

*Supporting Information for*

**Bifunctional squamide-catalyzed asymmetric  
synthesis of chiral  $\alpha$ -mercaptosilanes**

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## I: General Information

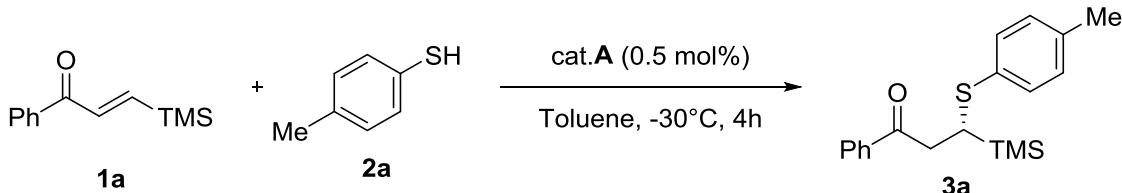
Commercially available materials were purchased from Alfa Aesar and Sigma-Aldrich. THF was distilled over sodium. Other solvents were dried over 4Å molecular sieve prior use. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm,  $\delta$ ) relative to tetramethylsilane ( $\delta$  0.00) or chloroform ( $\delta$  = 7.26, singlet).  $^1\text{H}$  NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), triplet of doublets (dt), triplet of triplets (tt), multiplets (m), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded on a Bruker (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on a Waters Q-TOF Premier Spectrometer. The determination of enantiomeric excess was performed *via* chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Jasco P-1030 polarimeter and are reported as follows:  $[\alpha]_D^{rt}$  ( $c$  is in gm per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness).

## II. General procedure

### a) Synthesis of $\beta$ -silylated enones 1

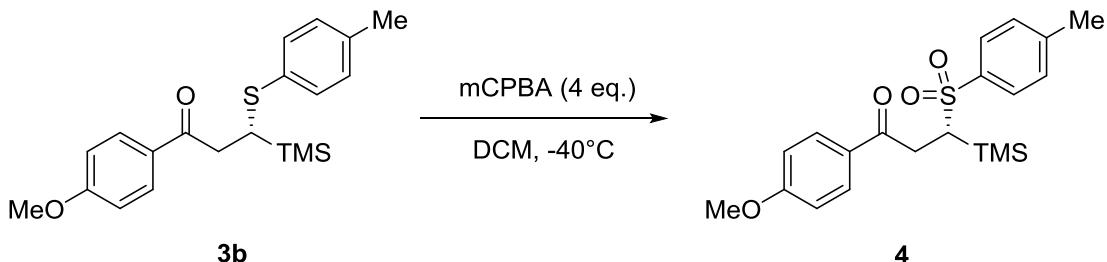
$\beta$ -silyl enones **1a~1q** were synthesized according to the literature.<sup>[1-5]</sup>

### b) General procedure for the reactions of 1 with 2 to synthesize products 3 (3a as an example)



To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar was added **1a** (0.1 mmol, 20.4 mg), **2a** (0.11 mmol, 13.6 mg) and Cat.A (0.0005 mmol, 0.3 mg). To this mixture was added dry Toluene (3.0 mL), then the reaction mixture was stirred at -30 °C for 4 hours. The reaction mixture was purified by flash column chromatography (silica gel, Petroleum ether/EtOAc, 20:1, v/v) to afford product **3a** (0.095 mmol, 31.2 mg) as a colorless oil in 95% yield and 92% ee.

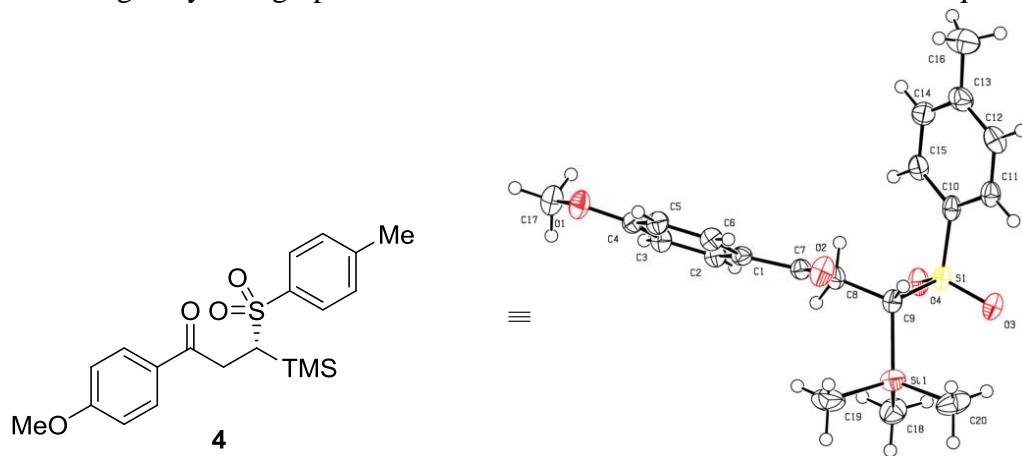
### c) General procedure for the reactions of 4 from 3b



To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar was added **3b** (0.1 mmol, 35.8 mg) and CH<sub>2</sub>Cl<sub>2</sub> (1 mL). The reaction mixture was cooled to -40 °C and added m-CPBA (0.4 mmol, 69.0 mg, 4.0 equiv). The was stirred at -40°C overnight. The reaction mixture was purified by flash column chromatography (silica gel, Petroleum ether/EtOAc, 10:1, v/v) to afford the product **4** (0.095 mmol, 37.1 mg) in 95% yield and 92% ee.

**d) Stereochemistry determination **4** via X-ray crystallographic analysis**

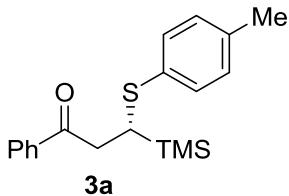
Product **4** was crystallized as a colorless crystal *via* vaporization of a hexane/Dichloromethane solution, and its absolute configuration was determined by x-ray structure analaysis. CCDC 2044606 (DOI: [10.5517/ccdc.csd.cc26ml1h](https://doi.org/10.5517/ccdc.csd.cc26ml1h)) contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



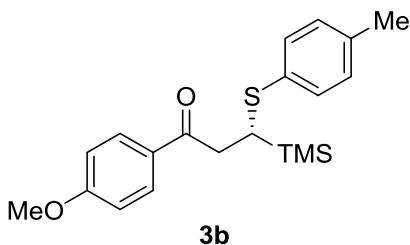
### III. Characterizations of products, reference

Structures of known compounds were confirmed by NMR spectral comparison with literature datas. The compound not reported before, <sup>1</sup>H NMR and <sup>13</sup>C NMR characterization and the corresponding spectra are provided.

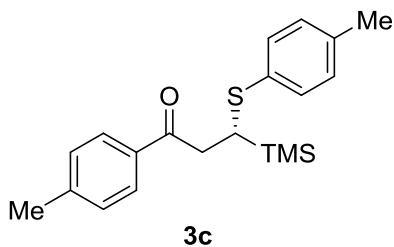
#### a) Characterizations of Products



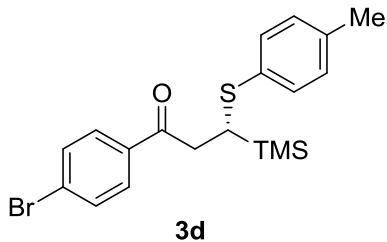
**(S)-1-phenyl-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3a):** colorless oil;  $[\alpha]_D^{23}$  (c 0.372, CHCl<sub>3</sub>) = +18.8; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.13 (s, 9H), 2.26 (s, 3H), 3.18 (dd, *J* = 17.6, 4.4 Hz, 1H), 3.26-3.29 (m, 1H), 3.36-3.42 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.82-7.85 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -2.2, 21.1, 28.2, 41.2, 128.1, 128.6, 129.8, 130.1, 132.9, 133.1, 136.2, 136.9, 199.2; HRMS(ESI) calcd for C<sub>19</sub>H<sub>24</sub>OSSi (M+Na)<sup>+</sup>: 351.1209, Found: 351.1204; 92% ee as determined by HPLC (Chiralcel AD, 95:5 hexanes/*i*-PrOH, 0.3 mL/min), t<sub>r</sub> (minor) = 14.8 min, t<sub>r</sub> (major) = 15.5 min.



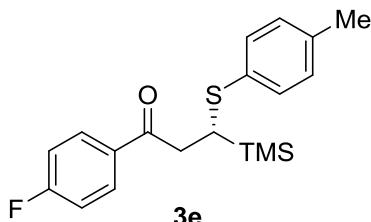
**(S)-1-(4-methoxyphenyl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one(3b):** colorless oil;  $[\alpha]_D^{23}$  (c 0.198, CHCl<sub>3</sub>) = +9.0; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.13 (s, 9H), 2.23 (s, 3H), 3.15 (dd, *J* = 17.2, 4.4 Hz, 1H), 3.26-3.38 (m, 2H), 3.85 (s, 3H), 7.25 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.04 (m, 2H), 7.25 (m, 2H), 7.84 (dt, *J* = 8.8, 2.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -2.2, 21.1, 28.2, 40.7, 55.6, 113.7, 129.8, 129.9, 130.1, 130.4, 133.1, 136.1, 163.5, 197.7; HRMS(ESI) calcd for C<sub>20</sub>H<sub>26</sub>O<sub>2</sub>SSi (M+Na)<sup>+</sup>: 381.1315, Found: 381.1325; 99% ee as determined by HPLC (Chiralcel ADH, 95:5 hexanes/*i*-PrOH, 0.3 mL/min), t<sub>r</sub> (minor) = 20.9 min, t<sub>r</sub> (major) = 23.3 min.



**(S)-1-(p-tolyl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3c):** colorless oil;  $[\alpha]_D^{23}$  (*c* 0.448,  $\text{CHCl}_3$ ) = +18.2;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.14 (s, 9H), 2.27 (s, 3H), 2.39 (s, 3H), 3.17 (dd, *J* = 17.2, 4.0 Hz, 1H), 3.26-3.29 (m, 1H), 3.38 (dd, *J* = 17.6, 8.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.20-7.26 (m, 4H), 7.75 (d, *J* = 8.4 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -2.2, 21.1, 21.7, 28.1, 41.0, 128.2, 129.3, 129.8, 129.9, 133.0, 134.5, 136.1, 143.9, 198.8; HRMS(ESI) calcd for  $\text{C}_{20}\text{H}_{26}\text{OSSi}$  ( $M+\text{Na}^+$ ): 365.1366, Found: 365.1366; 83% *ee* as determined by HPLC (Chiralcel ADH, 95:5 hexanes/*i*-PrOH, 0.3 mL/min),  $t_r$  (minor) = 17.1 min,  $t_r$  (major) = 18.4 min.

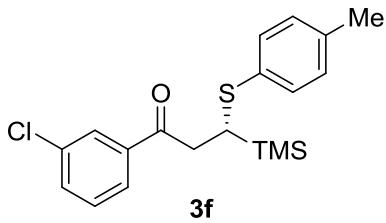


**(S)-1-(4-bromophenyl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3d):** colorless oil;  $[\alpha]_D^{23}$  (*c* 0.525,  $\text{CHCl}_3$ ) = +43.6;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.13 (s, 9H), 2.26 (s, 3H), 3.23 (m, 3H), 7.03 (d, *J* = 6.8 Hz, 2H), 7.23 (d, *J* = 6.8 Hz, 2H), 7.54 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -2.7, 18.2, 34.5, 38.7, 115.6, 115.8, 130.7, 130.8, 133.4, 133.5, 164.4, 166.9, 174.1, 198.3; HRMS(ESI) calcd for  $\text{C}_{19}\text{H}_{23}{^{79}\text{BrOSSi}}$  ( $M+\text{Na}^+$ ): 429.0314, Found: 429.0315. HRMS(ESI) calcd for  $\text{C}_{19}\text{H}_{23}{^{81}\text{BrOSSi}}$  ( $M+\text{Na}^+$ ): 431.0293, Found: 431.0289; 99% *ee* as determined by HPLC (Chiralcel AZH, 99:1 hexanes/*i*-PrOH, 0.2 mL/min),  $t_r$  (major) = 13.5 min,  $t_r$  (minor) = 15.2 min.



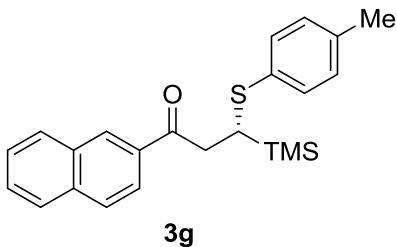
**(S)-1-(4-fluorophenyl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3e):** colorless oil;  $[\alpha]_D^{23}$  (*c* 0.825,  $\text{CHCl}_3$ ) = +88.5;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.13 (s, 9H), 2.26 (s, 3H), 3.13-3.60 (m, 3H), 7.01-7.08 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.83-8.00 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -2.3, 21.1, 28.4, 41.1, 115.6, 115.8, 129.8, 130.2, 130.7, 130.8, 132.8, 133.3, 133.4, 136.3, 164.50, 167.1, 197.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -105.64; HRMS(ESI) calcd for  $\text{C}_{19}\text{H}_{23}\text{FOSSi}$

(M+Na)<sup>+</sup>: 369.1115, Found: 369.1113; 99% ee as determined by HPLC (Chiralcel AZH, 95:5 hexanes/i-PrOH, 0.7 mL/min), t<sub>r</sub> (major) = 65.2 min, t<sub>r</sub> (minor) = 67.3 min.



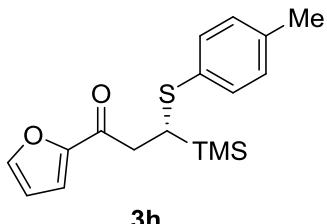
**(S)-1-(3-chlorophenyl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one(3f):**

colorless oil; [α]<sub>D</sub><sup>23</sup> (c 0.712, CHCl<sub>3</sub>) = +36.0; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 0.14 (s, 9H), 2.27 (s, 3H), 3.17 (dd, J = 16.8, 4.8 Hz, 1H), 3.22-3.25 (m, 1H), 3.32 (dd, J = 16.8, 6.8 Hz, 1H), 7.02 (d, J = 8 Hz, 2H), 7.22 (d, J = 8 Hz, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.48-7.50 (m, 1H), 7.69 (dt, J = 8.0, 1.6 Hz, 1H), 7.75 (t, J = 1.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = -2.3, 21.1, 28.6, 41.4, 126.1, 128.2, 129.8, 129.9, 130.4, 132.7, 133.0, 134.9, 136.5, 138.4, 198.1; HRMS(ESI) calcd for C<sub>19</sub>H<sub>23</sub><sup>35</sup>ClOSSi (M+Na)<sup>+</sup>: 385.0820, Found: 385.0818. HRMS(ESI) calcd for C<sub>19</sub>H<sub>23</sub><sup>37</sup>ClOSSi (M+Na)<sup>+</sup>: 387.0790, Found: 387.0791; 93% ee as determined by HPLC (Chiralcel IA, 98:2 hexanes/i-PrOH, 0.2 mL/min), t<sub>r</sub> (minor) = 22.8 min, t<sub>r</sub> (major) = 24.2 min.



**(S)-1-(naphthalen-2-yl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one(3g):**

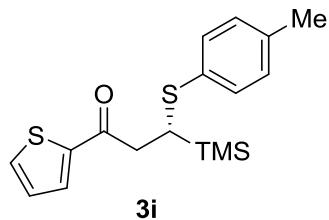
colorless oil; [α]<sub>D</sub><sup>23</sup> (c 0.656, CHCl<sub>3</sub>) = +31.2; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 0.17 (s, 9H), 2.25 (s, 3H), 3.31-3.37 (m, 2H), 3.49-3.56 (m, 1H), 7.03 (d, J = 8 Hz, 2H), 7.28 (d, J = 8 Hz, 2H), 7.53-7.58 (m, 2H), 7.83-7.85 (m, 2H), 7.89-7.93 (m, 2H), 8.32 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = -2.2, 21.1, 28.6, 41.3, 123.9, 126.9, 127.9, 128.5, 128.6, 129.7, 129.7, 129.8, 130.2, 132.5, 132.9, 134.3, 135.6, 136.3, 199.2; HRMS(ESI) calcd for C<sub>23</sub>H<sub>26</sub>OSSi (M+H)<sup>+</sup>: 379.1546, Found: 379.1548; 95% ee as determined by HPLC (Chiralcel ADH, 99:1 hexanes/i-PrOH, 0.3 mL/min), t<sub>r</sub> (minor) = 19.1 min, t<sub>r</sub> (major) = 21.1 min.



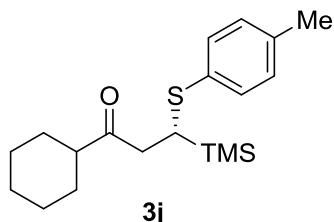
**(S)-1-(furan-2-yl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3h):**

colorless oil; [α]<sub>D</sub><sup>23</sup> (c 0.599, CHCl<sub>3</sub>) = +37.0; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 0.14 (s, 9H), 2.27 (s, 3H), 3.02-3.09 (m, 1H), 3.18-3.25 (m, 2H), 6.49 (q, J = 1.6 Hz, 1H),

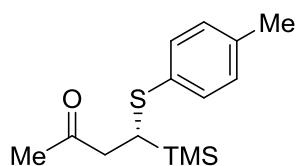
7.03 (d,  $J = 7.6$  Hz, 2H), 7.08 (dd,  $J = 3.6, 0.8$  Hz, 1H), 7.23-7.26 (m, 2H), 7.53 (dd,  $J = 1.6, 0.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = -2.3, 21.1, 28.6, 40.8, 112.3, 117.2, 129.7, 130.4, 132.8, 136.3, 146.4, 152.7, 188.3$ ; HRMS(ESI) calcd for  $\text{C}_{17}\text{H}_{22}\text{O}_2\text{SSi} (\text{M}+\text{H})^+$ : 319.1183, Found: 319.1186; 91% *ee* as determined by HPLC (Chiralcel ADH, 95:5 hexanes/*i*-PrOH, 0.3 mL/min),  $t_r$  ((minor) = 17.3 min,  $t_r$  (major) = 20.1 min.



**(S)-1-(thiophen-2-yl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3i):** colorless oil;  $[\alpha]_D^{23}$  (c 0.235,  $\text{CHCl}_3$ ) = +11.8;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.15$  (s, 9H), 2.27 (s, 3H), 3.13 (dd,  $J = 16, 4.4$  Hz, 1H), 3.21-3.32 (m, 2H), 7.03 (d,  $J = 7.6$  Hz, 2H), 7.08 (dd,  $J = 4.8, 4$  Hz, 1H), 7.24-7.27 (m, 2H), 7.60-7.61 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = -2.3, 21.1, 28.8, 41.7, 128.1, 129.8, 130.3, 131.9, 132.7, 133.8, 136.3, 144.3, 192.0$ ; HRMS(ESI) calcd for  $\text{C}_{17}\text{H}_{22}\text{OS}_2\text{Si} (\text{M}+\text{Na})^+$ : 357.0774, Found: 357.0776; 94% *ee* as determined by HPLC (Chiralcel IA, 99:1 hexanes/*i*-PrOH, 0.2 mL/min),  $t_r$  (major) = 38.5 min,  $t_r$  (minor) = 41.4 min.



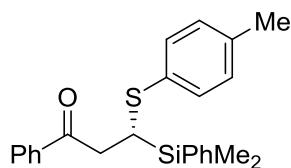
**(S)-1-cyclohexyl-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3j):** colorless oil;  $[\alpha]_D^{23}$  (c 0.674,  $\text{CHCl}_3\text{CHCl}_3$ ) = +54.5;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.09$  (s, 9H), 1.12-1.32 (m, 6H), 1.59-1.75 (m, 5H), 2.28 (s, 3H), 2.69 (dd,  $J = 18.4, 4.2$  Hz, 1H), 2.81 (dd,  $J = 18.4, 7.2$  Hz, 1H), 3.05 (dd,  $J = 7.2, 5.2$  Hz, 1H), 7.05 (d,  $J = 8.0$  Hz, 2H), 7.21 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = -2.3, 21.1, 25.7, 25.8, 25.9, 26.0, 27.2, 28.5, 28.6, 43.2, 51.1, 129.7, 129.8, 129.8, 133.2, 136.0, 162.8$ ; HRMS(ESI) calcd for  $\text{C}_{19}\text{H}_{30}\text{OSSi} (\text{M}+\text{Na})^+$ : 357.1679, Found: 357.1679; 83% *ee* as determined by HPLC (Chiralcel IA, 95:5 hexanes/*i*-PrOH, 0.3 mL/min),  $t_r$  (minor) = 12.5 min,  $t_r$  (major) = 13.2 min.



**3k**

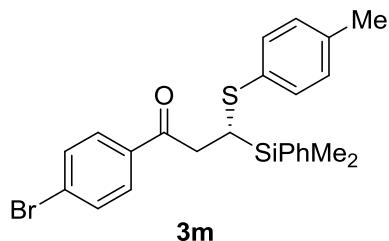
**(S)-4-(p-tolylthio)-4-(trimethylsilyl)butan-2-one (3k):** colorless oil;  $[\alpha]_D^{23}$  (c 0.375,  $\text{CHCl}_3$ ) = +35.2;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.10$  (s, 9H), 2.04 (s, 3H),

2.29 (s, 3H), 2.64-2.82 (m, 2H), 3.00-3.03 (m, 1H), 7.06 (d,  $J$  = 8.0 Hz, 1H), 7.23-7.25 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -2.5, 21.1, 27.9, 30.4, 46.0, 129.8, 130.2, 133.0, 136.3, 207.7; HRMS(ESI) calcd for  $\text{C}_{14}\text{H}_{22}\text{OSSi}$  ( $\text{M}+\text{Na}$ ) $^+$ : 289.1053, Found: 289.1047; 62% ee as determined by HPLC (Chiralcel ADH, 98:2 hexanes/i-PrOH, 0.5 mL/min),  $t_r$  (minor) = 9.0 min,  $t_r$  (major) = 10.3 min



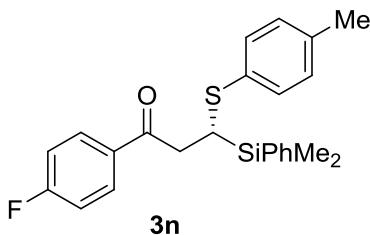
**3l**

**(S)-3-(dimethyl(phenyl)silyl)-1-phenyl-3-(p-tolylthio)propan-1-one (3l):** colorless oil;  $[\alpha]_D^{23}$  (c 0.302,  $\text{CHCl}_3$ ) = +10.4;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.44 (d,  $J$  = 1.6 Hz, 6H), 2.25 (s, 3H), 3.14 (dd,  $J$  = 17.6, 5.2 Hz, 1H), 3.30-3.37 (m, 1H), 3.43-3.46 (dd,  $J$  = 7.2, 5.2 Hz, 1H), 7.20-7.23 (m, 2H), 7.30-7.37 (m, 5H), 7.49 (tt,  $J$  = 7.2, 1.2 Hz, 1H), 7.57-7.60 (m, 2H), 7.70-7.71 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -4.0, -3.5, 21.1, 28.5, 41.3, 127.9, 128.0, 128.5, 129.6, 129.8, 130.5, 132.9, 133.0, 134.3, 136.4, 136.5, 136.9, 199.0; HRMS(ESI) calcd for  $\text{C}_{24}\text{H}_{26}\text{OSSi}$  ( $\text{M}+\text{Na}$ ) $^+$ : 413.1366, Found: 413.1368; 83% ee as determined by HPLC (Chiralcel AD, 95:5 hexanes/i-PrOH, 0.3 mL/min),  $t_r$  (major) = 18.3 min,  $t_r$  (minor) = 21.0 min.



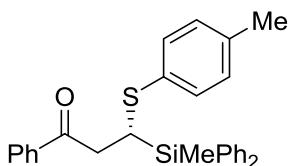
**3m**

**(S)-1-(4-bromophenyl)-3-(dimethyl(phenyl)silyl)-3-(p-tolylthio)propan-1-one (3m):** colorless oil;  $[\alpha]_D^{23}$  (c 0.765,  $\text{CHCl}_3$ ) = +61.7;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.37 (s, 6H), 2.18 (s, 3H), 3.03-3.09 (m, 1H), 3.27 (dd,  $J$  = 17.6, 7.2 Hz, 1H), 3.36-3.39 (m, 1H), 6.92 (d,  $J$  = 8.0 Hz, 2H), 7.14 (d,  $J$  = 8.0 Hz, 2H), 7.25-7.28 (m, 4H), 7.40-7.43 (m, 1H), 7.50-7.52 (m, 2H), 7.63 (d,  $J$  = 7.6 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -4.0, -3.5, 21.1, 28.3, 29.8, 41.2, 128.0, 128.0, 128.5, 128.6, 129.6, 129.8, 129.9, 130.4, 132.9, 133.0, 134.3, 136.4, 136.5, 136.9, 199.1; HRMS(ESI) calcd for  $\text{C}_{24}\text{H}_{25}{^{79}\text{BrOSSi}}$  ( $\text{M}+\text{Na}$ ) $^+$ : 491.0471, Found: 491.0472. HRMS(ESI) calcd for  $\text{C}_{24}\text{H}_{25}{^{81}\text{BrOSSi}}$  ( $\text{M}+\text{Na}$ ) $^+$ : 493.0450, Found: 493.0455; 86% ee as determined by HPLC (Chiralcel ADH, 95:5 hexanes/i-PrOH, 0.3 mL/min),  $t_r$  (major) = 21.7 min,  $t_r$  (minor) = 29.4 min.



**(S)-3-(dimethyl(phenyl)silyl)-1-(4-fluorophenyl)-3-(p-tolylthio)propan-1-one (3n):**

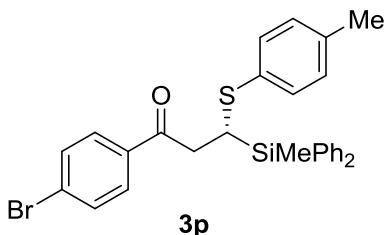
colorless oil;  $[\alpha]_D^{23}$  (c 0.375, CHCl<sub>3</sub>) = +56.5; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.44 (s, 6H), 2.25 (s, 3H), 3.08 (dd, *J* = 17.6, 5.6 Hz, 1H), 3.24-3.30 (m, 1H), 3.41 (dd, *J* = 7.2, 5.6 Hz, 1H), 6.99-7.03 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.30-7.34 (m, 3H), 7.56-7.58 (m, 2H), 7.68-7.72 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -4.2, -3.5, 21.1, 28.6, 41.1, 115.4, 115.6, 127.9, 129.6, 129.8, 130.5, 130.6, 130.7, 134.3, 136.4, 136.5, 197.5; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -105.64; HRMS(ESI) calcd for C<sub>24</sub>H<sub>25</sub>FO<sub>2</sub>Si (M+Na)<sup>+</sup>: 431.1272, Found: 431.1270; 90% ee as determined by HPLC (Chiralcel IA, 99:1 hexanes/*i*-PrOH, 0.2 mL/min), t<sub>r</sub> (minor) = 36.1 min, t<sub>r</sub> (major) = 52.2 min.



