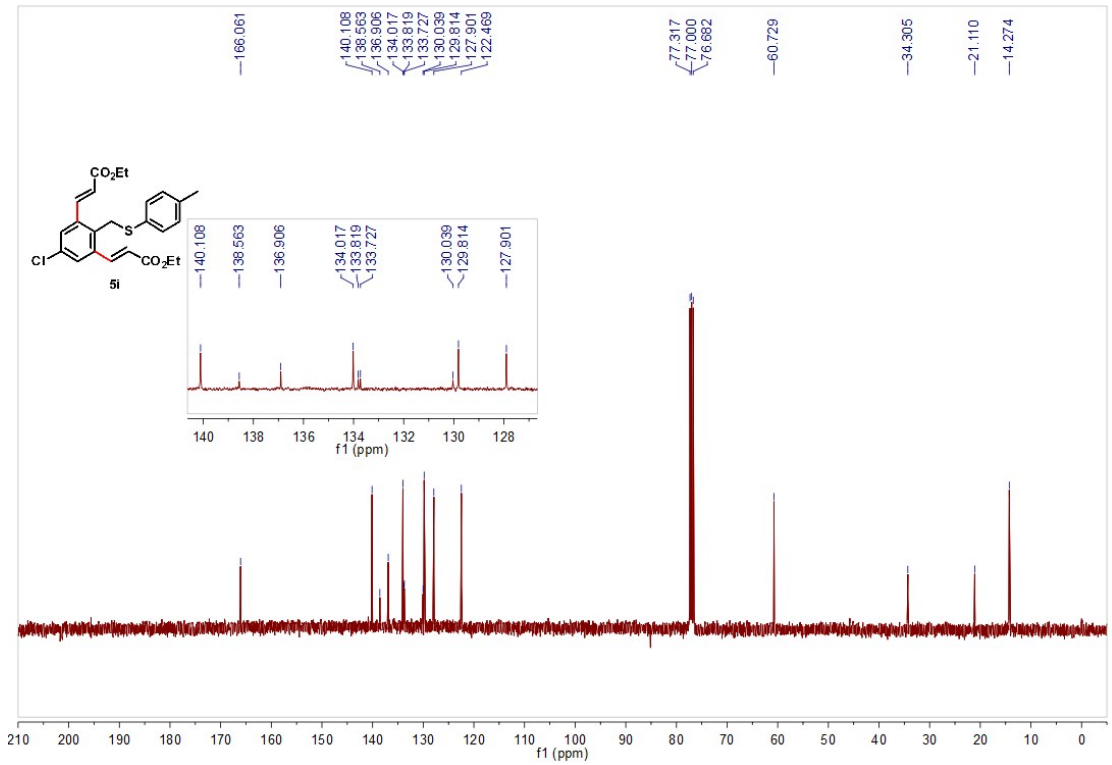

7.974
7.934
7.448
7.428
7.260
7.122
7.103
6.713
6.673
6.450
4.283
4.266
4.248
4.230
4.205
3.906
2.330
1.350
1.332
1.315
MeO
OMe
S
CO2Et
CO2Et
5g
2.12
2.05
2.04
2.00
1.09
4.15
2.06
6.08
3.07
6.05
f1 (ppm)

