Supporting Information

Palladium-Catalyzed Thiocarbonylation of Alkenes toward Branched Thioesters using CO_2

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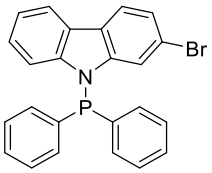
CONTENTS

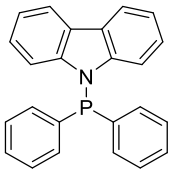
1. General information

All of the reagents except for the ligand **L1** and **L2** were purchased commercially and were used as received. Unless otherwise noted, all experiments were conducted under a nitrogen atmosphere. All chemicals were purchased from Adamas, Aldrich, TCI, Alfa etc. Unless otherwise noted, all commercial reagents were used without further purification. And the NMR spectroscopy was in full accordance with the data in the literature. The products of thiocarbonylation were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, GC, HRMS spectroscopy. NMR spectra were measured using a Bruker NMR (400 MHz). $CDCl_3$, C_6D_6 or DMSO-d_6 was used as the solvent and chemical shifts are reported in ppm relative to solvent: reference to $CDCl_3$: 7.26 ppm (^{1}H NMR) and 77.00 ppm (^{13}C NMR), to C_6D_6: 7.16 ppm (^{1}H NMR) and 128.00 ppm (^{13}C NMR) and to DMSO-d_6: 2.50 ppm (^{1}H NMR) and 39.50 ppm (^{13}C NMR). The coupling constant between fluorine and carbon is not discussed due to the complexity. Gas chromatographic analyses were performed on SHIMADZU GC-2010 Plus spectrometer. GC-MS was obtained using electron ionization (SHIMADZU GCMS-QP2010SE). ESI (electrospray ionization) high resolution mass spectra were recorded on an Agilent Technologies 6530 Q-TOF LC/MS spectrometer. High performance liquid chromatography (HPLC) was performed on Shimadzu LC-20AT instruments using Daicel Chiralcel OJH column.

2. Ligand synthesis

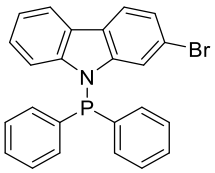


L1



L2

Ligand **L1** and **L2** were synthesized by following a literature procedure.[1] Other ligands (**L3**-**L11**) were purchased from commercial sources and used without further purification.



2-bromo-9-(diphenylphosphanyl)-9H-carbazole (L1)

White solid (Yield = 85%; 3.65 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (m, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.61 (m, 1H), 7.32 (m, 4H), 7.28 - 7.23 (m, 7H), 7.16 - 7.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.9, 133.8, 131.4, 131.2, 129.5, 128.8, 128.8, 126.0, 124.0, 121.1, 121.1, 120.1, 116.7, 116.5, 114.1, 114.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 33.68. HRMS (ESI) $[C_{24}H_{17}BrNP+H]^+$ calculated mass 430.0355, measured mass 430.0360.

Single-Crystal Structure Analysis

Single crystal of ligand **L1** was obtained by recrystallization in dichloromethane and n-hexane. CCDC: 2100007 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

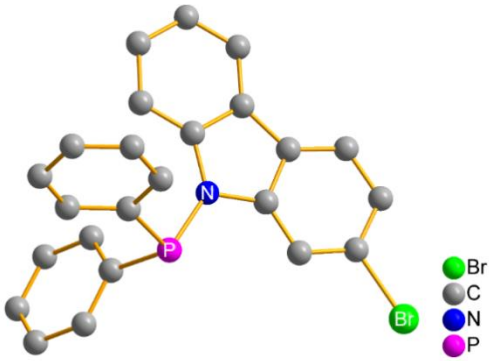
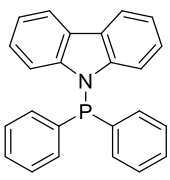


Figure S1. Thermal Ellipsoid Depiction of Compound **L1**

Table S1. Crystal data and structure refinement for compound **L1**

Empirical formula	$C_{24}H_{17}BrNP$
Formula weigh	430.26
Crystal system	monoclinic
Space group	P 21
a (Å)	10.659(2)
b (Å)	8.1881(16)
c (Å)	11.525(2)
α (°)	90.000
β (°)	101.380(3)
γ (°)	90.000
V ($Å^3$)	986.1(3)
Z	2
Temperature/K	296(2)
F (000)	436
Crystal size/mm^3	0.30 × 0.30 × 0.20
θ min, θ max (deg)	1.802, 24.992
Reflections collected	4998
Independent reflections	3353 (R_{int} = 0.0214, R_{sigma} = 0.0823)
Data/restraints/parameters	3353/1/244
Goodness-of-fit on F^2	0.974
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.0896
Final R indexes [all data]	R_1 = 0.0502, wR_2 = 0.0980
Largest diff. peak and hole/ e $Å^{-3}$	0.415/-0.262



9-(diphenylphosphanyl)-9H-carbazole (L2)[2]

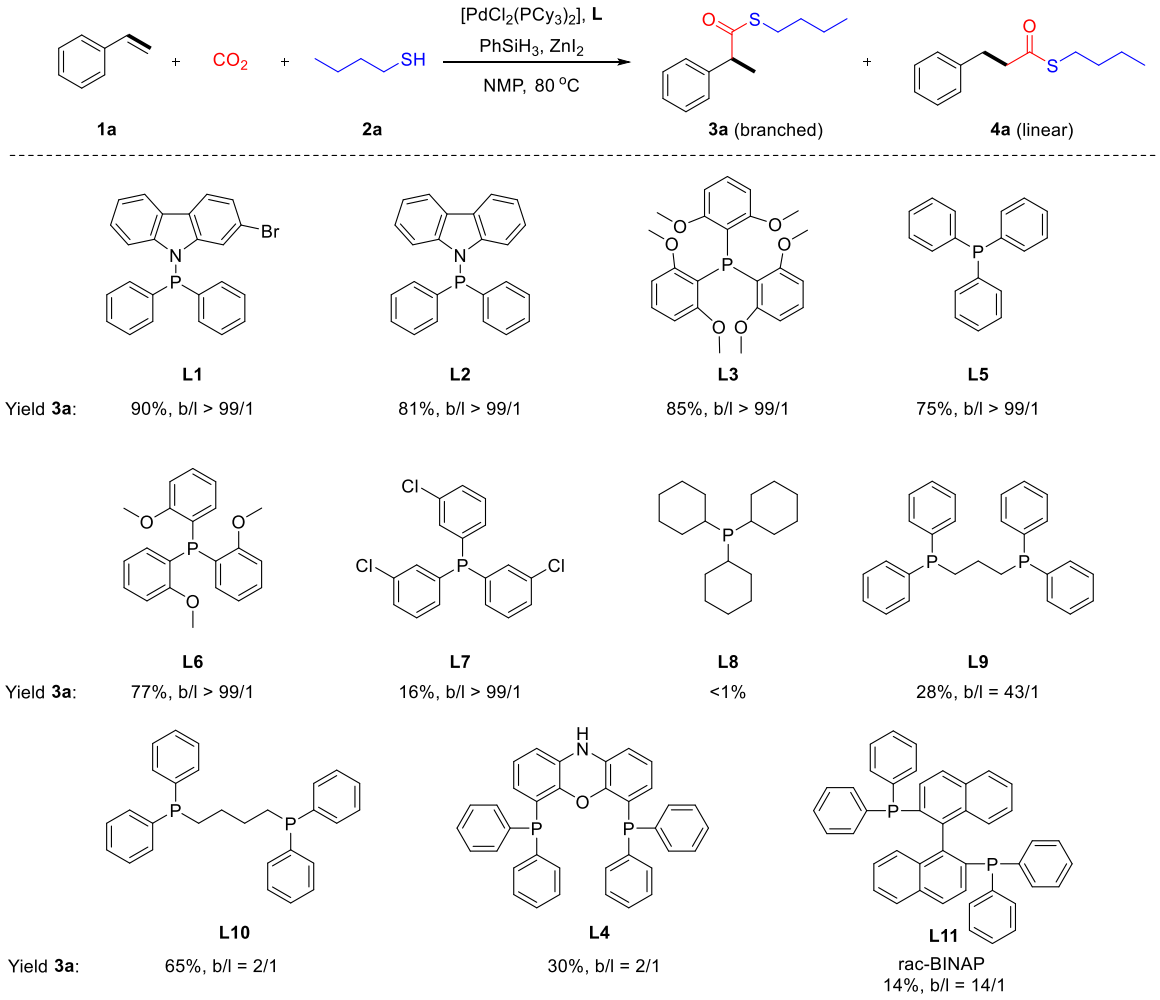
Yellow liquid (Yield = 80%; 2.80 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 - 8.02 (m, 2H), 7.73 (m, 2H), 7.52 (d, J = 4.0 Hz, 2H), 7.45 (m, 4H), 7.34 (t, J = 4.0 Hz, 5H), 7.26 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 134.3, 131.2, 129.2, 128.6, 125.6, 120.7, 120.1, 113.8, 113.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.87.

3. Typical procedure for thiocarbonylation of styrenes using CO_2

To a 4 mL sealing tube in a nitrogen-filled glovebox, the alkene (0.2 mmol), thiol (1.7 equiv, 0.34 mmol), palladium-catalyst (5.0 mmol%, 0.01 mmol), ligand (10.0 mmol%, 0.02 mmol), $PhSiH_3$ (1.8 equiv, 0.36 mmol), ZnI_2 (20.0 mmol%, 0.04 mmol)/DABCO (20.0 mmol%, 0.04 mmol) were added followed by addition of solvent *N*-methylpyrrolidone (NMP) (0.5 mL). Then the tube was sealed, taken out of the glovebox and placed into the autoclave. The autoclave was sealed and purged three times with CO_2 gas, then pressurized to 20 atm. Finally, the autoclave was heated at 80 ℃ for 18 h with stirring. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The result was measured by GC and GC-MS analysis using dodecane as internal standard or the product was purified by silica gel giving the isolated yield.

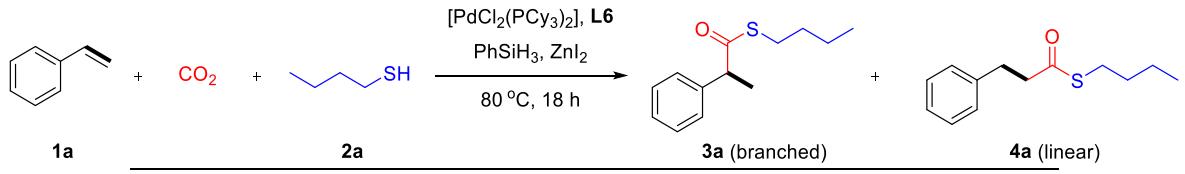
3.1 Screening of reaction conditions

Scheme S1. Ligand screening for the thiocarbonylation of styrene[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5.0 mol%), ligand (10.0 mol%), ZnI_2 (20.0 mol%), $PhSiH_3$ (1.8 equiv.), CO_2 (20 bar), NMP (0.5 mL), stirred at 80 ℃ for 18 h. Yield of **3a** and **4a** was determined by GC analysis using dodecane as the internal standard.

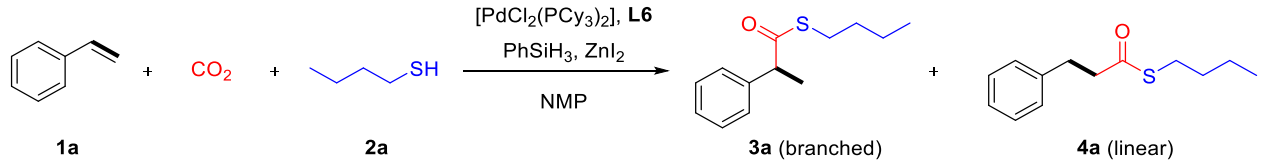
Table S2. Solvent screening for the thiocarbonylation of styrene[a]



Entry	Solvent/mL	Yield of **3a**/%	Yield of **4a**/%
1	**NMP**	**70**	**0.5**
2	Toluene	4	2
3	CH_3CN	0.3	0.2
4	DMF	40	3
5	DMSO	0.4	3
6	Diglyme	1	3
7	THF	0.5	0.2

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5.0 mol%), ligand (10.0 mol%), ZnI_2 (20 mol%), $PhSiH_3$ (1.8 equiv.), CO_2 (20 bar), solvent (0.5 mL), stirred at 80 °C for 18 h. Yield of **3a** and **4a** was determined by GC analysis using dodecane as the internal standard.

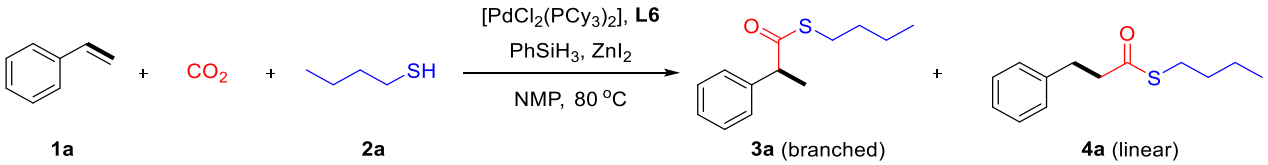
Table S3. Temperature and time screening for the thiocarbonylation of styrene[a]



Entry	Temperature/°C	Time/h	Yield of **3a**/%	Yield of **4a**/%
1	80	12	70	0.5
2	40	12	53	1
3	60	12	58	3
4	80	8	65	1
5	80	16	72	0.3
6	**80**	**18**	**77**	**0.5**

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5 mol%), ligand (10.0 mol%), ZnI_2 (20 mol%), $PhSiH_3$ (1.8 equiv.), CO_2 (20 bar), NMP (0.5 mL). Yield of **3a** and **4a** was determined by GC analysis using dodecane as the internal standard.

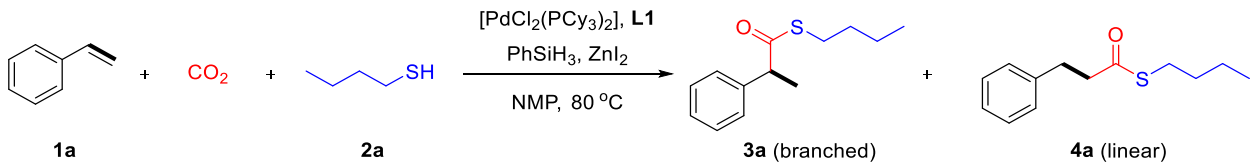
Table S4. The amount of solvent screening for the thiocarbonylation of styrene[a]



Entry	NMP/mL	Yield of **3a**/%	Yield of **4a**/%
1	**0.5**	**77**	**0.5**
2	0.3	69	1
3	0.7	75	1

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5.0 mol%), ligand (10.0 mol%), ZnI_2 (20 mol%), $PhSiH_3$ (1.8 equiv.), CO_2 (20 bar), stirred at 80 °C for 18 h. Yield of **3a** and **4a** was determined by GC analysis using dodecane as the internal standard.

Table S5. The pressure of carbon dioxide screening for the thiocarbonylation of styrene[a]



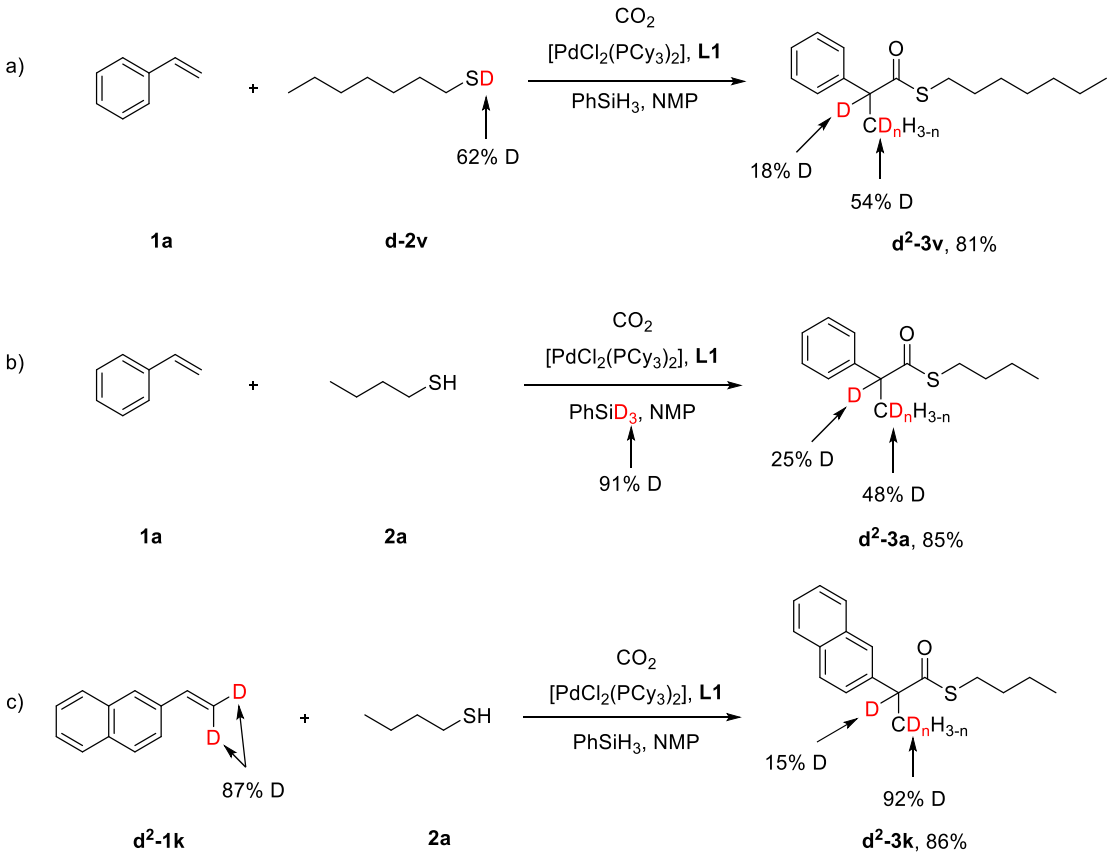
1a 2a 3a (branched) 4a (linear)

Entry	Pressure/bar	Yield of **3a**/%	Yield of **4a**/%
1	10	83	0.5
2	**20**	**90**	**0.4**
3	30	87	0.8

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5.0 mol%), ligand (10.0 mol%), ZnI_2 (20 mol%), $PhSiH_3$ (1.8 equiv.), NMP (0.5 mL), stirred at 80 °C for 18 h. Yield of **3a** and **4a** was determined by GC analysis using dodecane as the internal standard.

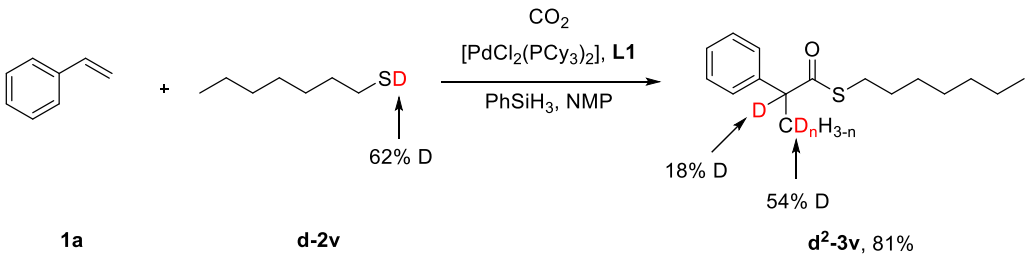
4. Deuterium-labelling experiments

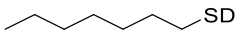
Scheme S2. Deuterium-labeling experiments[a]



[a]Reaction conditions: **d²-1k**/**1a** (0.2 mmol), **2a**/**d-2v** (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5.0 mol%), **L1** (10.0 mol%), [Si-H/D] (1.8 equiv.), CO_2 (20 bar), NMP (0.5 mL), and stirred at 80 °C for 18 h. Isolated yields of branched products.

4.1 Deuterium-labeled heptanethiol (d-2v) were synthesized by following a literature procedure.[3]

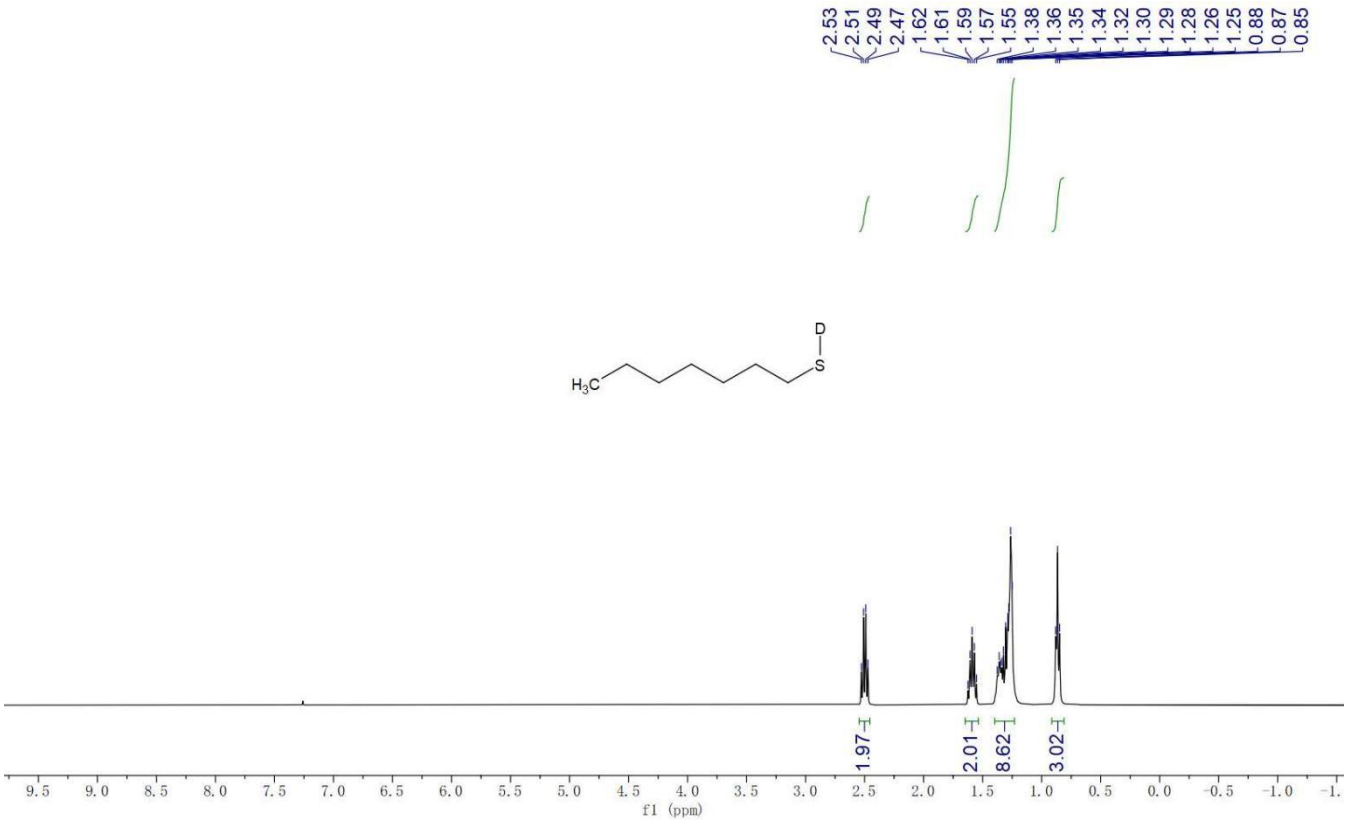


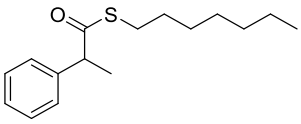


heptane-1-thiol-*d* (d-2v)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (q, J = 8.0 Hz, 2H), 1.59 (p, J = 8.2 Hz, 2H), 1.40 - 1.23 (m, 9H), 0.86 (t, J = 8.0 Hz, 3H).