**3o**

**(S)-3-(methyldiphenylsilyl)-1-phenyl-3-(p-tolylthio)propan-1-one (3o):**

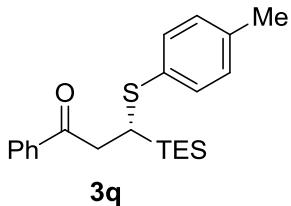
colorless oil;  $[\alpha]_D^{23}$  (c 0.564, CHCl<sub>3</sub>) = +20.0; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.72 (s, 3H), 2.24 (s, 3H), 3.24 (dd, *J* = 17.6, 6.0 Hz, 1H), 3.38-3.44 (m, 1H), 3.86 (t, *J* = 12.4, 6.4 Hz, 1H), 6.96 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8 Hz, 2H), 7.30-7.39 (m, 8H), 7.45-7.49(m, 1H) , 7.61-7.68 (m, 6H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -4.7, 21.1, 27.3, 41.6, 128.0, 128.0, 128.4, 129.7, 129.8, 130.8, 132.8, 132.9, 135.2, 135.2, 136.5, 136.9, 198.7; HRMS(ESI) calcd for C<sub>29</sub>H<sub>28</sub>OSSi (M+H)<sup>+</sup>: 453.1703, Found: 453.1700; 90% ee as determined by HPLC (Chiralcel AD, 95:5 hexanes/*i*-PrOH, 0.3 mL/min), t<sub>r</sub> (major) = 22.6 min, t<sub>r</sub> (minor) = 33.5 min.



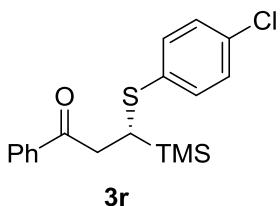
**(S)-1-(4-bromophenyl)-3-(methyldiphenylsilyl)-3-(p-tolylthio)propan-1-one**

**(3p):** colorless oil;  $[\alpha]_D^{23}$  (c 0.220, CHCl<sub>3</sub>) = +55.3; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.72 (s, 3H), 2.24 (s, 3H), 3.24 (dd, *J* = 17.6, 6.0 Hz, 1H), 3.38-3.44 (m, 1H), 3.86 (t, *J* = 12.4, 6.4 Hz, 1H), 6.96 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.30-7.39 (m, 7H), 7.45-7.49(m, 1H) , 7.61-7.68 (m, 6H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -4.7, 21.1, 27.3, 41.6, 127.9, 128.0, 128.4, 129.7, 129.8, 130.8, 132.8, 132.9, 135.2, 135.2,

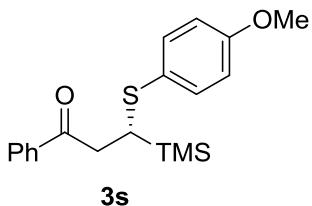
136.5, 136.9, 198.7; HRMS(ESI) calcd for  $C_{29}H_{27}{^{79}BrOSSi}$  ( $M+Na$ ) $^+$ : 553.0627, Found: 553.0625. HRMS(ESI) calcd for  $C_{29}H_{27}{^{81}BrOSSi}$  ( $M+Na$ ) $^+$ : 555.0606, Found: 555.0605; 90% *ee* as determined by HPLC (Chiralcel AD, 95:5 hexanes/*i*-PrOH, 1.0 mL/min),  $t_r$  (major) = 8.1 min,  $t_r$  (minor) = 17.4 min.



**(S)-1-phenyl-3-(p-tolylthio)-3-(triethylsilyl)propan-1-one (3q):** colorless oil;  $[\alpha]_D^{23}$  (c 0.420, CHCl<sub>3</sub>) = +45.3; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.69 (q,  $J$  = 8.0 Hz, 6H), 1.01 (t,  $J$  = 8.0 Hz, 9H), 2.25 (s, 3H), 3.19-3.27 (m, 1H), 3.37-3.46 (m, 2H), 7.00 (d,  $J$  = 4.0 Hz, 2H), 7.22 (d,  $J$  = 8.0 Hz, 2H), 7.31-7.41 (m, 2H), 7.49-7.54 (m, 1H), 7.79-7.82 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.8, 7.7, 21.1, 25.6, 41.7, 128.1, 128.2, 128.6, 129.7, 130.1, 133.0, 133.1, 136.1, 136.9, 199.1; HRMS(ESI) calcd for  $C_{22}H_{31}OSSi^+$  ( $M+H$ ) $^+$ : 371.1859, Found: 371.1860. 96% *ee* as determined by HPLC (Chiralcel OJH, 99:1 hexanes/*i*-PrOH, 0.2 mL/min),  $t_r$  (major) = 32.4 min,  $t_r$  (minor) = 35.1 min.

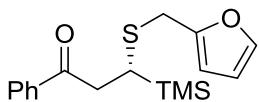


**(S)-3-((4-chlorophenyl)thio)-1-phenyl-3-(trimethylsilyl)propan-1-one (3r):** colorless oil;  $[\alpha]_D^{23}$  (c 0.764, CHCl<sub>3</sub>) = +37.9; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.13 (s, 9H), 3.16 (dd,  $J$  = 17.6, 7.6 Hz, 1H), 3.30 (dd,  $J$  = 7.2, 4.8 Hz, 1H), 3.41 (dd,  $J$  = 17.6, 7.6 Hz, 1H), 7.16 (d,  $J$  = 8.4 Hz, 2H), 7.25 (d,  $J$  = 8.4 Hz, 2H), 7.42 (t,  $J$  = 7.6 Hz, 2H), 7.52-7.56 (m, 1H), 7.84 (d,  $J$  = 7.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -2.3, 27.8, 41.0, 128.1, 128.7, 129.1, 130.6, 132.0, 133.3, 135.4, 136.7, 199.0; HRMS(ESI) calcd for  $C_{18}H_{21}{^{35}ClNaOSSi}^+$  ( $M+Na$ ) $^+$ : 371.0663, Found: 371.0662. HRMS(ESI) calcd for  $C_{18}H_{21}{^{37}ClNaOSSi}^+$  ( $M+Na$ ) $^+$ : 373.0633, Found: 373.0628; 25% *ee* as determined by HPLC (Chiralcel AZH, 99:1 hexanes/*i*-PrOH, 0.2 mL/min),  $t_r$  (major) = 31.5 min,  $t_r$  (minor) = 35.3 min.



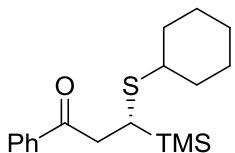
**(S)-3-((4-methoxyphenyl)thio)-1-phenyl-3-(trimethylsilyl)propan-1-one (3s):** colorless liquid;  $[\alpha]_D^{23}$  (c 0.375, CHCl<sub>3</sub>) = +56.1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.13 (s, 9H), 3.13-3.21 (m, 2H), 3.29-3.35 (m, 1H), 3.74 (s, 1H), 6.75 (d,  $J$  = 8.4 Hz,

2H), 7.31 (d,  $J$  = 8.0 Hz, 2H), 7.39-7.42 (m, 2H), 7.52 (t,  $J$  = 7.2 Hz, 2H), 7.81 (d,  $J$  = 7.6 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -2.2, 30.1, 41.1, 55.4, 114.6, 126.8, 128.1, 128.6, 132.8, 133.1, 133.3, 136.9, 159.0, 199.3.; HRMS(ESI) calcd for  $\text{C}_{19}\text{H}_{24}\text{O}_2\text{SSi}$  ( $\text{M}+\text{H}$ ) $^+$ : 345.1339, Found: 345.1340; 85% ee as determined by HPLC (Chiralcel IA, 99:1 hexanes/*i*-PrOH, 0.2 mL/min),  $t_r$ (major) = 47.7 min,  $t_r$ (minor) = 57.9 min.



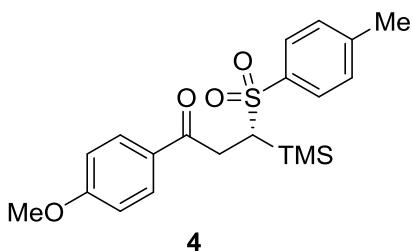
**3t**

**(S)-3-((furan-2-ylmethyl)thio)-1-phenyl-3-(trimethylsilyl)propan-1-one (3t):** colorless oil;  $[\alpha]_D^{23}$  (c 0.556,  $\text{CHCl}_3$ ) = +41.1;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.18 (s, 9H), 2.62 (dd,  $J$  = 6.8, 6.0 Hz, 1H), 3.26-3.28 (m, 2H), 3.65 (d,  $J$  = 14.4 Hz, 1H), 3.81 (d,  $J$  = 14.4 Hz, 1H), 6.15-7.23 (m, 2H), 7.28-7.29 (m, 1H), 7.45-7.49 (m, 2H), 7.55-7.59 (m, 1H), 7.94-7.96 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -2.7, 25.1, 30.4, 42.2, 108.0, 110.5, 128.2, 128.7, 133.22, 137.2, 142.1, 151.7, 199.7; HRMS(ESI) calcd for  $\text{C}_{17}\text{H}_{22}\text{O}_2\text{SSi}$  ( $\text{M}+\text{Na}$ ) $^+$ : 341.1002, Found: 341.1005; 25% ee as determined by HPLC (Chiralcel ADH, 99:1 hexanes/*i*-PrOH, 0.2 mL/min),  $t_r$ (minor) = 41.4 min,  $t_r$ (major) = 44.4 min.



**3u**

**(S)-3-(cyclohexylthio)-1-phenyl-3-(trimethylsilyl)propan-1-one (3u):** colorless oil;  $[\alpha]_D^{23}$  (c 0.343,  $\text{CHCl}_3$ ) = +42.1;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.09 (s, 9H), 1.20-1.24 (m, 5H), 1.53-1.56 (m, 1H), 1.67-1.79 (m, 3H), 2.00-2.05 (m, 1H), 2.57-2.62 (m, 1H), 2.74 (t,  $J$  = 6.4 Hz, 1H), 7.31 (dd,  $J$  = 6.4 Hz,  $J$  = 2.4 Hz, 2H), 7.45-7.49 (m, 2H), 7.55-7.59 (m, 1H), 7.96-7.98 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -2.5, 23.5, 25.9, 26.0, 26.3, 33.5, 33.9, 42.9, 44.6, 128.2, 128.7, 133.2, 137.3, 199.9; HRMS(ESI) calcd for  $\text{C}_{18}\text{H}_{28}\text{OSSi}$  ( $\text{M}+\text{H}$ ) $^+$ : 320.1630, Found: 320.1621; 99% ee as determined by HPLC (Chiralcel ASH, 98:2 hexanes/*i*-PrOH, 0.2 mL/min),  $t_r$  (major) = 24.3 min.



**4**

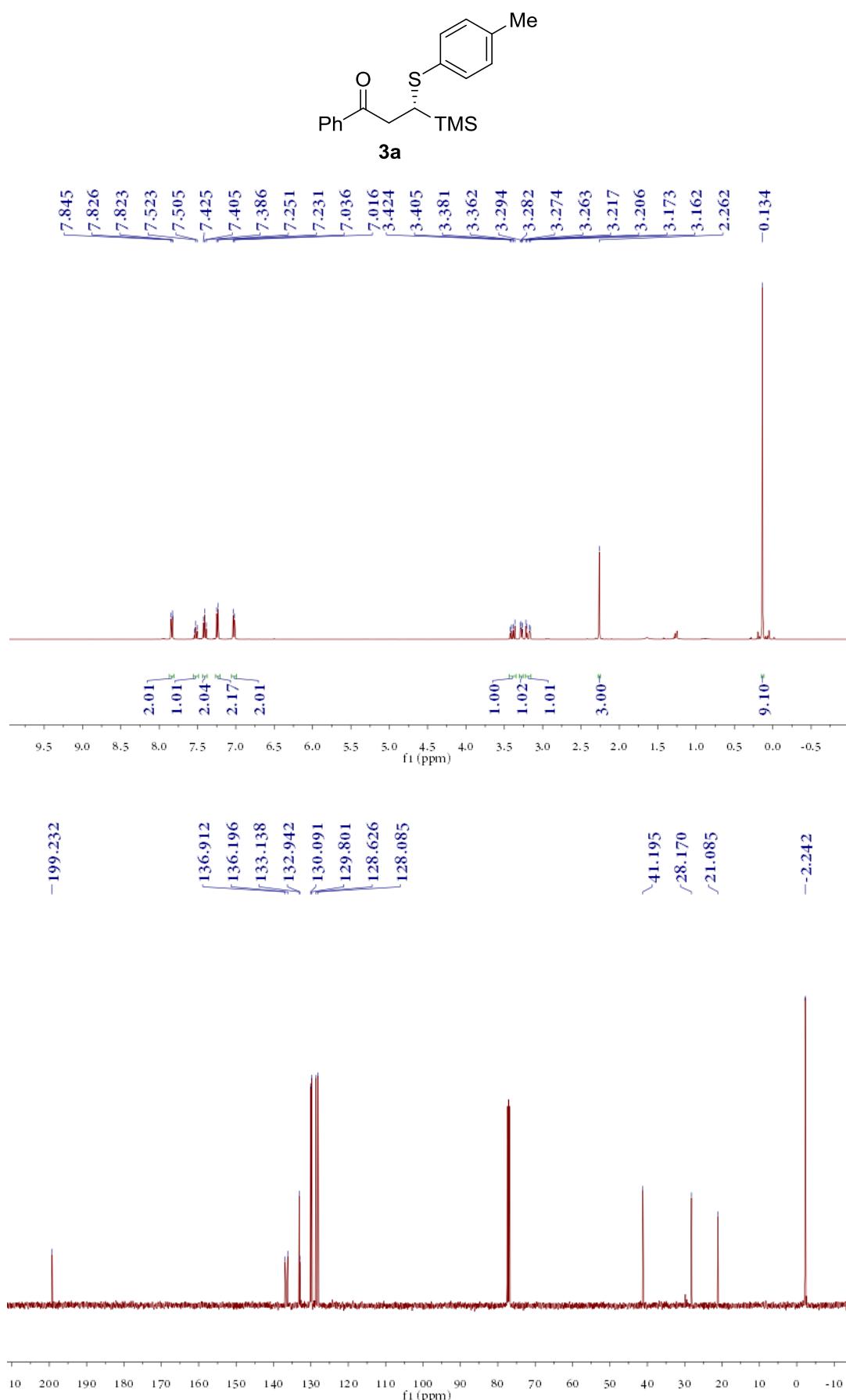
**(S)-1-(4-methoxyphenyl)-3-tosyl-3-(trimethylsilyl)propan-1-one (4):** white solid;  $[\alpha]_D^{23}$  (c 1.025,  $\text{CHCl}_3$ ) = +66.4;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.28 (s, 9H), 2.31 (s, 3H), 3.17 (dd,  $J$  = 18.4, 6.0 Hz, 1H), 3.31 (dd,  $J$  = 18.8, 5.2 Hz, 1H), 3.82 (dd,  $J$  =

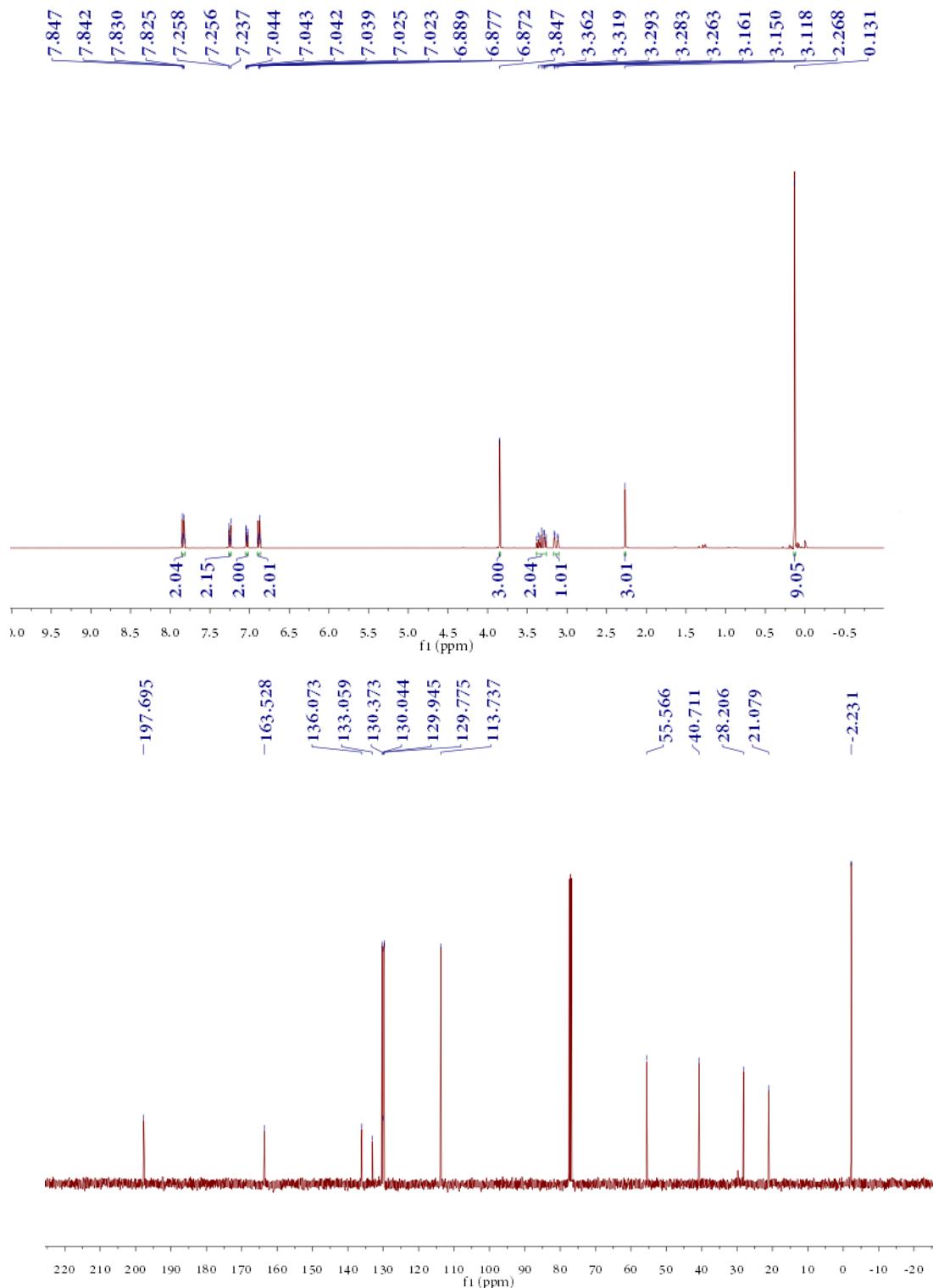
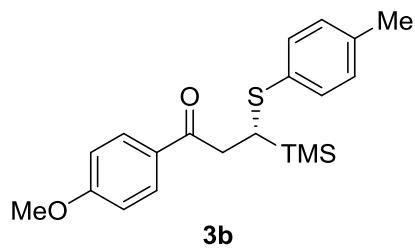
6.0, 5.2 Hz, 1H), 3.85 (s, 3H), 6.85-6.89 (m, 2H), 7.17 (d,  $J$  = 7.6 Hz, 2H), 7.68-7.70 (m, 2H), 7.73-7.77 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -1.0, 21.6, 34.8, 50.2, 55.6, 113.8, 128.1, 129.0, 129.7, 130.3, 137.5, 143.9, 163.9, 193.9; HRMS(ESI) calcd for  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{SSI} (\text{M}+\text{Na})^+$ : 413.1213, Found: 413.1213; 92% ee as determined by HPLC (Chiralcel ODH, 98:2 hexanes/*i*-PrOH, 0.5 mL/min),  $t_r$ (major) = 59.2 min,  $t_r$ (minor) = 80.1 min.

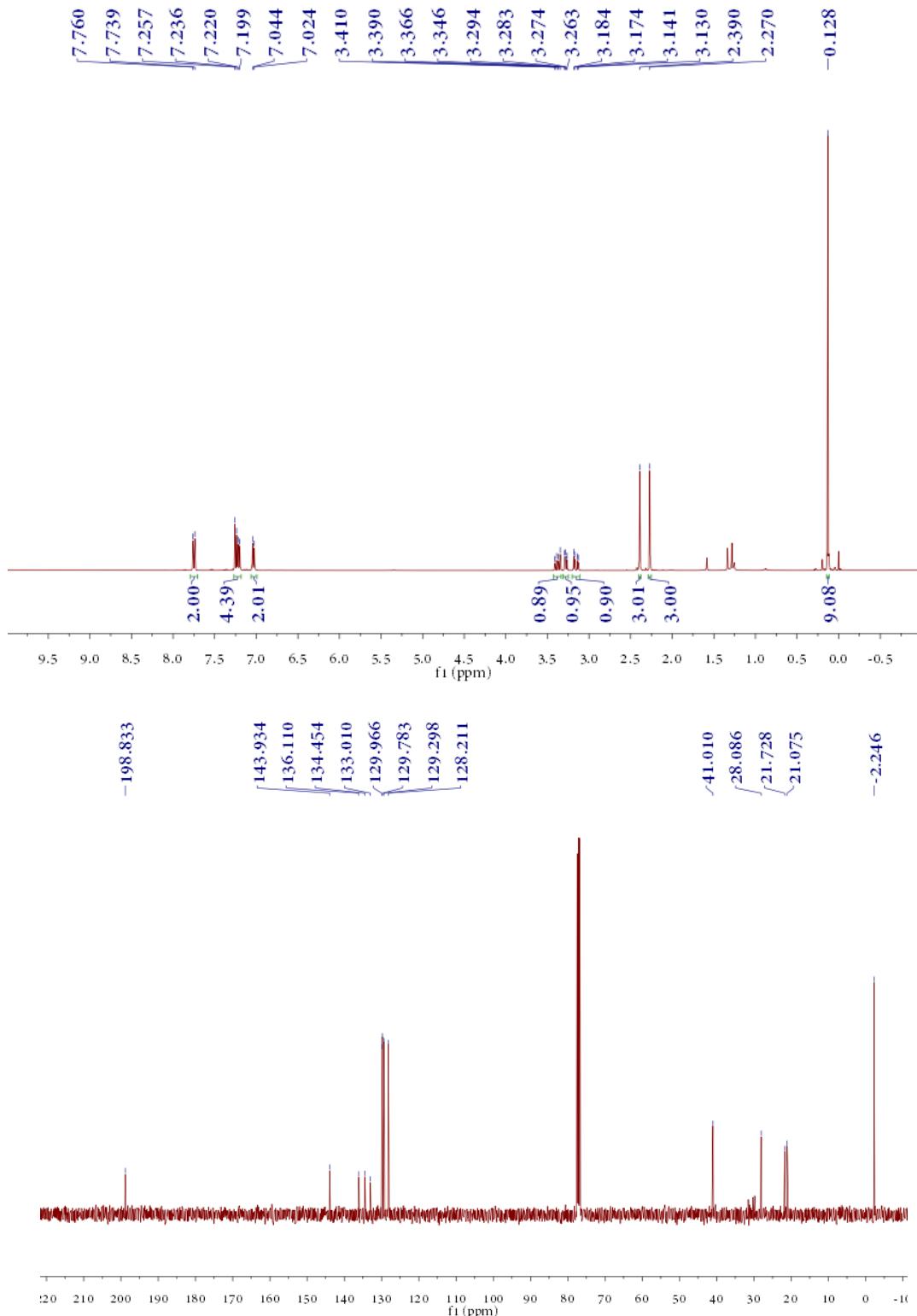
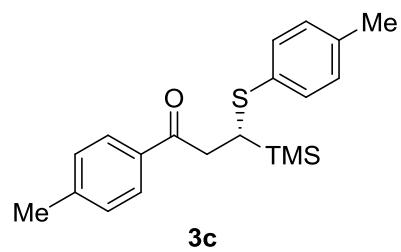
**b) References**