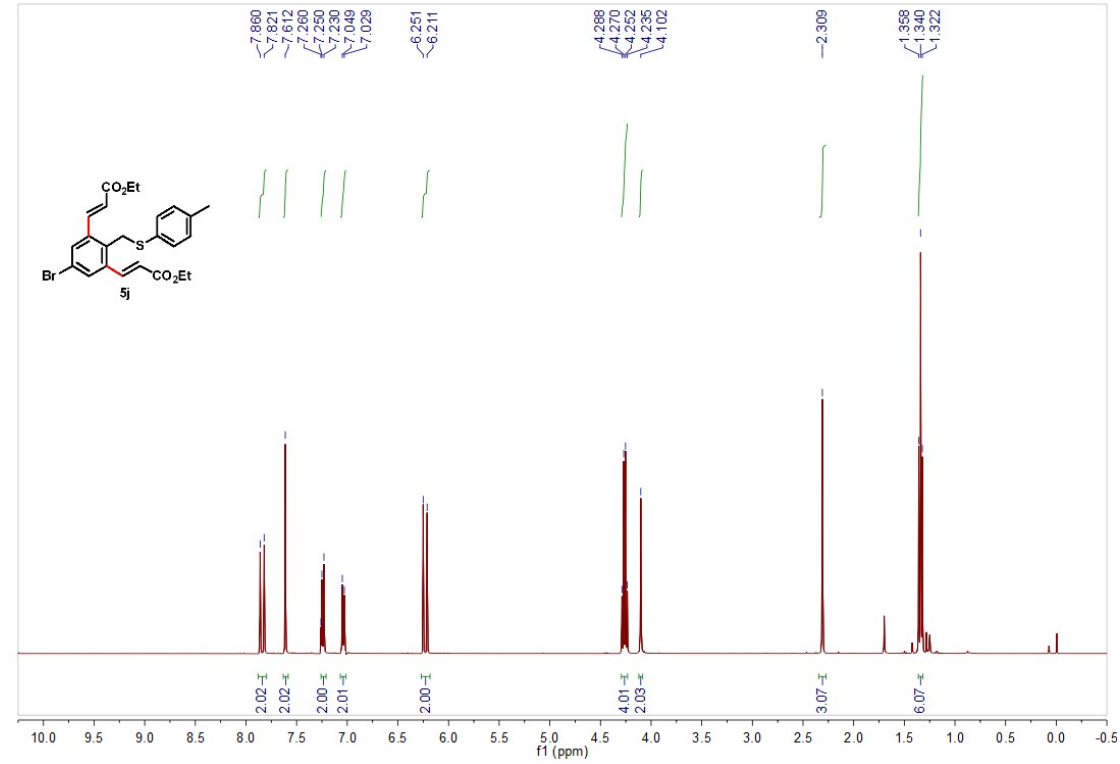

167.691
160.580
138.164
137.860
137.733
132.672
131.522
129.755
122.261
116.441
94.340
77.319
77.000
76.683
60.200
55.561
36.793
21.050
14.297
MeO
OMe
S
CO2Et
CO2Et
5g
f1 (ppm)