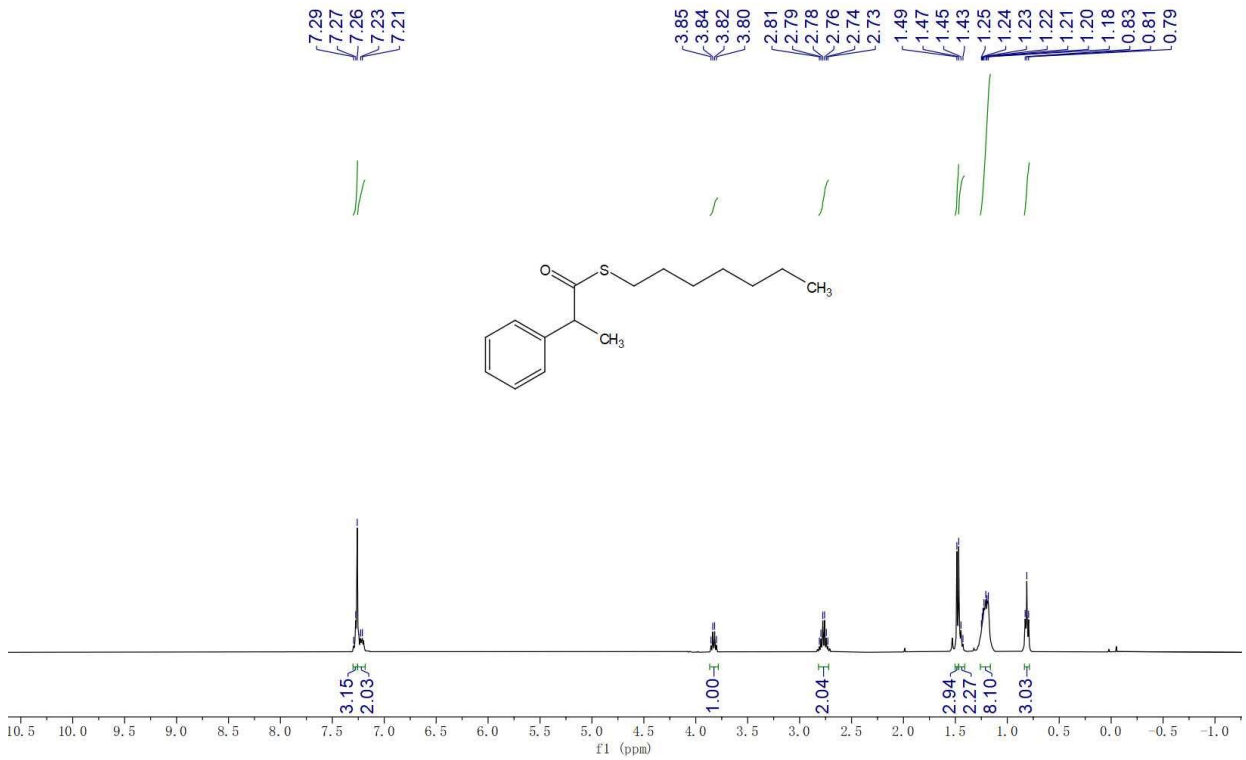
$$D\% = 1 - \frac{\frac{9.00 - 8.62}{1}}{\frac{1.97 + 2.01 + 8.00 + 3.02}{2 + 2 + 8 + 3}} = 1 - \frac{0.380}{1.000} = 62\%$$

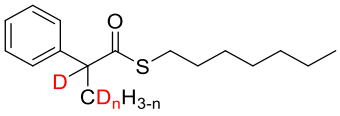




***S*-heptyl 2-phenylpropanethioate (3v)[4]**

Yellow liquid (Yield = 85%; 44.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (t, J = 8.0 Hz, 3H), 7.22 (d, J = 8.0 Hz, 2H), 3.83 (q, J = 8.0 Hz, 1H), 2.77 (m, 2H), 1.48 (m, J = 8.0 Hz, 3H), 1.45 (t, J = 8.0 Hz, 2H), 1.26 - 1.16 (m, 8H), 0.81 (t, J = 8.0 Hz, 3H).



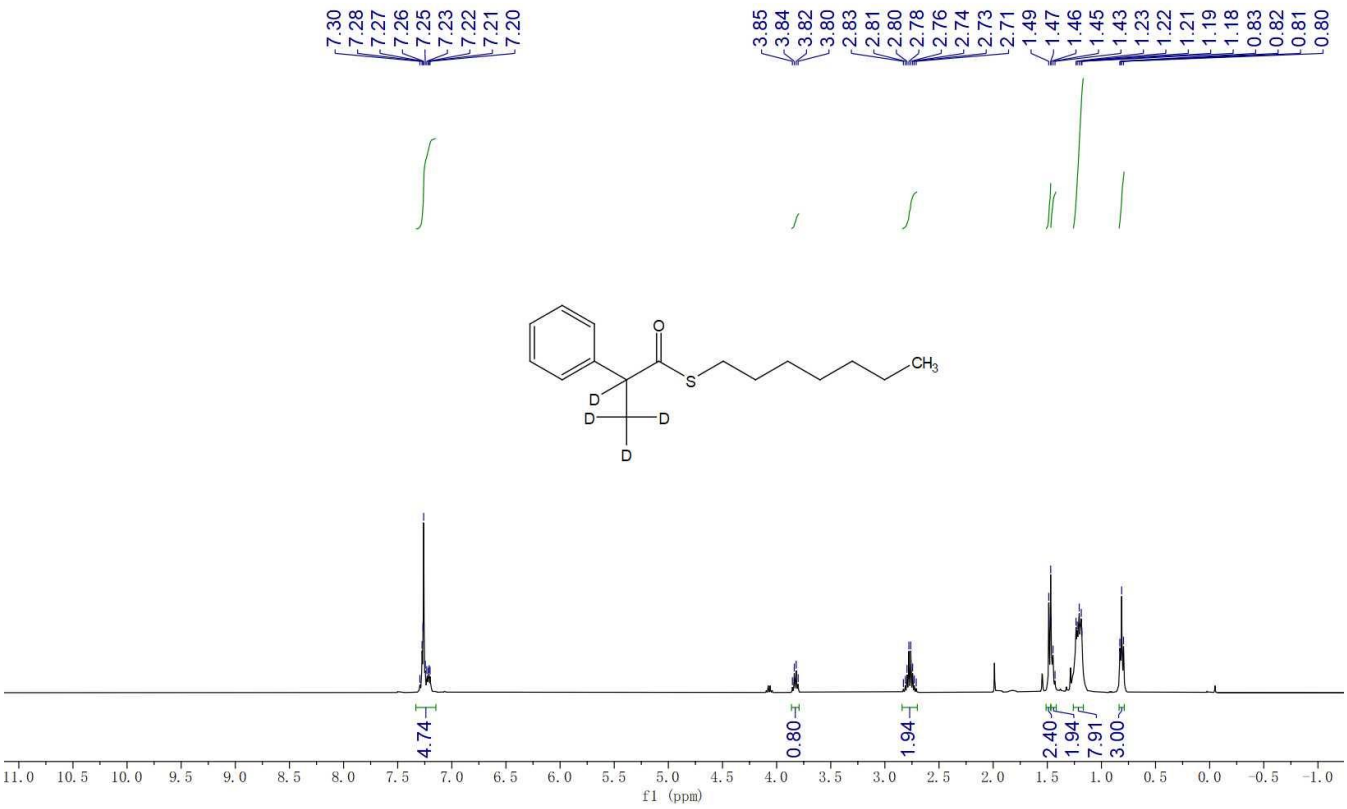


_S_-heptyl 2-phenylpropanethioate-2,3,3,3-d_4 (d^2-3v)

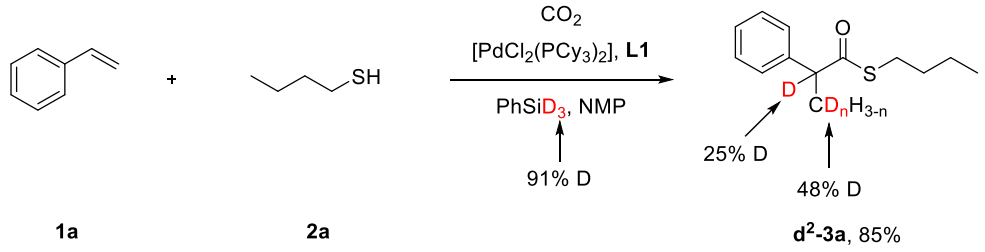
Yellow liquid (Yield = 81%; 42.8 mg);; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 - 7.15 (m, 5H), 3.83 (q, J = 8.0 Hz, 1H), 2.77 (m, 2H), 1.48 (d, J = 8.0 Hz, 2H), 1.46 (t, J = 8.0 Hz, 2H), 1.26 - 1.17 (m, 8H), 0.81 (t, J = 8.0 Hz, 3H).

$$D\ (D)\% = 1 - \frac{\frac{0.80}{1}}{\frac{4.74 + 1.94 + 1.94 + 7.91 + 3.00}{5 + 2 + 2 + 8 + 3}} = 1 - \frac{0.8}{0.977} = 18\%$$

$$D\ (CD_nH_{3-n})\% = 3 - \frac{2.40}{\frac{4.74 + 1.94 + 1.94 + 7.91 + 3.00}{5 + 2 + 2 + 8 + 3}} = 3 - \frac{2.40}{0.977} = 54\%$$



4.2 Deuterium-labeled phenylsilane were synthesized by following a literature procedure.[5]



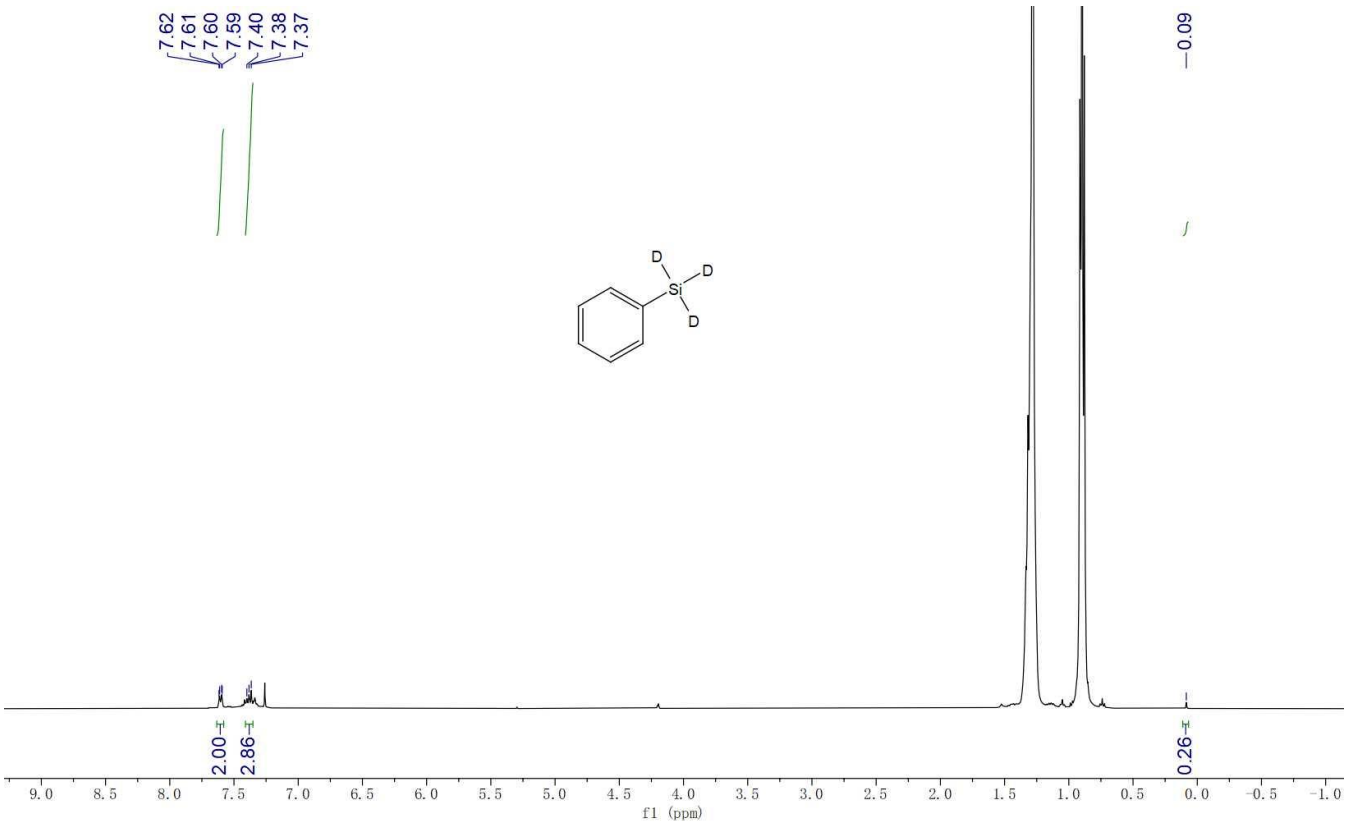
1a **2a** **d²-3a**, 85%

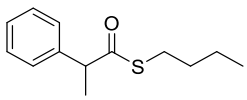
$PhSiD_3$

phenylsilane-*d*₃

^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 - 7.58 (m, 2H), 7.41 - 7.35 (m, 3H).

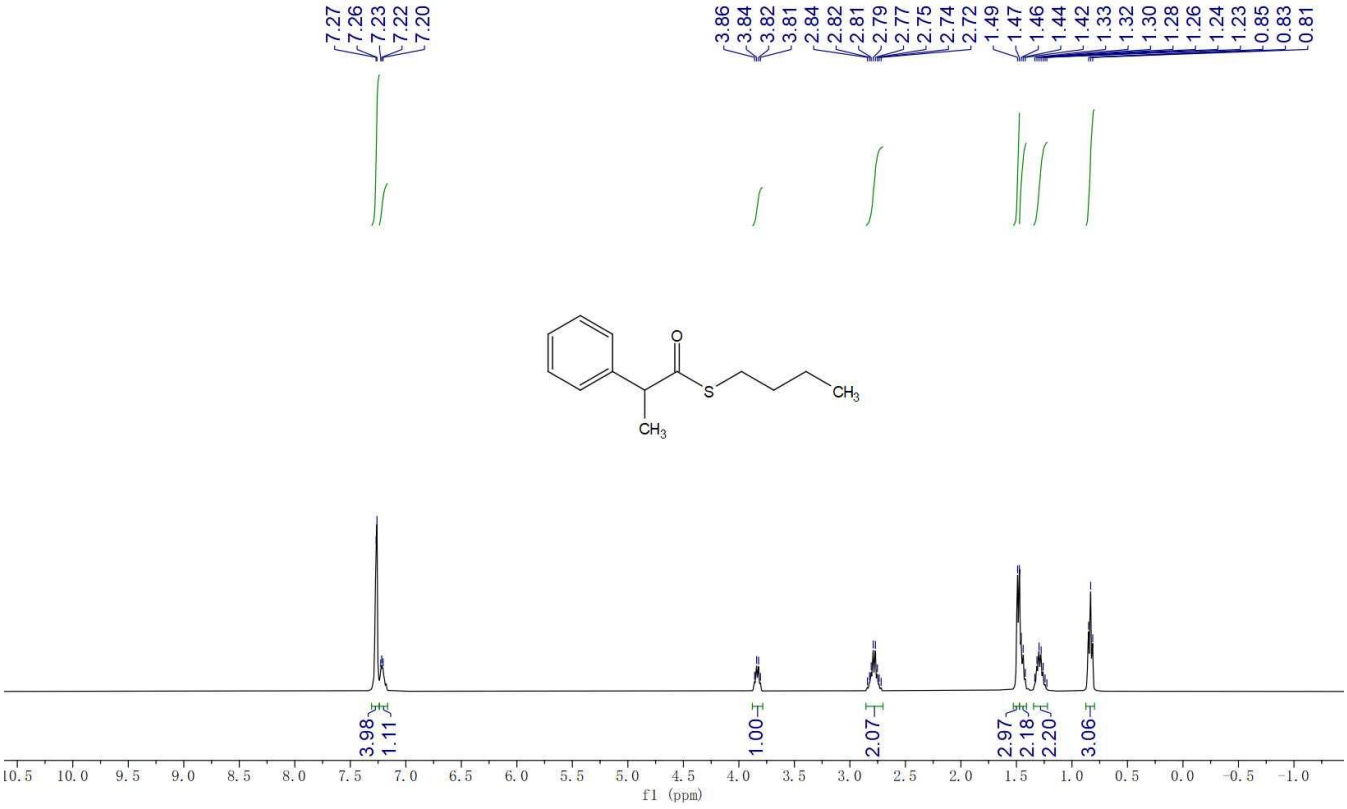
$$D\% = 1 - \frac{\frac{0.26}{3}}{\frac{2.00 + 3.08}{2 + 3}} = 1 - \frac{0.087}{1.016} = 91\%$$

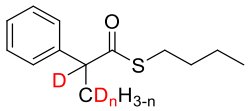




***S*-butyl 2-phenylpropanethioate (3a)[6]**

Yellow liquid (Yield = 90%; 40.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, J = 4.0 Hz, 4H), 7.22 (t, J = 4.0 Hz, 1H), 3.83 (q, J = 8.0 Hz, 1H), 2.77 (m, 2H), 1.48 (d, J = 8.0 Hz, 3H), 1.45 (t, J = 8.0 Hz, 2H), 1.28 (m, 2H), 0.83 (t, J = 8.0 Hz, 3H).



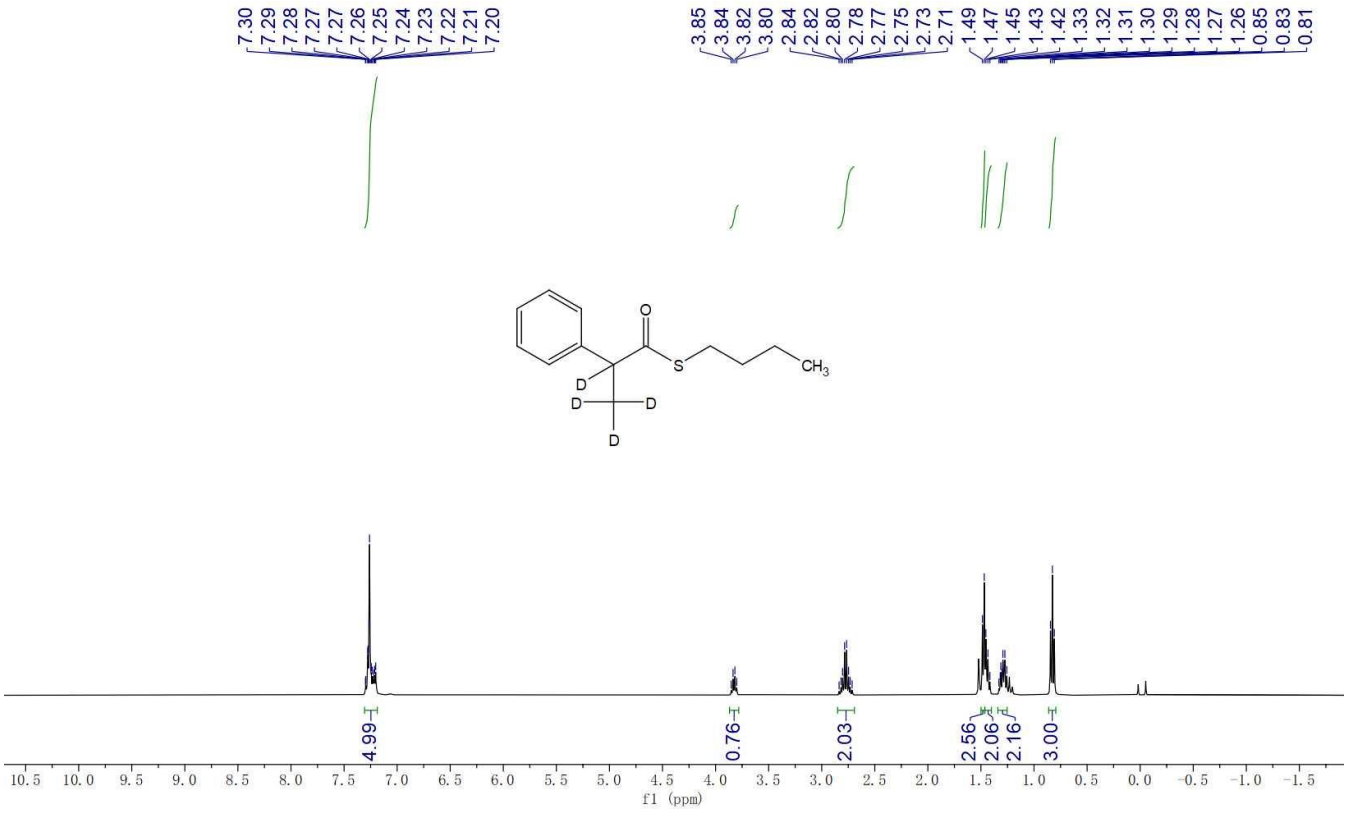


_S_-butyl 2-phenylpropanethioate-2,3,3,3-d_4 (d^2-3a)

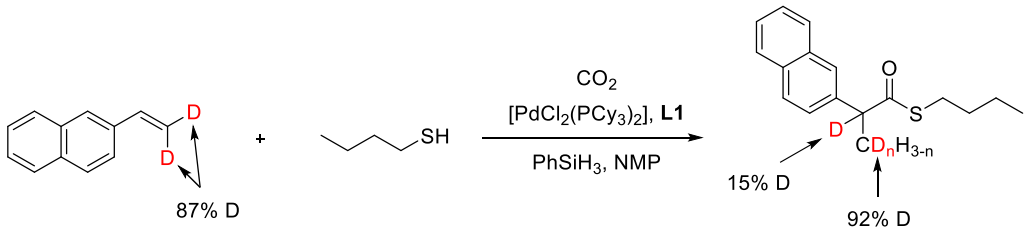
Yellow liquid (Yield = 85%; 37.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 - 7.19 (m, 5H), 3.83 (m, 1H), 2.85 - 2.69 (m, 2H), 1.48 (d, J = 8.0 Hz, 3H), 1.46 - 1.40 (m, 2H), 1.30 (m, 2H), 0.83 (t, J = 8.0 Hz, 3H).

$$D\,(D)\% = 1 - \frac{\frac{0.76}{1}}{\frac{4.99 + 2.03 + 2.06 + 2.16 + 3.00}{5 + 2 + 2 + 2 + 3}} = 1 - \frac{0.76}{1.017} = 25\%$$

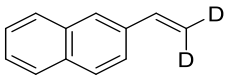
$$D\,(CD_nH_{3-n})\% = 3 - \frac{2.56}{\frac{4.99 + 2.03 + 2.06 + 2.16 + 3.00}{5 + 2 + 2 + 2 + 3}} = 3 - \frac{2.56}{1.017} = 48\%$$