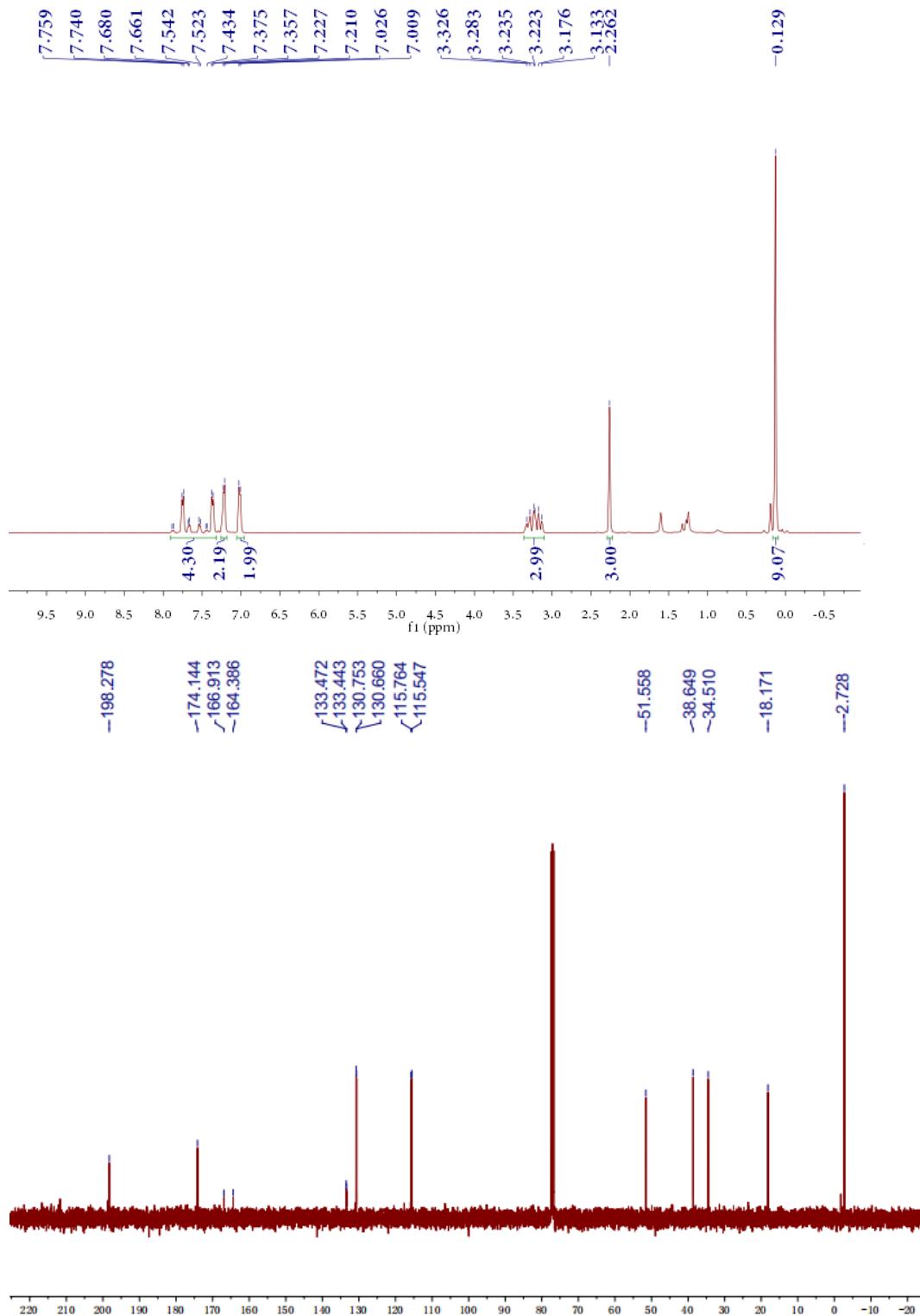
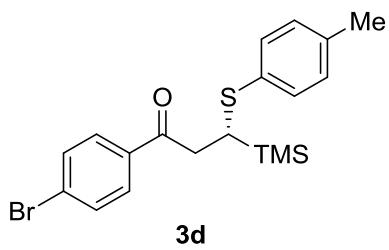
- (1) A. Mizuno, H. Kusama, N. Iwasawa, *Angew. Chem. Int. Ed.*, 2009, **48**, 8318-8320.
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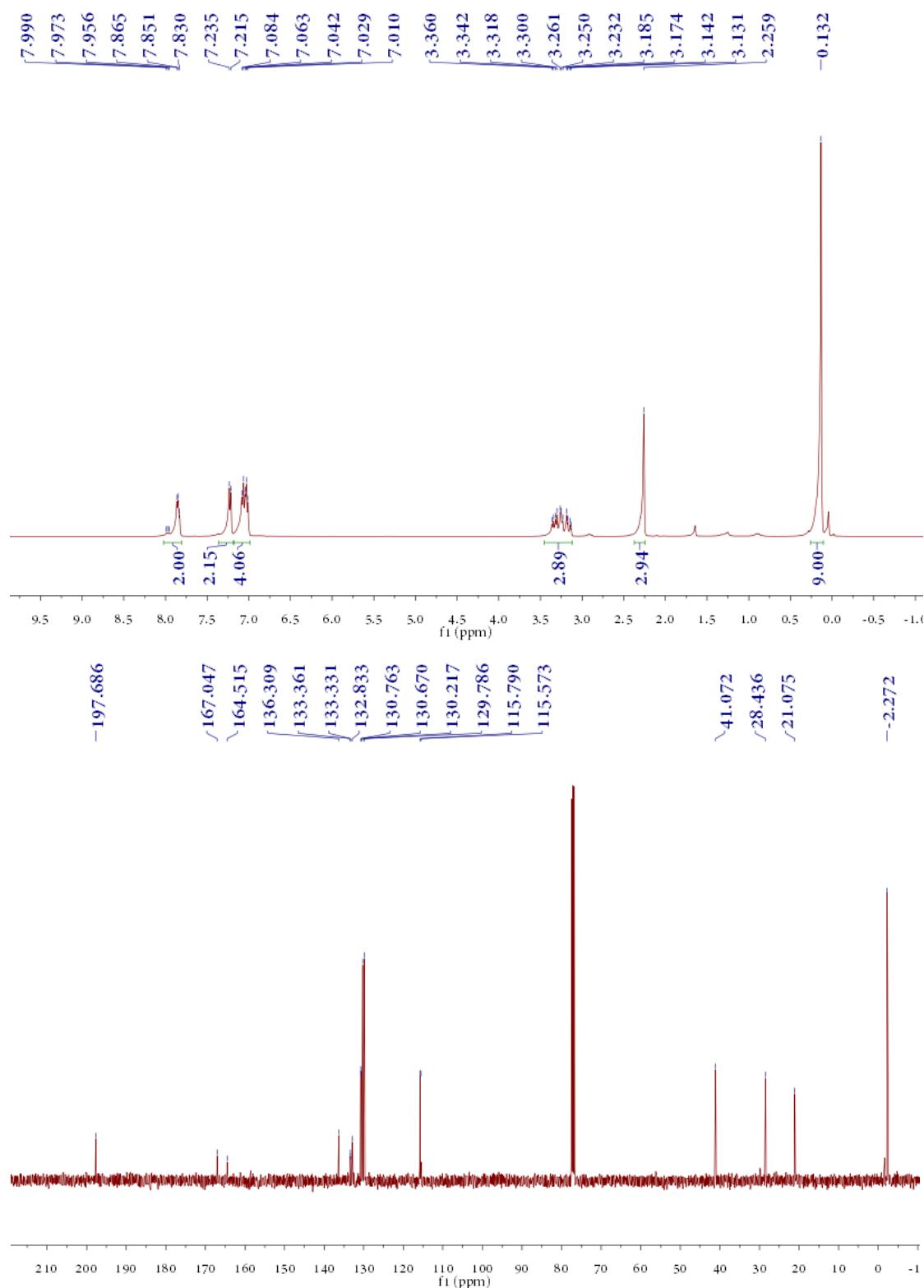
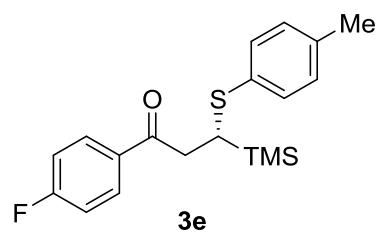
**IV:  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  NMR and HPLC dates of products**

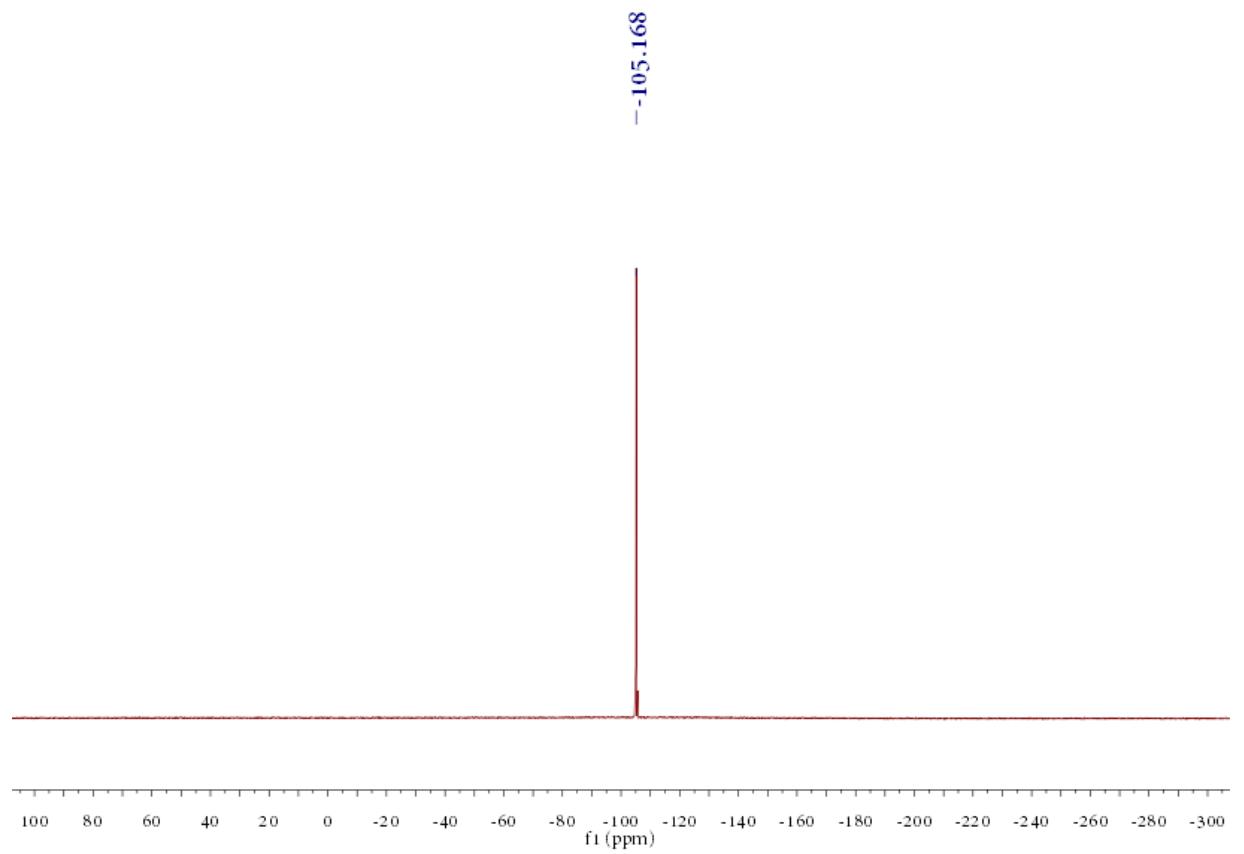


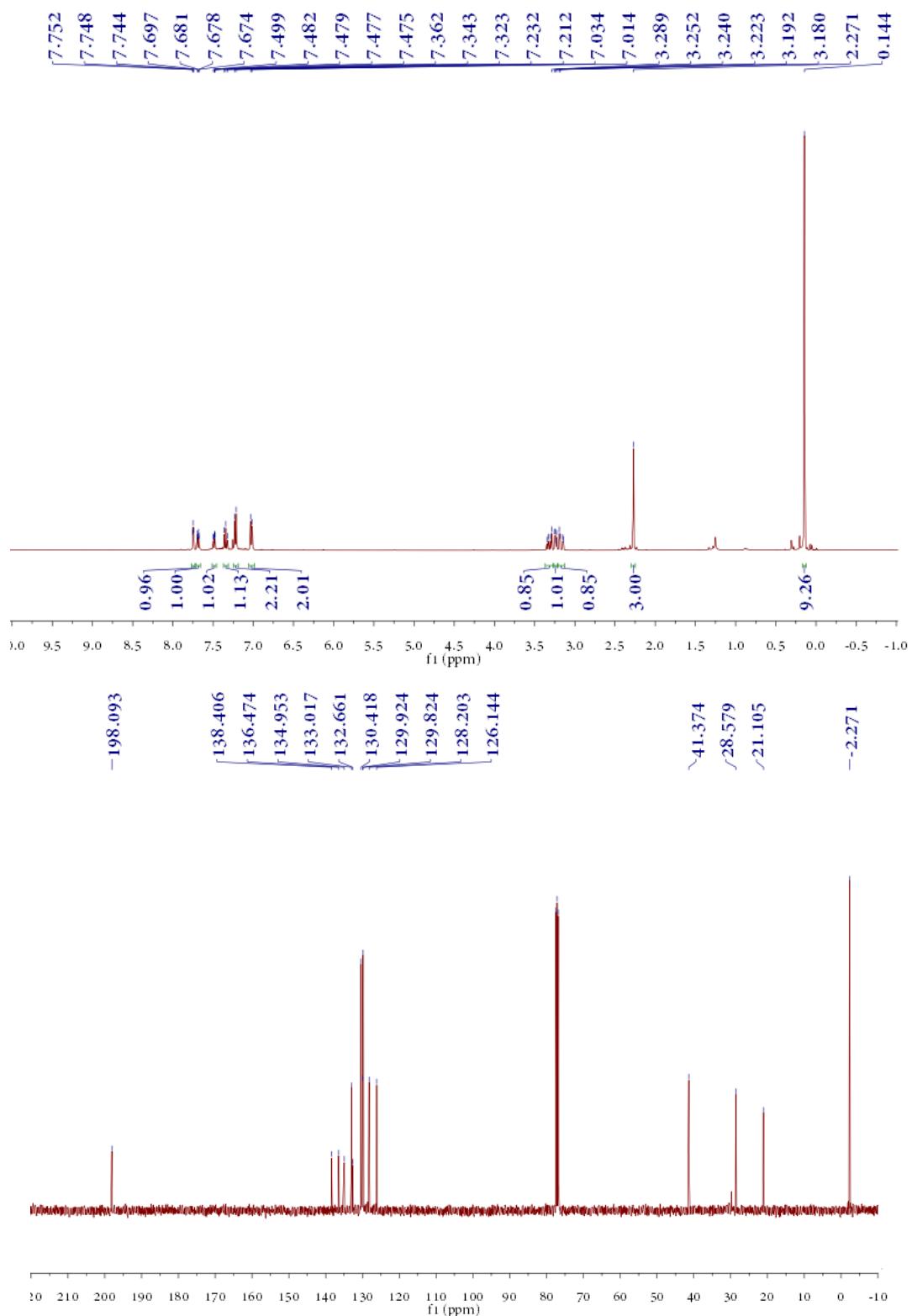
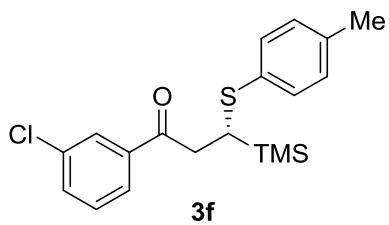


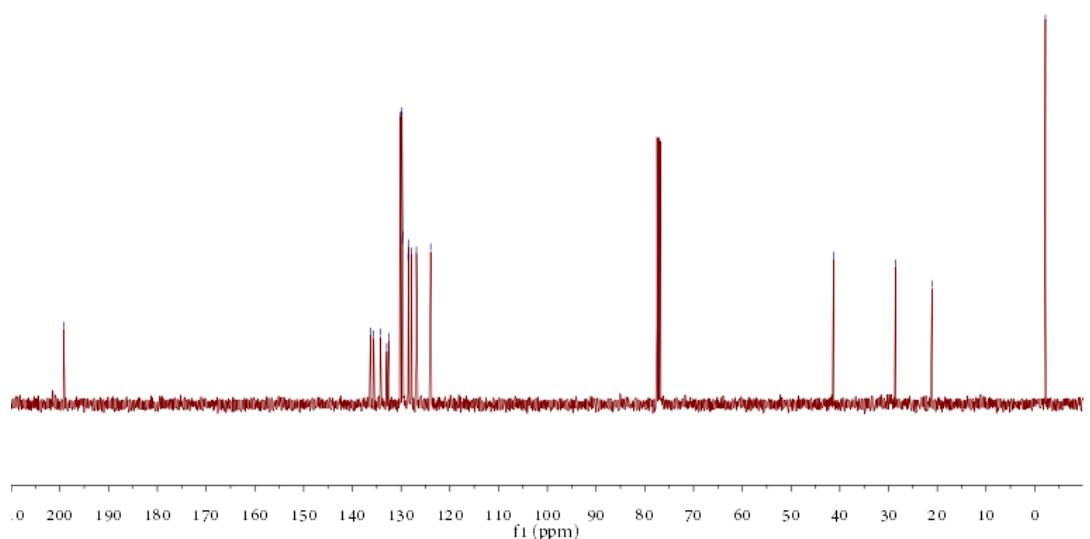
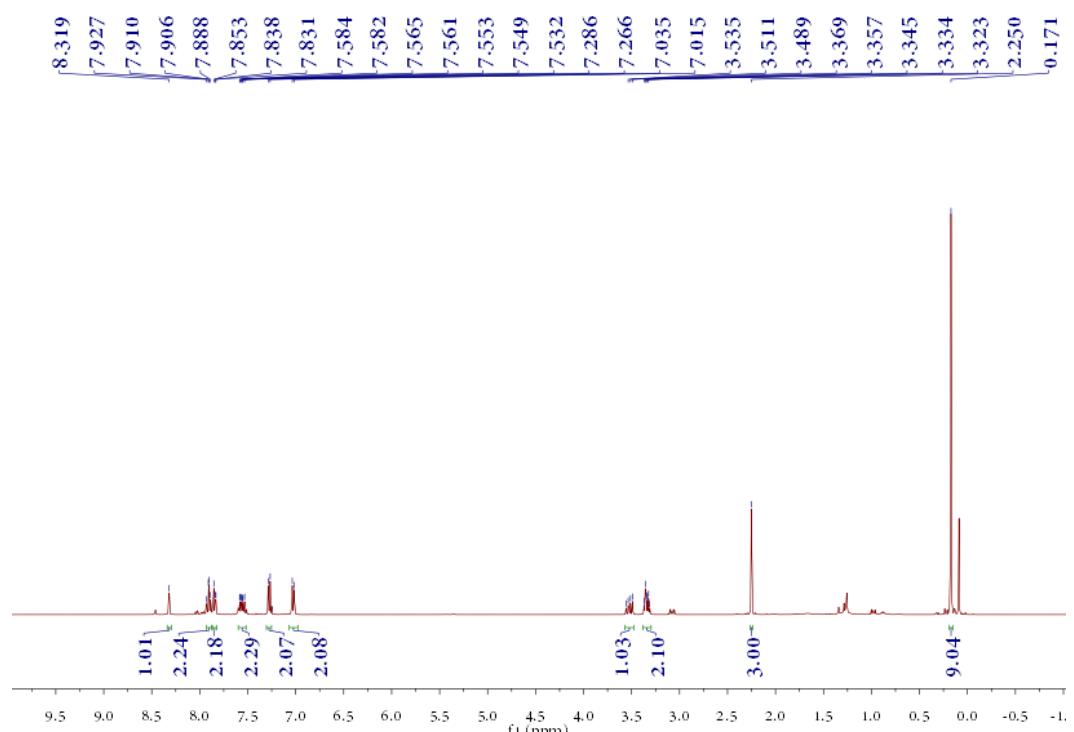
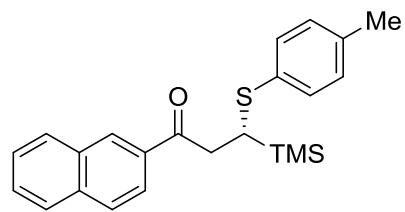


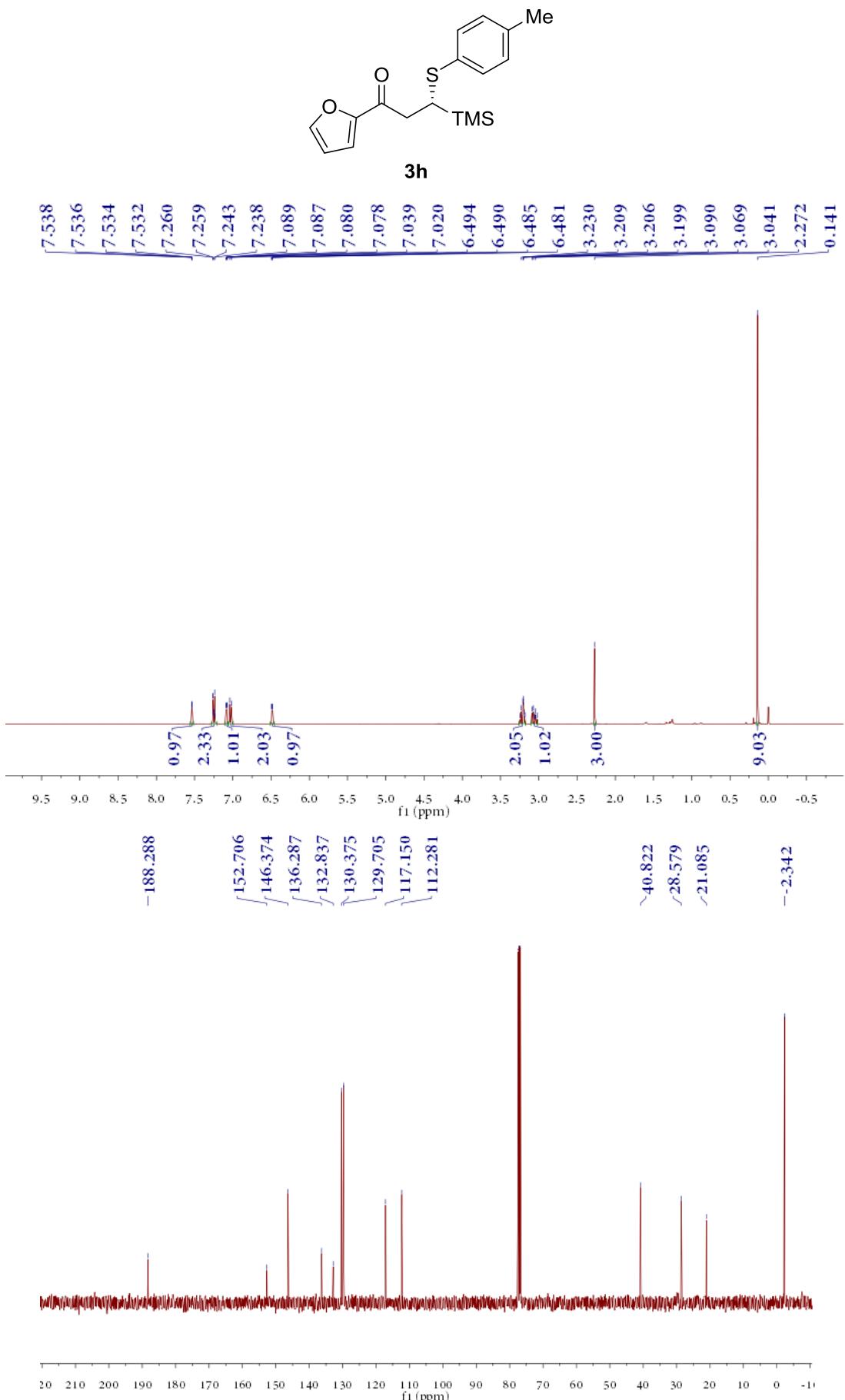


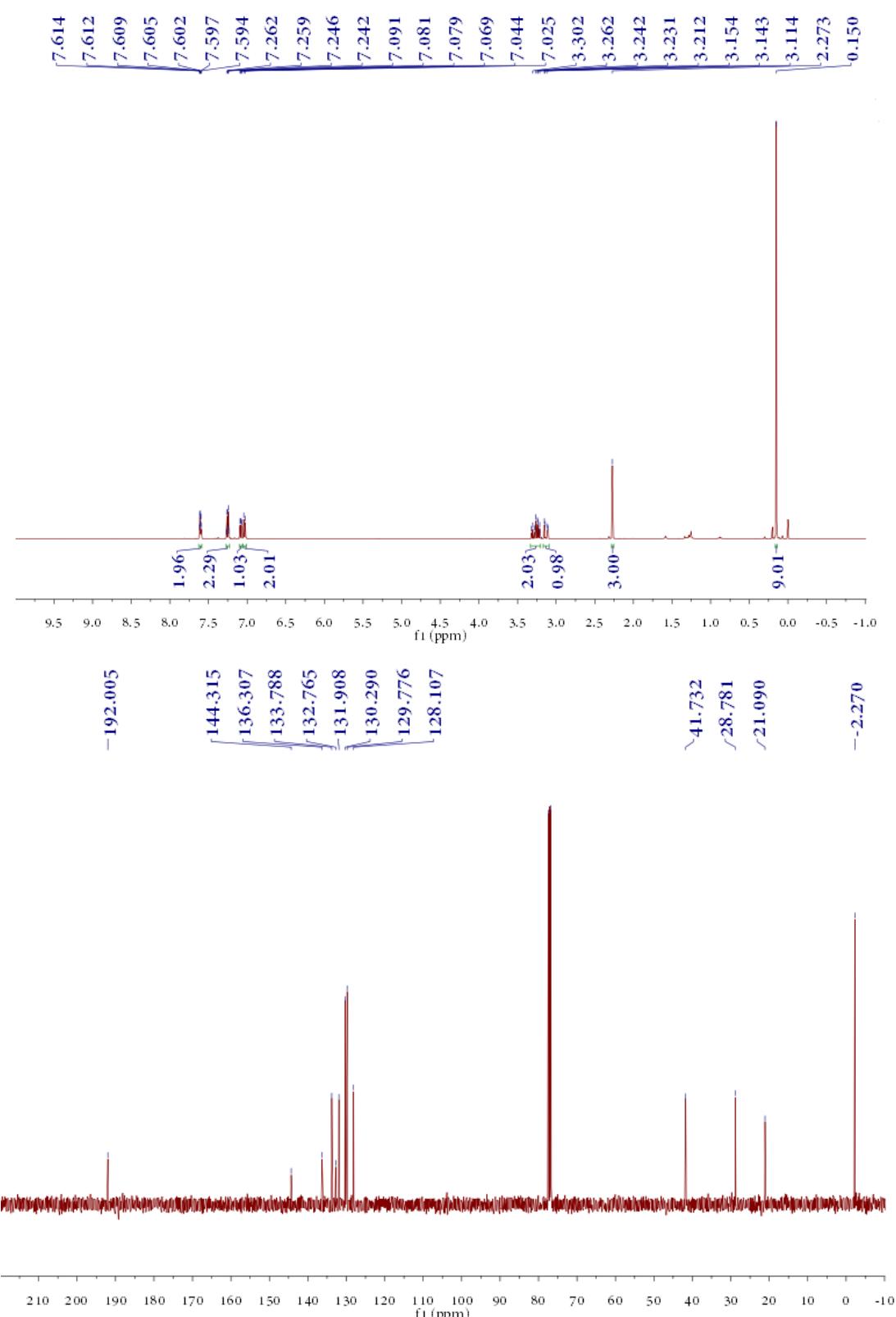
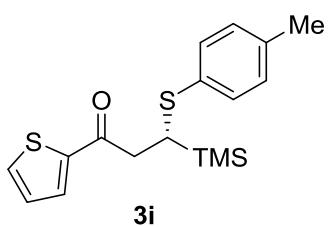


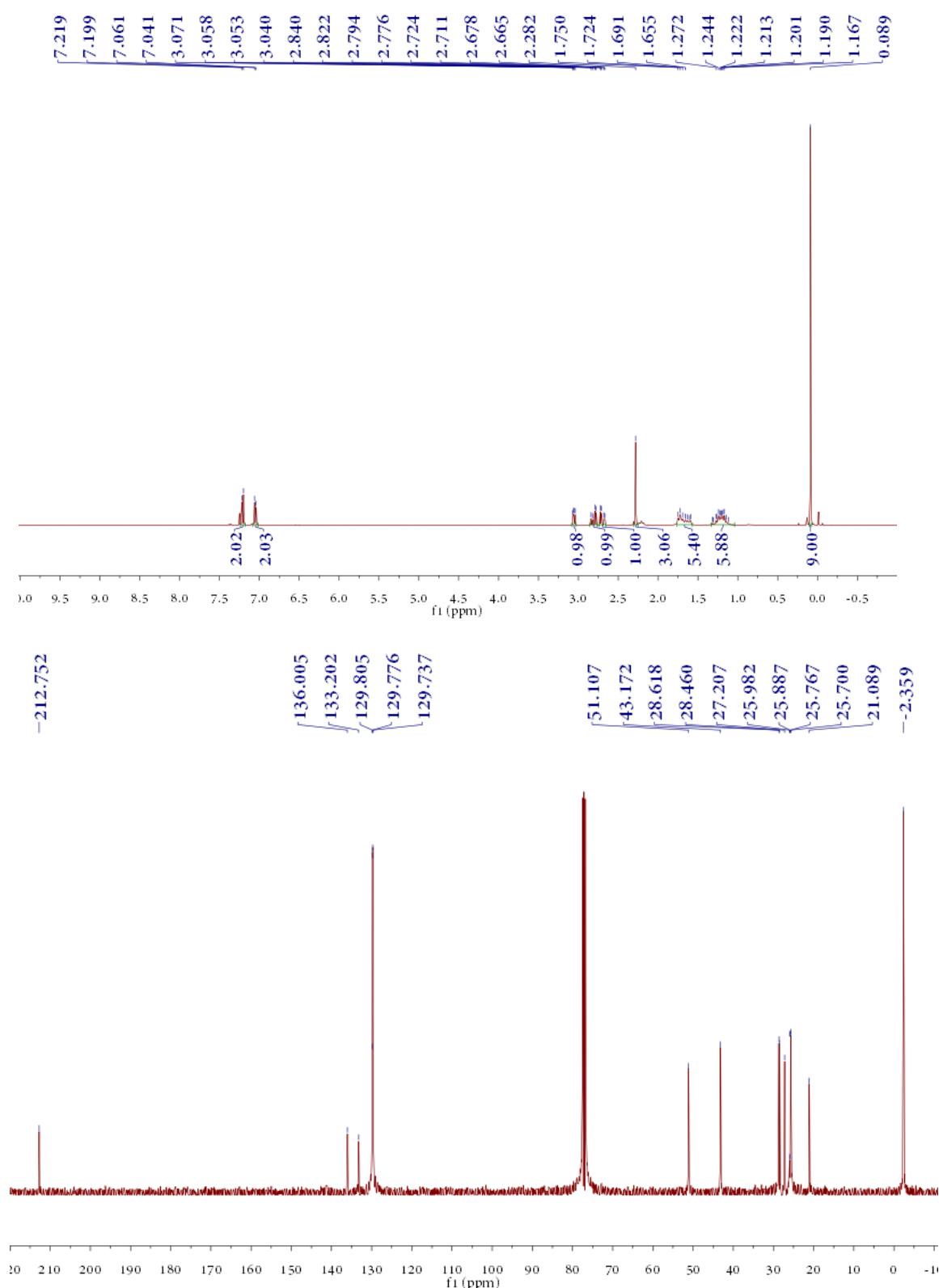
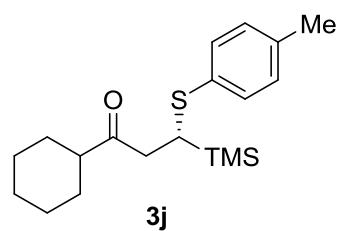