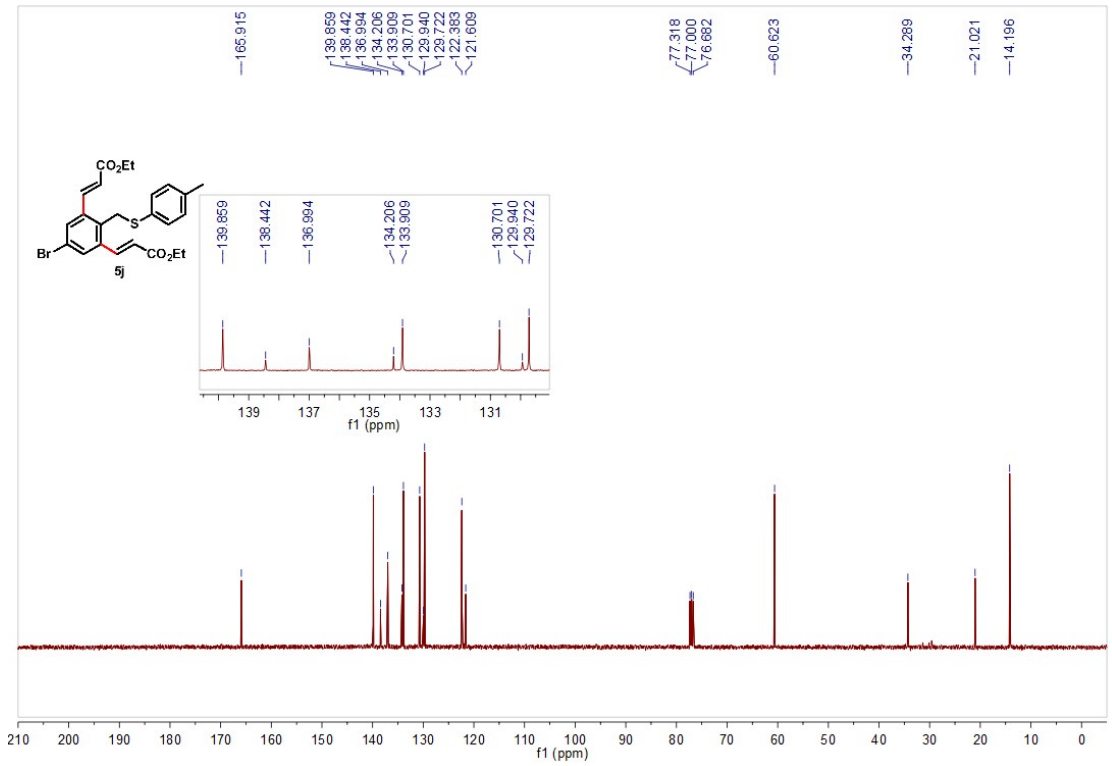

8.024
7.984
7.902
7.900
7.883
7.880
7.580
7.561
7.558
7.542
7.539
7.478
7.470
7.454
7.451
7.435
7.432
7.363
7.344
7.316
7.296
7.260
7.077
6.280
6.251
4.282
4.264
4.246
4.239
4.228
3.684
2.319
1.350
1.332
1.314
CO2Et
CO2Et
OMe
O
S
5h
2.06
0.96
1.03
3.08
1.04
2.00
2.01
2.02
6.05
3.03
3.09
6.01
f1 (ppm)