4.3 Deuterium-labeled 2-Vinylnaphthalene (d^2-1k) were synthesized by following a literature procedure.[7]



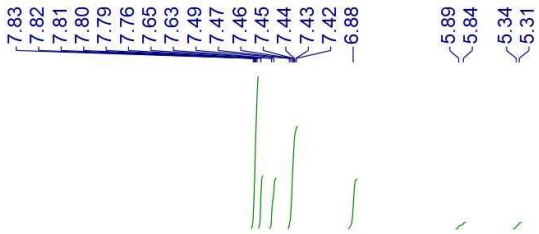
d²-1k **2a** **d²-3k**, 86%

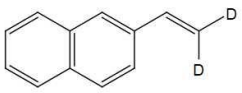


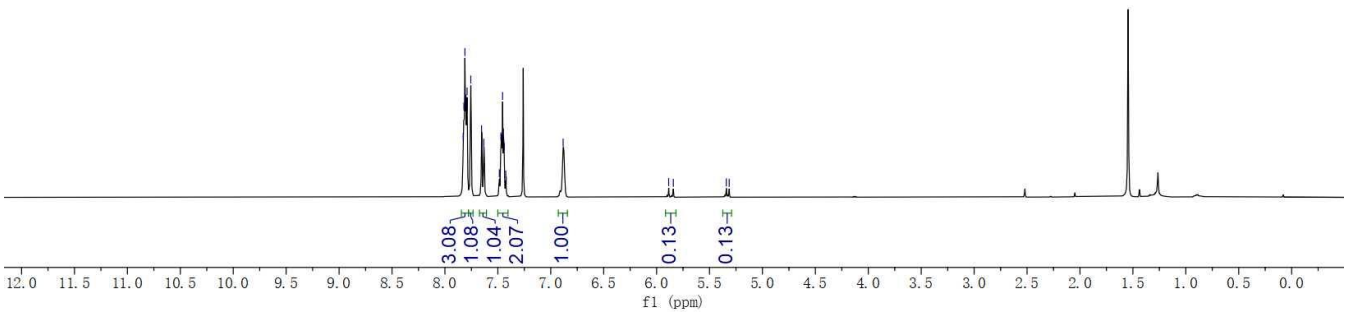
2-(vinyl-2,2-*d*₂)naphthalene (d²-1k)

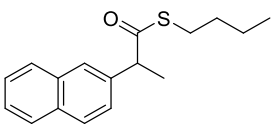
White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (m, 3H), 7.76 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.50 - 7.40 (m, 2H), 6.88 (s, 1H).

$$D\% = 1 - \frac{\frac{0.13 + 0.13}{1 + 1}}{\frac{3.08 + 1.08 + 1.04 + 2.07 + 1}{3 + 1 + 1 + 2 + 1}} = 1 - \frac{0.130}{1.034} = 87\%$$



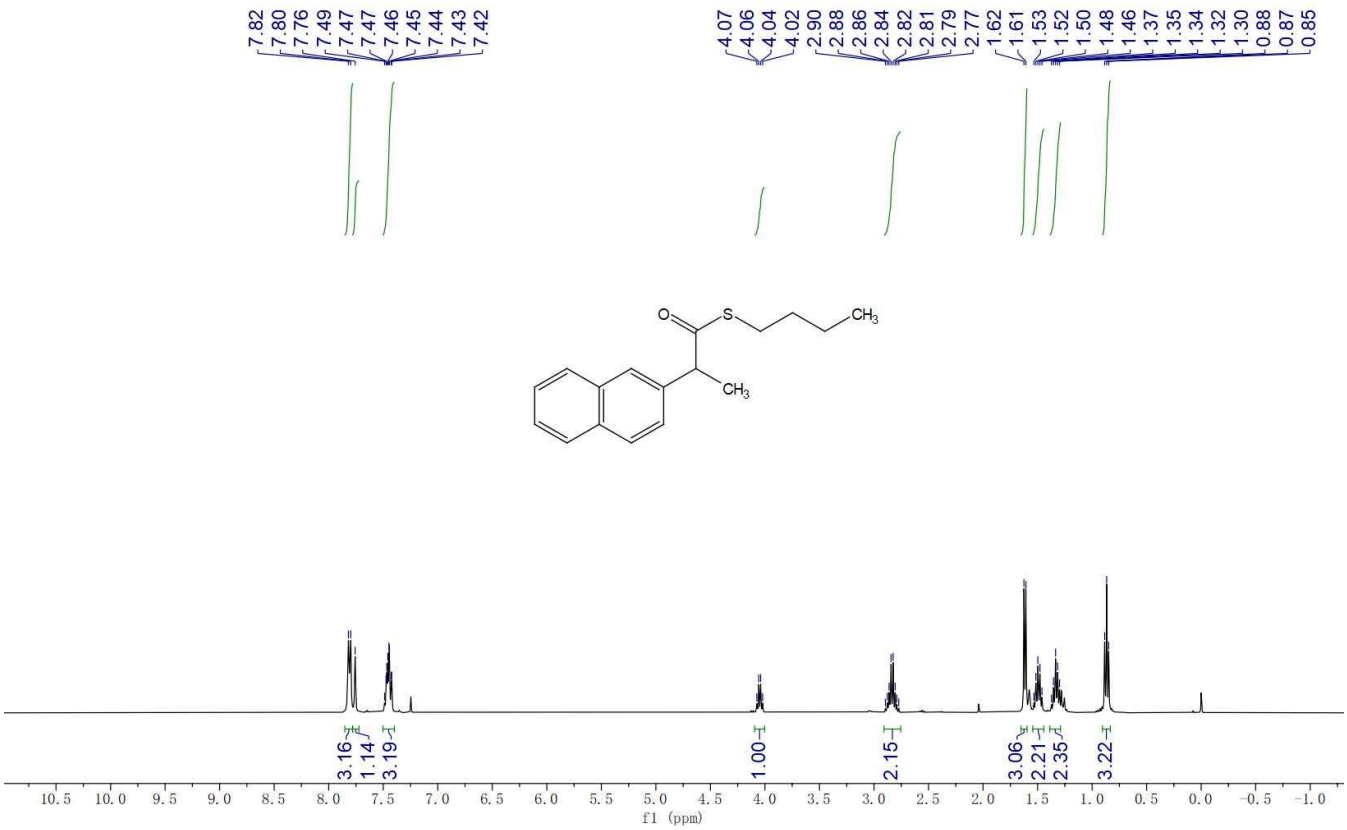


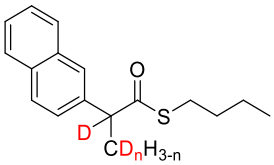




***S*-butyl 2-(naphthalen-2-yl) propanethioate (3k)**

Yellow liquid (Yield = 91%; 49.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.0 Hz, 3H), 7.76 (s, 1H), 7.45 (m, 3H), 4.05 (q, J = 8.0 Hz, 1H), 2.83 (m, 2H), 1.62 (d, J = 4.0 Hz, 3H), 1.50 (m, 2H), 1.34 (m, 2H), 0.87 (t, J = 8.0 Hz, 3H). HRMS (ESI) $[C_{17}H_{20}OS+H]^+$ calculated mass 273.1316, measured mass 273.1308.



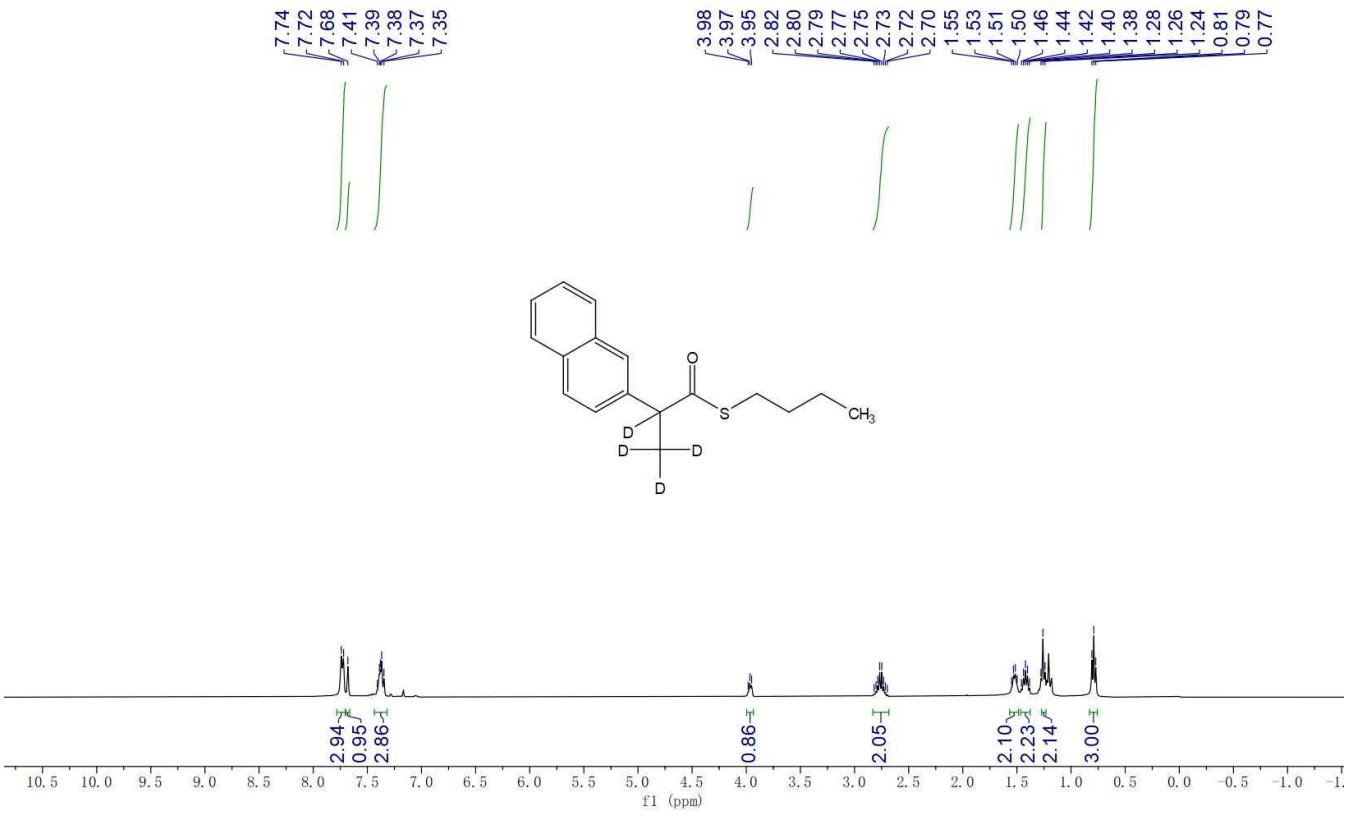


_S_-butyl 2-(naphthalen-2-yl) propanethioate-2,3,3,3-d_4 (d^2-3k)

Yellow liquid (Yield = 86%; 46.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.0 Hz, 3H), 7.68 (s, 1H), 7.44 - 7.32 (m, 3H), 3.97 (t, J = 8.0 Hz, 1H), 2.77 (m, 2H), 1.52 (m, 2H), 1.42 (m, 2H), 1.26 (m, 2H), 0.79 (t, J = 8.0 Hz, 3H).

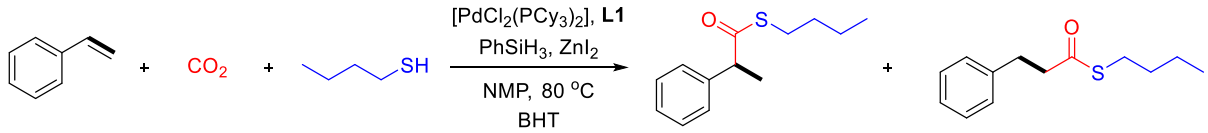
$$D\ (D)\% = 1 - \frac{\frac{0.86}{1}}{\frac{2.94 + 0.95 + 2.86 + 2.05 + 2.23 + 2.14 + 3}{3 + 1 + 3 + 2 + 2 + 2 + 3}} = 1 - \frac{0.86}{1.011} = 15\%$$

$$D\ (CD_nH_{3-n})\% = 3 - \frac{2.1}{\frac{2.94 + 0.95 + 2.86 + 2.05 + 2.23 + 2.14 + 3}{3 + 1 + 3 + 2 + 2 + 2 + 3}} = 3 - \frac{2.1}{1.011} = 92\%$$



5. Mechanism verification experiments

5.1 Mechanism of free radical elimination[a]



1a + CO_2 + **2a** → **3a** (branched) yield: 89% + **4a** (linear) <1%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5.0 mol%), ligand (10 mol%), ZnI_2 (20 mol%), $PhSiH_3$ (1.8 equiv.), butylated hydroxytoluene (1.0 equiv.), NMP (0.5 mL), CO_2 (20 bar), and stirred at 80 ℃ for 18 h. Yield of **3a** and **4a** was determined by GC analysis using dodecane as the internal standard.

5.2 Verification of palladium hydrogen species.

In the glove box, add 0.01mmol (8 mg) of $PdCl_2(PCy_3)_2$, 0.4 mmol (44 μL) of phenylsilane and 500 μL of deuterated benzene into the young tube, then remove the glove box and heat at 80 ℃ for 4 h to test ^{1}H NMR and ^{31}P NMR: negative hydrogen signals were not found and ^{31}P-NMR signal (25.09 ppm) of $PdCl_2(PCy_3)_2$ was observed (**experiment A**). After adding 0.4 mmol (36 μL) C_4H_9SH to the above reaction solution and heated at 80 ℃ for 1 h to test ^{1}H NMR and ^{31}P NMR: a new negative hydrogen signals at -14.36 ppm and a new ^{31}P-NMR signal at 42.10 ppm were observed might be due to the formation of trans $Pd(PCy_3)_2(H)(SC_4H_9)$ (**experiment B**). Furthermore, heating the above mixture at 80 ℃ for 4 h and 18 h increased the negative hydrogen signal and ^{31}P-NMR signal (42.10 ppm) (**experiments C and D**).

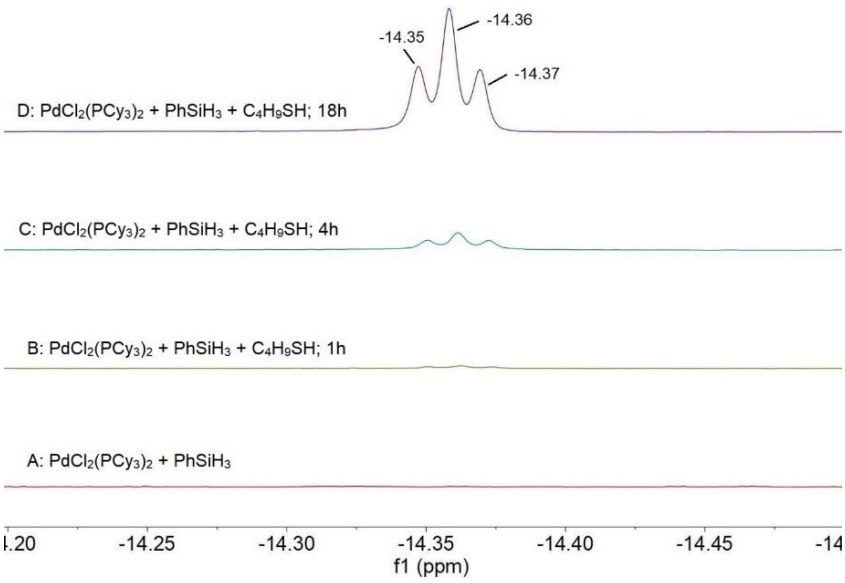


Figure S2. ^{1}H NMR spectra of various reaction components in C_6D_6. Reaction conditions: A: $PdCl_2(PCy_3)_2$ (0.01mmol), $PhSiH_3$ (0.4 mmol) in C_6D_6 at 80 ℃ for 4 h; B: $PdCl_2(PCy_3)_2$ (0.01mmol), $PhSiH_3$ (0.4 mmol), *n*BuSH (0.4 mmol) in C_6D_6 at 80 ℃ for 1 h; C: $PdCl_2(PCy_3)_2$ (0.01 mmol), $PhSiH_3$ (0.4 mmol) *n*BuSH (0.4 mmol) in C_6D_6 at 80 ℃ for 4 h; D: $PdCl_2(PCy_3)_2$ (0.01 mmol), $PhSiH_3$ (0.4 mmol) and *n*BuSH (0.4 mmol) in C_6D_6 at 80 ℃ for 18 h.

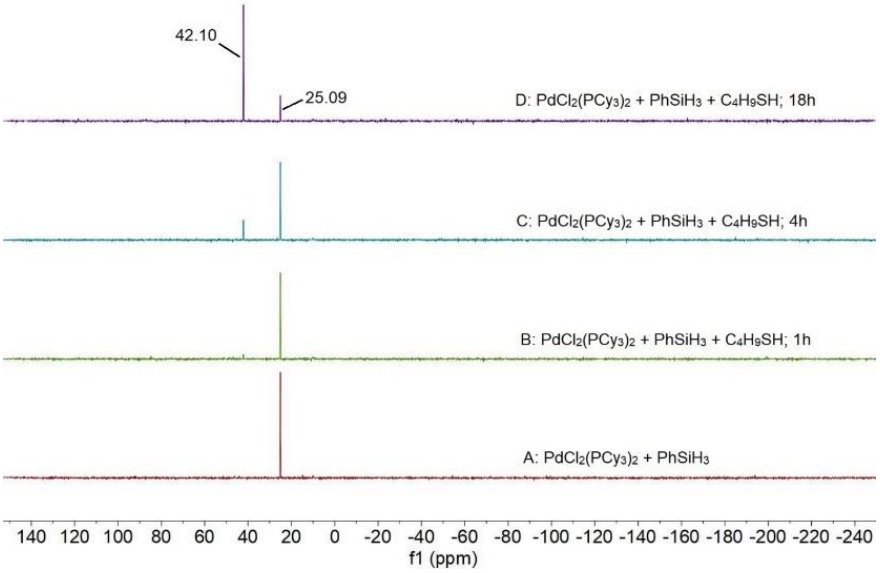
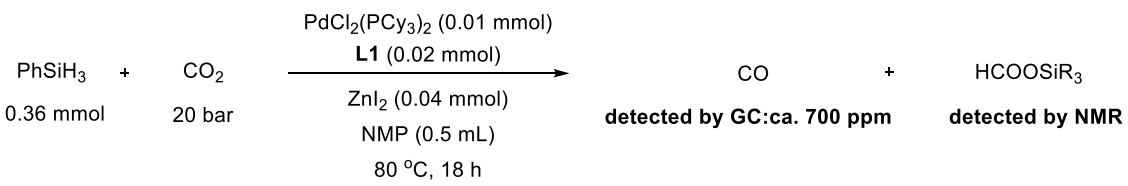


Figure S3. ^{31}P NMR spectra of various reaction componets in C_6D_6. Reaction conditions: A: $PdCl_2(PCy_3)_2$ (0.01mmol), $PhSiH_3$ (0.4 mmol) in C_6D_6 at 80 ℃ for 4 h; B: $PdCl_2(PCy_3)_2$ (0.01mmol), $PhSiH_3$ (0.4 mmol), *n*BuSH (0.4 mmol) in C_6D_6 at 80 ℃ for 1 h; C: $PdCl_2(PCy_3)_2$ (0.01 mmol), $PhSiH_3$ (0.4 mmol), *n*BuSH (0.4 mmol) in C_6D_6 at 80 ℃ for 4 h; D: $PdCl_2(PCy_3)_2$ (0.01 mmol), $PhSiH_3$ (0.4 mmol) and *n*BuSH (0.4 mmol) in C_6D_6 at 80 ℃ for 18 h.

5.3 Reduction of CO_2 with phenylsilane[4]



Scheme S3. Reaction conditions: $PdCl_2(PCy_3)_2$ (0.01 mmol), **L1** (0.02 mmol), ZnI_2 (0.04 mmol), $PhSiH_3$ (0.36 mmol), NMP (0.5 mL), CO_2 (20 bar) and stirred at 80 °C for 18 h.

In a glove box, a 4 mL sealing tube with a magnetic stirring bar was charged with phenylsilane (0.36 mmol), $PdCl_2(PCy_3)_2$ (0.01 mmol), **L1** (0.02 mmol), ZnI_2 (0.04 mmol), and NMP (0.5 mL). Then the tube was sealed, taken out of the glove box and placed into the autoclave. The autoclave was sealed and purged three times with CO_2 gas, then pressurized to 20 atm. Finally, the autoclave was heated at 80 ℃ for 18 h with stirring. After the reaction finished, the autoclave was cooled to room temperature and the gas phase was carefully vented to a balloon. GC analysis of the gas sample indicates the presence of a small amount of CO (ca. 700 ppm) and residual CO_2 in the gas phase of the reaction system (**Figure S4**). The sticky turbid mixture was filtered through a short cotton plug, and an aliquot of the filtrate was sampled and analyzed by ^{1}H-/^{13}C-NMR analyses. As shown in **Figures S5 and S6**, the signal corresponding to silyl formate was observed in ^{1}H- and ^{13}C-NMR spectra.

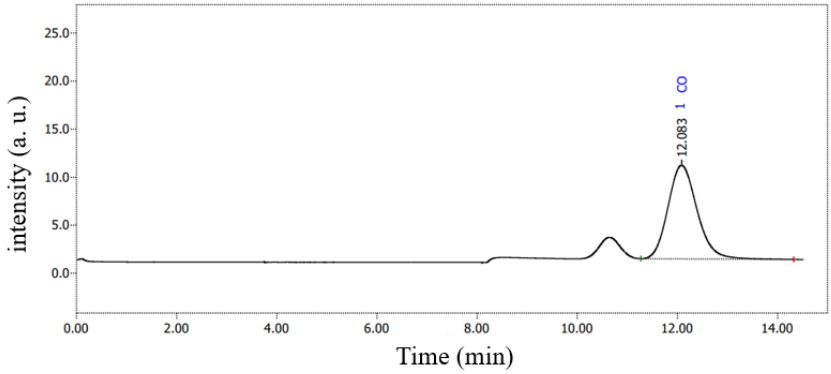


Figure S4. GC chromatograms for CO (t_R = 12.08 min) gases generated in situ from the reaction of $PhSiH_3$ and CO_2 in reaction conditions.

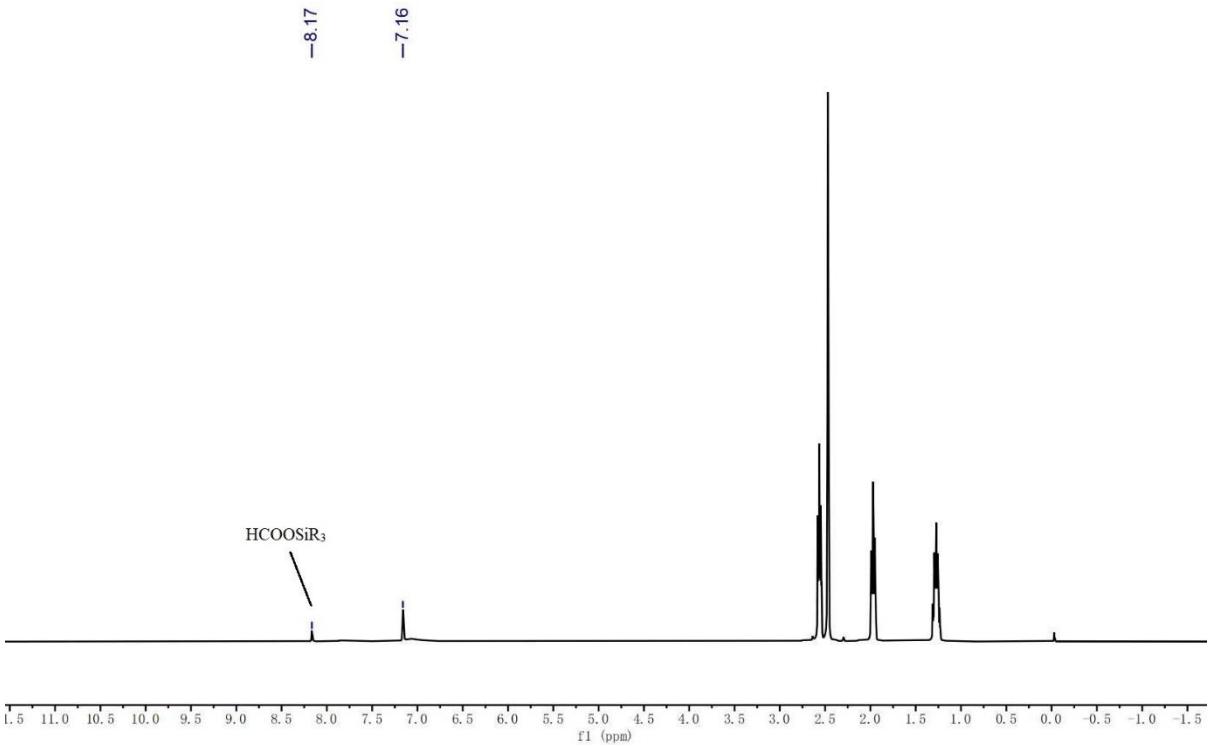


Figure S5. ^{1}H NMR spectra (C_6D_6) of the liquid phase in the reaction of CO_2 with $PhSiH_3$ in standard conditions, indicating the in-situ generation of $HCOOSiR_3$.