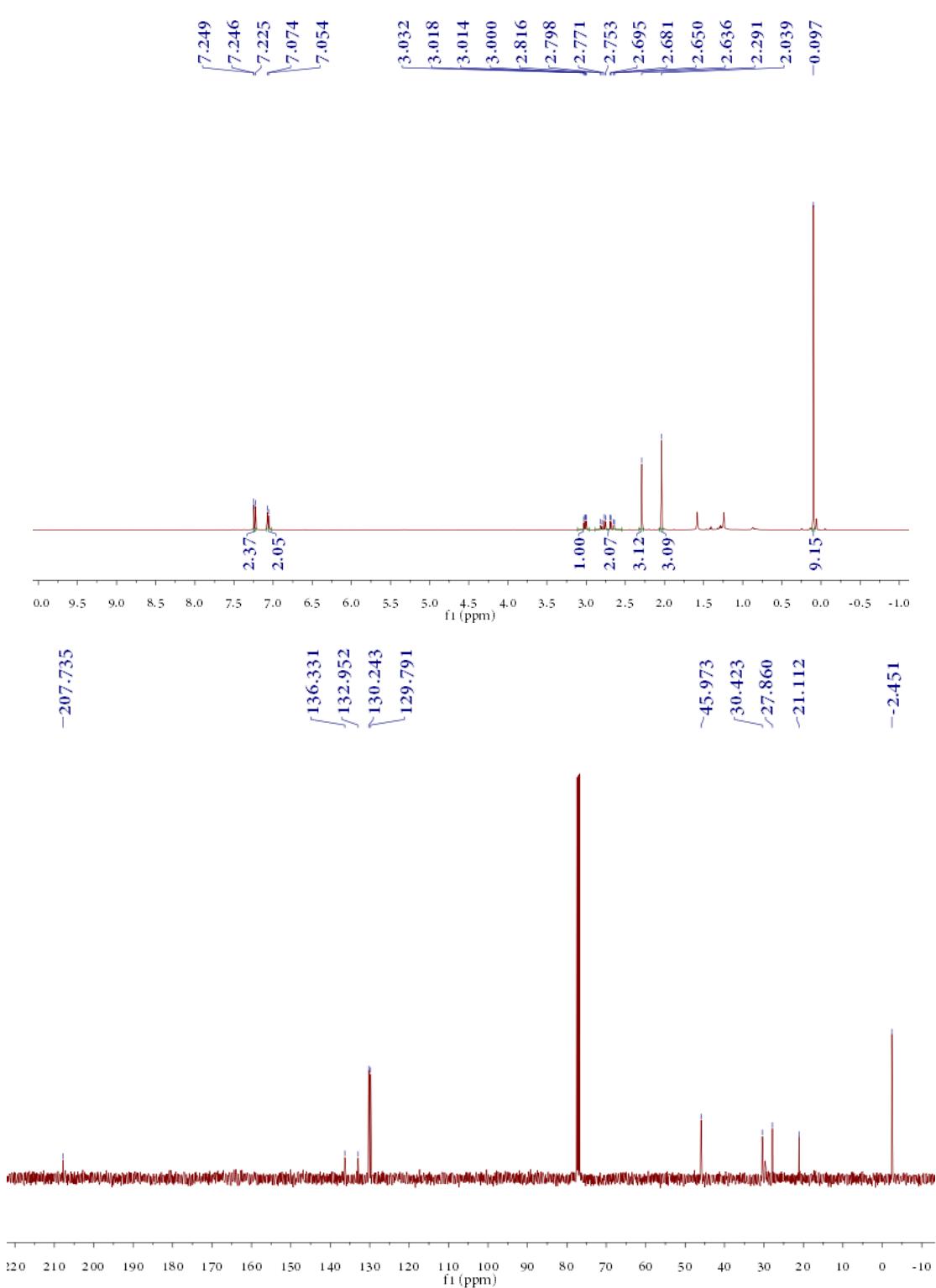
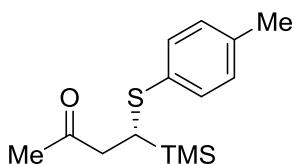


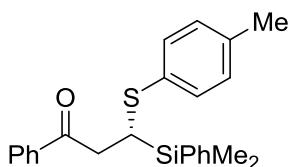




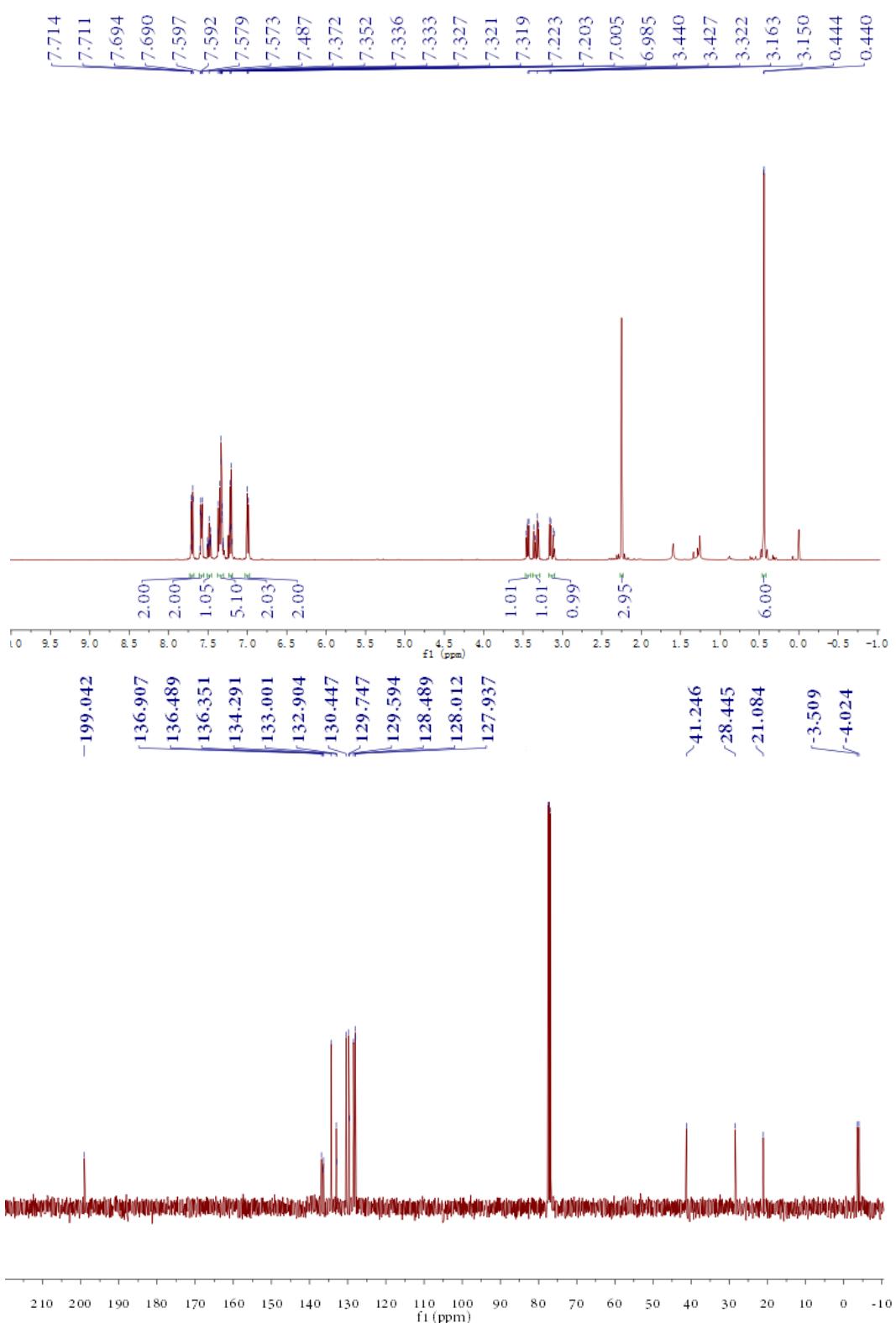


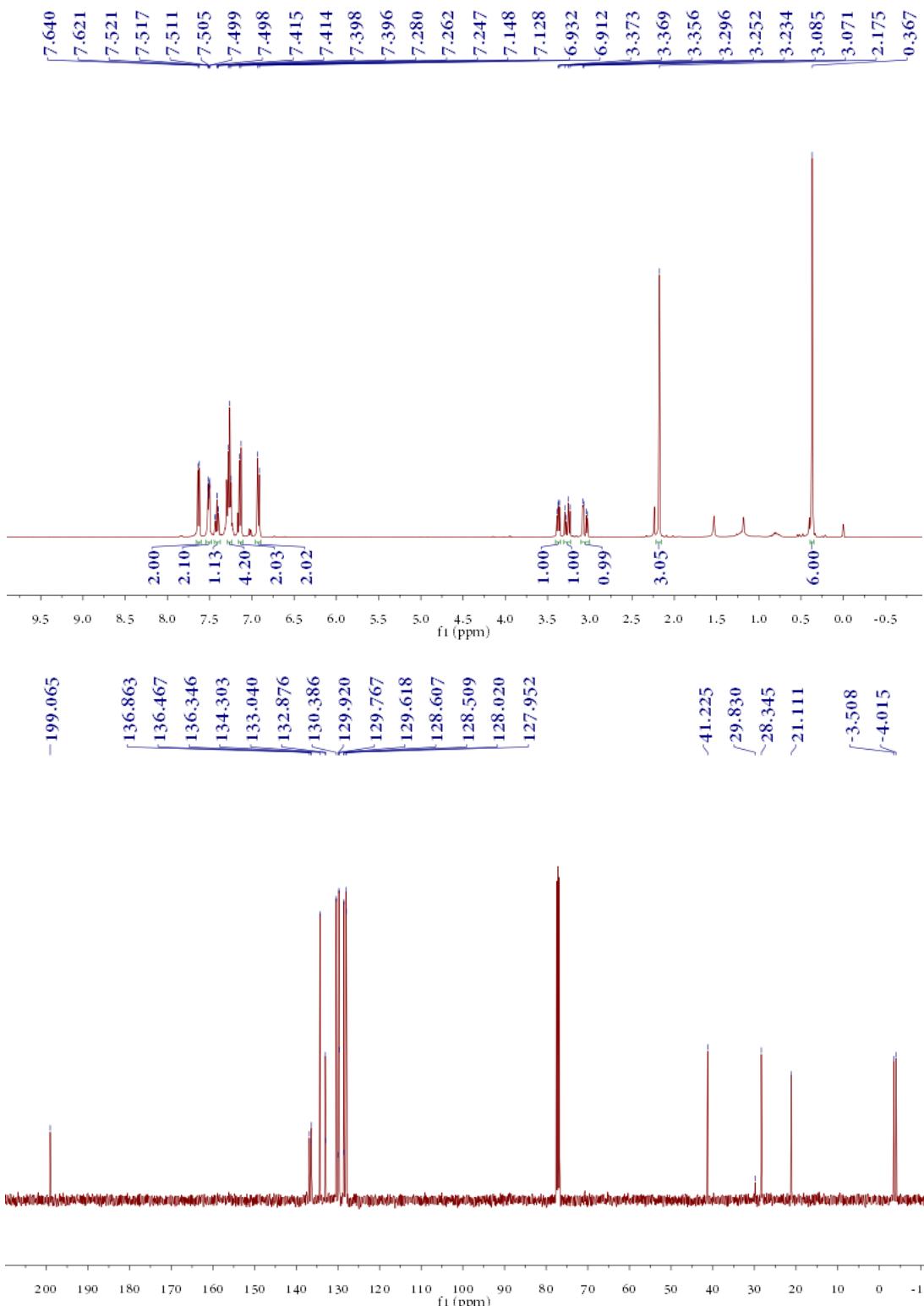
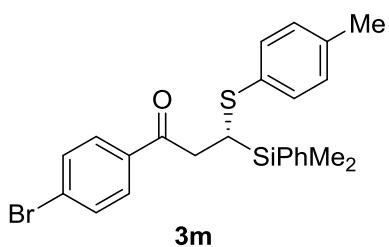


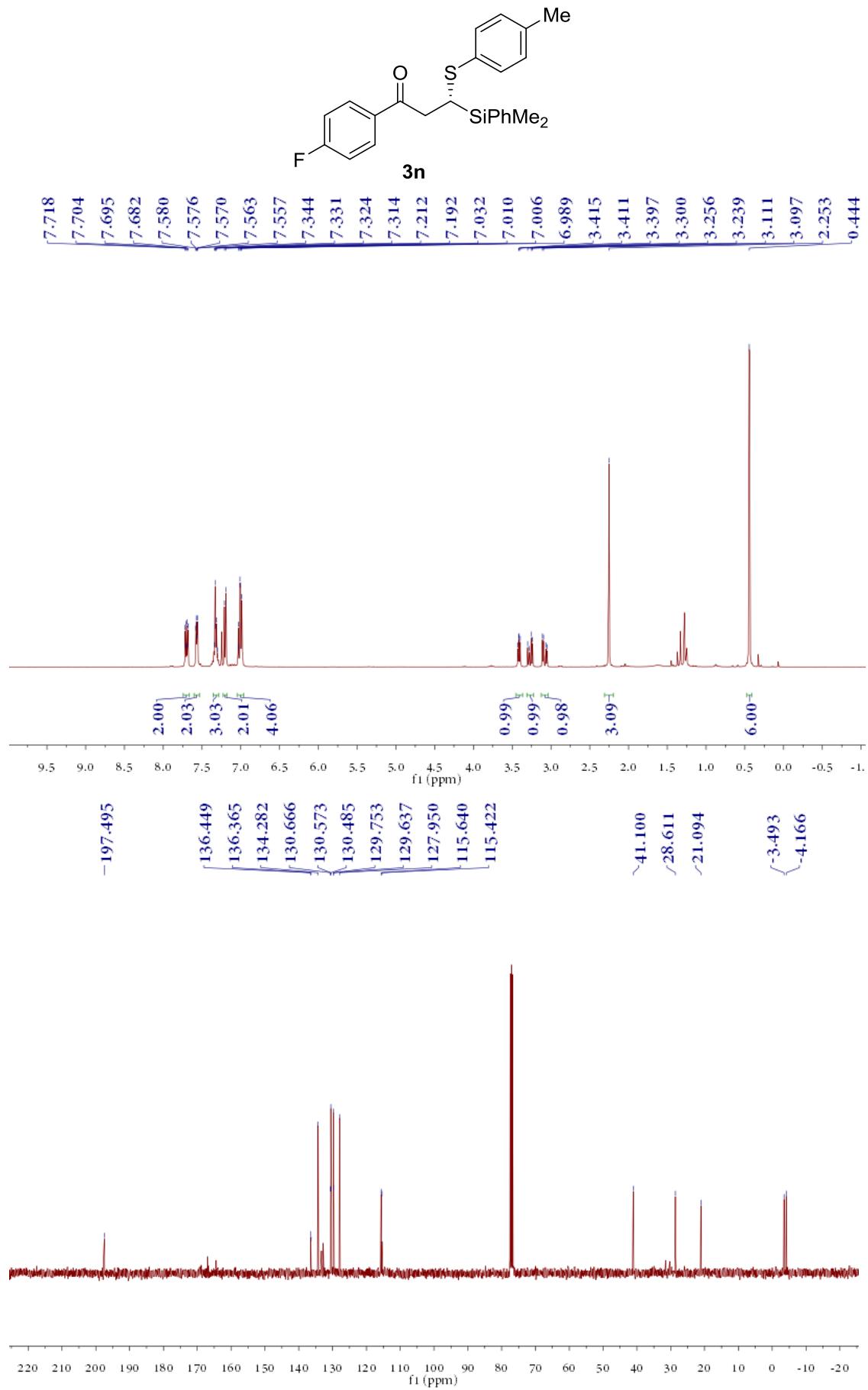


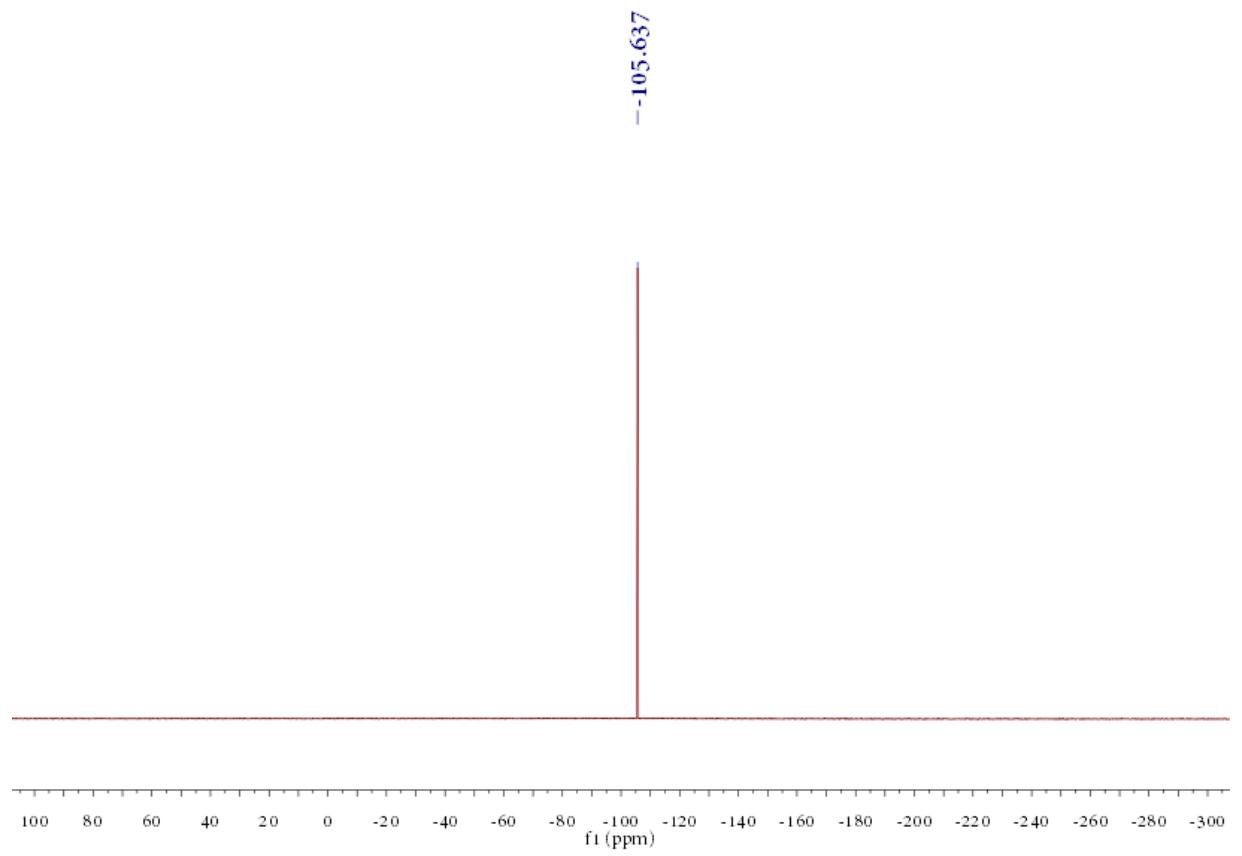


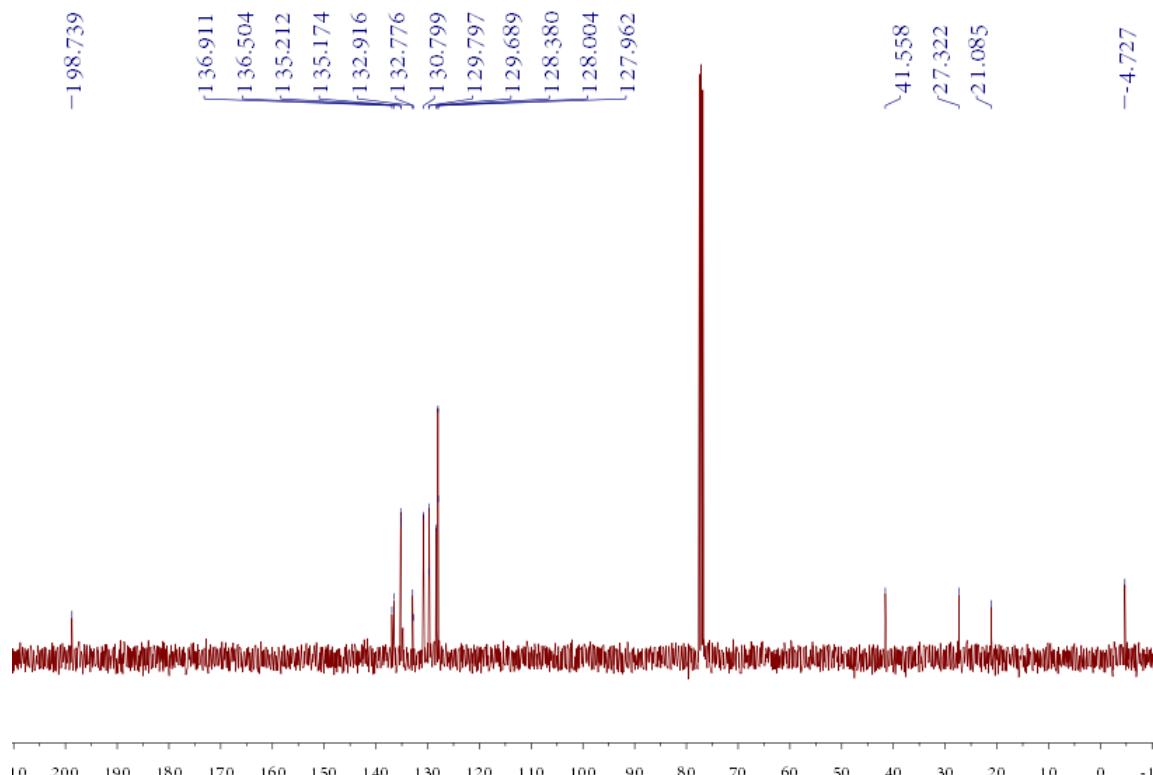
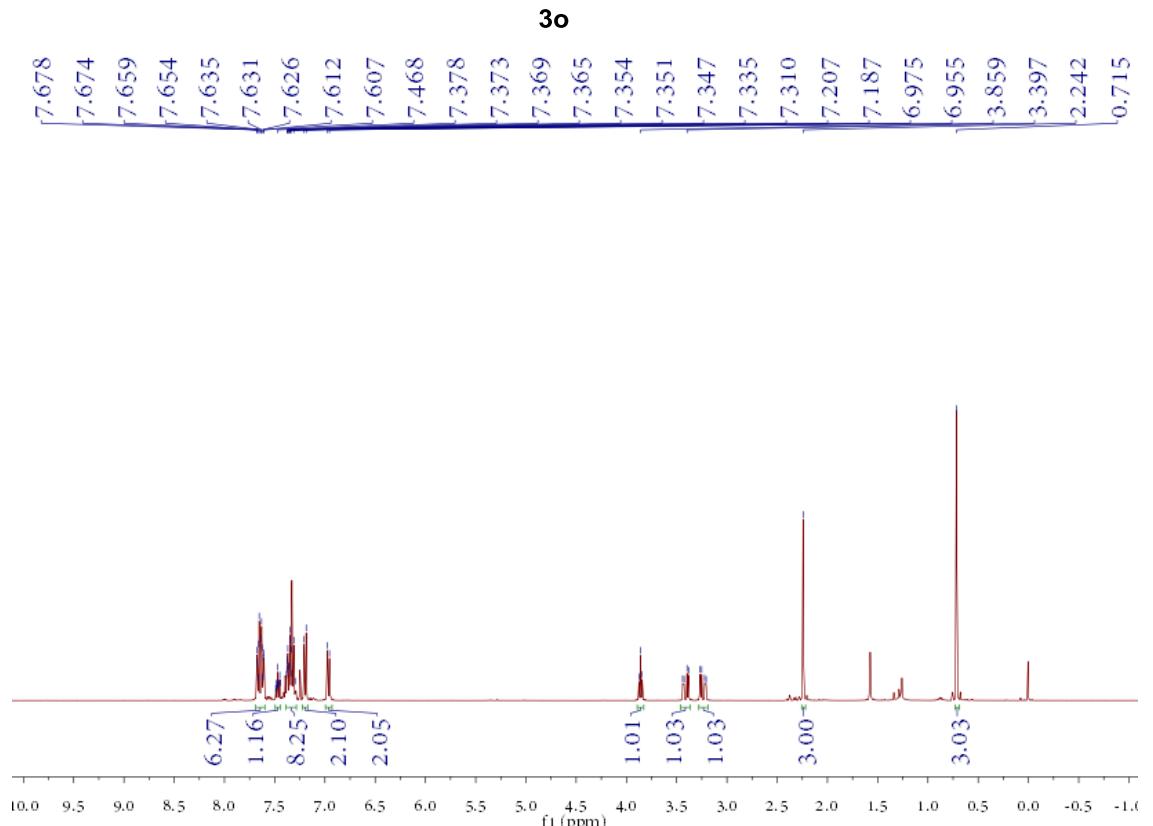
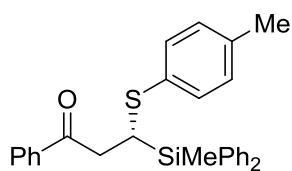
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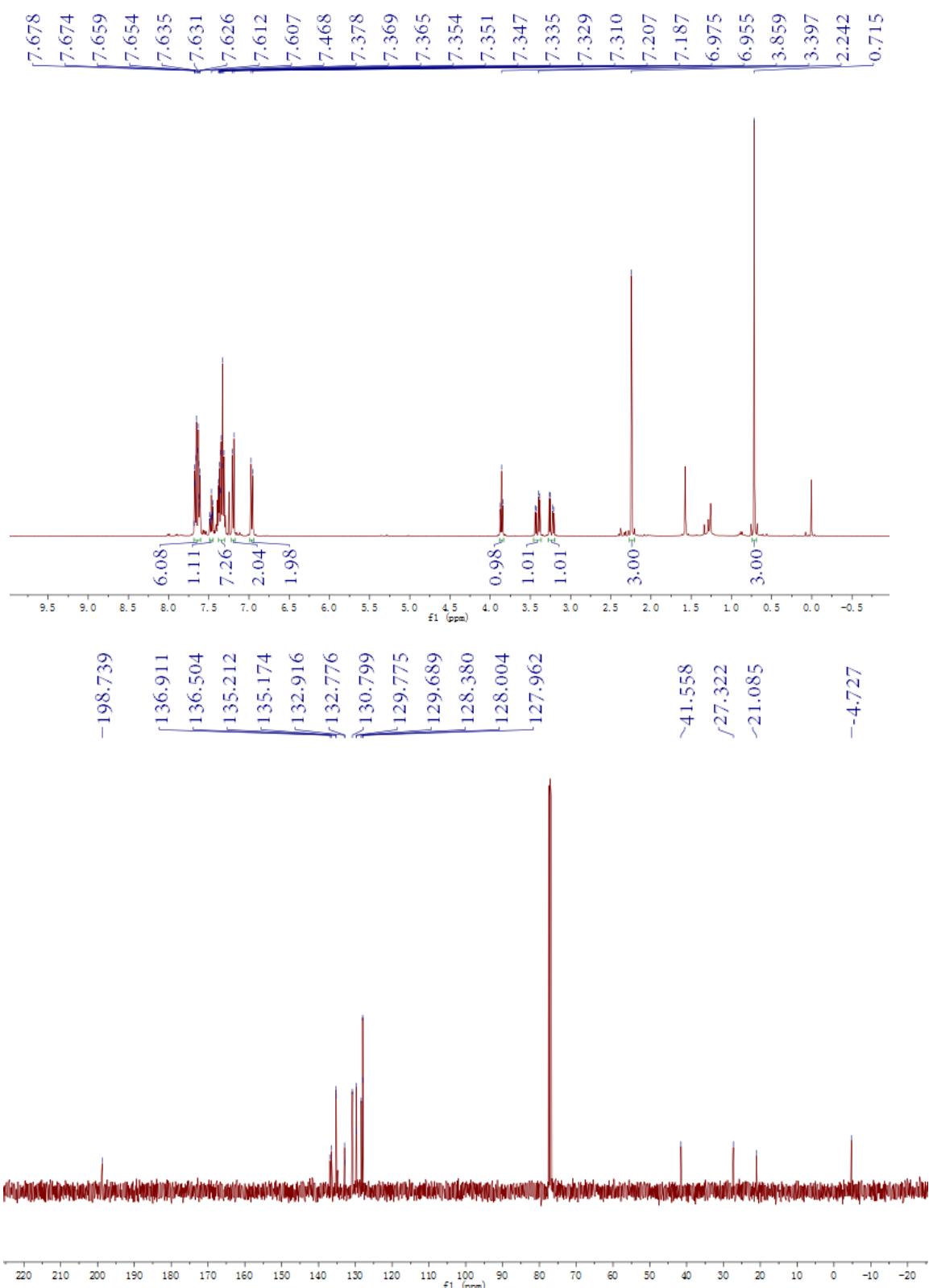
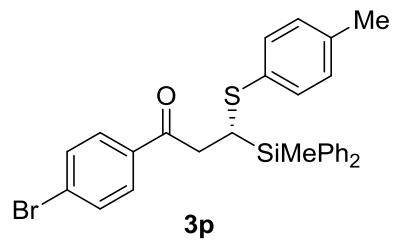