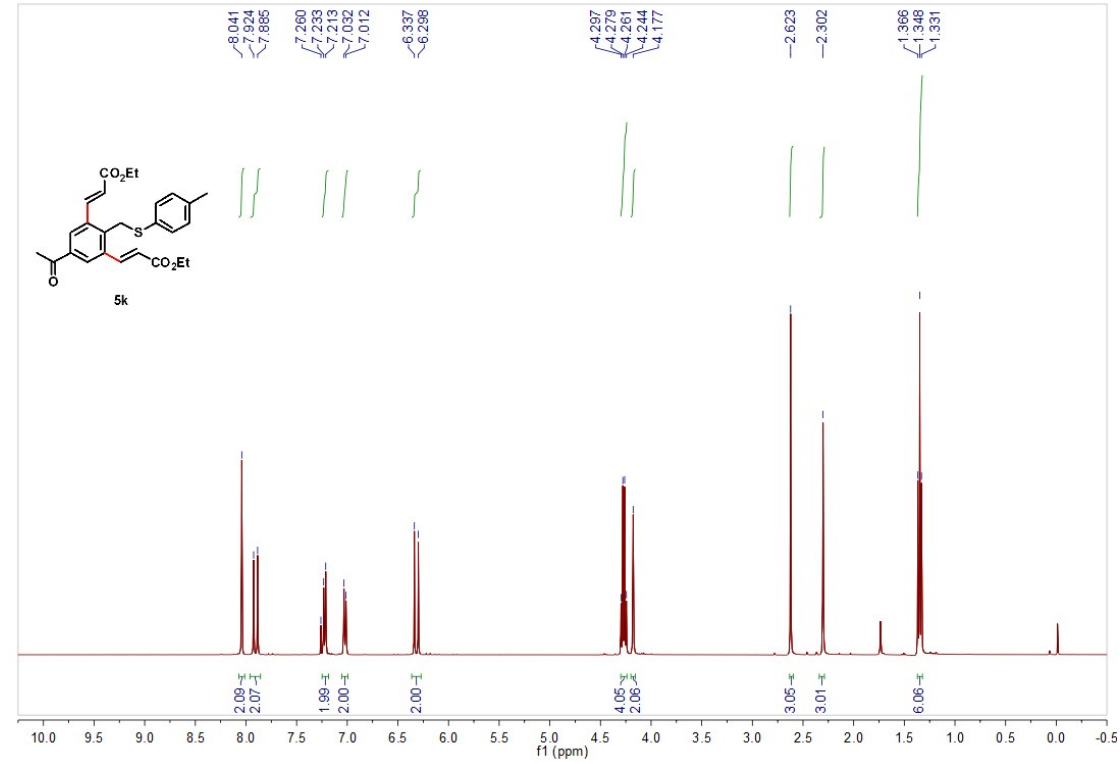

168.307
166.347
141.220
140.947
138.245
134.878
134.067
133.749
131.555
130.561
130.451
130.138
129.718
128.264
77.319
77.000
76.682
60.523
52.047
34.475
21.072
14.239
5h
141.220
140.993
140.947
138.245
134.878
134.067
133.749
131.555
130.561
130.451
130.332
130.138
129.718
128.264
127.795
f1 (ppm)
f1 (ppm)

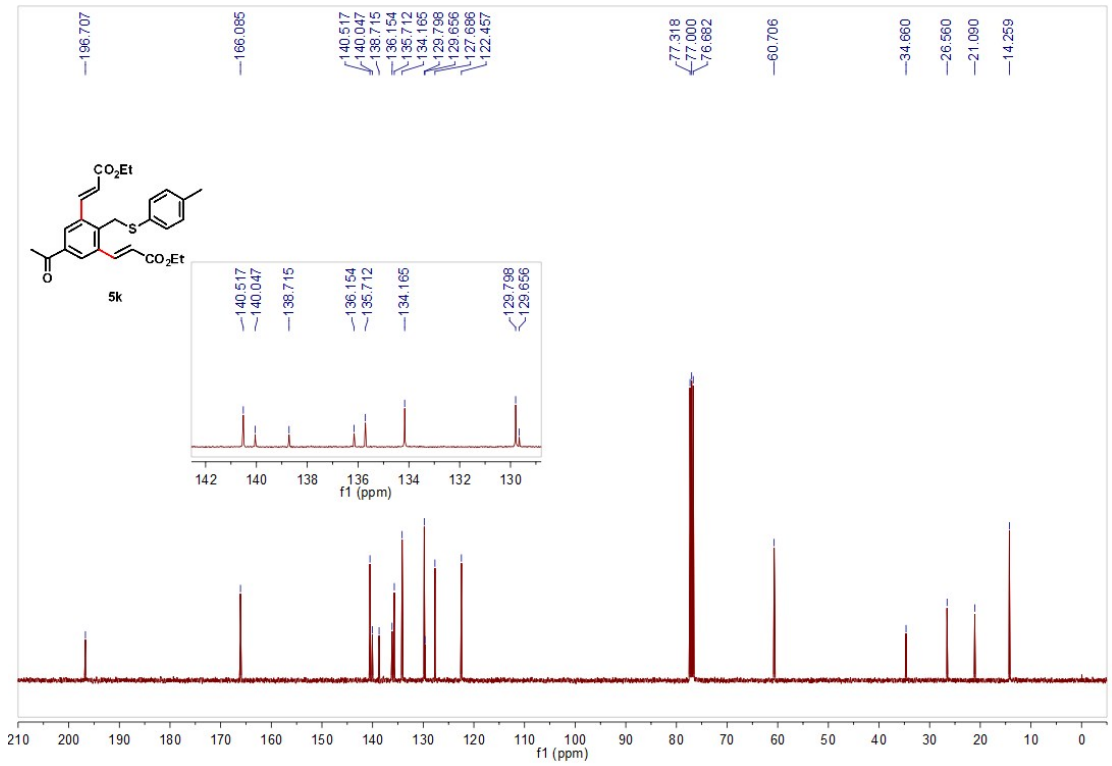

7.874
7.834
7.466
7.260
7.251
7.231
7.051
7.031
6.257
6.218
4.291
4.273
4.255
4.237
4.118
2.312
1.361
1.343
1.325
5i
2.05
2.01
2.02
2.00
2.00
4.05
2.03
3.08
6.06
f1 (ppm)