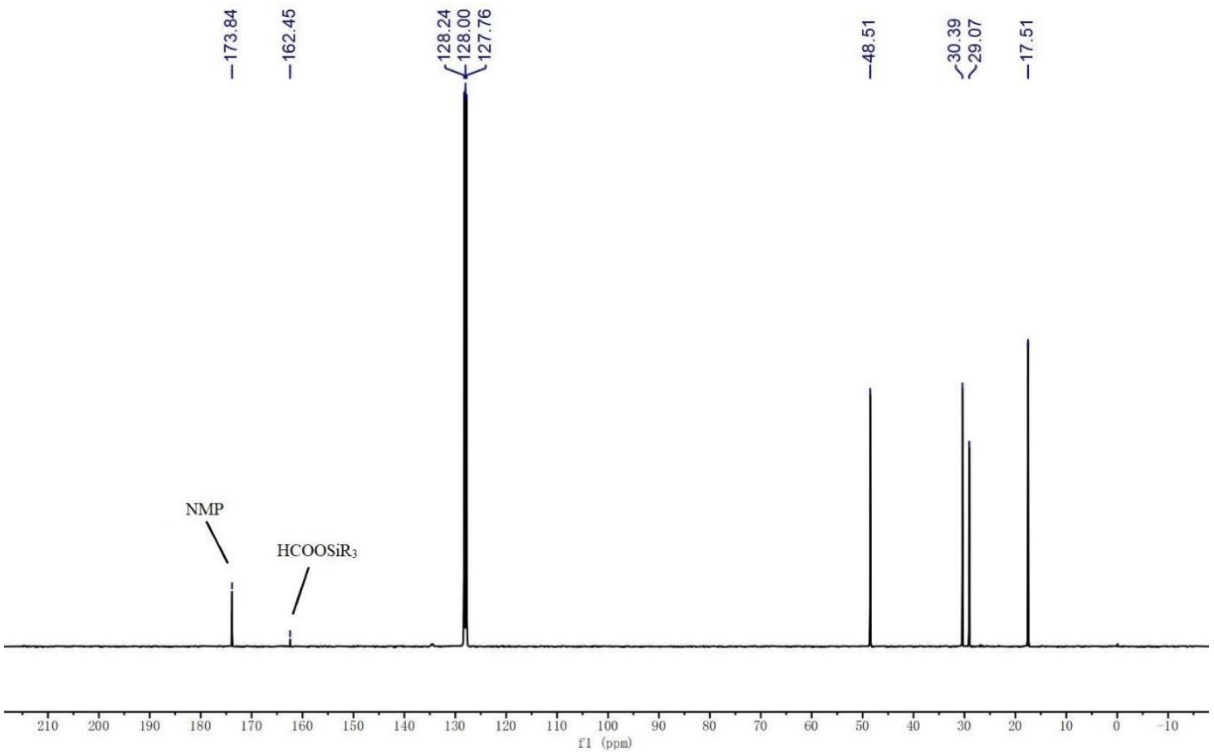


Figure S6. ^{13}C NMR spectra (C_6D_6) of the liquid phase in the reaction of CO_2 with $PhSiH_3$ in standard conditions, indicating the in-situ generation of $HCOOSiR_3$.

5.4 Carboxylic acid species capture experiment

In the glove box, add styrene (0.2 mmol), *n*BuSH (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5.0 mol%), **L1** (10.0 mol%), $PhSiH_3$ (1.8 equiv.), ZnI_2 (20 mol%), NMP (300 μL) and 100 μL of deuterated benzene into the J. Young/valved NMR tube, then remove the glove box and purge with $^{13}CO_2$, heat at 80 ℃ for 30 min to test ^{13}C NMR: a peak at 177.34 ppm in ^{13}C NMR was observed might correspond to the formation of carboxylate Pd species **D**, ^{13}C-labelled CO_2 NMR signals appeared at δ=128.24 ppm, NMP signal was observed at 173.73 ppm, product **3a** signal was detected at δ=200.34 ppm, demonstrating the formation of the thioester product **3a** using ^{13}C-labelled CO_2 under our conditions.

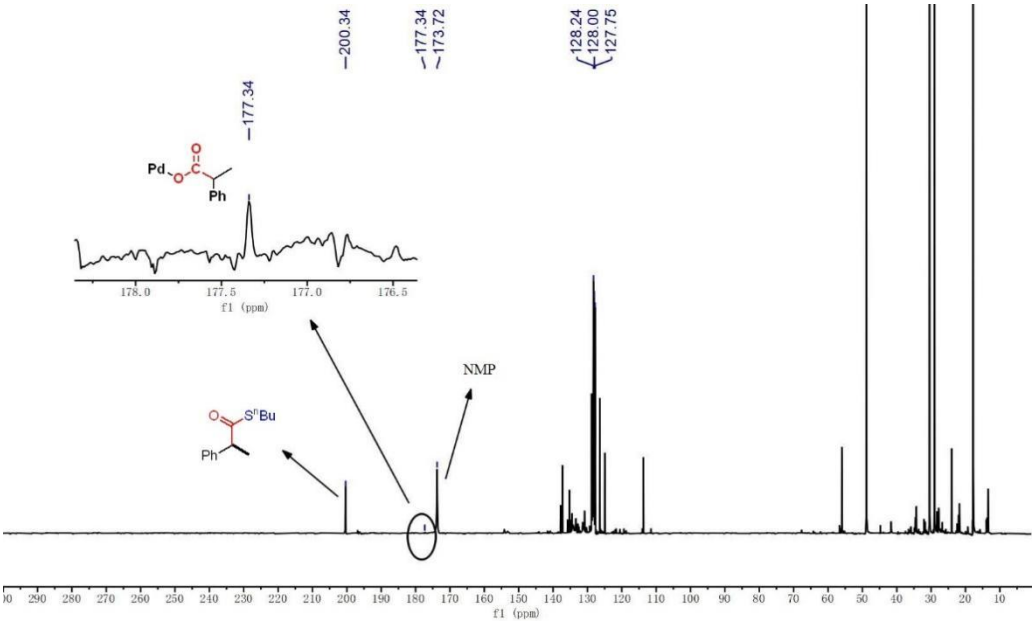


Figure S7. *In-situ* ^{13}C NMR spectra.

To a 4 mL sealing tube in a nitrogen-filled glovebox, the styrene (0.2 mmol), *n*BuSH (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5.0 mol%), **L1** (10.0 mol%), $PhSiH_3$ (1.8 equiv.), ZnI_2 (20 mol%), were added followed by addition of solvent *N*-methylpyrrolidone (NMP) (0.5 mL). Then the tube was sealed, taken out of the glovebox and placed into the autoclave. The autoclave was sealed and purged three times with CO_2 gas, then pressurized to 20 atm. At last, the autoclave was heated at 80 ℃ for 1 h with stirring. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. After that, the reaction system was quenched by adding aqueous hydrochloric acid, and the crude ^{1}H NMR spectrum was tested. Peaks were found for the 2-phenylpropionic acid species.

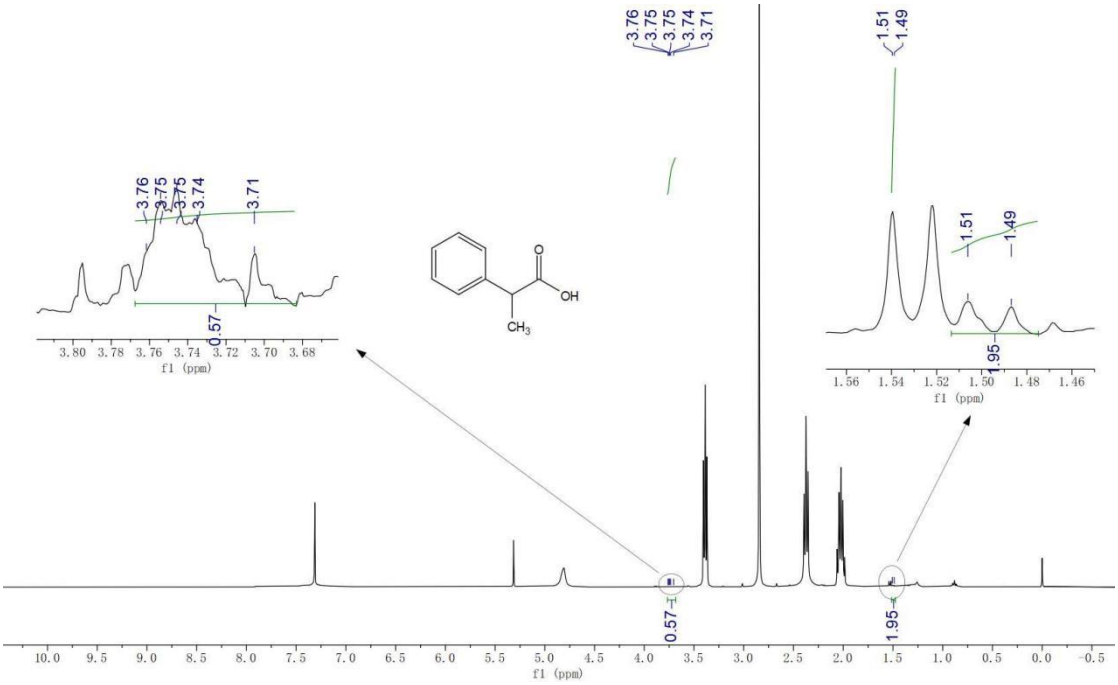


Figure S8. ^{1}H NMR spectra of hydrochloric acid quenching experiment.

In order to verify whether the peak marked in the **Figure S8** is the 2-phenylpropionic acid species, we added a drop of 2-phenylpropionic acid species to the NMR tube and found that it was indeed the peak of the 2-phenylpropionic acid.

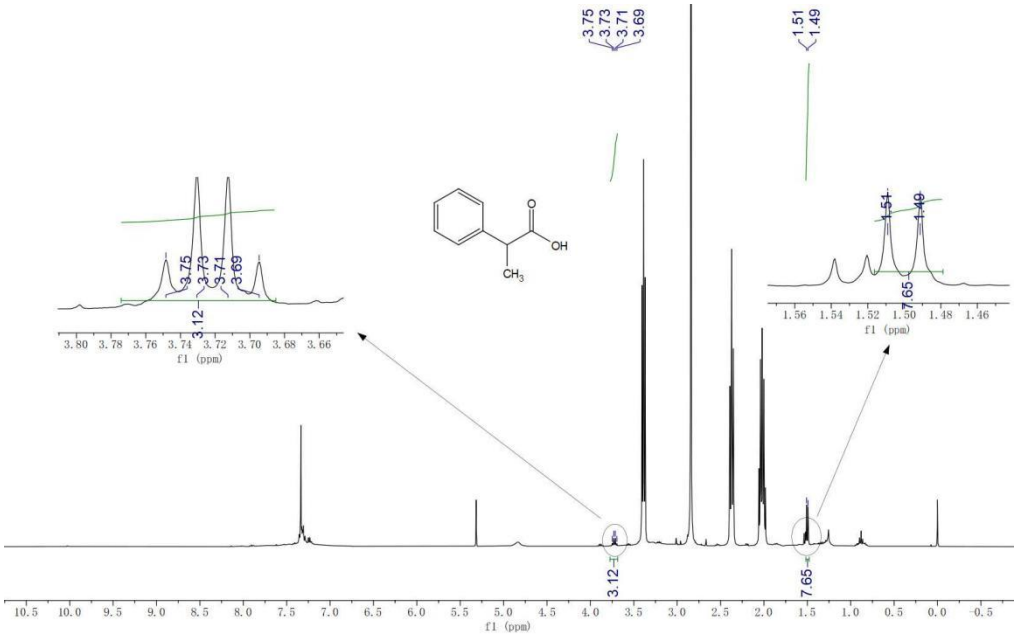
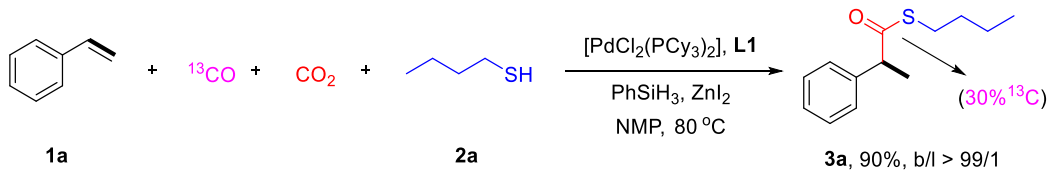
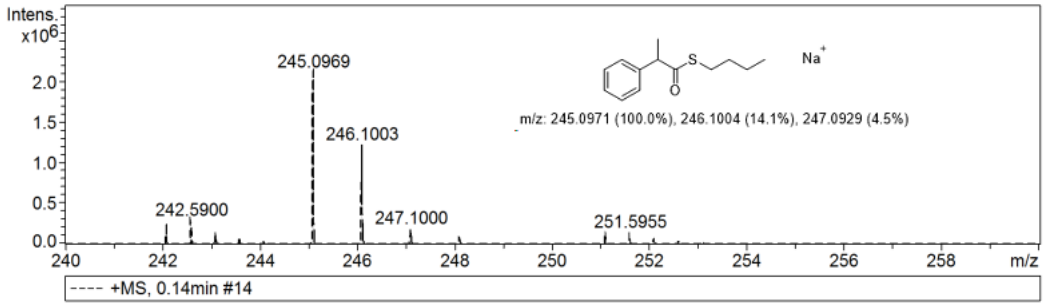


Figure S9. ^{1}H NMR spectra of hydrochloric acid quenching experiment.

5.5 CO_2 and ^{13}CO competition experiments

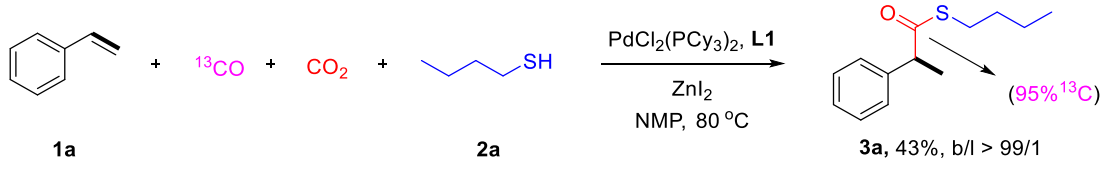


Experimental Procedure: To a 4 mL sealing tube in a nitrogen-filled glovebox, the styrene **1a** (0.2 mmol), *n*BuSH **2a** (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5 mol%), ligand **L1** (10 mol%), phenylsilane (1.8 equiv.), zinc iodide (20 mol%) and a stirring bar were added followed by addition of solvent *N*-methylpyrrolidone (NMP) (0.5 mL). Then the tube was sealed, taken out of the glovebox and placed into the autoclave. The autoclave was sealed and purged three times with CO_2 gas, then filled with 1bar ^{13}CO, then filled with 20 bar $^{12}CO_2$. At last, the autoclave was heated at 80 °C for 18 h with stirring. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The product was purified by silica gel giving the isolated yield. Only 30% ^{13}C incorporation was found in the carboxyl group of the thioester product form HRMS (Figure **S10**).

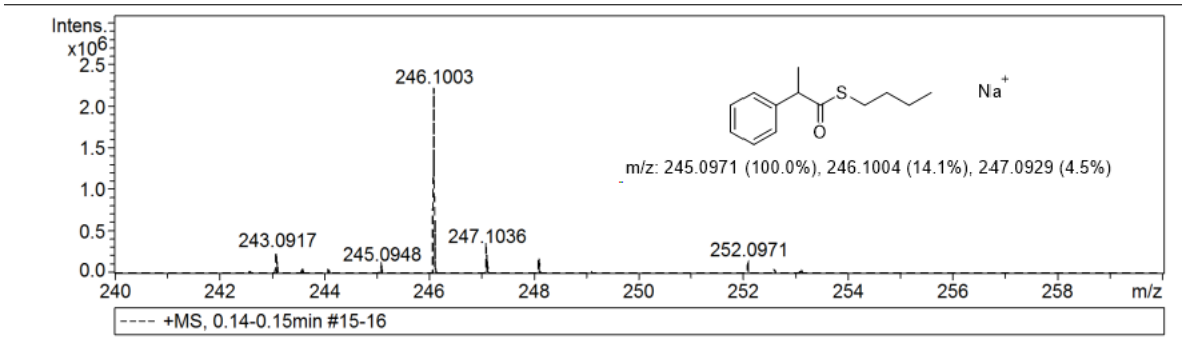


#	m/z	Res.	S/N	I	I %	FWHM
1	98.9752	10525	535.0	71377	3.4	0.0094
2	105.0698	10356	634.8	85969	4.1	0.0101
3	122.0577	10664	1122.1	153995	7.3	0.0114
4	149.0449	12361	383.0	58122	2.7	0.0121
5	158.0505	12484	1116.5	177795	8.4	0.0127
6	158.5521	12739	660.2	105342	5.0	0.0124
7	165.0583	12980	425.9	70027	3.3	0.0127
8	185.1139	11214	304.9	54777	2.6	0.0165
9	223.1154	12808	374.7	76068	3.6	0.0174
10	242.0884	14009	1191.8	256411	12.1	0.0173
11	242.5900	14103	1376.2	296383	14.0	0.0172
12	243.0912	13320	712.1	153668	7.3	0.0182
13	243.5913	12443	267.6	57851	2.7	0.0196
14	245.0969	13308	9758.5	2119519	100.0	0.0184
15	246.1003	13384	5626.7	1221953	57.7	0.0184
16	247.1000	10556	902.2	196348	9.3	0.0234
17	248.1006	11066	381.7	83363	3.9	0.0224
18	251.0940	14413	596.1	131337	6.2	0.0174
19	251.5955	14350	687.9	151757	7.2	0.0175
20	252.0982	10945	350.5	77472	3.7	0.0230
21	263.1077	13425	424.2	95457	4.5	0.0196
22	264.1105	13544	248.3	55908	2.6	0.0195
23	301.1410	14130	707.9	165817	7.8	0.0213
24	353.1421	15474	342.4	83691	3.9	0.0228
25	353.6439	15655	578.2	141410	6.7	0.0226
26	354.1462	13740	478.6	117055	5.5	0.0258
27	354.6500	11712	317.9	77707	3.7	0.0303
28	355.1542	10698	193.3	47262	2.2	0.0332
29	360.3235	14459	359.7	88016	4.2	0.0249
30	413.2660	14551	591.8	143673	6.8	0.0284

Figure S10. Mass spectrum of product **3a**.



Experimental Procedure: To a 4 mL sealing tube in a nitrogen-filled glovebox, the styrene **1a** (0.2 mmol), *n*BuSH **2a** (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5 mol%), ligand **L1** (10 mol%), zinc iodide (20 mol%) and a stirring bar were added followed by addition of solvent *N*-methylpyrrolidone (NMP) (0.5 mL). Then the tube was sealed, taken out of the glovebox and placed into the autoclave. The autoclave was sealed and purged three times with CO_2 gas, then filled with 1bar ^{13}CO, then filled with 20 bar $^{12}CO_2$. At last, the autoclave was heated at 80 ℃ for 18 h with stirring. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The product was purified by silica gel giving the isolated yield. 95% ^{13}C incorporation was found in the carboxyl group of the thioester product form HRMS (^{13}C-labeled product as the main product) (Figure **S11**).



#	m/z	Res.	S/N	I	I %	FWHM
1	98.9753	10017	2195.6	136766	6.2	0.0099
2	105.0699	10781	1295.5	82751	3.7	0.0097
3	116.9860	10908	923.6	60504	2.7	0.0107
4	149.5467	12183	469.1	36310	1.6	0.0123
5	158.5521	12341	1793.3	150476	6.8	0.0128
6	165.5600	13169	590.8	52624	2.4	0.0126
7	167.5576	13215	419.2	37919	1.7	0.0127
8	193.5732	13532	1012.2	106562	4.8	0.0143
9	224.1185	13000	892.1	109856	5.0	0.0172
10	233.0969	13263	440.7	56968	2.6	0.0176
11	243.0917	13927	1912.8	258178	11.7	0.0175
12	243.5932	13892	587.5	79469	3.6	0.0175
13	244.0927	12416	380.4	51628	2.3	0.0197
14	245.0948	10105	699.7	95435	4.3	0.0243
15	246.1003	13307	16201.6	2215455	100.0	0.0185
16	247.1036	13092	2274.1	311668	14.1	0.0189
17	248.1010	11129	1208.6	166090	7.5	0.0223
18	252.0971	14408	1074.4	150268	6.8	0.0175
19	252.5989	13846	313.8	44000	2.0	0.0182
20	253.1055	7686	239.0	33623	1.5	0.0329
21	264.1110	13521	780.9	113704	5.1	0.0195
22	301.1408	13912	1187.8	185920	8.4	0.0216
23	302.1445	14150	213.2	33498	1.5	0.0214
24	354.6472	15680	569.8	97278	4.4	0.0226
25	355.1494	14760	272.4	46532	2.1	0.0241
26	355.6550	10544	245.2	41878	1.9	0.0337
27	360.3236	14077	739.1	126608	5.7	0.0256
28	413.2662	14664	1002.2	176781	8.0	0.0282
29	414.2698	14621	262.9	46433	2.1	0.0283
30	441.2975	14910	464.7	83870	3.8	0.0296

Figure S11. Mass spectrum of product **3a**.

5.6 Details of DFT calculations

To further probe the nature of the regioselective thiocarbonylation of alkenes with carbon dioxide, DFT calculations at the GAUSSIAN 09[8] series of programs at the ωB97X-D level were carried out on the whole catalytic cycles shown in **Figure S12**. The LANL2DZ basis set for the Pd center and the 6-311+G (d, p) basis sets were used for all the other atoms for the geometry

optimizations. To roughly evaluate the effect of the solvent, the polarized continuous model (PCM) in *N*-methylpyrrolidone as the solvent was employed in the calculations. For the convenience of calculation, the molecular treatment is simplified. As shown in **Figure S12**, active Pd-H species **B** is generated from the oxidative addition of methyl thiol with Pd(0) species **A** with the sulfur atom at the *trans* position,[9] which is endothermic by 1.44 kcal/mol and the calculated results agree well with experiments present in **Scheme S2-a** and **Figures S2-S3**. After insertion by styrene, benzyl-Pd complex **C** is generated, and this reaction is exothermic by 1.98 kcal/mol. Then benzyl-Pd complex **C** was transformed into carboxylate Pd species R(CO_2)Pd **D** upon the migratory insertion of CO_2 into the Pd-C bond. One O atom of CO_2 approaches the Pd center and C of CO_2 interacts with C connected to the α-C of styrene to form a five-membered ring, which the length of the Pd-O and Pd-H bond is 2.12 and 2.78 Å, respectively. And the reaction is exothermic by 5.60 kcal/mol, which is favorable in energy.