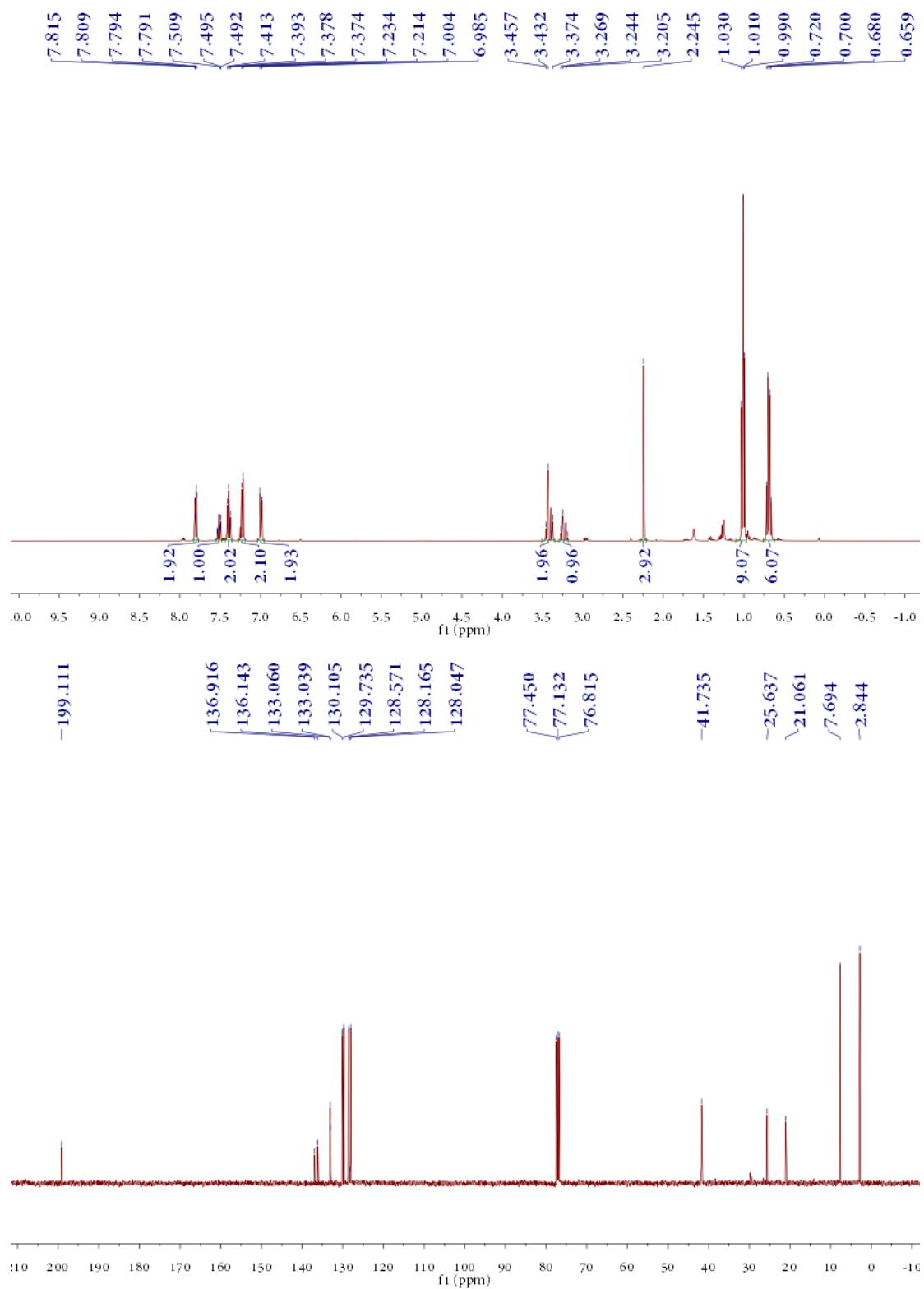
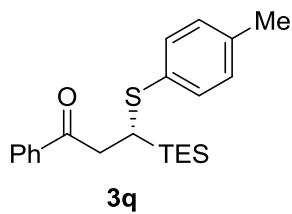


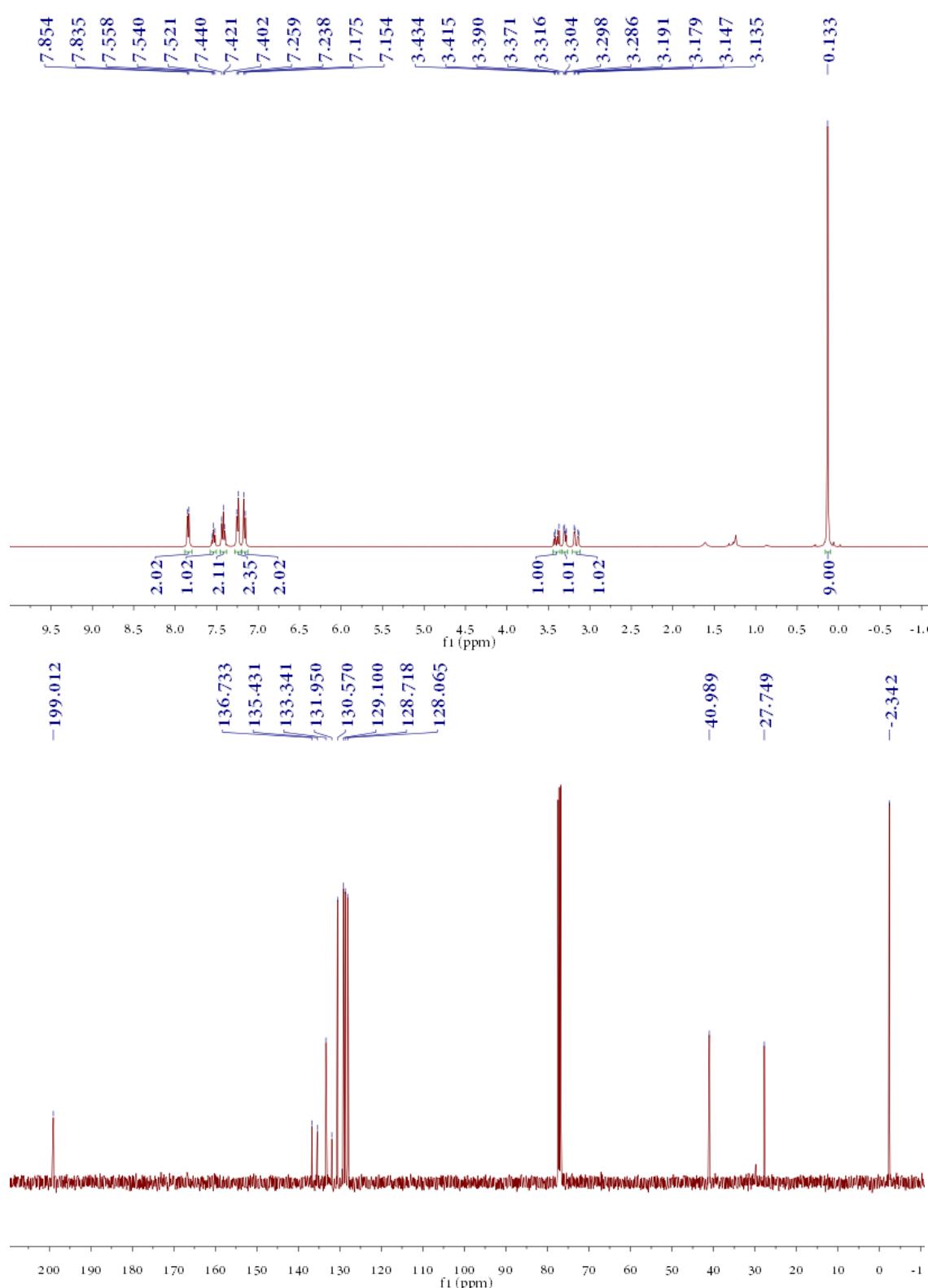
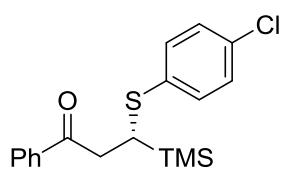


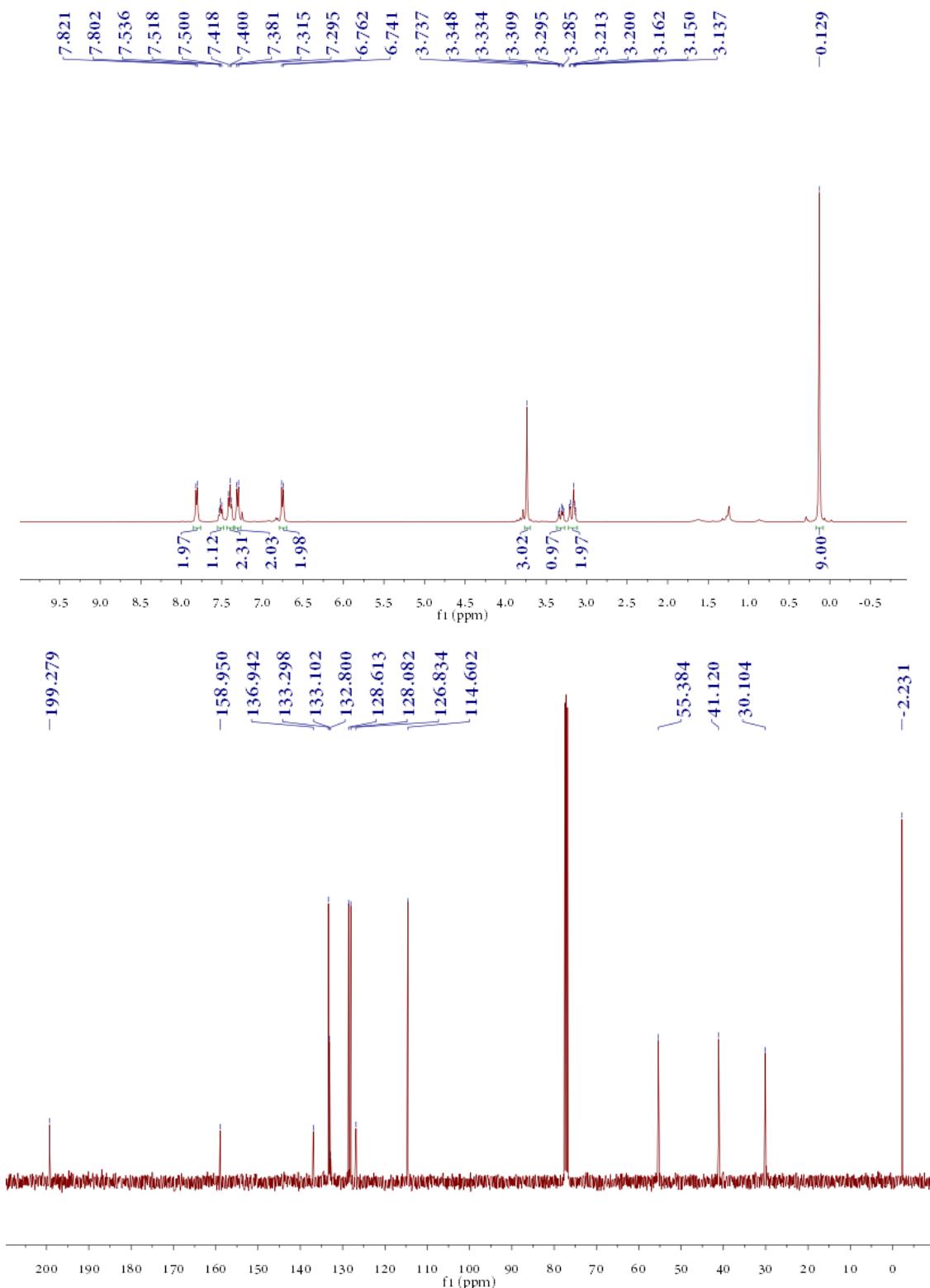
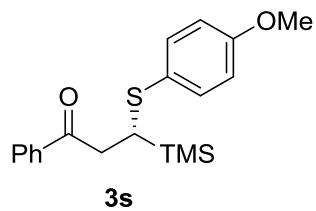


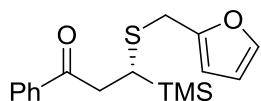




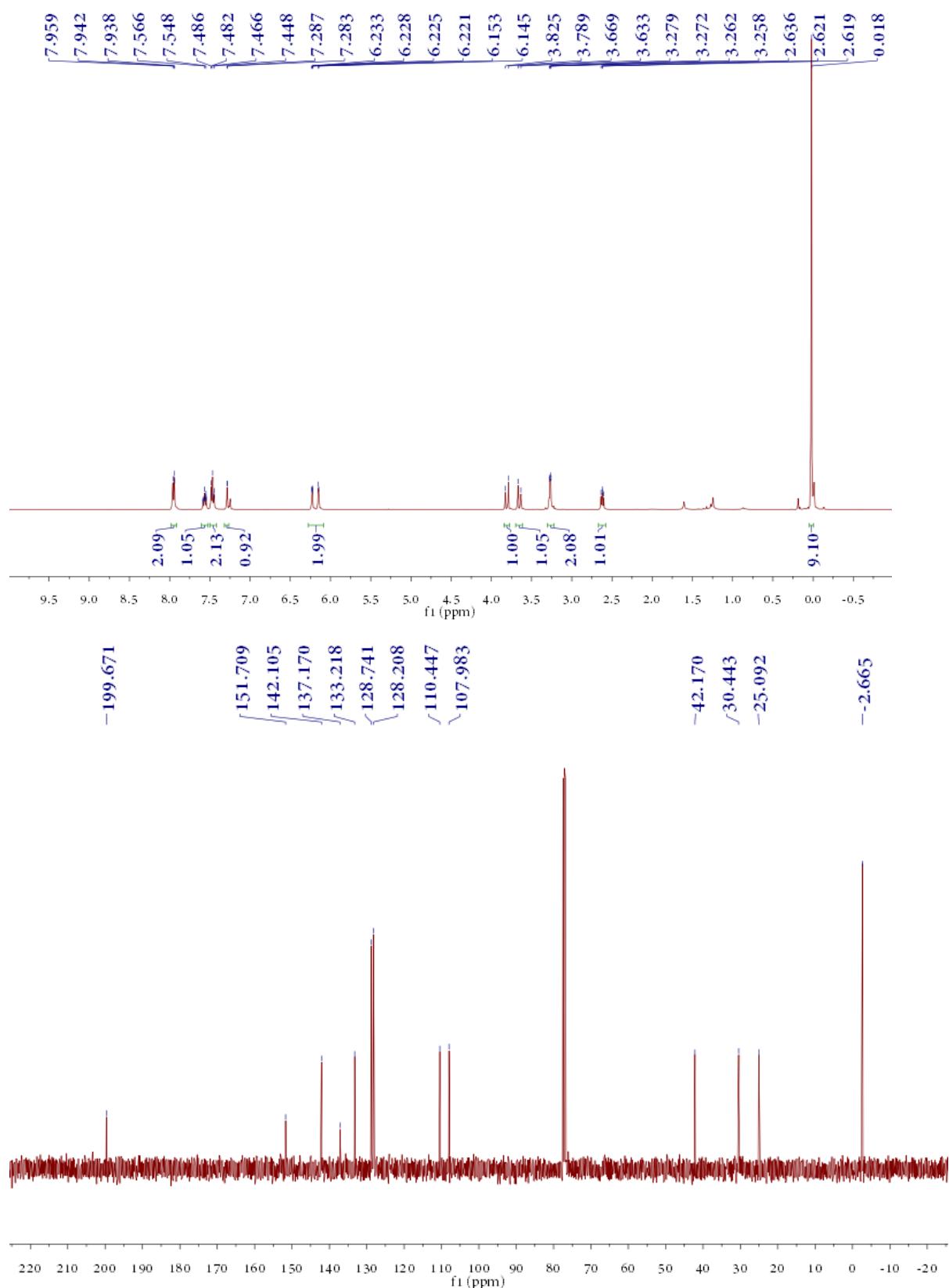


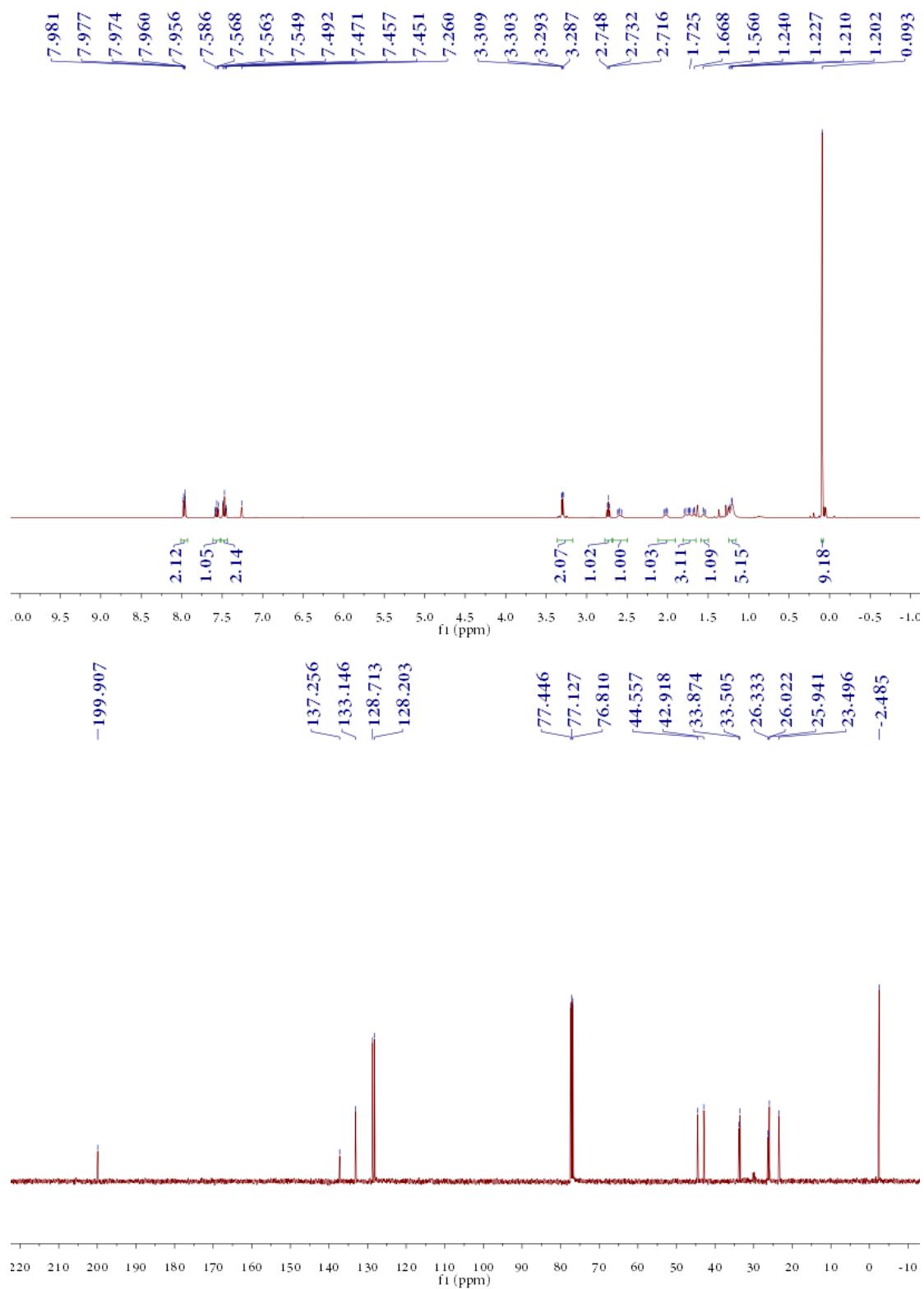
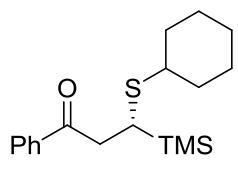


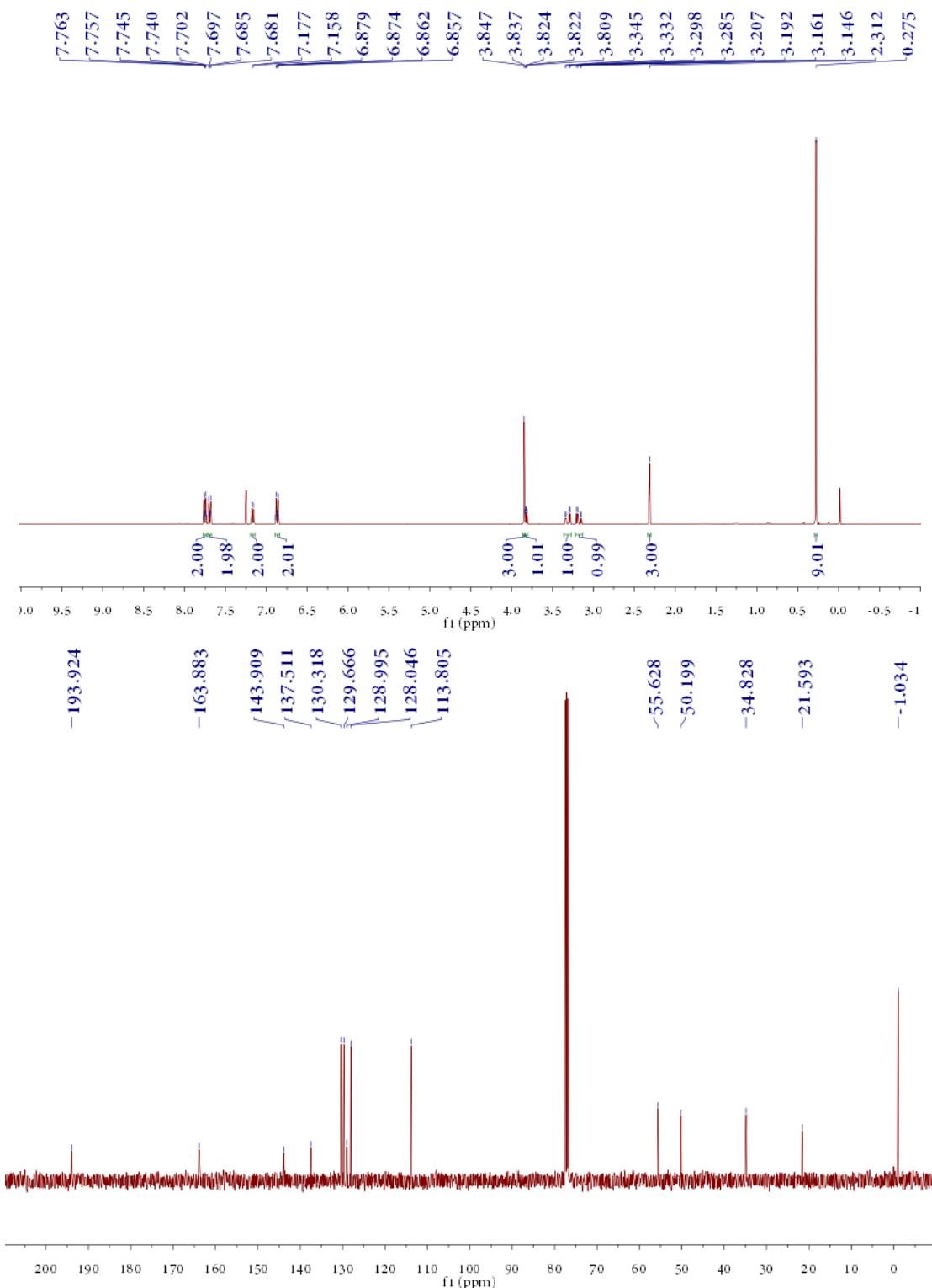
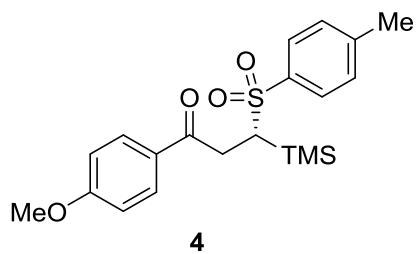