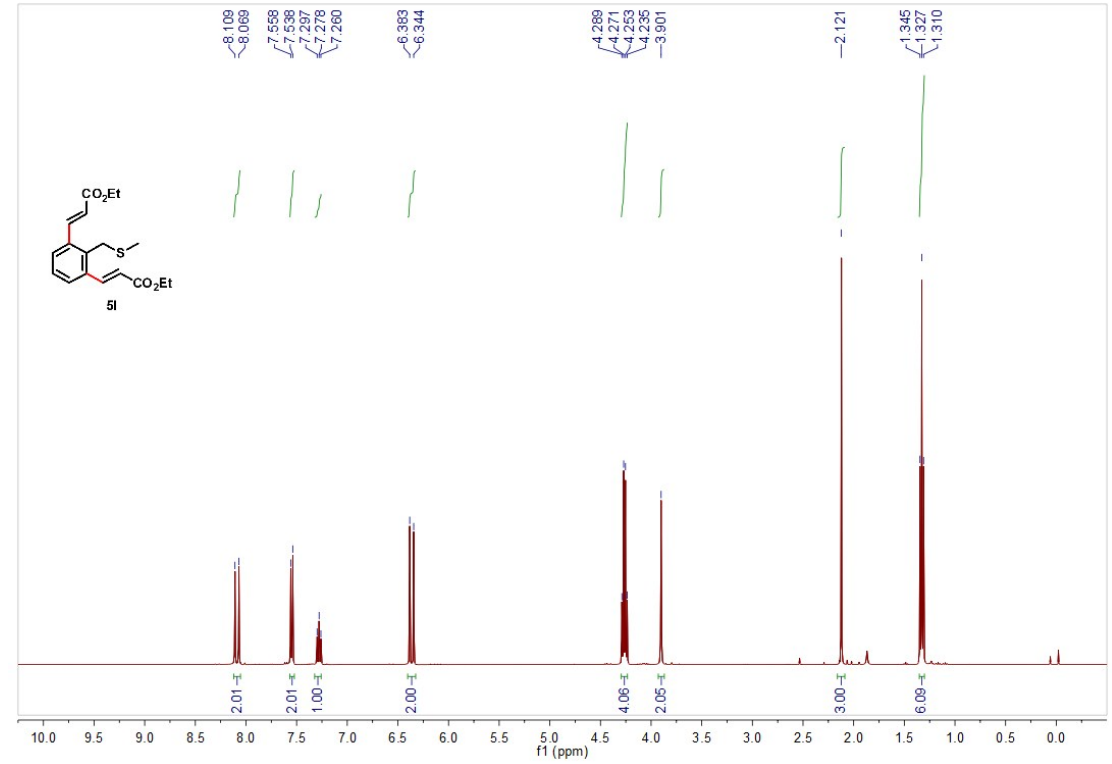

166.061
140.108
138.563
136.906
134.017
133.819
133.727
130.039
129.814
127.901
122.469
77.317
77.000
76.682
60.729
34.305
21.110
14.274
CO2Et
S
Cl
CO2Et
5i
f1 (ppm)
f1 (ppm)