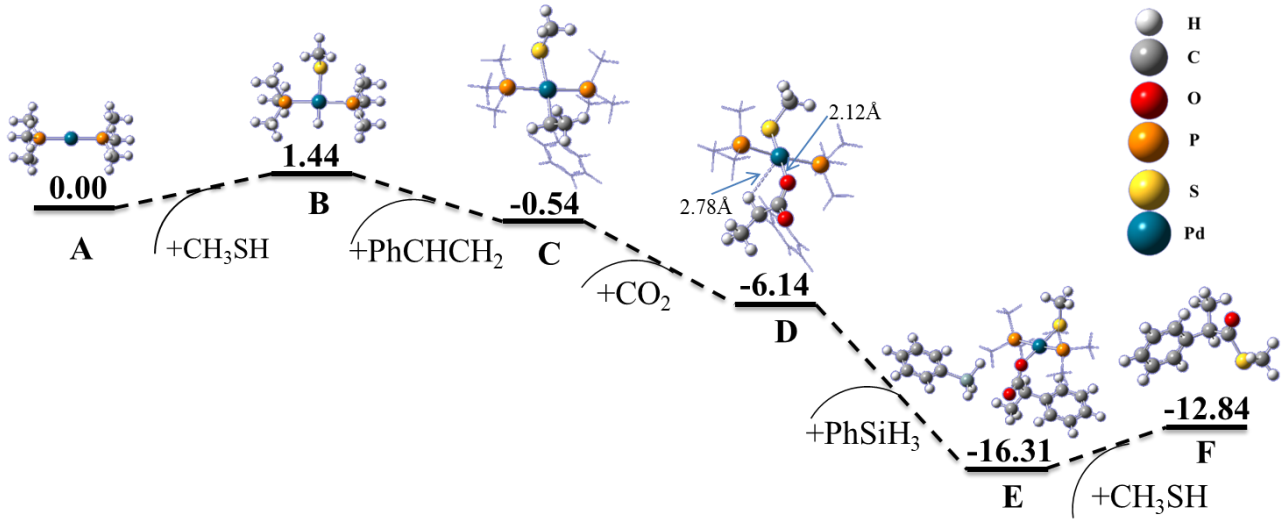


Figure S12. Mechanistic studies for Pd-catalyzed thiocarbonylation of alkene using CO_2 by DFT (kcal/mol).

Optimized energies in *N*-methylpyrrolidone solvent

Table S6. Optimized energies in *N*-methylpyrrolidone solvent (a.u., ωB97X-D, 298.15K)

Intermediate	E(a.u.)
A-PdL_2	-1048.846925
CH_3SH	-438.687864
B-$L_2PdHSCH_3$	-1487.532497
$PhCHCH_2$	-309.511727
C	-1797.047381
CO_2	-188.592907
D	-1985.649209
$PhSiH_3$	-522.836131
E	-2508.470862
F	-1562.760348

Cartesian coordinates of key stationary points in DFT study (unit in Å).

A	Coordinates (Angstroms) X	Y	Z
P	2.32251100	-0.00029800	0.00006900
C	3.15082600	-0.46645100	1.57220700
H	2.85100400	-1.47705800	1.85653500
H	4.23908200	-0.42923100	1.46772900

H	2.84172000	0.21880200	2.36391900
C	3.14681600	1.59632000	-0.38155000
H	4.23539200	1.49081400	-0.35861000
H	2.83914000	1.93786700	-1.37176700
H	2.84228800	2.34730200	0.35012400
C	3.15098800	-1.12723000	-1.19106600
H	2.85167100	-2.15705500	-0.98691600
H	2.84172400	-0.87471000	-2.20724700
H	4.23923100	-1.04633000	-1.11481400
Pd	-0.00000900	-0.00010100	-0.00002800
P	-2.32250600	0.00040400	-0.00001100
C	-3.14688400	-1.59649400	0.38052000
H	-4.23544300	-1.49093200	0.35749500
H	-2.84228100	-2.34699700	-0.35160300
H	-2.83933600	-1.93866200	1.37057200
C	-3.15109700	1.12650300	1.19184300
H	-2.85186400	2.15650500	0.98845300
H	-4.23935500	1.04559400	1.11559000
H	-2.84174400	0.87329400	2.20781600
C	-3.15062000	0.46769300	-1.57190700
H	-2.84149000	-0.21710400	-2.36397400
H	-4.23887800	0.43047400	-1.46753600
H	-2.85070800	1.47844000	-1.85562300

CH_3SH	Coordinates (Angstroms)		
	X	Y	Z
C	0.04832900	1.15611700	0.00000000
H	1.09320300	1.46492400	0.00000000
H	-0.43658300	1.54627300	0.89332900
H	-0.43658300	1.54627300	-0.89332900
S	0.04832900	-0.66578600	0.00000000
H	-1.28328300	-0.84160400	0.00000000

B	Coordinates (Angstroms)		
	X	Y	Z
P	2.32787900	-0.47074400	-0.02995900
C	3.17736900	0.88492300	-0.91044700
H	2.85099700	1.83458400	-0.48364600
H	4.26089200	0.78787700	-0.80630700
H	2.91239800	0.85962200	-1.96897700
C	3.12880400	-1.96989200	-0.69899400
H	4.21526700	-1.90958700	-0.59691400
H	2.75969100	-2.84452000	-0.16096800
H	2.86902800	-2.07782100	-1.75348500
C	2.99779300	-0.35327100	1.66533300
H	2.65048300	0.57809700	2.11535300
H	2.63053100	-1.19069400	2.26110400
H	4.09044900	-0.37046100	1.65104200
P	-2.32772500	-0.47095100	-0.02991900
C	-2.99794700	-0.35276100	1.66519900
H	-4.09060100	-0.36987300	1.65068900
H	-2.63088600	-1.19000000	2.26135200
H	-2.65064200	0.57875300	2.11491000
C	-3.17704400	0.88426500	-0.91126100

H	-2.91205800	0.85820000	-1.96976800
H	-4.26057900	0.78739500	-0.80708300
H	-2.85056200	1.83415600	-0.48506500
C	-3.12851800	-1.97041000	-0.69841200
H	-2.75941700	-2.84480600	-0.15999900
H	-4.21499200	-1.91012300	-0.59645600
H	-2.86865100	-2.07874700	-1.75284000
Pd	0.00007700	-0.35725600	-0.05659900
H	0.00022300	-1.83789800	-0.56191900
S	-0.00045300	1.99261400	0.73300900
C	-0.00031700	2.87432800	-0.87202300
H	-0.88405500	2.62236100	-1.46213800
H	-0.00293400	3.95155100	-0.69178300
H	0.88598400	2.62622200	-1.45990900

$PhCHCH_2$	Coordinates (Angstroms)		
	X	Y	Z
C	-1.77599700	-1.04173100	0.00000100
C	-0.40567900	-1.27849100	0.00000000
C	0.51052400	-0.22159400	-0.00000100
C	0.01112300	1.08729100	-0.00000200
C	-1.35573500	1.32576900	0.00000000
C	-2.25646700	0.26256100	0.00000100
H	-2.46780400	-1.87666400	0.00000300
H	-0.03683500	-2.29961800	0.00000000
H	0.69327600	1.93008600	-0.00000300
H	-1.72271700	2.34623500	-0.00000100
H	-3.32395500	0.45198500	0.00000200
C	1.95331200	-0.53184000	-0.00000200
H	2.18832100	-1.59438500	-0.00000800
C	2.96316800	0.33793000	0.00000300
H	2.81451100	1.41294600	0.00000900
H	3.98970700	-0.00996100	0.00000100

C	Coordinates (Angstroms)		
	X	Y	Z
P	-2.16626800	-1.61666500	0.00272600
C	-3.82244800	-1.19732100	0.65037600
H	-4.20604900	-0.33329200	0.10813300
H	-4.50375400	-2.04234900	0.52496100
H	-3.74546800	-0.95118400	1.71113300
C	-1.83320100	-3.20907800	0.84615200
H	-2.70328400	-3.86332600	0.75398800
H	-0.97187100	-3.70580300	0.39605900
H	-1.62661700	-3.03631100	1.90431200
C	-2.49352600	-2.15504900	-1.71257400
H	-2.81328700	-1.29205600	-2.29695800
H	-1.57553000	-2.55758600	-2.14522000
H	-3.26873200	-2.92498500	-1.73321000
P	0.89015400	2.00339900	0.10970100
C	1.94967300	1.95855100	-1.38153600
H	2.57537200	2.85321400	-1.43409900
H	2.58263900	1.06990800	-1.35343400
H	1.31419000	1.90819900	-2.26802900

C	0.12659900	3.66247300	0.00128000
H	-0.38324000	3.88978100	0.93927900
H	0.90088000	4.41418600	-0.17114600
H	-0.59873200	3.67753500	-0.81177800
C	2.10007800	2.30456000	1.45035200
H	2.79009900	1.46882200	1.54221100
H	2.66936500	3.21029300	1.22617000
H	1.57371600	2.44290200	2.39650700
Pd	-0.60332500	0.14505000	0.11973700
S	-2.27321100	1.44688900	-1.17448300
C	-3.16504100	2.36677300	0.13017400
H	-2.52900300	3.12236100	0.59405000
H	-4.02878600	2.86801100	-0.31212300
H	-3.52168400	1.69262200	0.91149700
C	0.78022100	-1.14560100	1.08960000
H	0.32696200	-2.12905200	0.98646200
C	2.05640500	-1.21166700	0.31157100
C	3.30785200	-0.89390500	0.84888900
C	2.02465900	-1.64318000	-1.02628100
C	4.46753300	-0.95800500	0.07749000
H	3.38959700	-0.60053500	1.88952000
C	3.17539600	-1.71846500	-1.79430000
H	1.06662600	-1.90287400	-1.46763600
C	4.40984600	-1.36326600	-1.24913800
H	5.42086600	-0.69564700	0.52439800
H	3.11212000	-2.04828000	-2.82605100
H	5.31116400	-1.41151400	-1.84986800
C	0.90377200	-0.85863500	2.57963000
H	1.55799300	-1.58785000	3.07881300
H	1.30203600	0.13504300	2.79396600
H	-0.07844500	-0.92287900	3.05540600

CO_2	Coordinates (Angstroms)		
	X	Y	Z
C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.15651600
O	0.00000000	0.00000000	-1.15651600

D	Coordinates (Angstroms)		
	X	Y	Z
P	-2.27252700	-1.62952300	-0.24574200
C	-4.03561700	-1.30312300	0.07871300
H	-4.36482100	-0.48033000	-0.55678400
H	-4.63201000	-2.19393900	-0.13129900
H	-4.16281600	-1.02060400	1.12518100
C	-1.90978600	-3.09659600	0.77766600
H	-2.64658000	-3.88015700	0.58566000
H	-0.91573700	-3.48128500	0.54706600
H	-1.93777000	-2.81785700	1.83162900
C	-2.22281700	-2.25796500	-1.95611400
H	-2.50531500	-1.45391300	-2.63674600
H	-1.20900500	-2.58509600	-2.19481700
H	-2.91074300	-3.09833300	-2.07398900
P	0.28796000	2.18413400	0.79570100

C	0.51051900	3.49426600	-0.44906500
H	1.01336000	4.35671800	-0.00549400
H	1.11500900	3.10077900	-1.26851600
H	-0.45875700	3.79331700	-0.84907200
C	-0.55380000	3.00607300	2.19432700
H	-0.57876500	2.31579900	3.03964700
H	-0.01860100	3.91338900	2.48480200
H	-1.57922100	3.25991900	1.92431800
C	1.96837800	1.90074600	1.43737100
H	2.62110700	1.58330600	0.62428400
H	2.35960100	2.82007000	1.88007500
H	1.93278600	1.11116600	2.18847200
Pd	-0.89504400	0.22388100	0.19433100
S	-2.14905900	1.34939000	-1.43177800
C	-3.25706100	2.43551100	-0.47329300
H	-2.71728200	3.26559500	-0.01418400
H	-3.99281000	2.84634000	-1.16739300
H	-3.78276500	1.87624100	0.30185300
C	1.53556600	-2.02732200	-0.04604100
H	0.60704600	-1.96333000	-0.61849700
C	2.47373200	-0.97714500	-0.61151300
C	3.76338300	-0.82317100	-0.09830600
C	2.06546400	-0.14169400	-1.65124600
C	4.61872900	0.14764800	-0.60491100
H	4.09350000	-1.45785800	0.71711200
C	2.91845400	0.83349000	-2.15996300
H	1.06823900	-0.25220800	-2.06586300
C	4.19753300	0.98345200	-1.63606500
H	5.61339100	0.25927400	-0.18755100
H	2.58109300	1.47619400	-2.96588800
H	4.86326900	1.74430900	-2.02768900
C	2.10260000	-3.43941600	-0.18846000
H	2.29980600	-3.65744700	-1.24121000
H	3.03327600	-3.54784700	0.37055100
H	1.39733300	-4.18356000	0.19094700
C	1.19980100	-1.67616800	1.42082100
O	0.26404200	-0.82589300	1.63272500
O	1.84710400	-2.20011700	2.33099000

$PhSiH_3$	Coordinates (Angstroms) X	Y	Z
C	-0.01138400	-1.64634500	1.20370900
C	-0.01138400	-0.25502600	1.20149700
C	-0.00827000	0.46501200	0.00000000
C	-0.01138400	-0.25502600	-1.20149700
C	-0.01138400	-1.64634500	-1.20370900
C	-0.01042500	-2.34391600	0.00000000
H	-0.01511300	-2.18518000	2.14482000
H	-0.01753700	0.27194700	2.15114400
H	-0.01753700	0.27194700	-2.15114400
H	-0.01511300	-2.18518000	-2.14482000
H	-0.01239800	-3.42840900	0.00000000
Si	0.02547400	2.34179800	0.00000000

H	1.42169000	2.85243300	0.00000000
H	-0.65762200	2.85357100	-1.21507700
H	-0.65762200	2.85357100	1.21507700

E	Coordinates (Angstroms) X	Y	Z
P	0.13008700	-2.01982500	-1.31053100
C	0.41738300	-3.78069600	-0.94039100
H	-0.53063700	-4.31539800	-1.00727400
H	1.13236200	-4.20485400	-1.64926800
H	0.81196500	-3.87644000	0.07264400
C	1.80552000	-1.29873200	-1.28319000
H	2.47270500	-1.86569400	-1.93662500
H	1.77335500	-0.26100600	-1.61635300
H	2.18508900	-1.31914900	-0.26075700
C	-0.34152100	-1.98735500	-3.07098500
H	-1.31502400	-2.46561700	-3.18593600
H	-0.41276200	-0.95228200	-3.41037500
H	0.40045900	-2.51502900	-3.67454100
P	-2.86122100	-0.11713500	1.79453400
C	-4.65671300	-0.29358900	1.54798800
H	-5.19660000	0.12434900	2.40080200
H	-4.94038900	0.24031000	0.63909400
H	-4.91401200	-1.34572800	1.42524000
C	-2.53237500	-0.91560200	3.40516300
H	-1.49343300	-0.72777200	3.68231000
H	-3.19216600	-0.51141100	4.17674000
H	-2.68169100	-1.99299400	3.32875000
C	-2.65093100	1.65452800	2.15902500
H	-3.01439900	2.24450400	1.31770700
H	-3.21361900	1.91837300	3.05790100
H	-1.59197700	1.86686800	2.30806700
Pd	-1.38395400	-0.98068000	0.15665400
S	-2.93390300	-2.58475800	-0.55833400
C	-3.01063700	-3.77131800	0.82391500
H	-3.48377800	-3.33711000	1.70616400
H	-3.61208500	-4.62070500	0.49414200
H	-2.01567900	-4.13046000	1.09069300
C	-0.23554400	1.80231700	-1.25376600
H	-0.35772400	0.81973100	-1.71477200
C	-1.61946400	2.41689800	-1.15310300
C	-1.79231700	3.70853700	-0.65086500
C	-2.74834000	1.70037100	-1.55077900
C	-3.06087200	4.26435200	-0.53921300
H	-0.92640100	4.27514300	-0.32614000
C	-4.02112900	2.25148800	-1.43579000
H	-2.63281500	0.69919200	-1.95389000
C	-4.18217400	3.53507000	-0.92673500
H	-3.17680000	5.26534800	-0.13844600
H	-4.88635800	1.67630300	-1.74721300
H	-5.17235700	3.96662200	-0.83329200
C	0.70602600	2.63706700	-2.12085200
H	0.27747400	2.77016800	-3.11748800

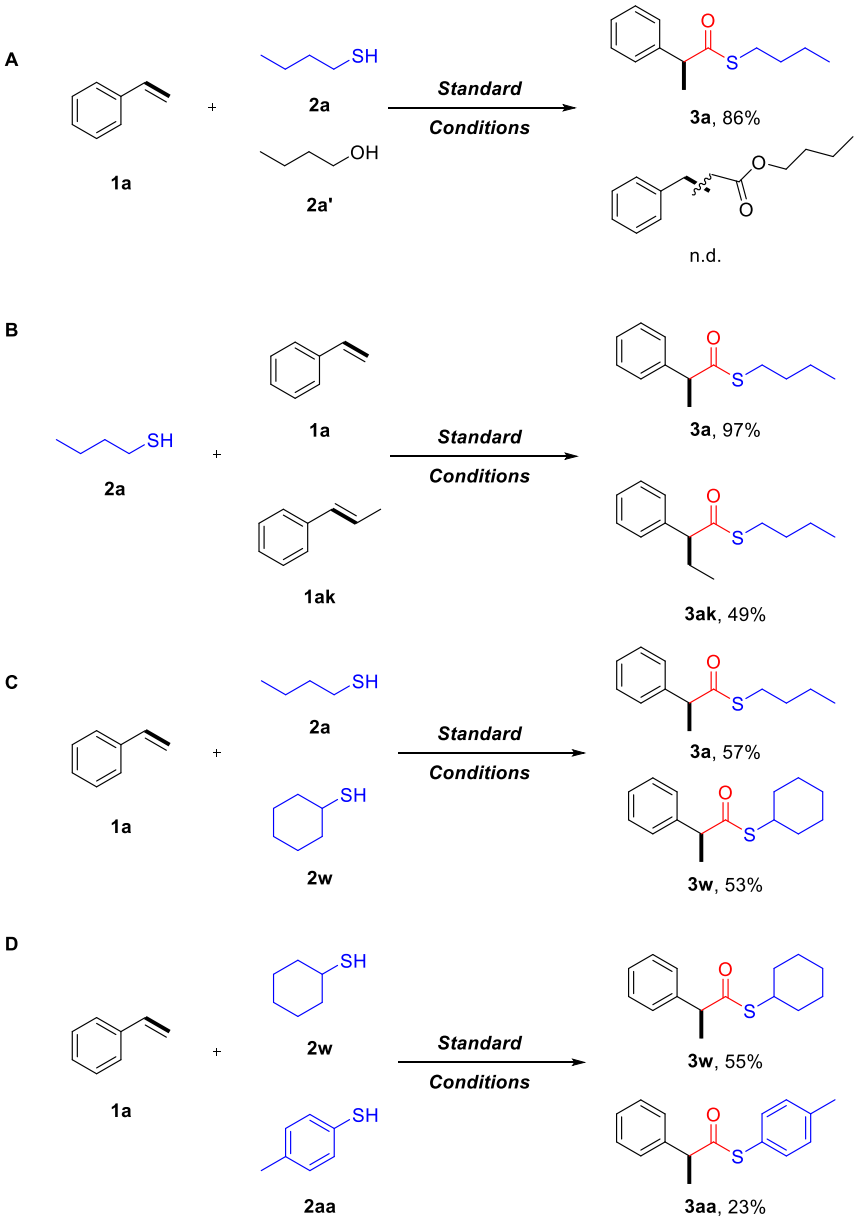
H	0.87797700	3.61978000	-1.67915400
H	1.67699100	2.14576200	-2.22450500
C	0.32529600	1.58098200	0.16908600
O	0.01288000	0.49475000	0.77334600
O	1.02925000	2.45536100	0.68166500
C	7.17290700	-1.26500500	-0.17528200
C	5.91210800	-0.68304400	-0.10950400
C	5.71739600	0.55820900	0.51212400
C	6.83266600	1.19697200	1.06597100
C	8.09793900	0.61869100	1.00333200
C	8.26950900	-0.61365900	0.38315700
H	7.30158200	-2.22613300	-0.66100400
H	5.06948400	-1.20728500	-0.55263600
H	6.71708500	2.16027800	1.55384200
H	8.94908900	1.13015900	1.43956200
H	9.25365000	-1.06634800	0.33287400
Si	3.99905900	1.32149800	0.60448100
H	3.11673100	0.44203700	1.40708700
H	4.11393900	2.65980100	1.23248700
H	3.44986300	1.43773900	-0.76789700

F	Coordinates (Angstroms)		
	X	Y	Z
C	0.26033800	1.03891600	-0.72759000
H	0.44735800	0.77923400	-1.77330000
C	-1.01391100	0.32834300	-0.29476100
C	-1.50144000	0.46319900	1.00649000
C	-1.72032600	-0.46131200	-1.20008800
C	-2.67329600	-0.17705600	1.39101700
H	-0.95976700	1.06824700	1.72592700
C	-2.89483600	-1.10167500	-0.81756500
H	-1.34927500	-0.57723500	-2.21336800
C	-3.37492500	-0.96075400	0.47945200
H	-3.04034200	-0.06310400	2.40495600
H	-3.43449300	-1.71039400	-1.53443900
H	-4.28998600	-1.45864100	0.77962000
C	0.15999900	2.56035100	-0.60081000
H	-0.67794700	2.92152100	-1.20010100
H	-0.00067100	2.85862600	0.43638200
H	1.07483800	3.03901300	-0.95725600
C	1.42584200	0.49693000	0.09619100
O	1.80072000	0.98151700	1.13559300
S	2.16708500	-0.96042000	-0.60090200
C	3.37995800	-1.35434600	0.68237700
H	2.87949500	-1.52685600	1.63372300
H	3.88386200	-2.26474200	0.35982900
H	4.10339900	-0.54666600	0.77943800

6. Competition reactions[a]

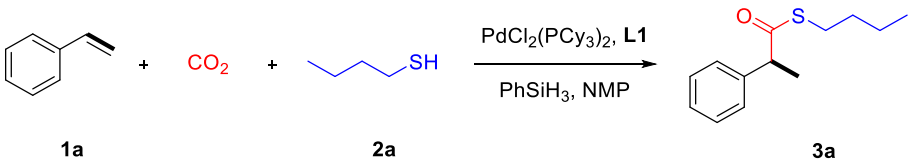
Competition reactions between different substrates were carried out (**Scheme S4**). Interestingly, the carbonylation of styrene in the presence of both *O*- and *S*-nucleophiles exclusively produced thioester **3a**, with no loss in activity (86% **Scheme S4**, eq **A**). This might indicate that the stronger Pd-S interaction of *n*BuSH than Pd-O interaction of *n*BuOH is

critical to give the product. When using 1:1 mixture of styrene (**1a**) and *β*-methylstyrene (**1ak**), both products **3a** and **3ak** can be detected, indicating the impact of steric effect of internal alkenes (97% vs 49% **Scheme S4**, eq **B**). Competition reaction of primary and secondary thiols was tested, and similar yields of the corresponding thioesters were formed (57% vs 53% **Scheme S4**, eq **C**). Steric hindrance effect of thiols is minor. In the competition reaction of styrene with alkyl thiol and aryl thiol, the yield of thioester from alkyl thiol **2w** was much higher than the yield from aryl thiol **2aa**, probably due to the weaker S-H polarity and Pd-S interaction of arylthiol (55% vs 23% **Scheme S4**, eq **D**).