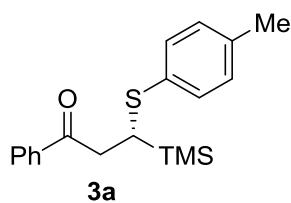


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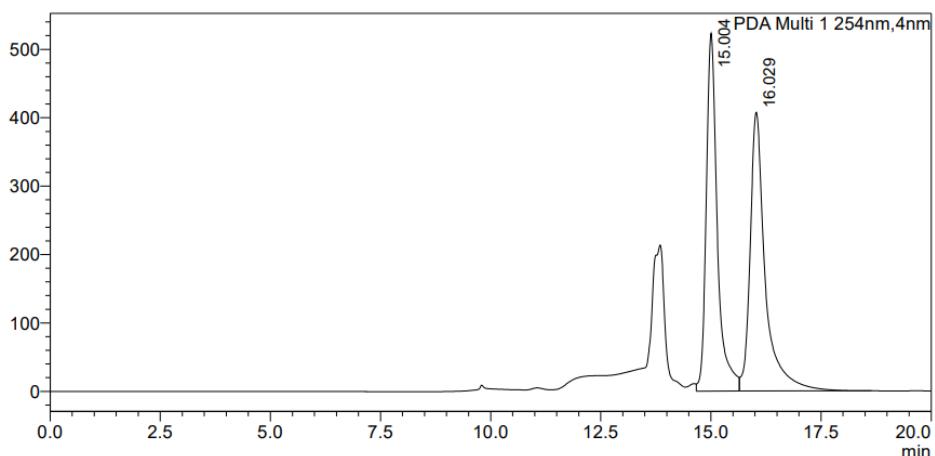






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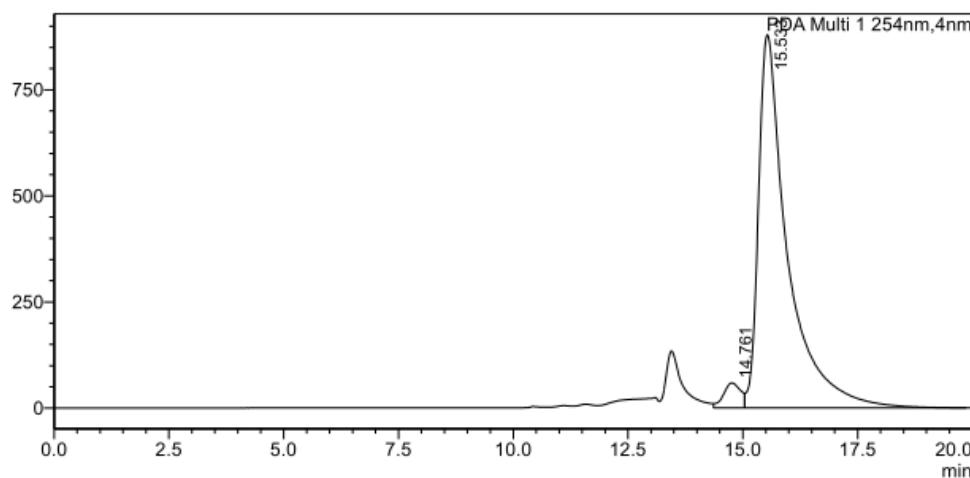
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	15.004	9145690	48.427	522962
2	16.029	9740015	51.573	407395
Total		18885705	100.000	930358

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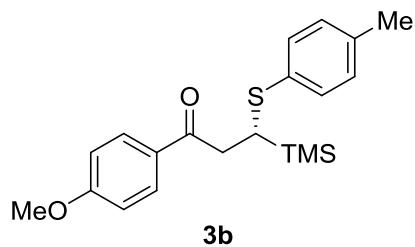
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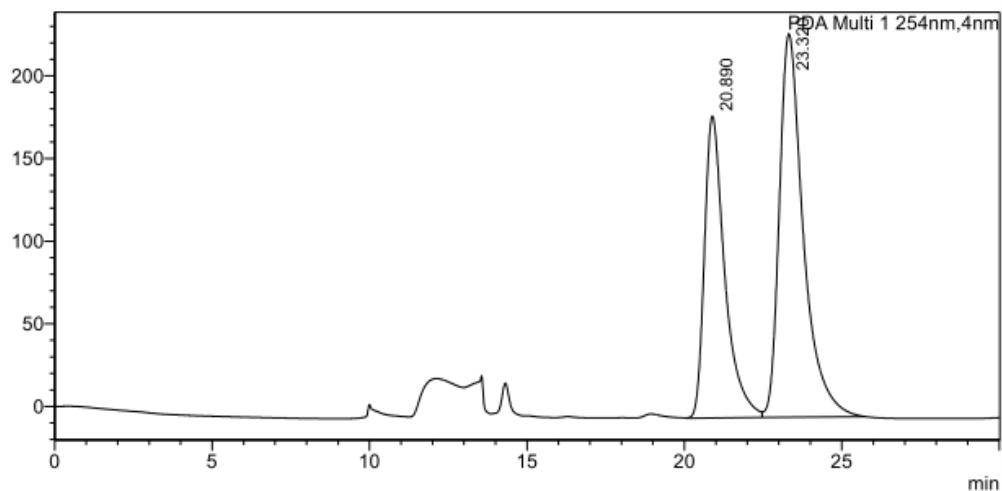
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.761	1548628	3.840	58715
2	15.533	38780608	96.160	879152
Total		40329237	100.000	937867



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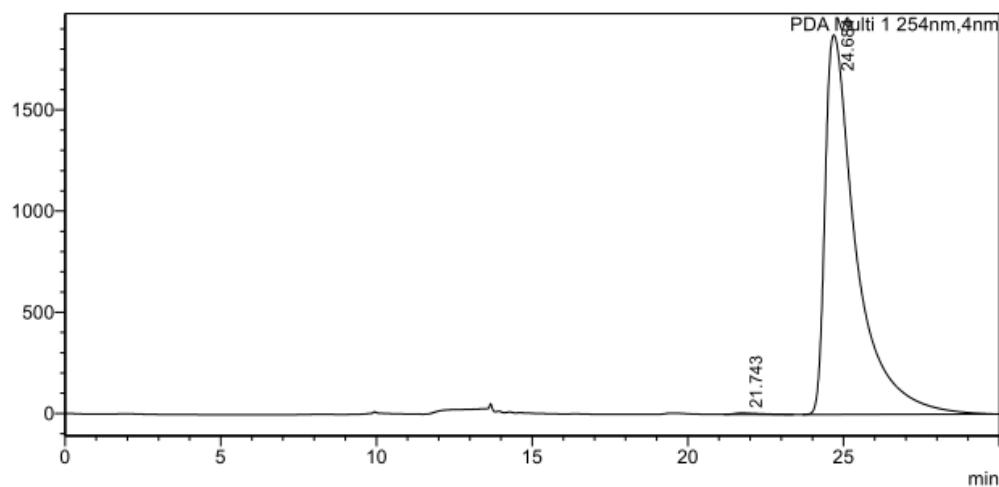
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	20.890	8218805	40.057	182537
2	23.320	12299165	59.943	231966
Total		20517970	100.000	414503

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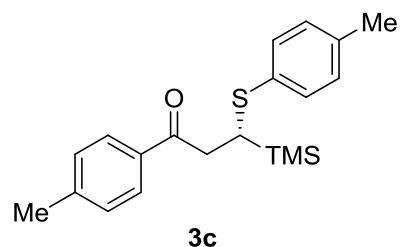
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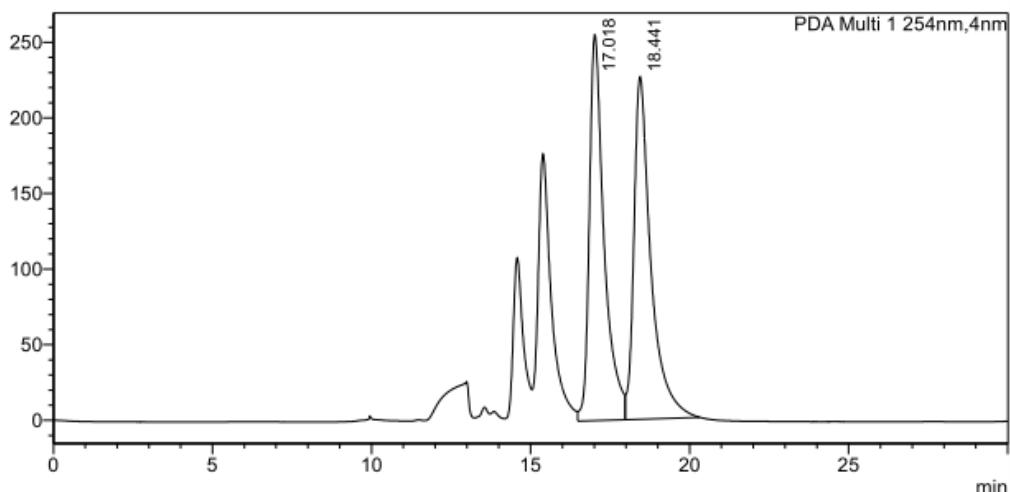
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	21.743	352020	0.270	6783
2	24.684	130040414	99.730	1874870
Total		130392434	100.000	1881653



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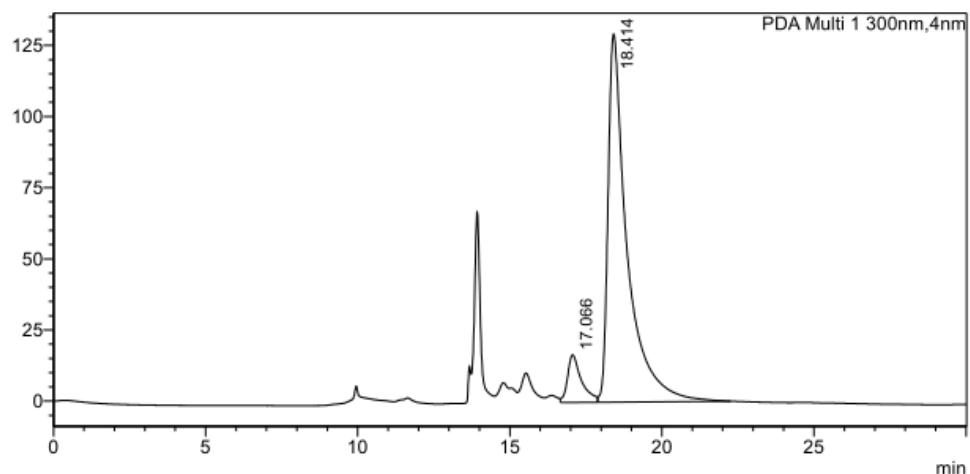
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	17.018	8228090	49.402	255180
2	18.441	8427267	50.598	226534
Total		16655357	100.000	481713

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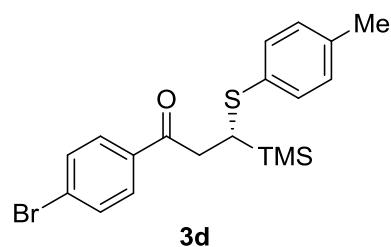
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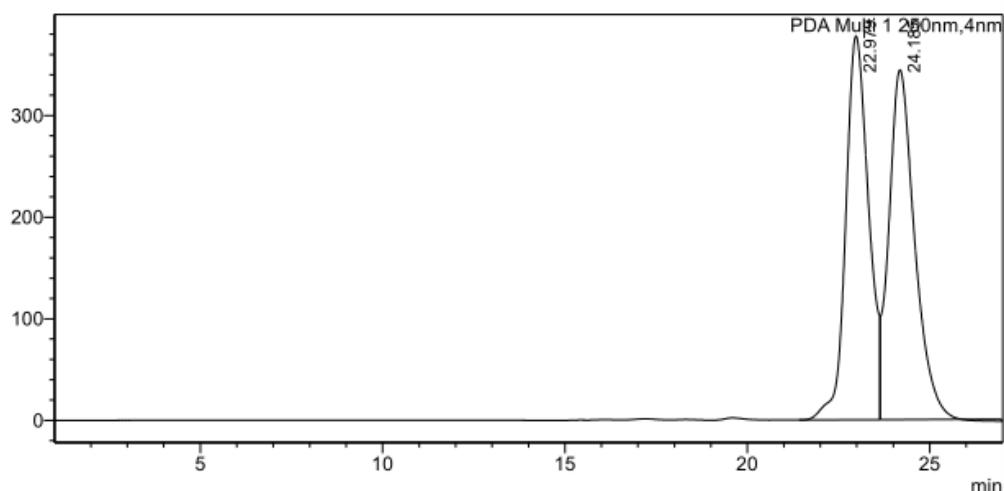
PDA Ch1 300nm

Peak#	Ret. Time	Area	Area%	Height
1	17.066	534434	8.635	16751
2	18.414	5655064	91.365	129392
Total		6189498	100.000	146143



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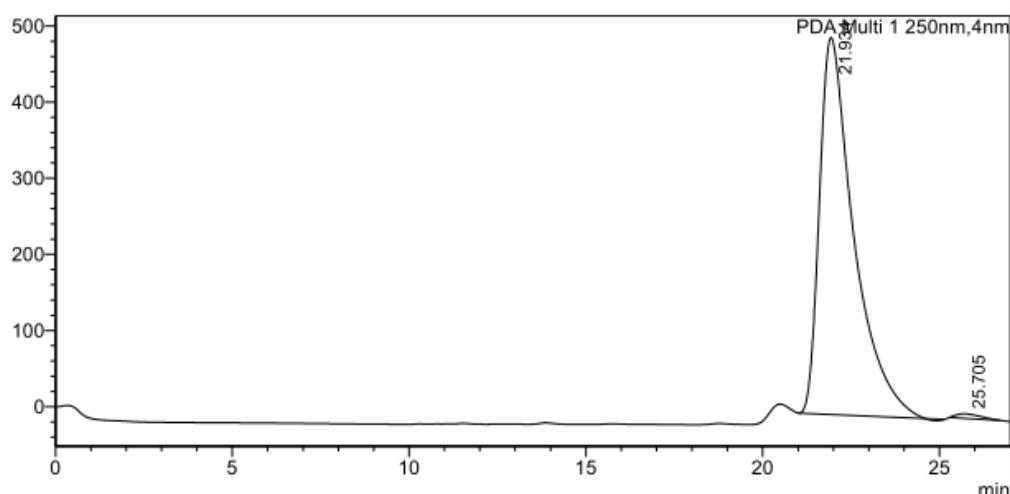
**<Peak Table>**

PDA Ch1 250nm

Peak#	Ret. Time	Area	Area%	Height
1	22.979	16548769	49.520	377557
2	24.185	16869875	50.480	344158
Total		33418645	100.000	721715

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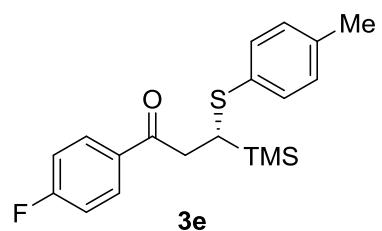
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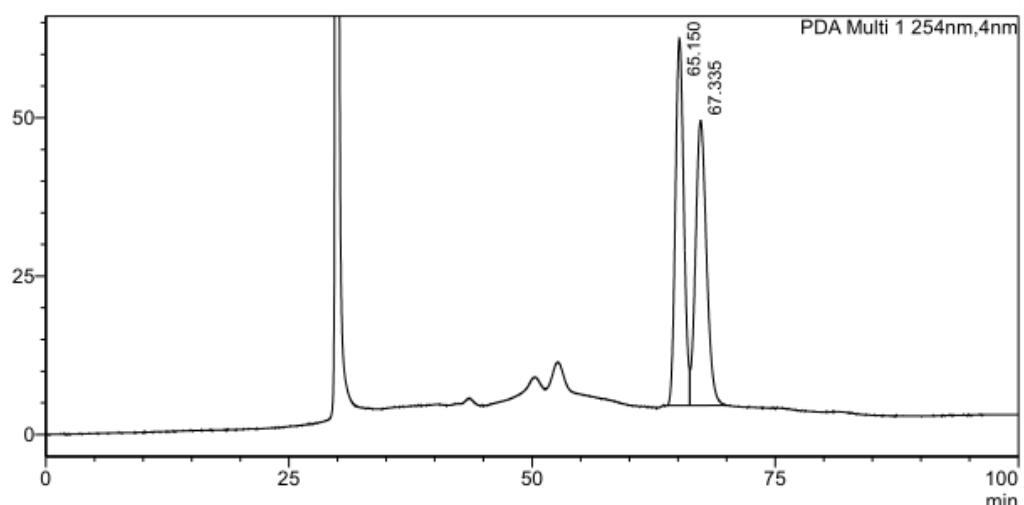
PDA Ch1 250nm

Peak#	Ret. Time	Area	Area%	Height
1	21.934	33359907	99.169	494941
2	25.705	279591	0.831	5866
Total		33639499	100.000	500807



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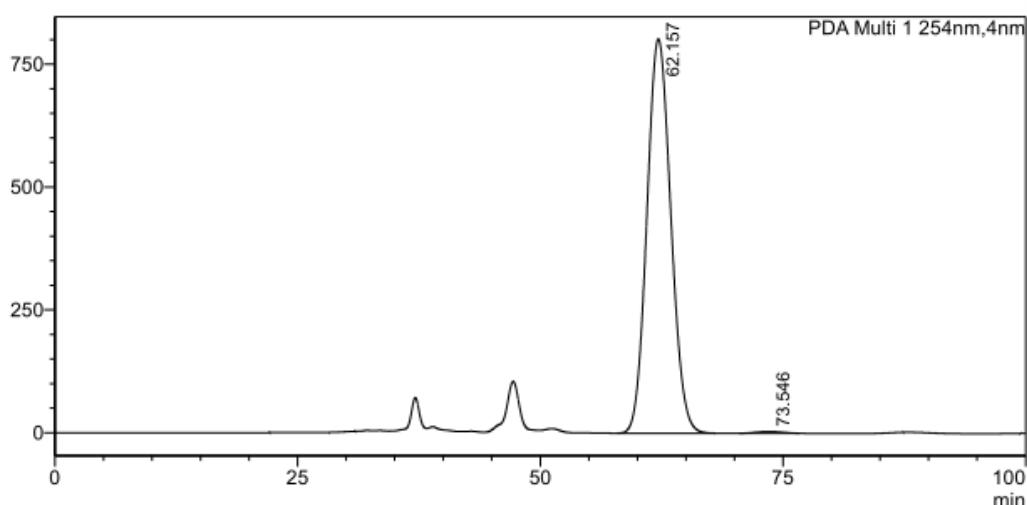
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	65.150	3490872	49.810	57954
2	67.335	3517483	50.190	44970
Total		7008355	100.000	102923

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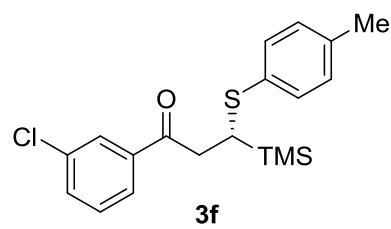
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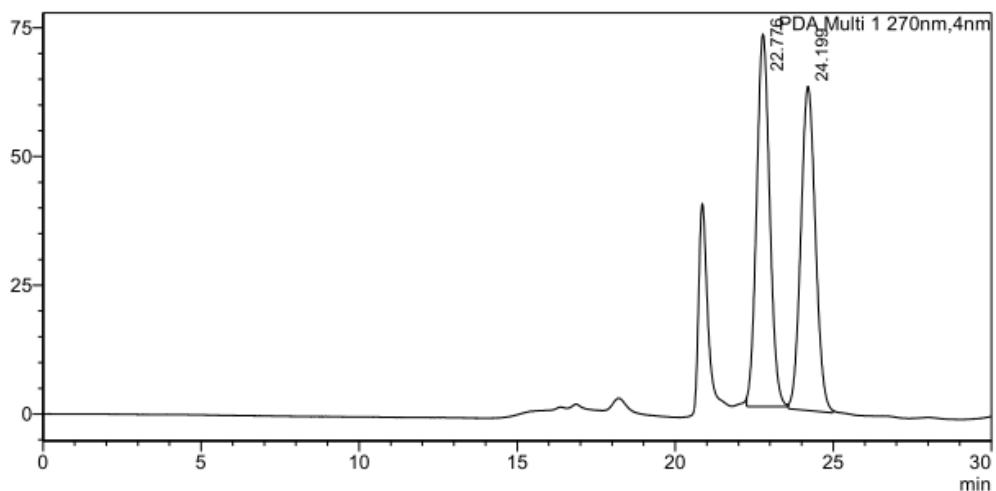
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	62.157	137433536	99.506	802291
2	73.546	682588	0.494	3578
Total		138116124	100.000	805868



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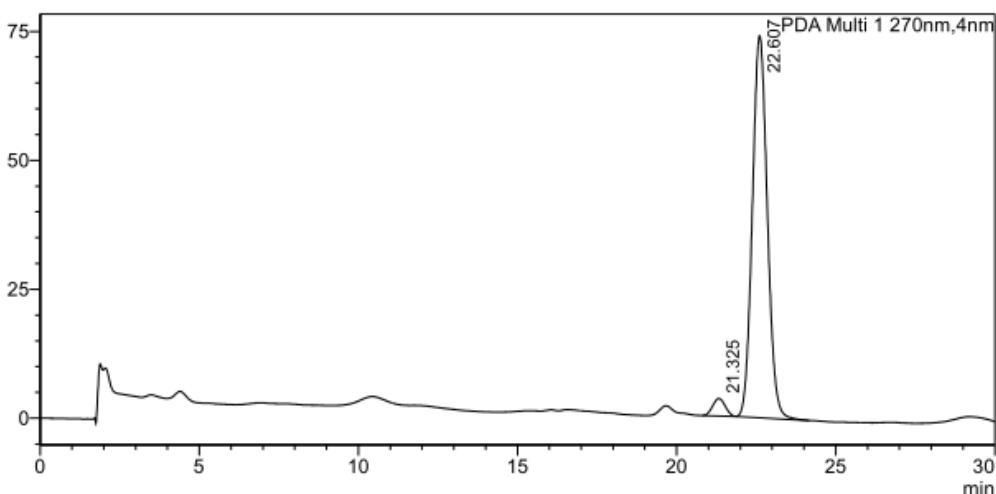
**<Peak Table>**

PDA Ch1 270nm

Peak#	Ret. Time	Area	Area%	Height
1	22.776	2082464	50.744	72204
2	24.199	2021394	49.256	62886
Total		4103857	100.000	135090

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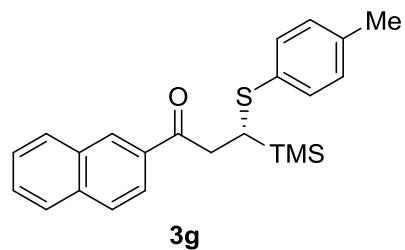
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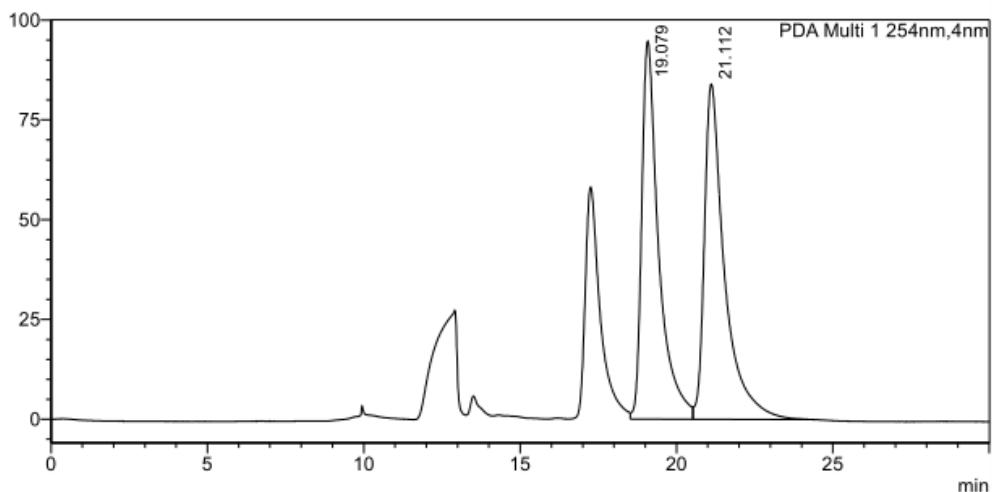
PDA Ch1 270nm

Peak#	Ret. Time	Area	Area%	Height
1	21.325	92628	3.684	3392
2	22.607	2421794	96.316	74049
Total		2514423	100.000	77440



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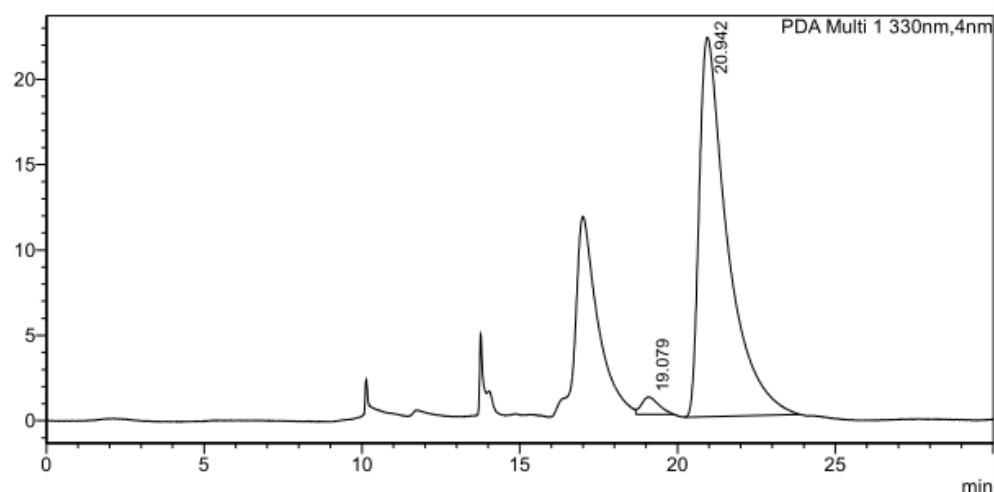
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	19.079	3578551	48.678	94695
2	21.112	3772859	51.322	83954
Total		7351410	100.000	178649