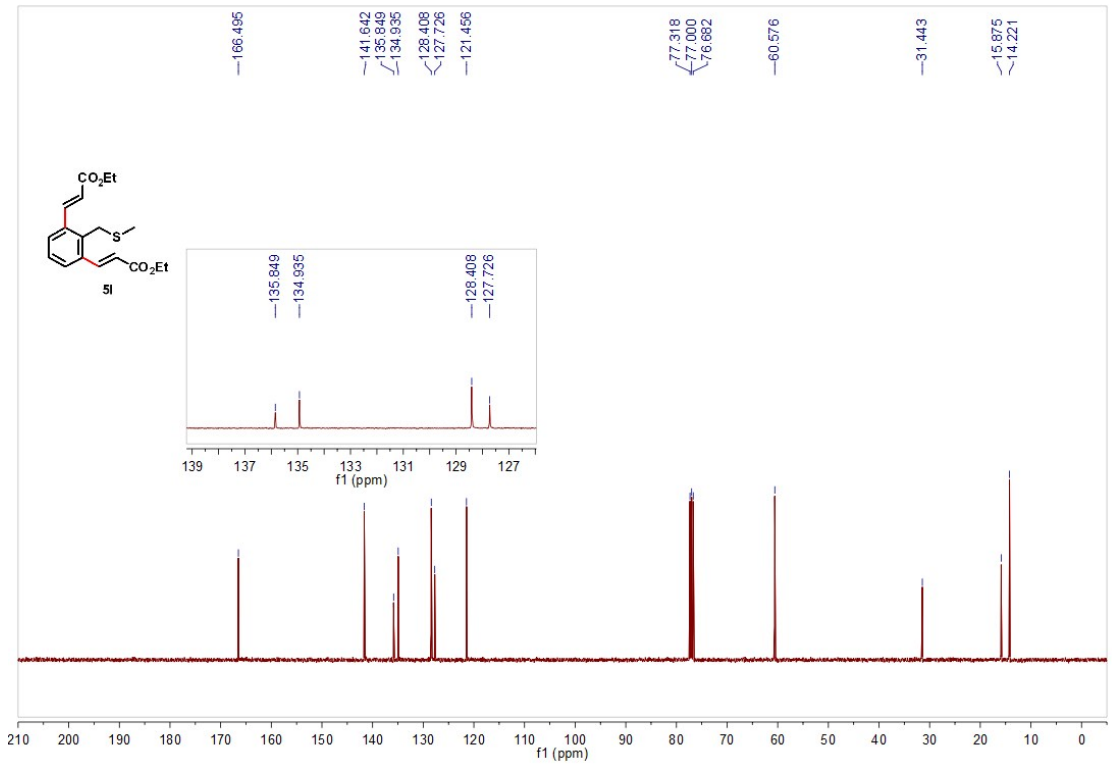

7.860
7.821
7.612
7.260
7.250
7.230
7.049
7.029
6.251
6.211
4.288
4.270
4.252
4.235
4.102
2.309
1.358
1.340
1.322
CO2Et
S
Br
CO2Et
5j
2.02
2.02
2.00
2.01
2.00
4.01
2.03
3.07
6.07
f1 (ppm)


165.915
139.859
138.442
136.994
134.206
133.909
130.701
129.940
129.722
122.383
121.609
77.318
77.000
76.682
60.623
34.289
21.021
14.196
CO2Et
Br
S
CO2Et
5j
f1 (ppm)
f1 (ppm)


8.041
7.924
7.885
7.260
7.233
7.213
7.032
7.012
6.337
6.298
4.297
4.279
4.261
4.244
4.177
2.623
2.302
1.366
1.348
1.331
CO2Et
S
CO2Et
O
5k
2.09
2.07
1.99
2.00
2.00
4.05
2.06
3.05
3.01
6.06
f1 (ppm)


196.707
166.085
140.517
140.047
138.715
136.154
135.712
134.165
129.798
129.656
127.886
122.457
77.318
77.000
76.682
60.706
34.660
26.560
21.090
14.259
CO2Et
S
CO2Et
O
5k
f1 (ppm)
f1 (ppm)


8.109
8.069
7.558
7.538
7.297
7.278
7.260
6.383
6.344
4.289
4.271
4.253
4.235
3.901
2.121
1.345
1.327
1.310
CO2Et
S
CO2Et
5l
2.01
2.01
1.00
2.00
4.06
2.05
3.00
6.09
f1 (ppm)


166.495
141.642
135.849
134.935
128.408
127.726
121.456
77.318
77.000
76.682
60.576
31.443
15.875
14.221
CO2Et
S
CO2Et
5l
135.849
134.935
128.408
127.726
139 137 135 133 131 129 127
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)