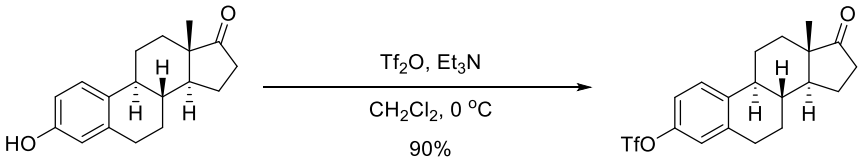
Scheme S4. [a]Standard conditions: **1a**/**1ak** (0.2 mmol), **2a**/**2a'**/**2w**/**2aa** (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5 mol%), **L1** (10.0 mol%), $PhSiH_3$ (1.8 equiv.), CO_2 (20 bar), NMP (0.5 mL), and stirred at 80 °C for 18 h. Yields were determined by quant. NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.

7. Procedures for gram-scale experiment



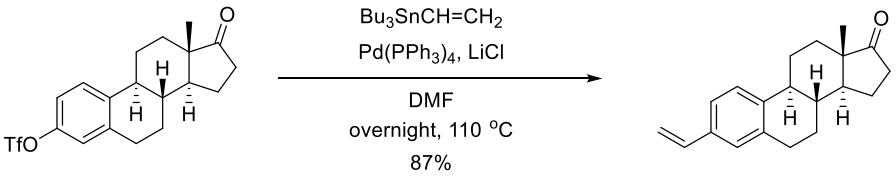
Experimental Procedure for product 3a (5 mmol scale): The substrate **1a** (5 mmol), thiol **2a** (1.7 equiv.), palladium catalyst (5 mol%), ligand **L1** (10 mol%), phenylsilane (1.8 equiv.), and a stirring bar were added to a 35 mL autoclave, followed by addition of solvent *N*-methylpyrrolidone (NMP) (6 mL). The autoclave was sealed and purged three times with CO_2 gas, then pressurized to 20 atm. At last, the autoclave was heated at 80 °C for 18 h with stirring. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The solution was diluted with water and extracted with ethyl acetate (50 mL). The combined organic extracts were washed with brine, dried with anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (200:1 petroleum ether:ethyl acetate, visualized with UV) to afford product **3a** (936 mg, 84% yield, b/l > 99:1).

8. General procedure for the preparation of Estrone Derivatives



Estrone **S1**

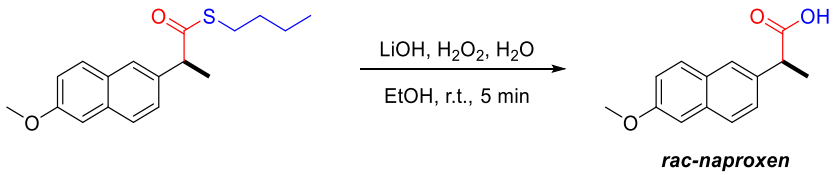
To estrone (1.00 g, 3.70 mmol, 1.00 equiv.) in CH_2Cl_2 (19 mL) at 0 ºC was added triethylamine (1.03 mL, 7.40 mmol, 2.00 equiv.) and trifluoromethanesulfonic anhydride (684 µL, 4.07 mmol, 1.10 equiv.). The reaction mixture was stirred at 0 ºC for 20 min before the addition of saturated aqueous $NaHCO_3$ (20 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic phases are washed with brine (40 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 4:1 (v/v) to afford 1.30 g of the title compound **S1**[10] as a colorless oil (1.34 g, 90% yield).



S1 **1an**

3-Vinyl-estrone **1an**[10] was synthesized by using 3-(Trifluoromethanesulfonyl)estrone **S1** (600 mg, 1.49 mmol, 1 equiv.), vinyltributylstannane (436 µL, 1.49 mmol, 1 equiv.), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.02 equiv.), LiCl (316 mg, 7.45 mmol, 5 equiv.), and DMF (23 mL, 0.067M solution). The crude product was purified by flash column chromatography using gradient elution (500 mL of 100% hexanes, 200 mL of 5% ethyl acetate in hexanes, and 300 mL of 8% ethyl acetate in hexanes) to obtain 363 mg (87%) white solid.

9. General procedure for the preparation of naproxen (3am')[11]



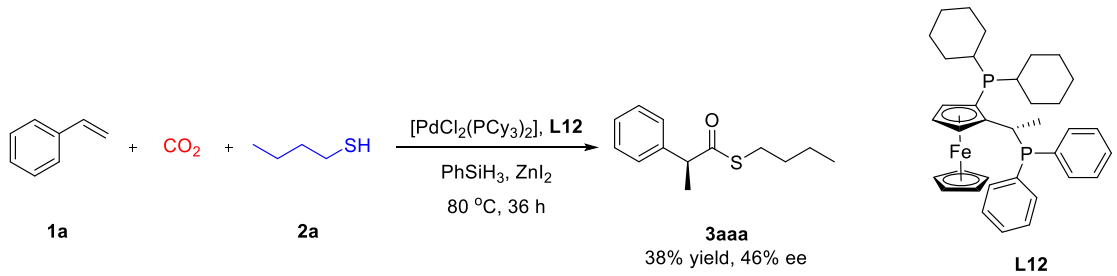
3am ***rac-naproxen***

3am', 91%, b/l > 99/1

A solution of **3am** (0.2 mmol) in EtOH (2 mL), was added a previously prepared solution of LiOH in H_2O_2 (LiOH 0.92 g, 38.4 mmol; 30% H_2O_2 6.2 mL; H_2O 11.5 mL). The mixture was stirred at rt for 3 min, then quenched with dil. HCl. Afterwards extraction with CH_2Cl_2 and usual work up are performed. The residue purified by column chromatography with petro ether/ethyl acetate (100:1 to 10:1) as the eluent to get *rac*-naproxen **3am'** (41.9 mg, 91% yield) as a white solid.

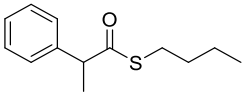
10. Asymmetric thiocarbonylation reation[a]

To a 4 mL sealing tube in a nitrogen-filled glovebox, the alkene (0.2 mmol), thiol (1.7 equiv, 0.34 mmol), palladium-catalyst (5.0 mmol%, 0.01 mmol), **L12** (10.0 mmol%, 0.02 mmol), $PhSiH_3$ (1.8 equiv, 0.36 mmol), ZnI_2 (20.0 mmol%, 0.04 mmol) were added followed by addition of solvent *N*-methylpyrrolidone (NMP) (0.5 mL). Then the tube was sealed, taken out of the glovebox and placed into the autoclave. The autoclave was sealed and purged three times with CO_2 gas, then pressurized to 20 atm. Finally, the autoclave was heated at 80 ℃ for 36 h with stirring. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The results were measured by GC and HPLC analysis.



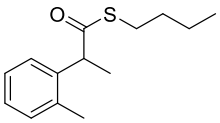
[a]Reaction conditions: styrene (0.2 mmol), butyl thiol (1.7 equiv.), $PdCl_2(PCy_3)_2$ (5.0 mol%), **L12** (10.0 mol%), $PhSiH_3$ (1.8 equiv.), ZnI_2 (20.0 mol%), CO_2 (20 bar), NMP (0.5 mL), and stirred at 80 ℃ for 36 h. Yield of **3aaa** was determined by GC analysis using dodecane as the internal standard. Enantiomeric excess was determined by chiral HPLC analysis.

11. Characterization spectra data of compounds.



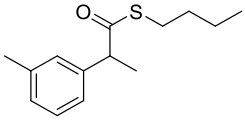
***S*-butyl 2-phenylpropanethioate (3a)[6]**

Yellow liquid (Yield = 90%; 40.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, J = 4.0 Hz, 4H), 7.22 (t, J = 4.0 Hz, 1H), 3.83 (q, J = 8.0 Hz, 1H), 2.77 (m, 2H), 1.48 (d, J = 8.0 Hz, 3H), 1.45 (t, J = 8.0 Hz, 2H), 1.28 (m, 2H), 0.83 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.2, 140.1, 128.7, 127.9, 127.4, 54.3, 31.5, 28.8, 22.0, 18.5, 13.6.



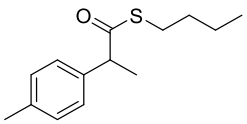
***S*-butyl 2-(*o*-tolyl) propanethioate (3b)**

Yellow liquid (Yield = 89%; 42.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 3H), 4.19 (q, J = 8.0 Hz, 1H), 2.91 (m, 2H), 2.46 (s, 3H), 1.60 (d, J = 4.0 Hz, 3H), 1.57 (t, J = 8.0 Hz, 2H), 1.43 (m, 2H), 0.96 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.7, 138.4, 136.2, 130.5, 127.3, 127.2, 126.4, 50.1, 31.5, 28.8, 22.0, 19.9, 18.1, 13.6. HRMS (ESI) $[C_{14}H_{20}OS+Na]^+$ calculated mass 259.1127, measured mass 259.1127.



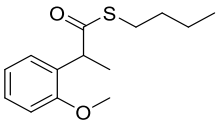
***S*-butyl 2-(*m*-tolyl) propanethioate (3c)**

Yellow liquid (Yield = 90%; 42.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 - 7.19 (m, 1H), 7.12 (s, 1H), 7.09 (d, J = 8.0 Hz, 2H), 3.85 (q, J = 8.0 Hz, 1H), 2.89 - 2.78 (m, 2H), 2.35 (s, 3H), 1.53 (s, 3H), 1.51 (d, J = 4.0 Hz, 2H), 1.35 (q, J = 8.0 Hz, 2H), 0.89 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 140.0, 138.3, 128.6, 128.5, 128.2, 125.0, 54.3, 31.5, 28.8, 22.0, 21.4, 18.5, 13.6. HRMS (ESI) $[C_{14}H_{20}OS+Na]^+$ calculated mass 259.1127, measured mass 259.1128.



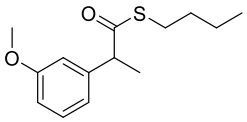
***S*-butyl 2-(*p*-tolyl) propanethioate (3d)**

Yellow liquid (Yield = 94%; 44.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 3.85 (q, J = 8.0 Hz, 1H), 2.88 - 2.79 (m, 2H), 2.34 (s, 3H), 1.52 (d, J = 8.0 Hz, 3H), 1.49 (t, J = 8.0 Hz, 2H), 1.39 - 1.32 (m, 2H), 0.89 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5, 137.1, 129.4, 128.4, 127.8, 53.9, 31.5, 28.8, 22.0, 21.1, 18.5, 13.6. HRMS (ESI) $[C_{14}H_{20}OS+Na]^+$ calculated mass 259.1127, measured mass 259.1133.



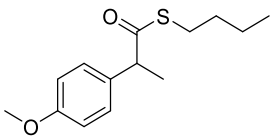
***S*-butyl 2-(2-methoxyphenyl) propanethioate (3e)**

Yellow liquid (Yield = 81%; 40.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 4.25 (q, J = 8.0 Hz, 1H), 3.82 (s, 3H), 2.81 (t, J = 8.0 Hz, 2H), 1.53 - 1.48 (m, 3H), 1.47 (s, 2H), 1.38 - 1.32 (m, 2H), 0.88 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 157.1, 128.7, 128.5, 128.4, 120.7, 110.7, 55.5, 47.3, 31.6, 28.6, 21.9, 17.2, 13.6. HRMS (ESI) $[C_{14}H_{20}O_2S+Na]^+$ calculated mass 275.1076, measured mass 275.1079.



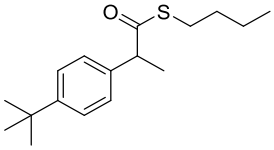
***S*-butyl 2-(3-methoxyphenyl) propanethioate (3f)**

Yellow liquid (Yield = 86%; 43.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (t, J = 8.0 Hz, 1H), 6.91 (d, J = 4.0 Hz, 1H), 6.87 (s, 1H), 6.83 (d, J = 8.0 Hz, 1H), 3.87 (q, J = 8.0 Hz, 1H), 3.82 (s, 3H), 2.90 - 2.81 (m, 2H), 1.55 (d, J = 8.0 Hz, 3H), 1.52 (t, J = 8.0 Hz, 2H), 1.38 (t, J = 8.0 Hz, 2H), 0.90 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 159.8, 141.6, 129.6, 120.3, 113.7, 112.7, 55.2, 54.3, 31.5, 28.8, 22.0, 18.4, 13.5. HRMS (ESI) $[C_{14}H_{20}O_2S+Na]^+$ calculated mass 275.1076, measured mass 275.1086.



***S*-butyl 2-(4-methoxyphenyl) propanethioate (3g)**

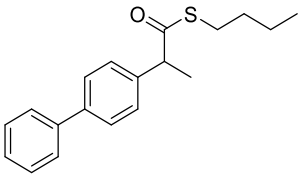
Yellow liquid (Yield = 87%; 43.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, J = 12.0 Hz, 2H), 6.86 (d, J = 12.0 Hz, 2H), 3.82 (q, J = 8.0 Hz, 1H), 3.79 (s, 3H), 2.81 (m, 2H), 1.50 (d, J = 8.0 Hz, 3H), 1.37 - 1.32 (m, 2H), 1.28 (t, J = 8.0 Hz, 2H), 0.88 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.7, 159.0, 132.1, 129.0, 114.0, 55.2, 53.4, 31.5, 28.8, 22.0, 18.5, 13.5. HRMS (ESI) $[C_{14}H_{20}O_2S+Na]^+$ calculated mass 275.1076, measured mass 275.1083.



***S*-butyl 2-(4-(tert-butyl) phenyl) propanethioate (3h)**

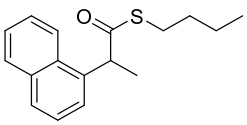
Yellow liquid (Yield = 94%; 52.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 3.79 (q, J = 8.0 Hz, 1H), 2.80 - 2.71 (m, 2H), 1.45 (d, J = 8.0 Hz, 3H), 1.42 (t, J = 8.0 Hz, 2H), 1.31 - 1.25 (m, 2H), 1.24 (s,

9H), 0.81 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5, 150.2, 136.9, 127.5, 125.6, 53.8, 34.5, 31.5, 31.4, 28.8, 22.0, 18.5, 13.6. HRMS (ESI) $[C_{17}H_{26}OS+Na]^+$ calculated mass 301.1597, measured mass 301.1601.



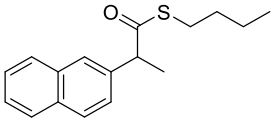
***S*-butyl 2-([1,1'-biphenyl]-4-yl) propanethioate (3i)**

Yellow liquid (Yield = 92%; 54.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (t, *J* = 8.0 Hz, 4H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 4.0 Hz, 2H), 7.38 (d, *J* = 12.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 3.94 (q, *J* = 8.0 Hz, 1H), 2.94 - 2.78 (m, 2H), 1.58 (d, *J* = 8.0 Hz, 3H), 1.52 (t, *J* = 8.0 Hz, 2H), 1.40 - 1.34 (m, 2H), 0.90 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.3, 140.8, 140.4, 139.1, 128.8, 128.3, 127.4, 127.3, 127.1, 54.0, 31.5, 28.9, 22.0, 18.5, 13.6. HRMS (ESI) $[C_{19}H_{22}OS+Na]^+$ calculated mass 321.1284, measured mass 321.1280.



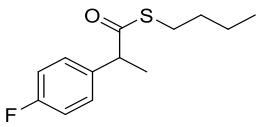
***S*-butyl 2-(naphthalen-1-yl) propanethioate (3j)**

Yellow liquid (Yield = 93%; 50.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.58 - 7.47 (m, 4H), 4.68 (q, *J* = 8.0 Hz, 1H), 2.83 (t, *J* = 8.0 Hz, 2H), 1.70 (d, *J* = 4.0 Hz, 3H), 1.48 (m, 2H), 1.35 - 1.29 (m, 2H), 0.86 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.0, 136.0, 134.0, 131.6, 129.1, 128.1, 126.4, 125.7, 125.6, 125.4, 123.2, 50.0, 31.4, 28.8, 21.9, 18.4, 13.5. HRMS (ESI) $[C_{17}H_{20}OS+H]^+$ calculated mass 273.1308, measured mass 273.1298.



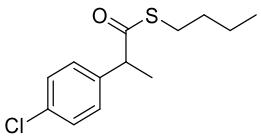
***S*-butyl 2-(naphthalen-2-yl) propanethioate (3k)**

Yellow liquid (Yield = 91%; 49.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 3H), 7.77 (s, 1H), 7.47 (m, 3H), 4.06 (q, *J* = 8.0 Hz, 1H), 2.84 (m, 2H), 1.63 (d, *J* = 8.0 Hz, 3H), 1.51 (m, 2H), 1.35 (m, 2H), 0.88 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.3, 137.5, 133.5, 132.8, 128.4, 127.9, 127.7, 126.8, 126.2, 125.9, 54.4, 31.5, 28.9, 22.0, 18.5, 13.6. HRMS (ESI) $[C_{17}H_{20}OS+H]^+$ calculated mass 273.1308, measured mass 273.1316.



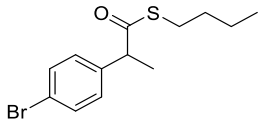
***S*-butyl 2-(4-fluorophenyl) propanethioate (3l)**

Yellow liquid (Yield = 81%; 38.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (m, 2H), 6.94 (t, *J* = 8.0 Hz, 2H), 3.79 (q, *J* = 8.0 Hz, 1H), 2.82 - 2.69 (m, 2H), 1.44 (d, *J* = 4.0 Hz, 3H), 1.42 (m, 2H), 1.30 - 1.23 (m, 2H), 0.81 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.2, 162.2 (d, *J* = 244.0 Hz), 135.7 (d, *J* = 3.0 Hz), 129.4 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 22.0 Hz), 53.4, 31.4, 28.8, 21.9, 18.6, 13.5. ^{19}F NMR (377 MHz, $CDCl_3$): δ = -115.29. HRMS (ESI) $[C_{13}H_{18}FOS+H]^+$ calculated mass 241.1057, measured mass 241.1064.



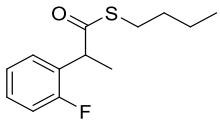
***S*-butyl 2-(4-chlorophenyl) propanethioate (3m)**

Yellow liquid (Yield = 83%; 42.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.85 (q, *J* = 8.0 Hz, 1H), 2.90 - 2.77 (m, 2H), 1.52 (s, 3H), 1.49 (d, *J* = 8.0 Hz, 2H), 1.38 - 1.30 (m, 2H), 0.88 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.9, 138.5, 133.3, 129.2, 128.8, 53.6, 31.4, 28.9, 22.0, 18.5, 13.6. HRMS (ESI) $[C_{13}H_{17}ClOS+H]^+$ calculated mass 257.0761, measured mass 257.0765.



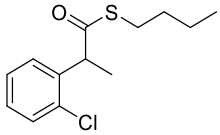
***S*-butyl 2-(4-bromophenyl) propanethioate (3n)**

Yellow liquid (Yield = 84%; 50.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 3.83 (q, *J* = 8.0 Hz, 1H), 2.83 (m, 2H), 1.50 (d, *J* = 8.0 Hz, 3H), 1.48 (t, *J* = 8.0 Hz, 2H), 1.34 (m, 2H), 0.88 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.9, 137.1, 129.9, 127.7, 119.5, 51.7, 29.5, 27.0, 20.0, 16.5, 11.6. HRMS (ESI) $[C_{13}H_{17}BrOS+Na]^+$ calculated mass 323.0076, measured mass 323.0077.



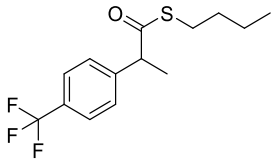
***S*-butyl 2-(2-fluorophenyl) propanethioate (3o)**

Yellow liquid (Yield = 80%; 38.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.95 (q, *J* = 8.0 Hz, 1H), 2.85 (m, 2H), 1.55 (d, *J* = 4.0 Hz, 3H), 1.53 - 1.45 (m, 2H), 1.35 (m, 2H), 0.89 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.7, 160.5 (d, *J* = 246.0 Hz), 129.0 (d, *J* = 3.0 Hz), 129.0 (d, *J* = 6.0 Hz), 127.2 (d, *J* = 14 Hz), 124.3 (d, *J* = 3.0 Hz), 115.5 (d, *J* = 22 Hz), 46.5 (d, *J* = 3.0 Hz), 31.5, 28.8, 21.9, 17.5, 13.6. ^{19}F NMR (377 MHz, $CDCl_3$): δ = -117.51. HRMS (ESI) $[C_{13}H_{17}FOS+H]^+$ calculated mass 241.1057, measured mass 241.1056.



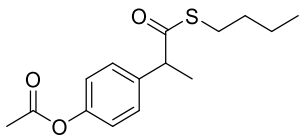
***S*-butyl 2-(2-chlorophenyl) propanethioate (3p)**

Yellow liquid (Yield = 83%; 42.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (t, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 4.42 (q, *J* = 8.0 Hz, 1H), 2.85 (m, 2H), 1.53 -1.52 (d, *J* = 4.0 Hz, 3H), 1.50 (t, *J* = 8.0 Hz, 2H), 1.39 - 1.32 (m, 2H), 0.89 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.7, 137.7, 134.2, 129.7, 128.9, 128.6, 127.2, 50.2, 31.5, 28.8, 21.9, 17.8, 13.5. HRMS (ESI) $[C_{13}H_{17}ClOS+H]^+$ calculated mass 257.0761, measured mass 257.0755.



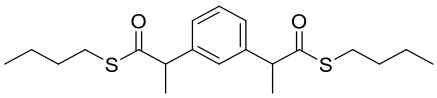
***S*-butyl 2-(4-(trifluoromethyl) phenyl) propanethioate (3q)**

Yellow liquid (Yield = 85%; 49.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.95 (q, *J* = 8.0 Hz, 1H), 2.85 (m, 2H), 1.55 (d, *J* = 4.0 Hz, 3H), 1.53 - 1.45 (m, 2H), 1.35 (m, 2H), 0.89 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.5, 143.9, 129.7 (q, *J* = 33.0 Hz), 128.2, 125.6 (q, *J* = 4.0 Hz), 124.1 (d, *J* = 270 Hz), 54.01, 31.40, 28.92, 21.95, 18.51, 13.53. ^{19}F NMR (377 MHz, $CDCl_3$): δ = -62.56. HRMS (ESI) $[C_{14}H_{17}F_3OS+Na]^+$ calculated mass 313.0844, measured mass 313.0837.



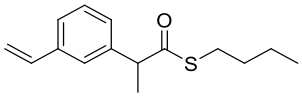
4-(1-(butylthio)-1-oxopropan-2-yl) phenyl acetate (3r)

Yellow liquid (Yield = 84%; 47.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 3.81 (q, J = 8.0 Hz, 1H), 2.76 (m, 2H), 2.22 (s, 3H), 1.45 (d, J = 8.0 Hz, 3H), 1.42 (t, J = 8.0 Hz, 2H), 1.32 - 1.25 (m, 2H), 0.82 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.0, 169.4, 150.0, 137.5, 128.9, 121.7, 53.6, 31.4, 28.8, 22.0, 21.1, 18.6, 13.5. HRMS (ESI) $[C_{15}H_{20}O_3S+Na]^+$ calculated mass 303.1025, measured mass 303.1027.