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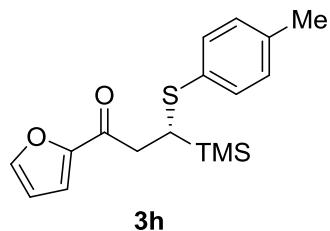
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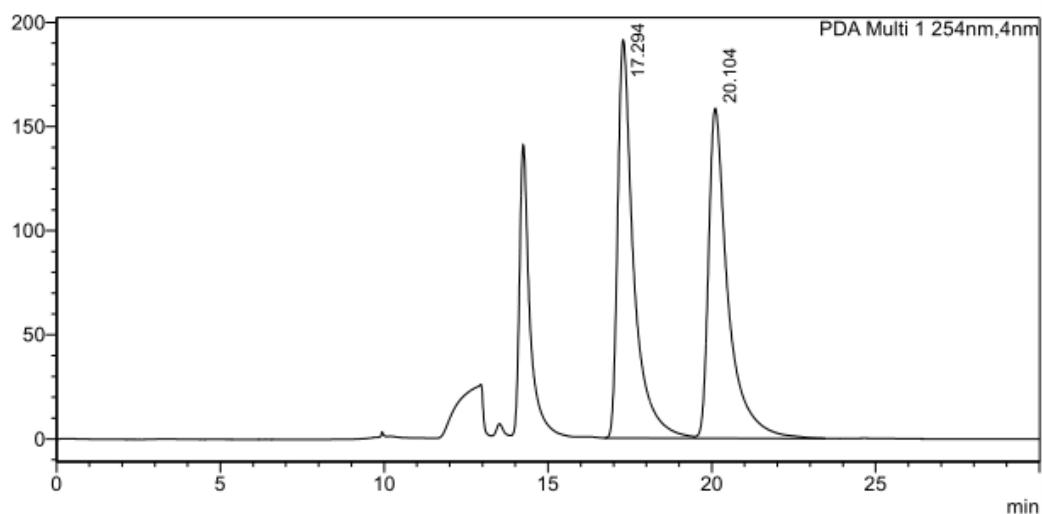
PDA Ch1 330nm

Peak#	Ret. Time	Area	Area%	Height
1	19.079	38767	2.722	1019
2	20.942	1385274	97.278	22214
Total		1424041	100.000	23234



**<Chromatogram>**

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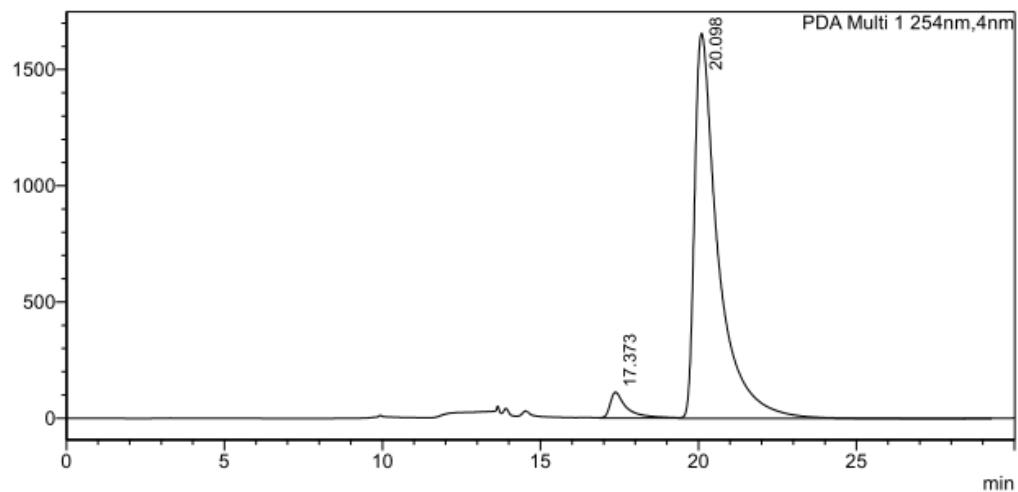
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	17.294	6493004	49.828	191138
2	20.104	6537718	50.172	158399
Total		13030723	100.000	349536

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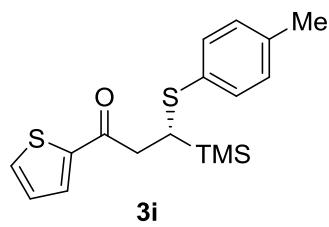
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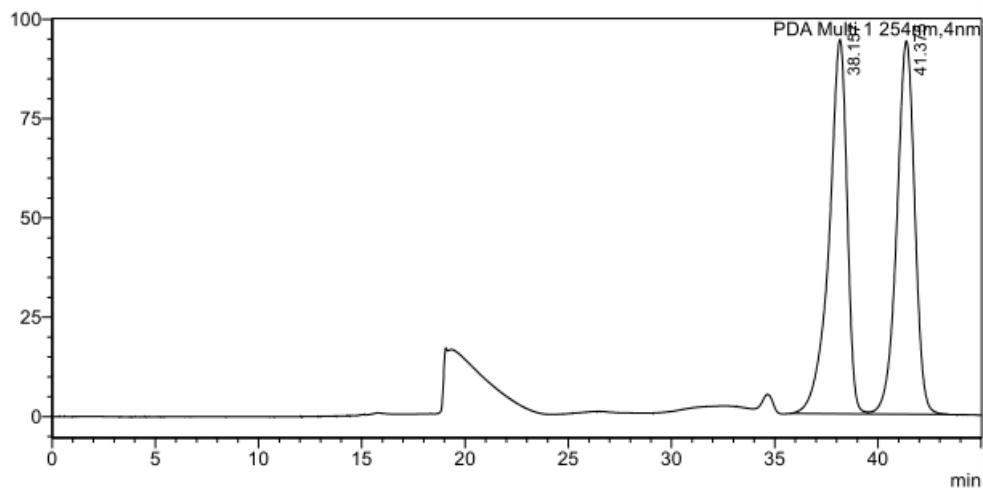
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	17.373	4095681	4.546	111324
2	20.098	85994142	95.454	1656125
Total		90089822	100.000	1767449



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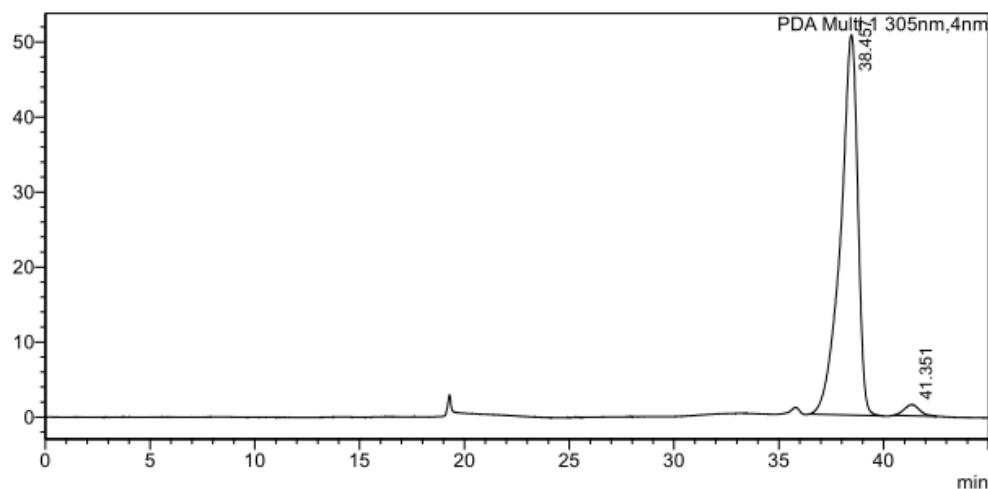
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	38.157	5709408	50.123	94176
2	41.375	5681409	49.877	93949
Total		11390818	100.000	188125

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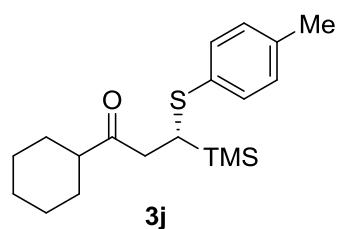
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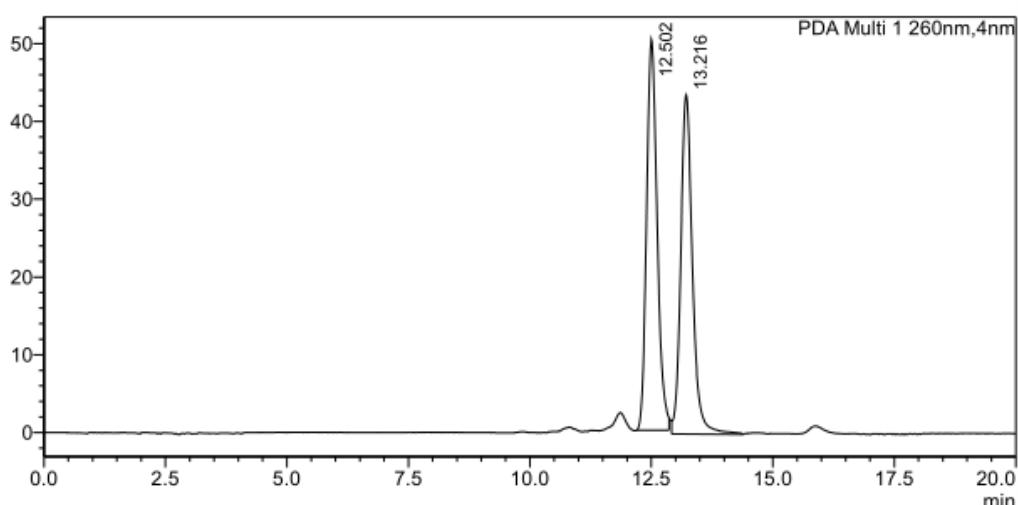
PDA Ch1 305nm

Peak#	Ret. Time	Area	Area%	Height
1	38.457	2902104	97.451	50712
2	41.351	75908	2.549	1476
Total		2978012	100.000	52188



**<Chromatogram>**

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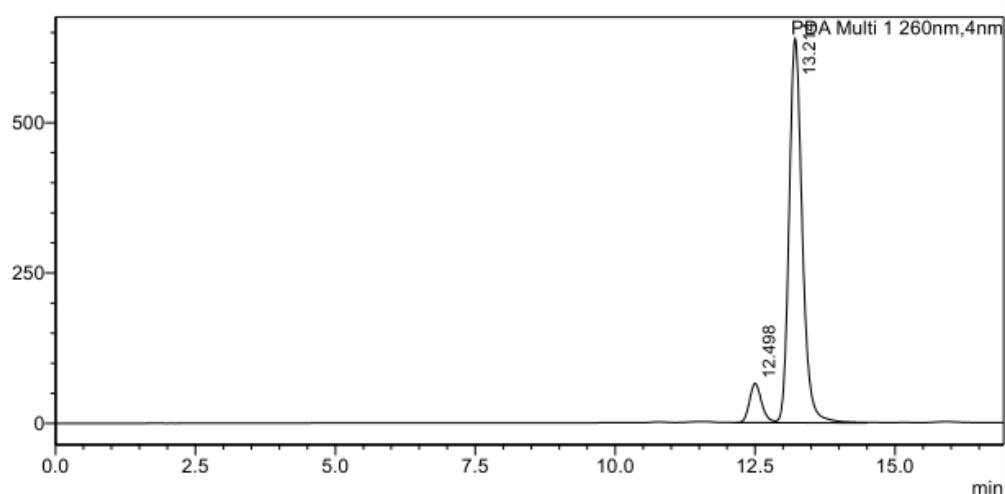
**<Peak Table>**

PDA Ch1 260nm

Peak#	Ret. Time	Area	Area%	Height
1	12.502	759683	50.980	50277
2	13.216	730466	49.020	43600
Total		1490149	100.000	93878

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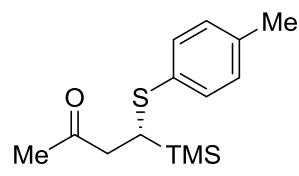
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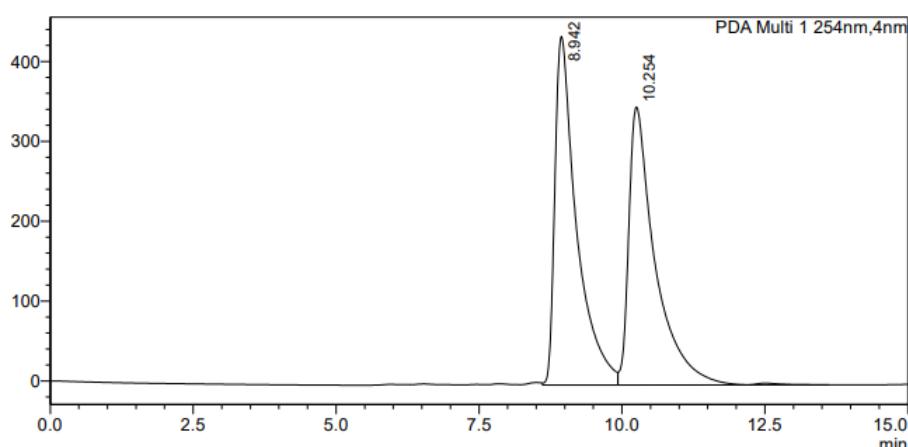
PDA Ch1 260nm

Peak#	Ret. Time	Area	Area%	Height
1	12.498	990602	8.656	65165
2	13.214	10453229	91.344	638762
Total		11443831	100.000	703927



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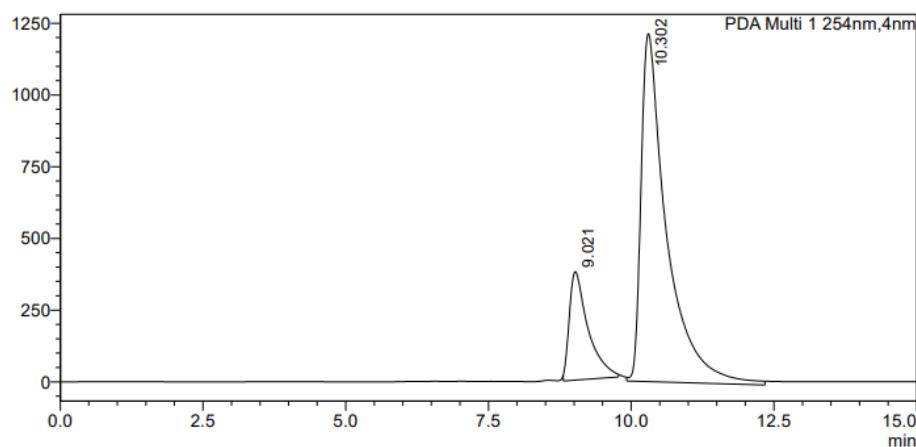
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	8.942	11527446	50.813	436151
2	10.254	11158533	49.187	348053
Total		22685979	100.000	784204

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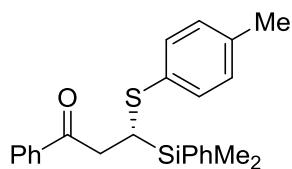
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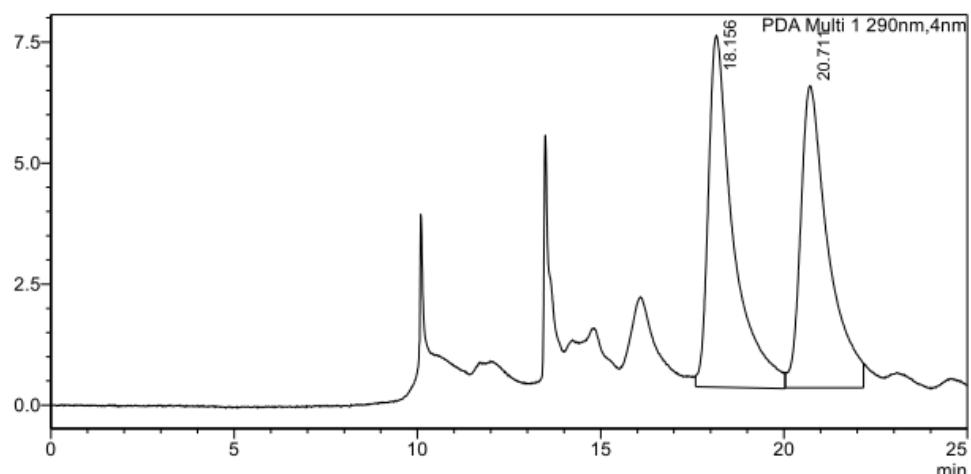
Peak#	Ret. Time	Area	Area%	Height
1	9.021	8651222	18.623	378379
2	10.302	37802140	81.377	1212863
Total		46453362	100.000	1591242



**3I**

**<Chromatogram>**

mAU



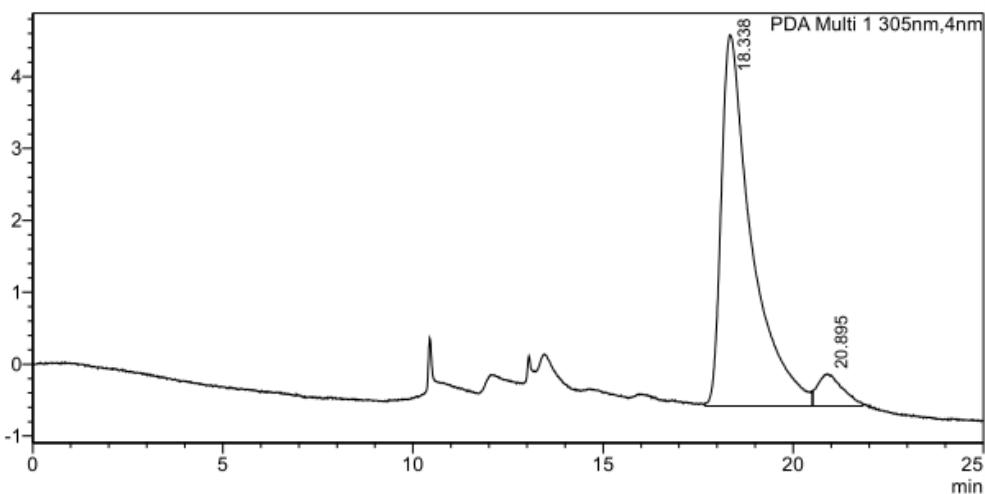
**<Peak Table>**

PDA Ch1 290nm

Peak#	Ret. Time	Area	Area%	Height
1	18.156	344234	51.437	7261
2	20.711	325003	48.563	6234
Total		669238	100.000	13496

**<Chromatogram>**

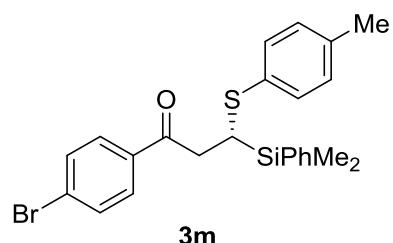
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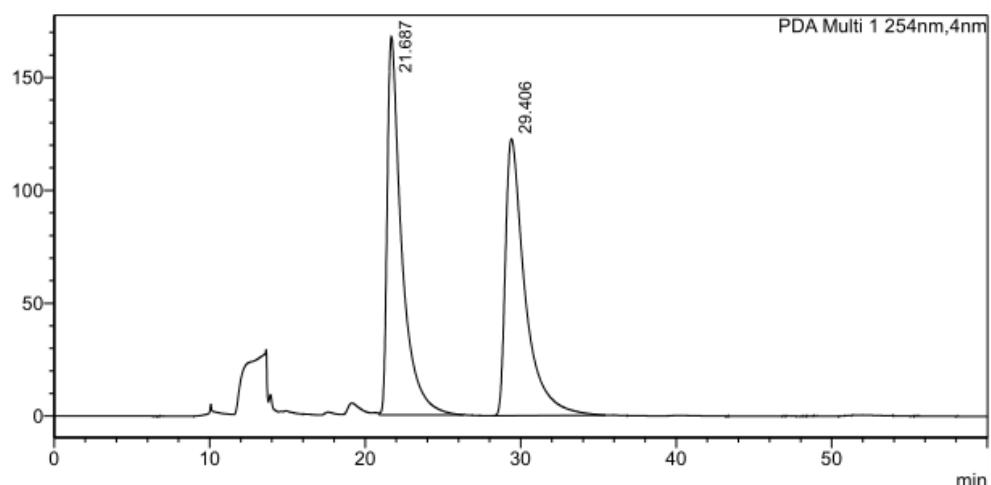
PDA Ch1 305nm

Peak#	Ret. Time	Area	Area%	Height
1	18.338	285370	93.342	5162
2	20.895	20354	6.658	445
Total		305724	100.000	5607



**<Chromatogram>**

mAU



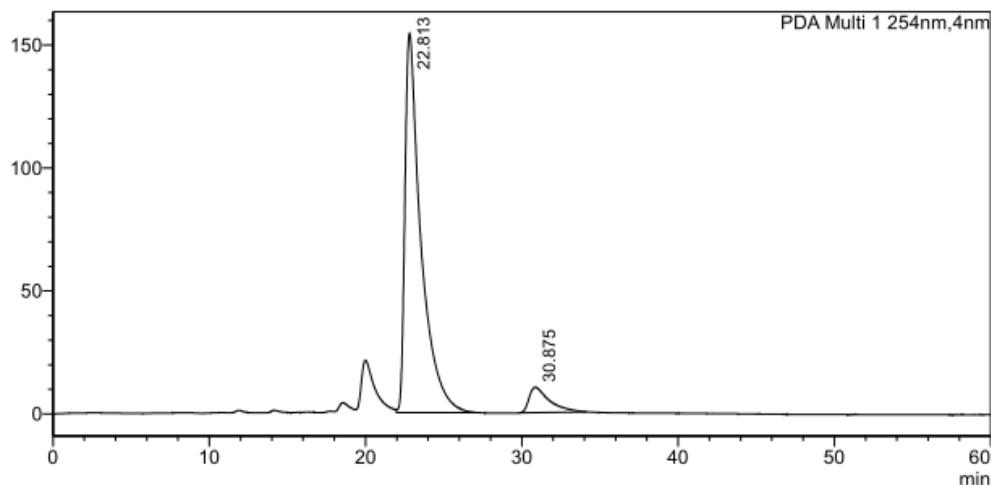
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	21.687	10835607	50.211	167676
2	29.406	10744664	49.789	122753
Total		21580270	100.000	290429

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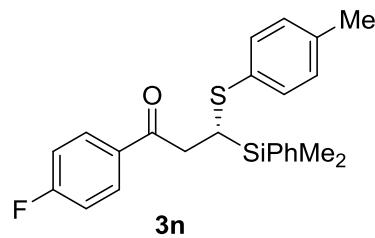
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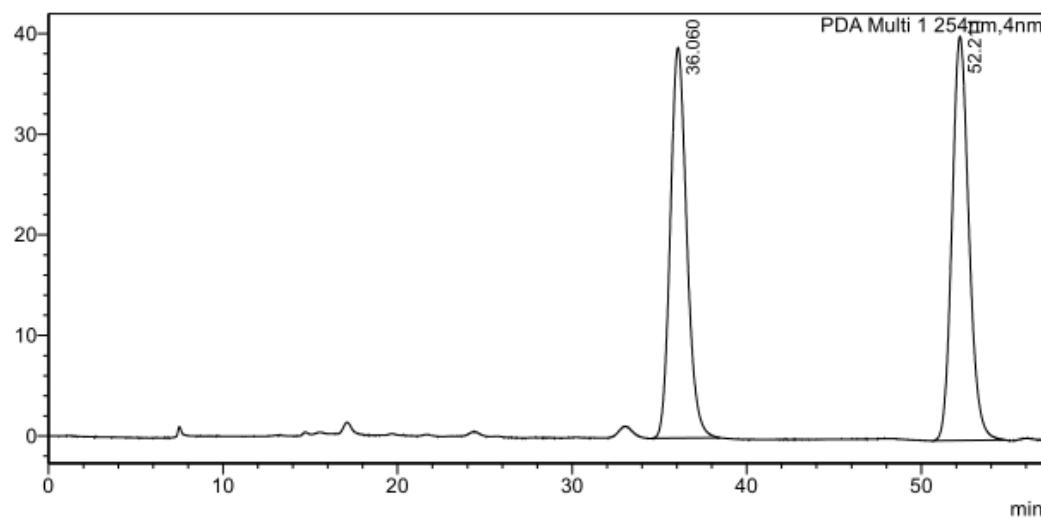
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	22.813	10988359	92.165	154349
2	30.875	934155	7.835	10351
Total		11922514	100.000	164700



**<Chromatogram>**

mAU



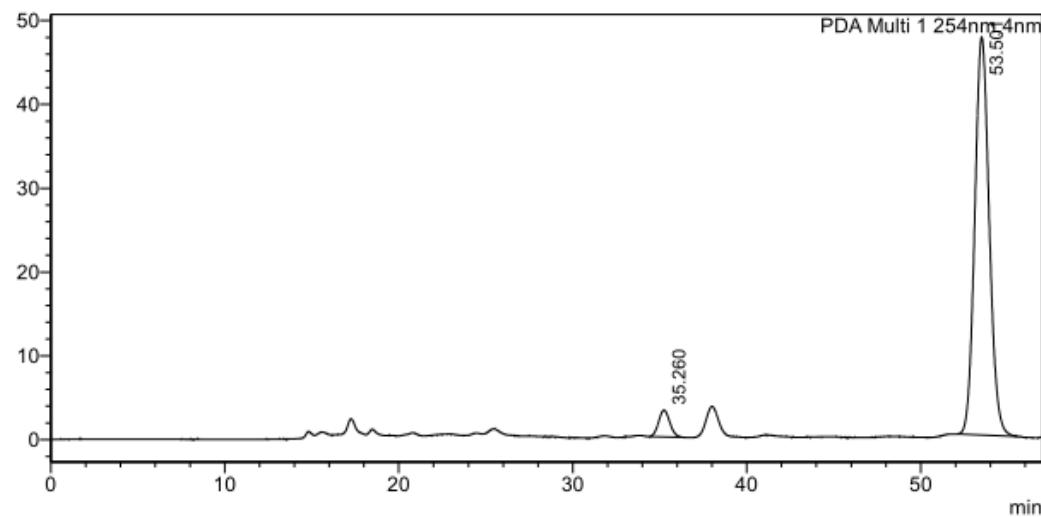
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	36.060	2539125	48.549	38806
2	52.211	2690920	51.451	40138
Total		5230045	100.000	78945

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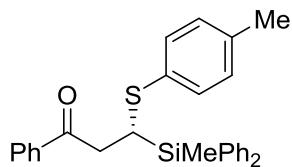
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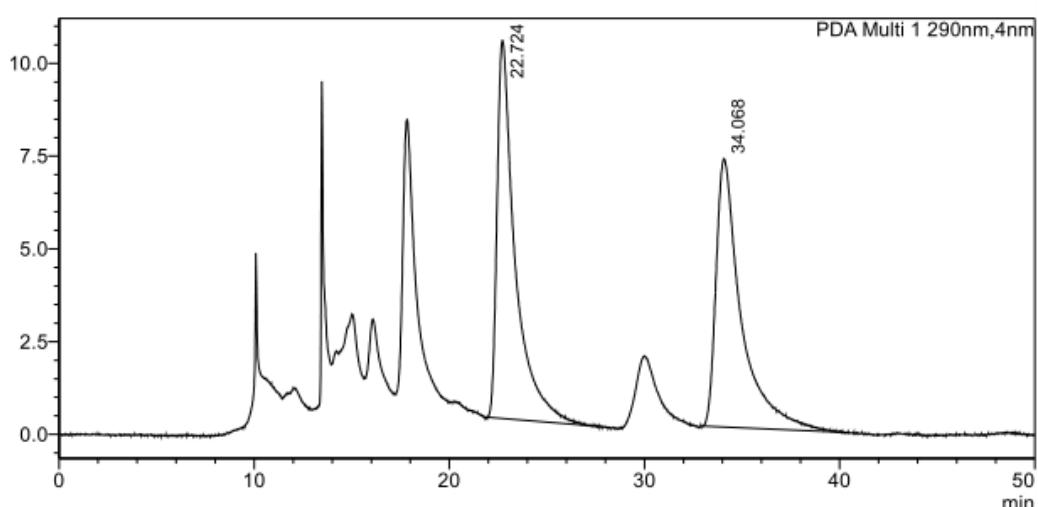
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	35.260	141873	4.909	3191
2	53.501	2748252	95.091	47485
Total		2890125	100.000	50676