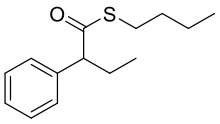
***S, S'*-dibutyl 2, 2'-(1,3-phenylene)dipropanethioate (3s)[12]**

Yellow liquid (Yield = 58%; 42.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 - 7.29 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.17 (s, 1H), 3.90 (m, 2H), 2.89 - 2.83 (m, 4H), 1.56 (s, 6H), 1.56 - 1.50 (m, 4H), 1.37 (m, 4H), 0.91 (t, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.2, 140.4, 128.9, 127.8, 126.8, 54.2, 31.5, 28.8, 21.9, 18.5, 13.6.



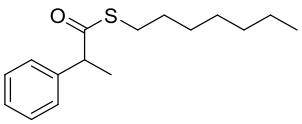
***S*-butyl 2-(3-vinylphenyl)propanethioate (3t)**

Yellow liquid (Yield = 29%; 14.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 - 7.31 (m, 2H), 7.29 - 7.26 (m, 1H), 7.21 (d, J = 8.0 Hz, 1H), 6.71 (m, 1H), 5.76 (d, J = 16.0 Hz, 1H), 5.26 (d, J = 8.0 Hz, 1H), 3.88 (q, J = 8.0 Hz, 1H), 2.90 - 2.77 (m, 2H), 1.53 (d, J = 4.0 Hz, 3H), 1.51 - 1.48 (m, 2H), 1.38 - 1.32 (m, 2H), 0.88 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.2, 140.3, 140.0, 136.7, 128.8, 127.3, 125.9, 125.2, 114.2, 54.2, 31.5, 28.8, 22.0, 18.5, 13.5. HRMS (ESI) $[C_{15}H_{20}OS+Na]^+$ calculated mass 271.1128, measured mass 271.1127.



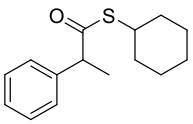
***S*-butyl 2-phenylbutanethioate (3u/3ak)**

Yellow liquid; Yield (**3ak**) = 67% (31.6 mg); Yield (**3u**) =88% (41.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, J = 8.0 Hz, 3H), 7.22 (d, J = 8.0 Hz, 2H), 3.58 (t, J = 8.0 Hz, 1H), 2.80 (m, 2H), 2.13 (m, 1H), 1.80 (m, 1H), 1.49 - 1.42 (m, 2H), 1.33 - 1.26 (m, 2H), 0.84 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.7, 138.7, 128.6, 128.2, 127.3, 62.3, 31.5, 28.8, 26.6, 21.9, 13.5, 12.1. HRMS (ESI) $[C_{14}H_{20}OS+Na]^+$ calculated mass 259.1127, measured mass 259.1131.



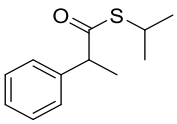
***S*-heptyl 2-phenylpropanethioate (3v)[4]**

Yellow liquid (Yield = 85%; 44.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (t, J = 8.0 Hz, 3H), 7.22 (d, J = 8.0 Hz, 2H), 3.83 (q, J = 8.0 Hz, 1H), 2.77 (m, 2H), 1.48 (m, J = 8.0 Hz, 3H), 1.45 (t, J = 8.0 Hz, 2H), 1.26 - 1.16 (m, 8H), 0.81 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.3, 140.1, 128.6, 127.9, 127.4, 54.3, 31.7, 29.4, 29.1, 28.8, 28.7, 22.6, 18.5, 14.0.



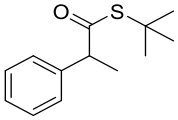
***S*-cyclohexyl 2-phenylpropanethioate (3w)[13]**

Yellow liquid (Yield = 87%; 43.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (t, J = 8.0 Hz, 3H), 7.22 (d, J = 8.0 Hz, 2H), 3.79 (q, J = 8.0 Hz, 1H), 3.41 (m, 1H), 1.90 - 1.72 (m, 2H), 1.69 - 1.56 (m, 2H), 1.47 (d, J = 8.0 Hz, 3H), 1.39 - 1.32 (m, 2H), 1.32 - 1.26 (m, 2H), 1.27 - 1.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.0, 140.2, 128.6, 127.9, 127.3, 54.3, 42.5, 33.1, 32.9, 26.0, 26.0, 25.6, 18.5.



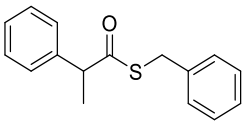
_S_-isopropyl 2-phenylpropanethioate (3x)[14]

Yellow liquid (Yield = 80%; 33.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 - 7.29 (m, 3H), 7.26 (d, J = 4.0 Hz, 2H), 3.84 (q, J = 8.0 Hz, 1H), 3.59 (m, 1H), 1.52 (d, J = 8.0 Hz, 3H), 1.28 (d, J = 8.0 Hz, 3H), 1.22 (d, J = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.3, 140.1, 128.6, 127.9, 127.3, 54.2, 34.8, 22.9, 22.8, 18.4.



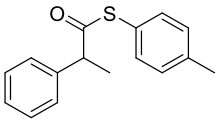
_S_-(tert-butyl) 2-phenylpropanethioate (3y)[13]

Yellow liquid (Yield = 77%; 34.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.14 (m, 5H), 3.72 (q, J = 8.0 Hz, 1H), 1.40 (d, J = 8.0 Hz, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5, 140.3, 128.5, 127.7, 127.1, 54.5, 47.8, 29.7, 18.5.



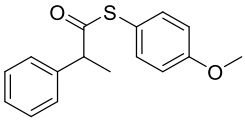
_S_-benzyl 2-phenylpropanethioate (3z)[4]

Yellow liquid (Yield = 68%; 34.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (t, J = 8.0 Hz, 6H), 7.27 (d, J = 4.0 Hz, 4H), 4.17 - 4.03 (m, 2H), 3.92 (q, J = 8.0 Hz, 1H), 1.58 (d, J = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.5, 139.7, 137.4, 128.8, 128.7, 128.6, 128.0, 127.5, 127.2, 54.1, 33.5, 18.4.



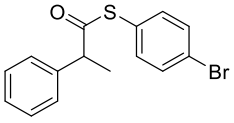
_S_-(p-tolyl) 2-phenylpropanethioate (3aa)[13]

Yellow liquid (Yield = 64%; 32.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, J = 4.0 Hz, 4H), 7.15 (t, J = 8.0 Hz, 3H), 7.09 (d, J = 8.0 Hz, 2H), 3.90 (q, J = 8.0 Hz, 1H), 2.26 (s, 3H), 1.48 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 139.7, 139.5, 134.4, 129.9, 128.8, 128.1, 127.5, 124.4, 54.0, 21.3, 18.7.



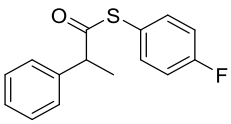
_S_-(4-methoxyphenyl) 2-phenylpropanethioate (3ab)

Yellow liquid (Yield = 65%; 35.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 - 7.22 (m, 5H), 7.17 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 3.91 (q, J = 8.0 Hz, 1H), 3.72 (s, 3H), 1.49 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.0, 160.6, 139.7, 136.0, 132.7, 128.7, 128.0, 127.5, 114.8, 55.3, 53.8, 18.7. HRMS (ESI) $[C_{16}H_{16}O_2S+H]^+$ calculated mass 273.0944, measured mass 273.0950.



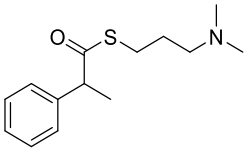
_S_-(4-bromophenyl) 2-phenylpropanethioate (3ac)[13]

Yellow liquid (Yield = 58%; 37.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 5H), 7.20 (d, J = 8.0 Hz, 2H), 3.99 (q, J = 4.0 Hz, 1H), 1.58 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 139.3, 135.9, 132.3, 128.8, 128.1, 127.7, 127.1, 123.9, 54.2, 18.5.



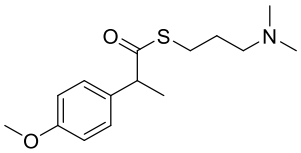
***S*-(4-fluorophenyl) 2-phenylpropanethioate (3ad)**

Yellow liquid (Yield = 75%; 39 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.0 Hz, 2H), 7.35 - 7.28 (m, 5H), 7.06 (t, *J* = 8.0 Hz, 2H), 3.99 (q, *J* = 8.0 Hz, 1H), 1.58 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.1, 163.4 (d, *J* = 249.0 Hz), 139.4, 136.5 (d, *J* = 8.0 Hz), 128.8, 128.0, 127.7, 123.2 (d, *J* = 3.0 Hz), 116.4 (d, *J* = 23.0 Hz), 54.0, 18.6. ^{19}F NMR (377 MHz, $CDCl_3$): δ = -111.35. HRMS (ESI) $[C_{15}H_{13}FOS+H]^+$ calculated mass 261.0744, measured mass 261.0748.



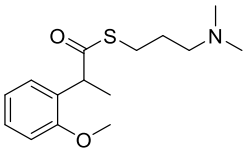
***S*-(3-(dimethylamino)propyl) 2-phenylpropanethioate (3ae)**

Yellow liquid (Yield = 63%; 31.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 - 7.21 (m, 5H), 3.83 (q, *J* = 8.0 Hz, 1H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.20 (t, *J* = 7.3 Hz, 2H), 2.12 (s, 6H), 1.63 (m, 2H), 1.48 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 140.0, 128.7, 127.9, 127.4, 58.4, 54.3, 45.4, 27.6, 27.0, 18.4. HRMS (ESI) $[C_{14}H_{21}NOS+H]^+$ calculated mass 252.1420, measured mass 252.1417.



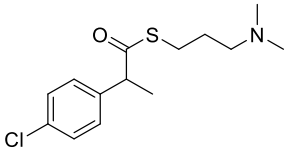
***S*-(3-(dimethylamino)propyl) 2-(4-methoxyphenyl)propanethioate (3af)**

Yellow liquid (Yield = 85%; 47.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 3.83 (m, 1H), 3.78 (s, 3H), 2.84 (m, 2H), 2.25 (t, *J* = 8.0 Hz, 2H), 2.17 (s, 6H), 1.68 (m, 2H), 1.49 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5, 159.0, 132.0, 129.0, 114.1, 58.4, 55.2, 53.4, 45.4, 27.6, 27.0, 18.4. HRMS (ESI) $[C_{15}H_{23}NO_2S+H]^+$ calculated mass 282.1523, measured mass 282.1528.



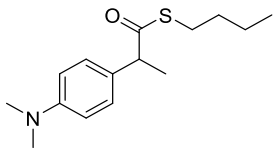
***S*-(3-(dimethylamino)propyl) 2-(2-methoxyphenyl)propanethioate (3ag)**

Yellow liquid (Yield = 80%; 45.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (t, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.25 (q, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.26 (t, *J* = 8.0 Hz, 2H), 2.18 (s, 6H), 1.68 (m, 2H), 1.48 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.0, 157.1, 128.6, 128.6, 128.4, 120.7, 110.7, 58.5, 55.5, 47.3, 45.4, 27.7, 26.9, 17.2. HRMS (ESI) $[C_{15}H_{23}NO_2S+H]^+$ calculated mass 282.1526, measured mass 282.1522.



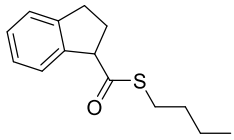
***S*-(3-(dimethylamino)propyl) 2-(4-chlorophenyl)propanethioate (3ah)**

Yellow liquid (Yield = 42%; 23.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.86 (m, 1H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.27 (t, *J* = 8.0 Hz, 2H), 2.19 (s, 6H), 1.70 (m, 2H), 1.52 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.7, 138.4, 133.3, 129.2, 128.8, 58.4, 53.6, 45.4, 27.5, 27.1, 18.4. HRMS (ESI) $[C_{14}H_{20}ClNOS+H]^+$ calculated mass 286.1029, measured mass 286.1027.



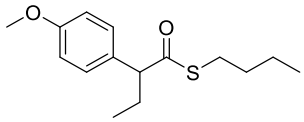
***S*-butyl (*S*)-2-(4-(dimethylamino)phenyl)propanethioate (3ai)**

Yellow liquid (Yield = 73%; 38.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, J = 12.0 Hz, 2H), 6.70 (d, J = 12.0 Hz, 2H), 3.78 (q, J = 8.0 Hz, 1H), 2.94 (s, 6H), 2.81 (m, 2H), 1.50 (d, J = 8.0 Hz, 3H), 1.49 (m, 2H), 1.36 - 1.32 (m, 2H), 0.89 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 150.0, 128.7, 127.7, 112.6, 53.4, 40.6, 31.6, 28.8, 22.0, 18.4, 13.6. HRMS (ESI) $[C_{15}H_{23}NOS+H]^+$ calculated mass 266.1575, measured mass 266.1573.



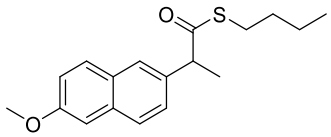
***S*-butyl 2,3-dihydro-1H-indene-1-carbothioate (3aj)**

Yellow liquid (Yield = 79%; 37.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 8.0 Hz, 2H), 4.23 (q, J = 4.0 Hz, 1H), 3.15 (m, 1H), 2.99 - 2.87 (m, 3H), 2.50 - 2.33 (m, 2H), 1.59 - 1.54 (m, 2H), 1.40 (m, 2H), 0.92 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 144.6, 140.7, 127.8, 126.5, 125.1, 124.8, 59.1, 31.9, 31.6, 30.0, 28.8, 22.0, 13.6. HRMS (ESI) $[C_{14}H_{18}OS+Na]^+$ calculated mass 257.0971, measured mass 257.0971.



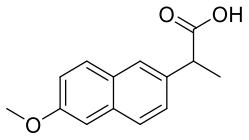
***S*-butyl 2-(4-methoxyphenyl) butanethioate (3al)**

Yellow liquid (Yield = 73%; 38.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, J = 12.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 3.79 (s, 3H), 3.57 (t, J = 8.0 Hz, 1H), 2.82 (m, 2H), 2.13 (m, 1H), 1.80 (m, 1H), 1.50 (m, 2H), 1.35 (m, 2H), 0.88 (t, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 158.9, 130.7, 129.2, 114.0, 61.4, 55.2, 31.5, 28.7, 26.6, 22.0, 13.5, 12.1. HRMS (ESI) $[C_{15}H_{22}O_2S+Na]^+$ calculated mass 289.1233, measured mass 289.1234.



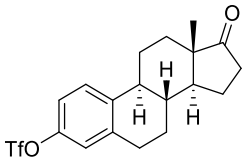
***S*-butyl 2-(6-methoxynaphthalen-2-yl) propanethioate (3am)[15]**

Yellow liquid (Yield = 89%; 53.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 - 7.71 (m, 3H), 7.43 (m, 1H), 7.19 - 7.13 (m, 2H), 4.04 (q, J = 8.0 Hz, 1H), 3.91 (s, 3H), 2.93 - 2.80 (m, 2H), 1.64 (d, J = 8.0 Hz, 3H), 1.57 - 1.49 (m, 2H), 1.36 (m, 2H), 0.90 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 157.8, 135.2, 133.9, 129.4, 129.0, 127.2, 126.6, 126.5, 119.1, 105.7, 55.3, 54.3, 31.5, 28.9, 22.0, 18.5, 13.6.



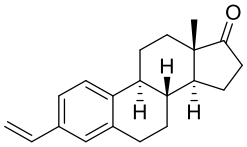
2-(6-methoxynaphthalen-2-yl) propanoic acid (3am')[16]

White solid (Yield = 91%; 41.9 mg); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.29 (s, 1H), 7.76 (t, J = 8.0 Hz, 2H), 7.69 (s, 1H), 7.38 (m, 1H), 7.26 (d, J = 4.0 Hz, 1H), 7.13 (m, 1H), 3.84 (s, 3H), 3.78 (q, J = 8.0 Hz, 1H), 1.42 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 176.0, 157.6, 136.8, 133.7, 129.6, 128.9, 127.3, 126.9, 126.1, 119.2, 106.2, 55.6, 45.1, 18.9.



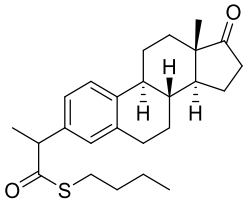
(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate (S1)[11]

White solid (Yield = 90%; 1.34 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.99 (s, 1H), 2.94 (m, 2H), 2.51 (m, 1H), 2.45 - 2.36 (m, 1H), 2.30 (m, 1H), 2.22 - 2.12 (m, 1H), 2.05 (m, 2H), 2.01 - 1.94 (m, 1H), 1.70 - 1.59 (m, 3H), 1.55 - 1.47 (m, 3H), 0.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 220.3, 147.6, 140.3, 139.3, 127.2, 121.2, 118.3, 50.4, 47.9, 44.1, 37.8, 35.8, 31.5, 29.4, 26.1, 25.7, 21.6, 13.8.



(8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (1an)[10]

White solid (Yield = 87%; 363 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.14 (s, 1H), 6.66 (m, 1H), 5.70 (d, J = 8.0 Hz, 1H), 5.19 (d, J = 8.0 Hz, 1H), 2.92 (m, 2H), 2.58 - 2.37 (m, 2H), 2.30 (m, 1H), 2.21 - 2.11 (m, 1H), 2.10 - 2.00 (m, 2H), 2.00 - 1.89 (m, 1H), 1.65 - 1.56 (m, 3H), 1.54 - 1.45 (m, 3H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 220.8, 139.6, 136.6, 136.6, 135.3, 126.9, 125.5, 123.6, 113.2, 50.6, 48.0, 44.5, 38.2, 35.9, 31.6, 29.4, 26.5, 25.7, 21.6, 13.9.



***S*-butyl 2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)propanethioate (3an)**

Yellow liquid (Yield = 83%; 66 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.04 (s, 1H), 3.83 (q, J = 8.0 Hz, 1H), 2.91 (m, 2H), 2.88 - 2.75 (m, 2H), 2.50 (m, 1H), 2.41 (m, 1H), 2.29 (m, 1H), 2.15 (m, 1H), 2.10 - 2.03 (m, 2H), 2.03 - 1.90 (m, 2H), 1.64 - 1.58 (m, 2H), 1.58 - 1.53 (m, 2H), 1.52 (s, 3H), 1.49 - 1.44 (m, 2H), 1.39 - 1.32 (m, 2H), 1.30 - 1.24 (m, 1H), 0.90 (m, 3H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 220.6, 201.3, 138.9, 137.5, 136.8, 128.3, 125.6, 125.2, 53.8, 50.6, 48.0, 44.4, 38.1, 35.8, 31.7, 31.5, 29.4, 28.8, 26.5, 25.7, 22.0, 21.6, 18.6, 13.9, 13.6. HRMS (ESI) $[C_{25}H_{34}O_2S+Na]^+$ calculated mass 421.2174, measured mass 421.2177.