**<Chromatogram>**

mAU



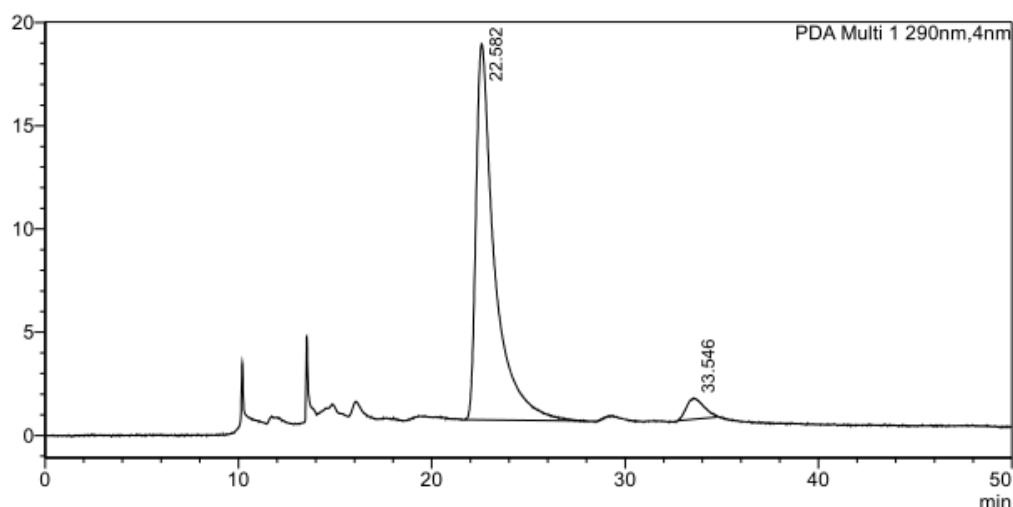
**<Peak Table>**

PDA Ch1 290nm

Peak#	Ret. Time	Area	Area%	Height
1	22.724	657282	50.426	10185
2	34.068	646181	49.574	7220
Total		1303462	100.000	17405

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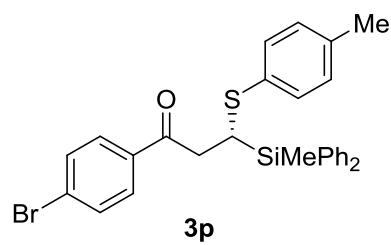
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**<Peak Table>**

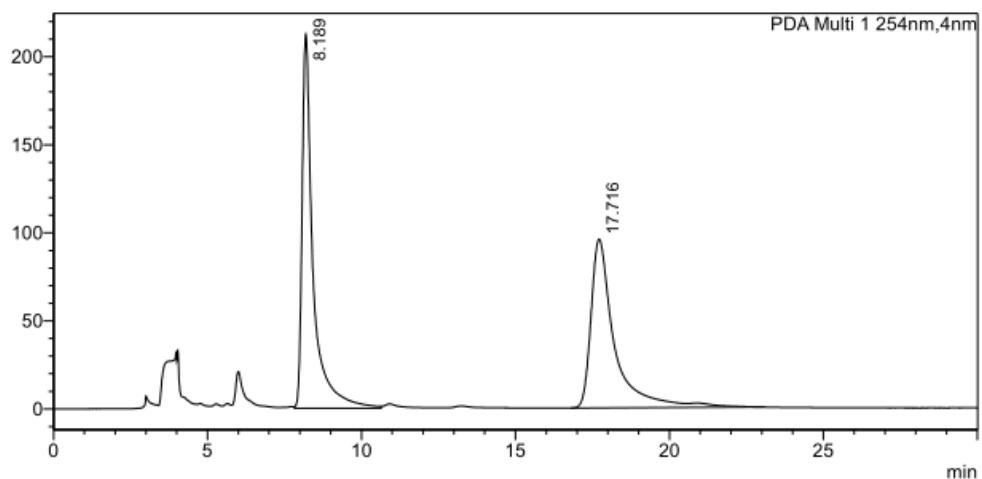
PDA Ch1 290nm

Peak#	Ret. Time	Area	Area%	Height
1	22.582	1211779	95.010	18199
2	33.546	63648	4.990	1000
Total		1275427	100.000	19199



**<Chromatogram>**

mAU



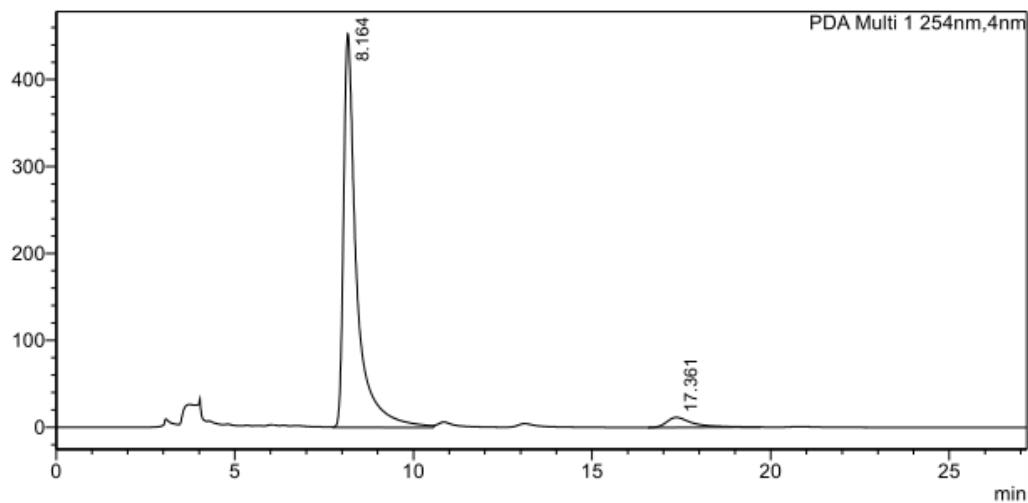
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	8.189	5232353	50.596	212254
2	17.716	5109006	49.404	95801
Total		10341358	100.000	308055

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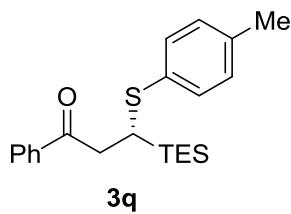
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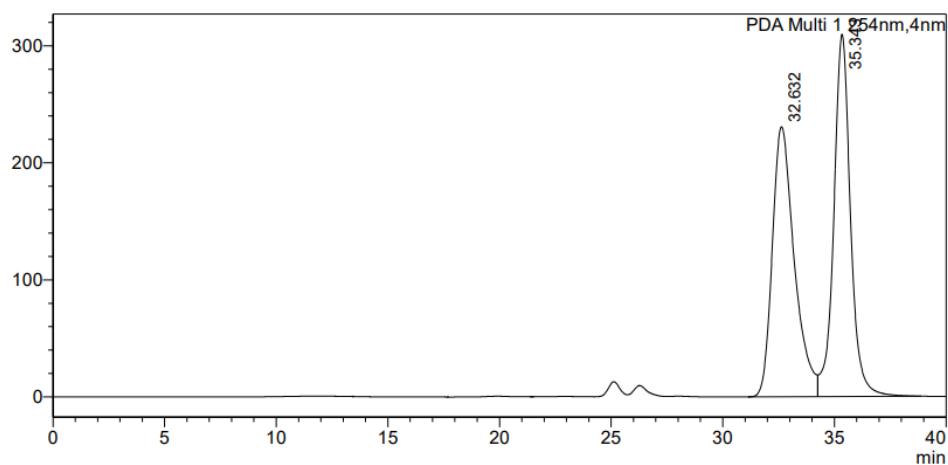
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	8.164	11544524	95.181	452899
2	17.361	584510	4.819	11470
Total		12129034	100.000	464369



**<Chromatogram>**

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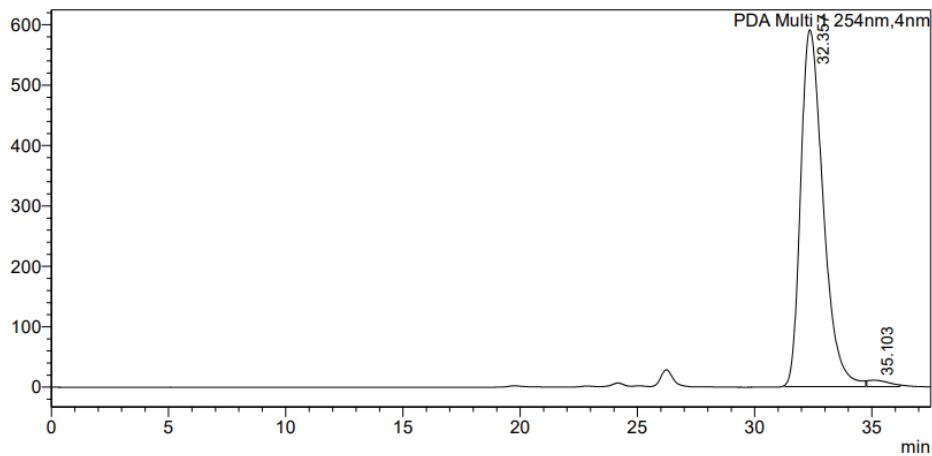
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	32.632	15795983	49.551	230662
2	35.343	16082071	50.449	309465
Total		31878055	100.000	540127

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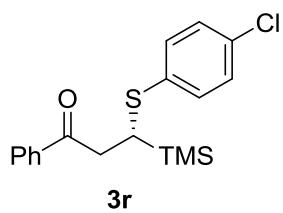
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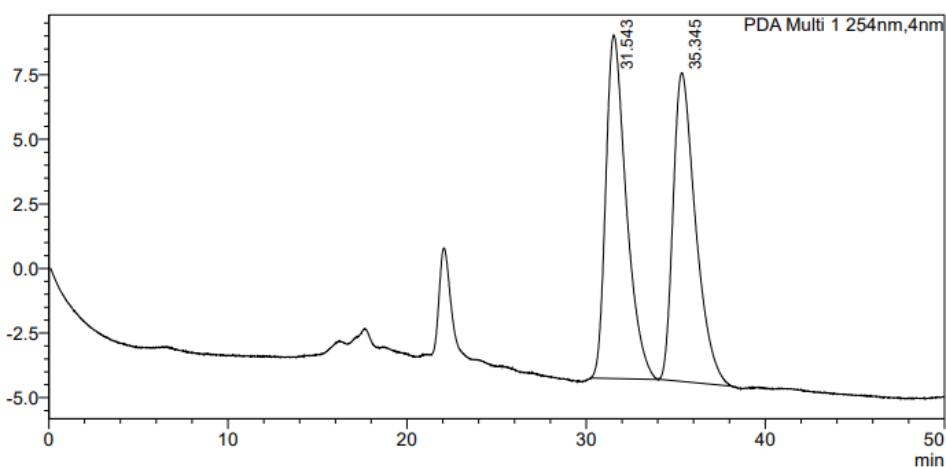
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	32.357	39337528	98.402	590462
2	35.103	638642	1.598	10300
Total		39976170	100.000	600761



**<Chromatogram>**

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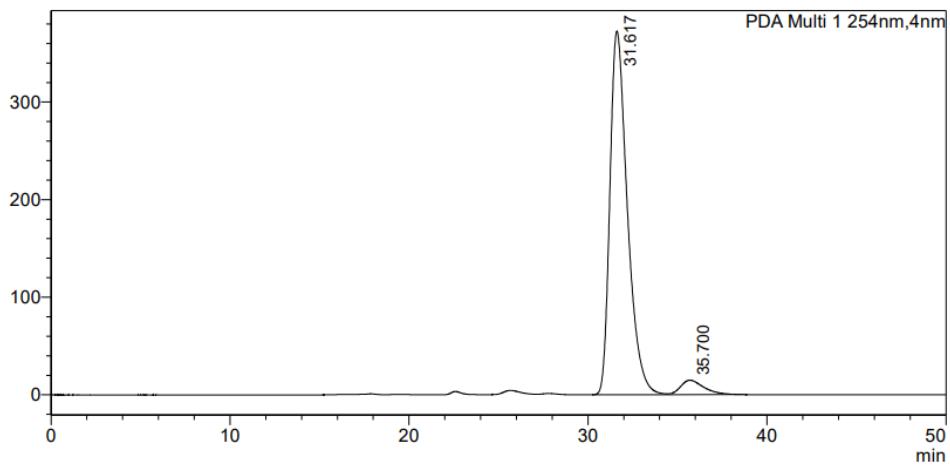
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	31.543	1058906	50.403	13291
2	35.345	1041977	49.597	11946
Total		2100883	100.000	25237

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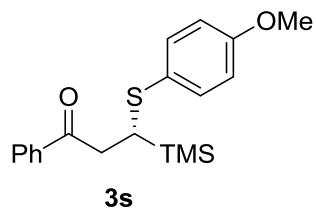
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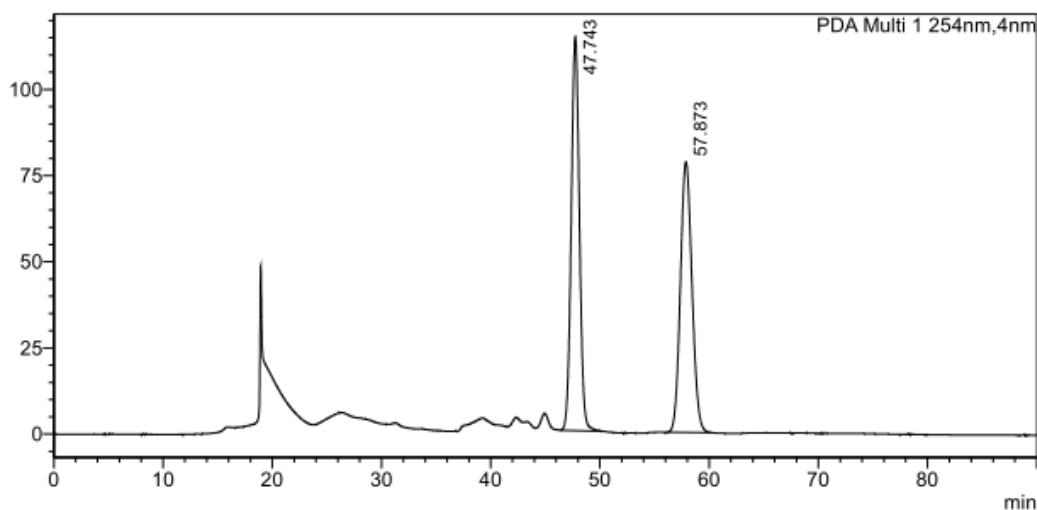
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	31.617	25293424	94.974	372716
2	35.700	1338394	5.026	14766
Total		26631818	100.000	387482



**<Chromatogram>**

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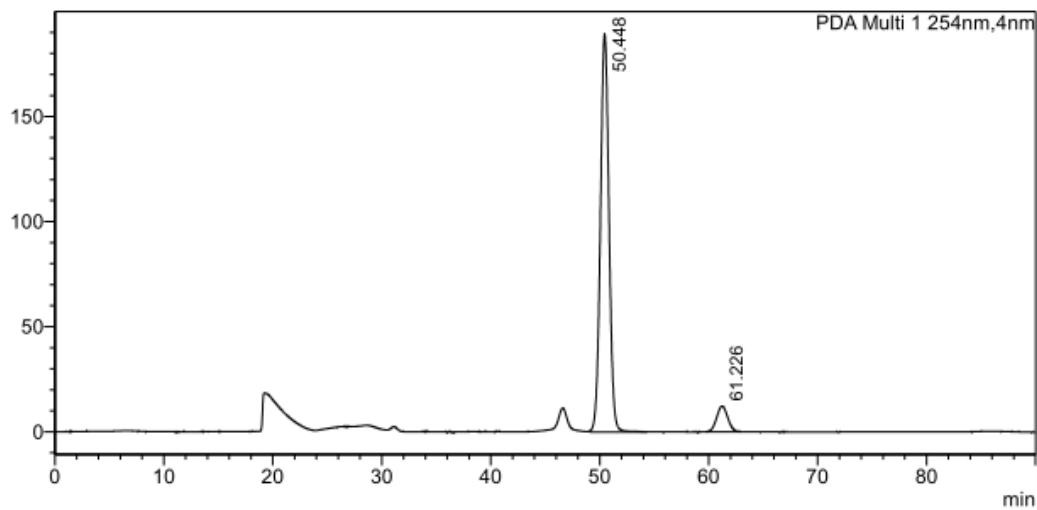
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	47.743	5937768	50.715	114371
2	57.873	5770367	49.285	78515
Total		11708136	100.000	192886

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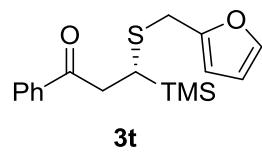
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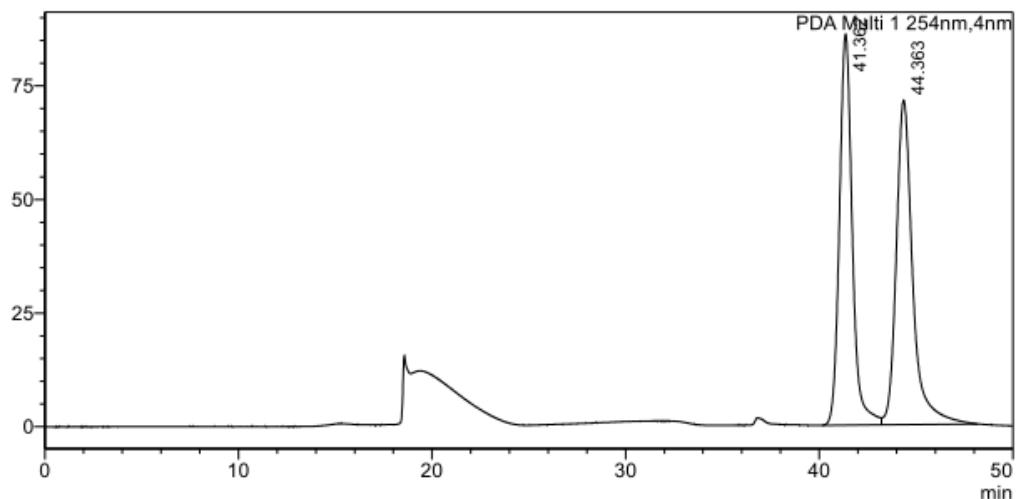
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	50.448	10398147	92.365	189396
2	61.226	859489	7.635	12227
Total		11257637	100.000	201623



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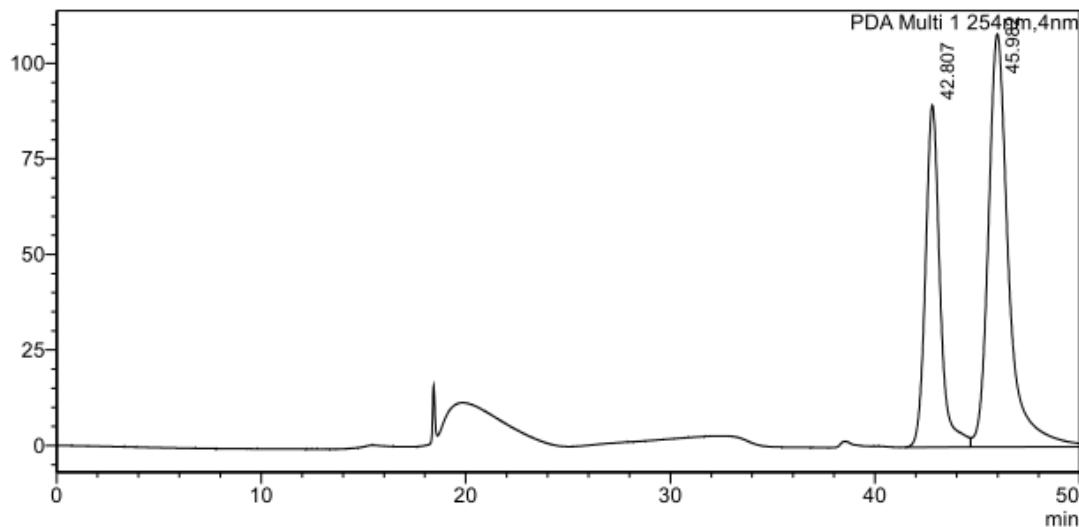
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	41.362	3974228	48.462	86028
2	44.363	4226515	51.538	71401
Total		8200743	100.000	157429

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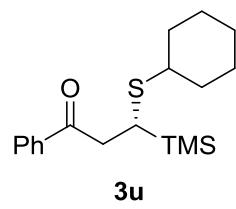
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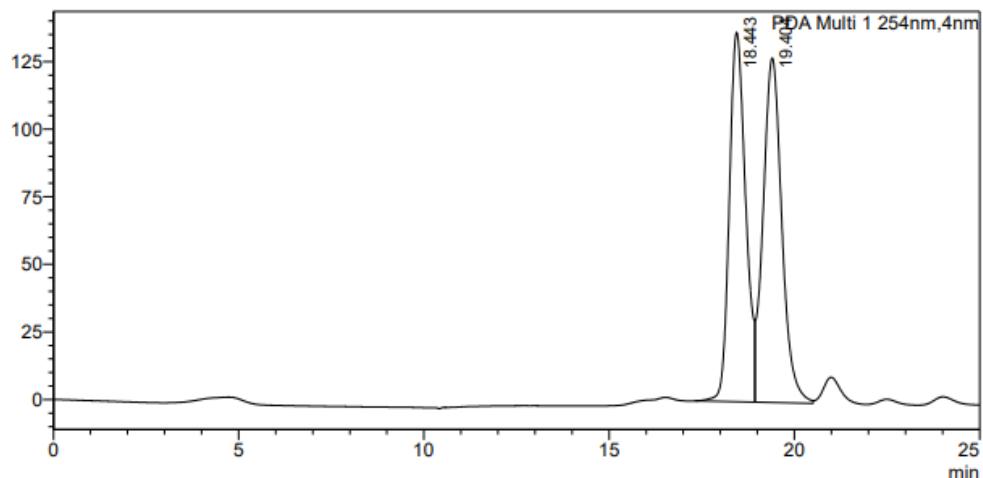
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	42.807	4435099	37.282	89476
2	45.982	7461146	62.718	108028
Total		11896245	100.000	197504



**<Chromatogram>**

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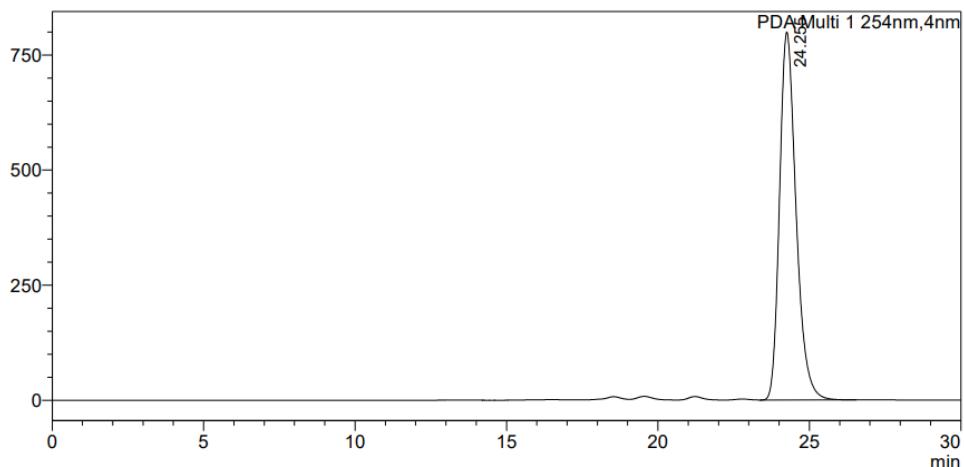
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	18.443	4179183	48.130	136592
2	19.404	4503969	51.870	127399
Total		8683152	100.000	263991

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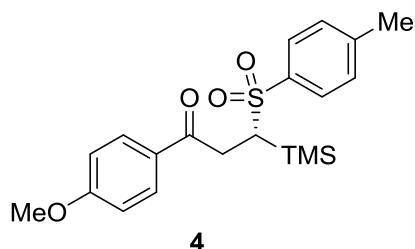
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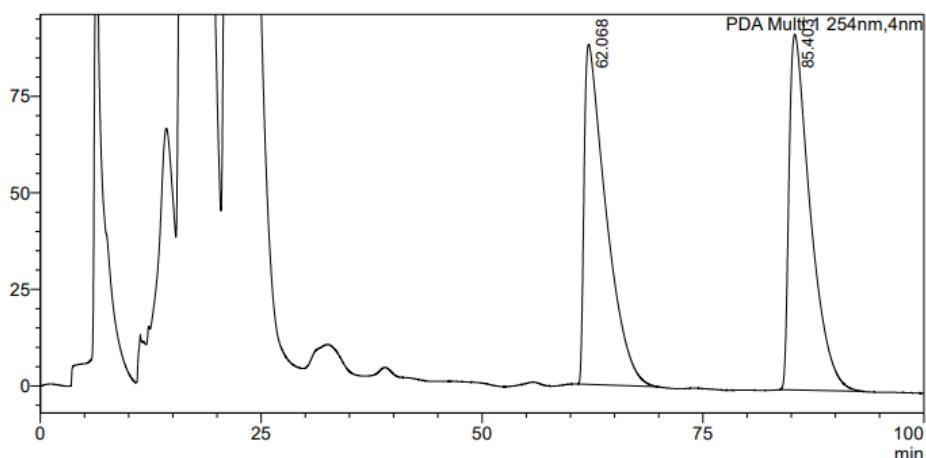
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	24.255	30343869	100.000	799335
Total		30343869	100.000	799335



**<Chromatogram>**

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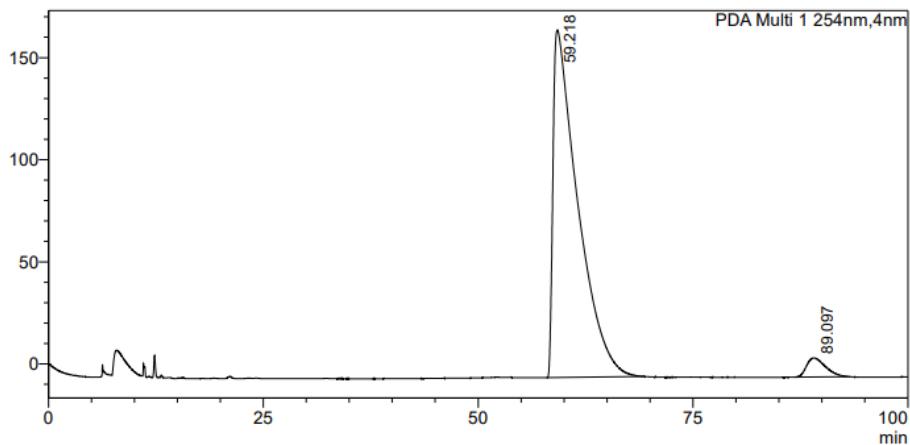
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	62.068	15201578	49.653	88036
2	85.403	15413838	50.347	92080
Total		30615416	100.000	180116

**<Chromatogram>**

mAU



**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	59.218	34017475	95.996	170209
2	89.097	1418700	4.004	9292
Total		35436175	100.000	179501