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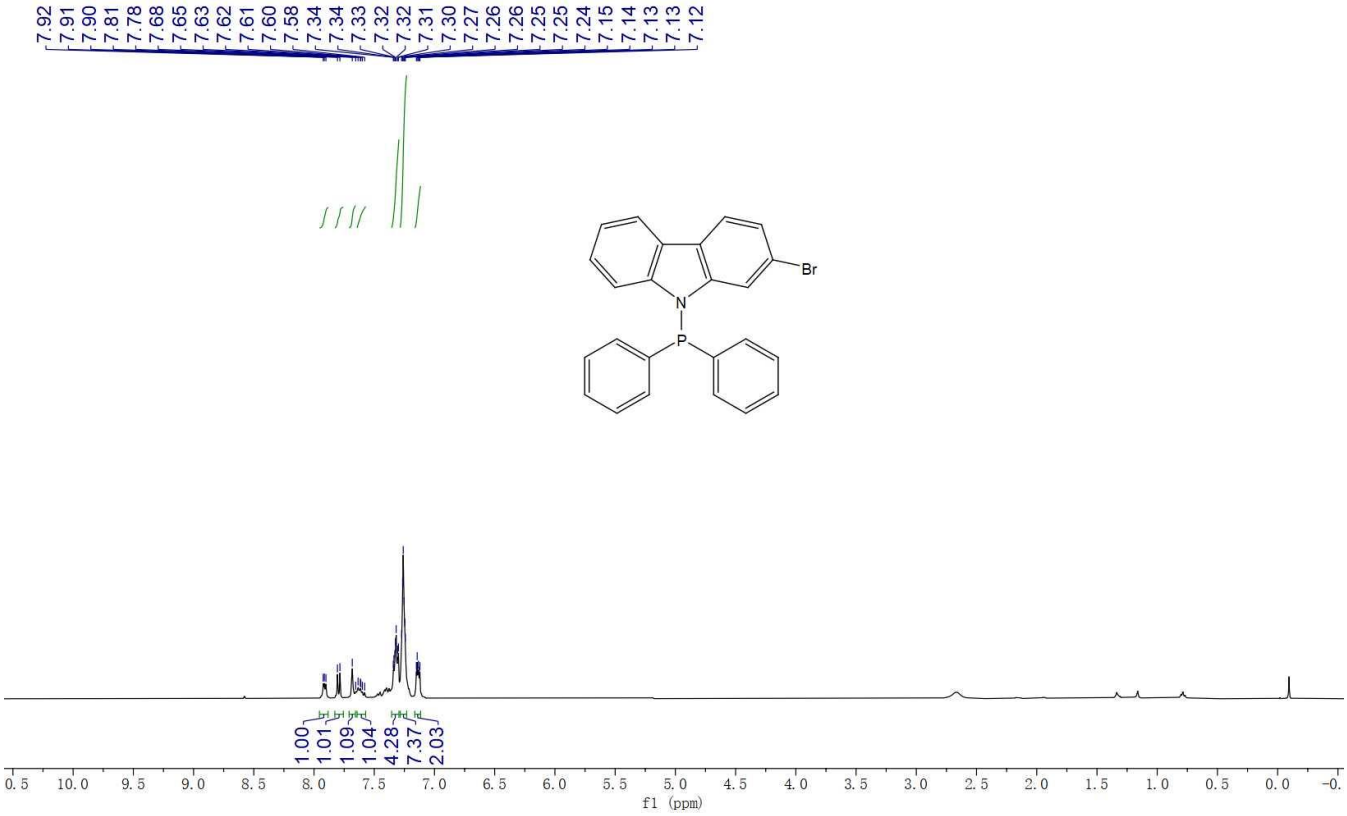
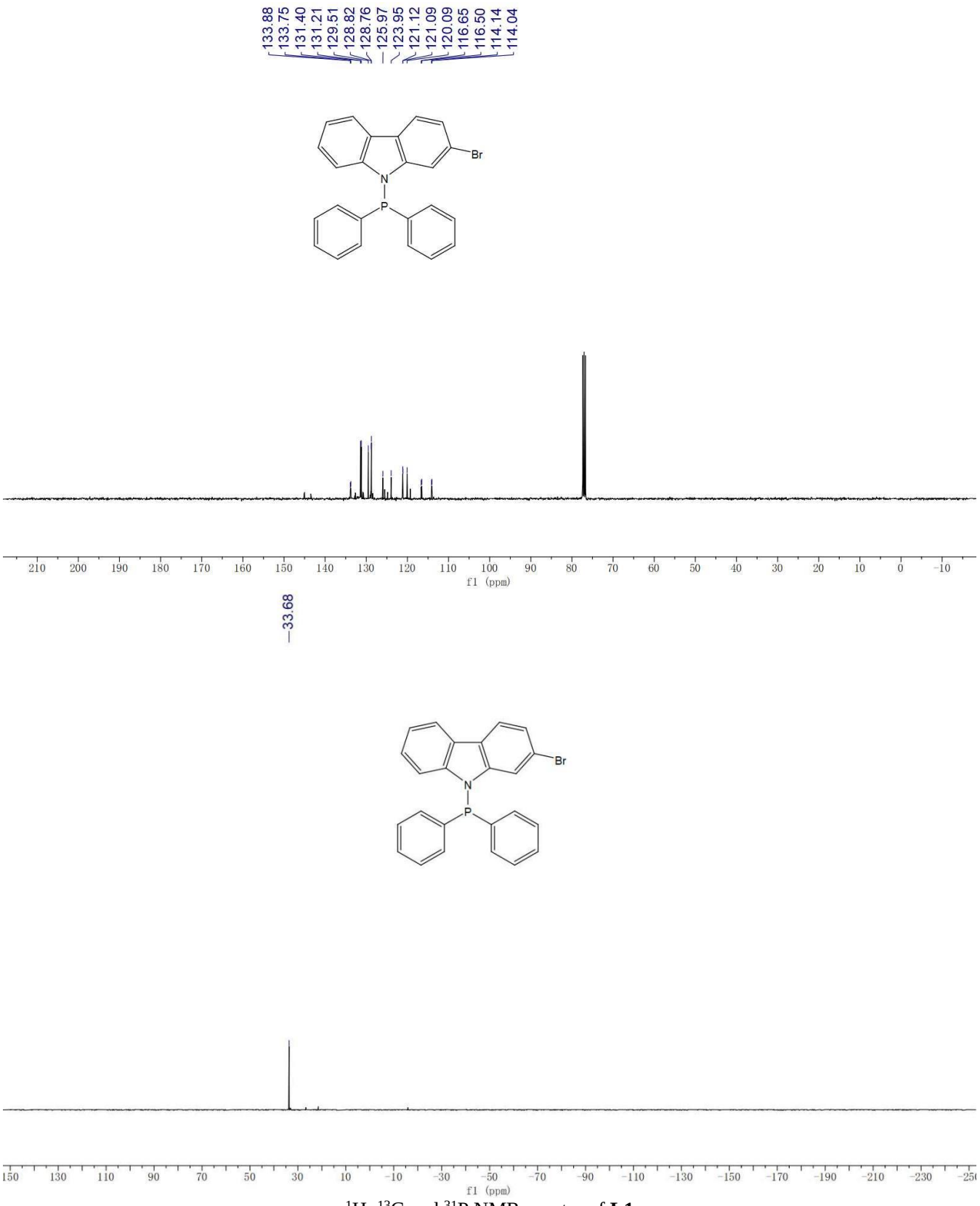
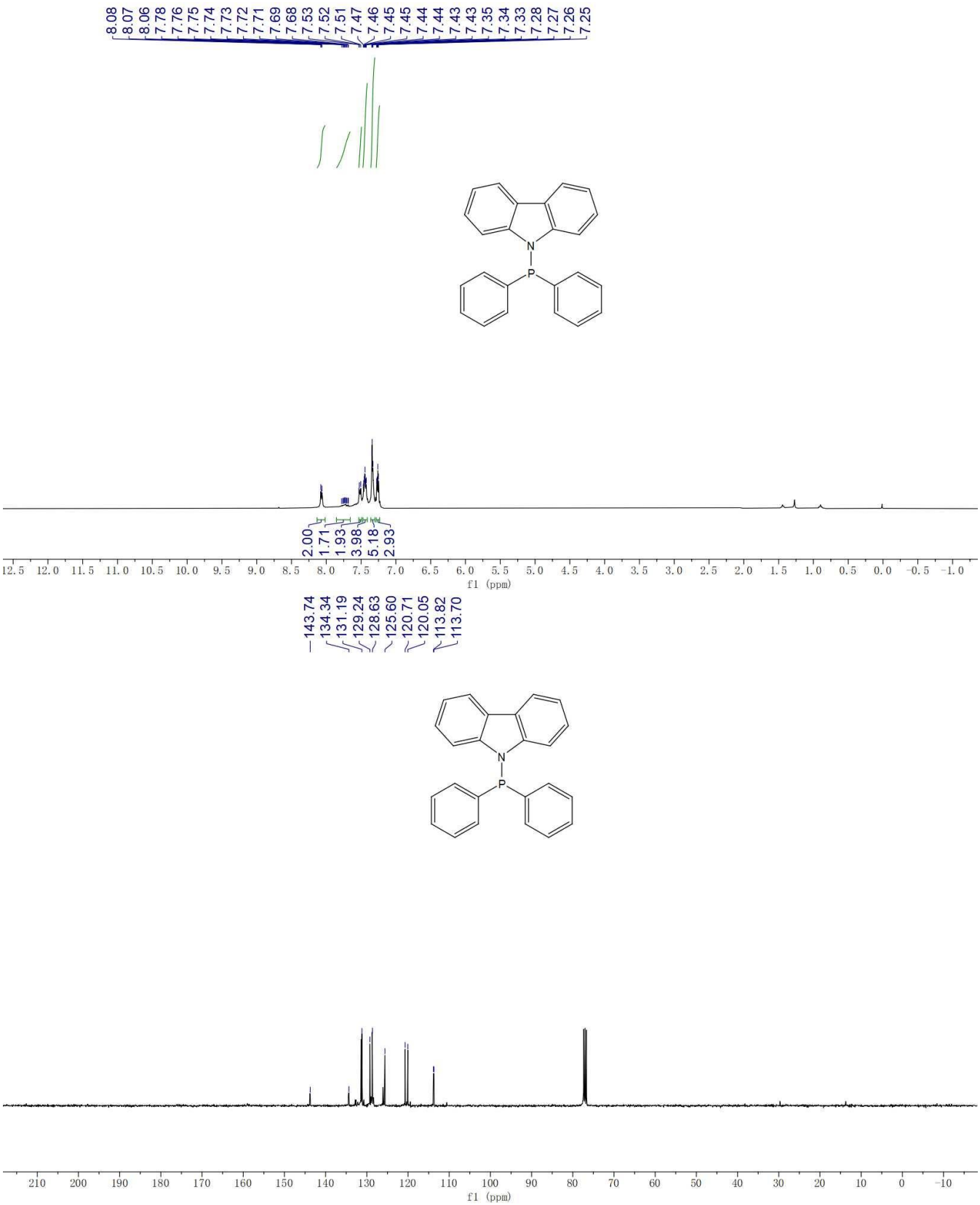
13. NMR spectrums





^{1}H, ^{13}C and ^{31}P NMR spectra of **L1**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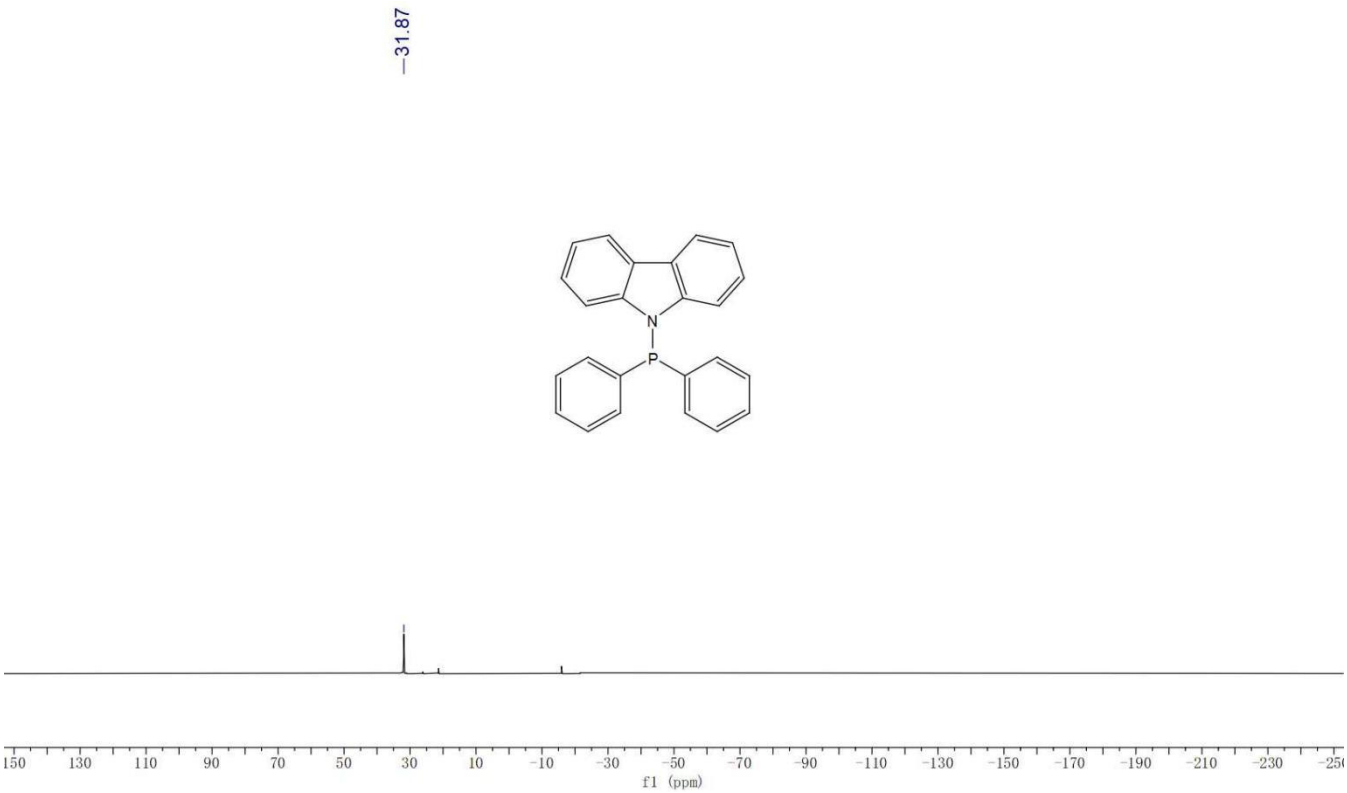

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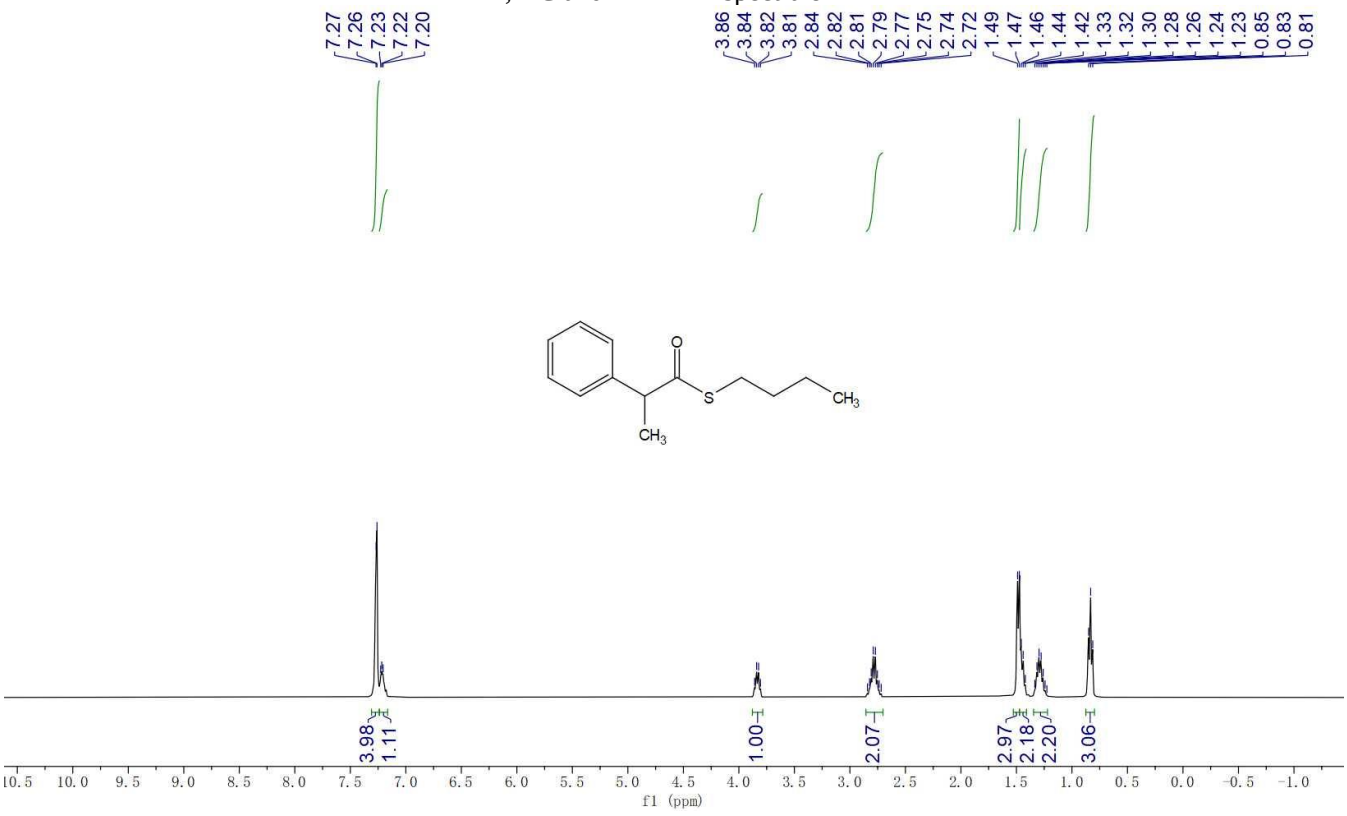
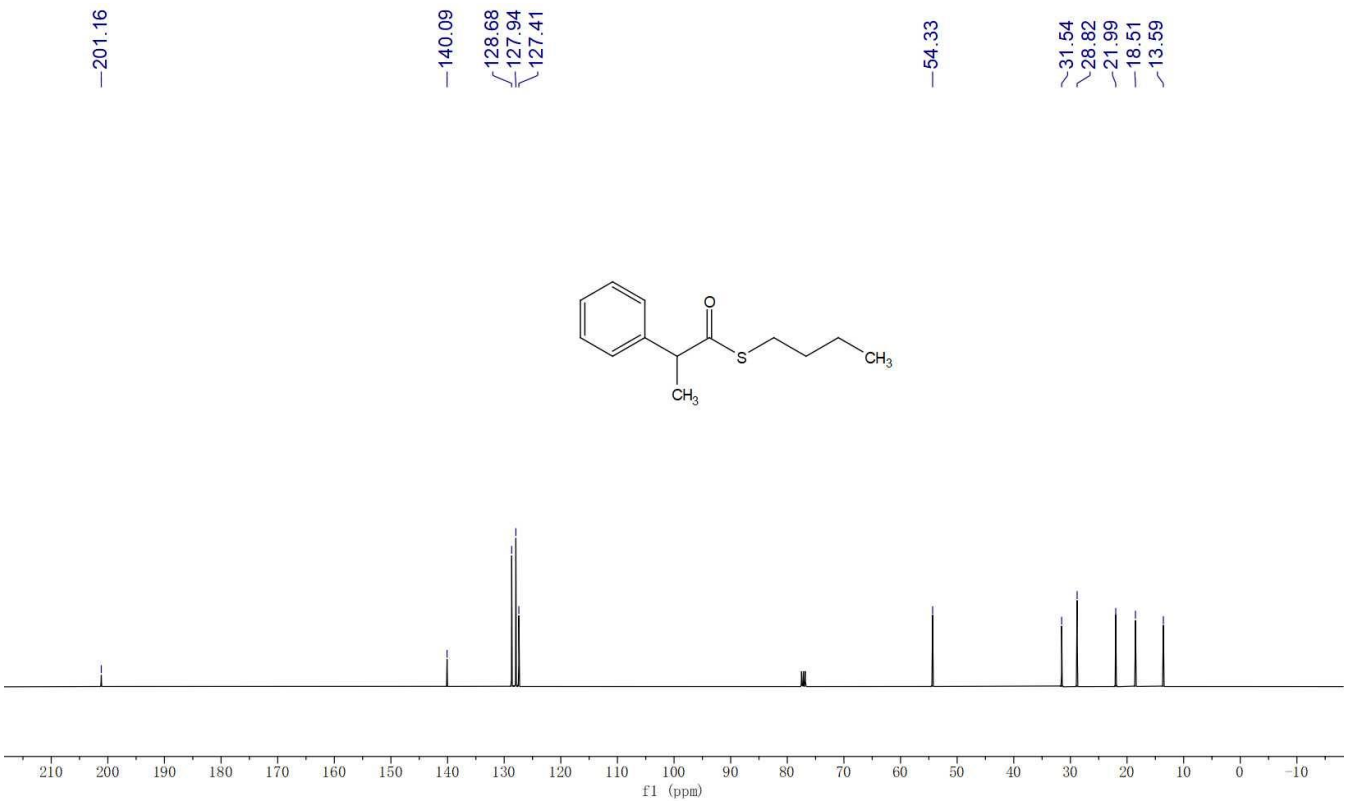
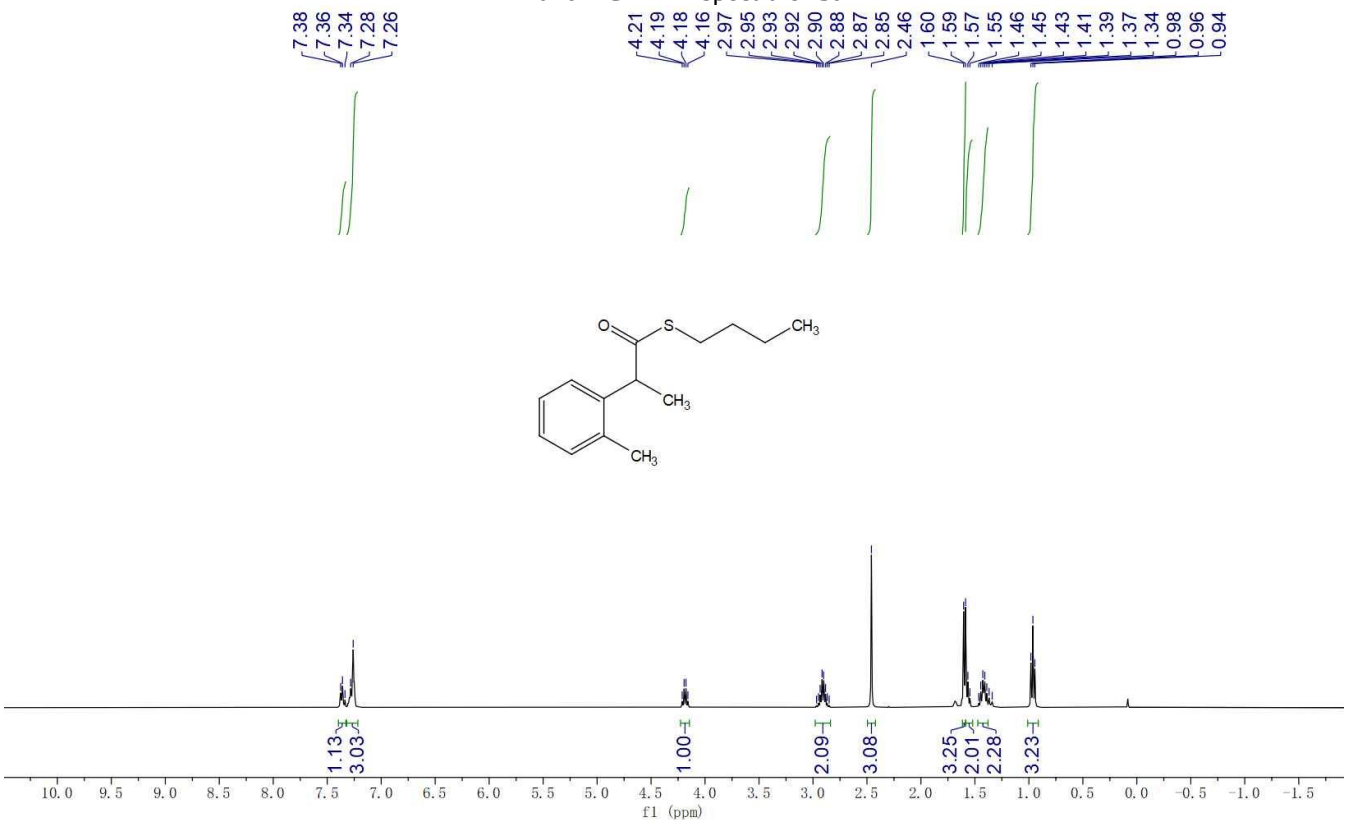
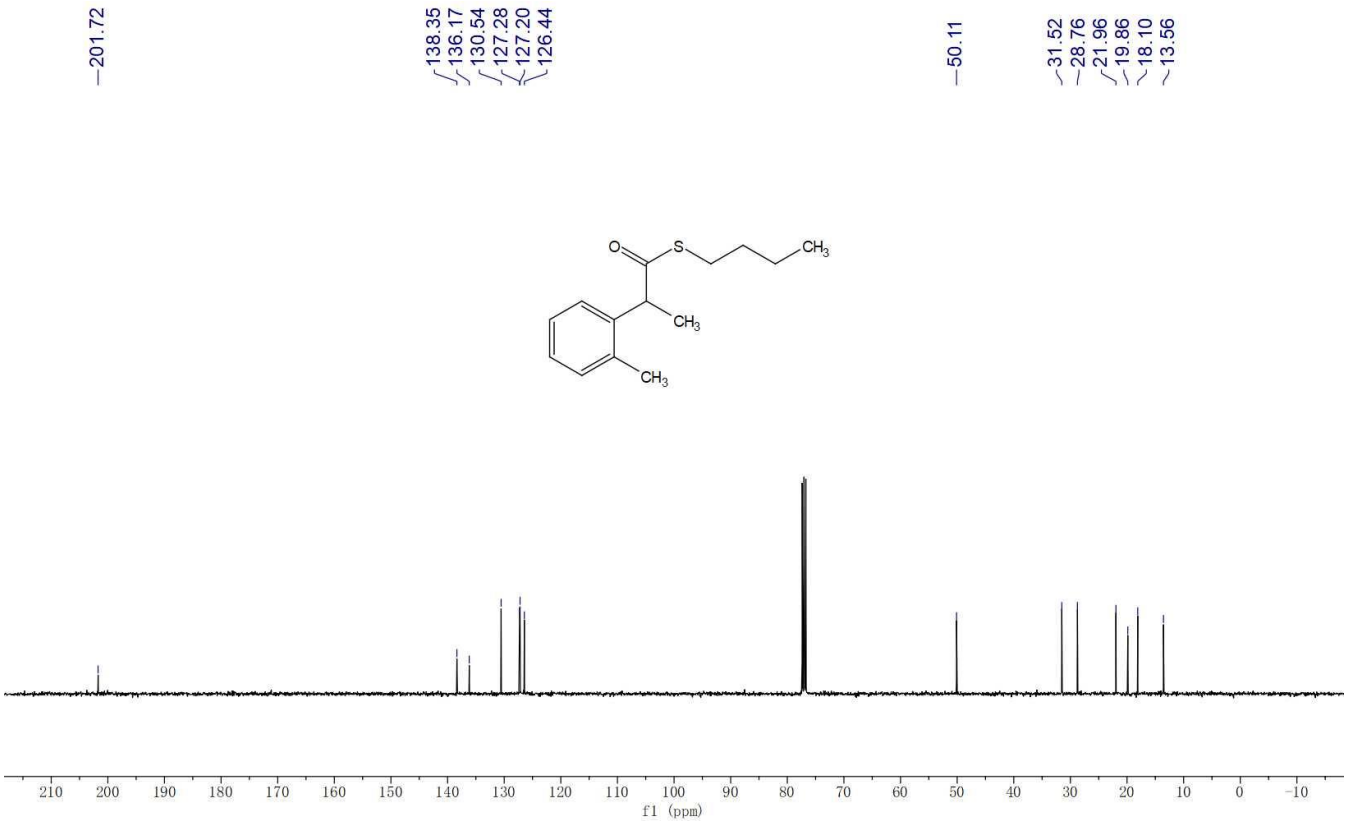


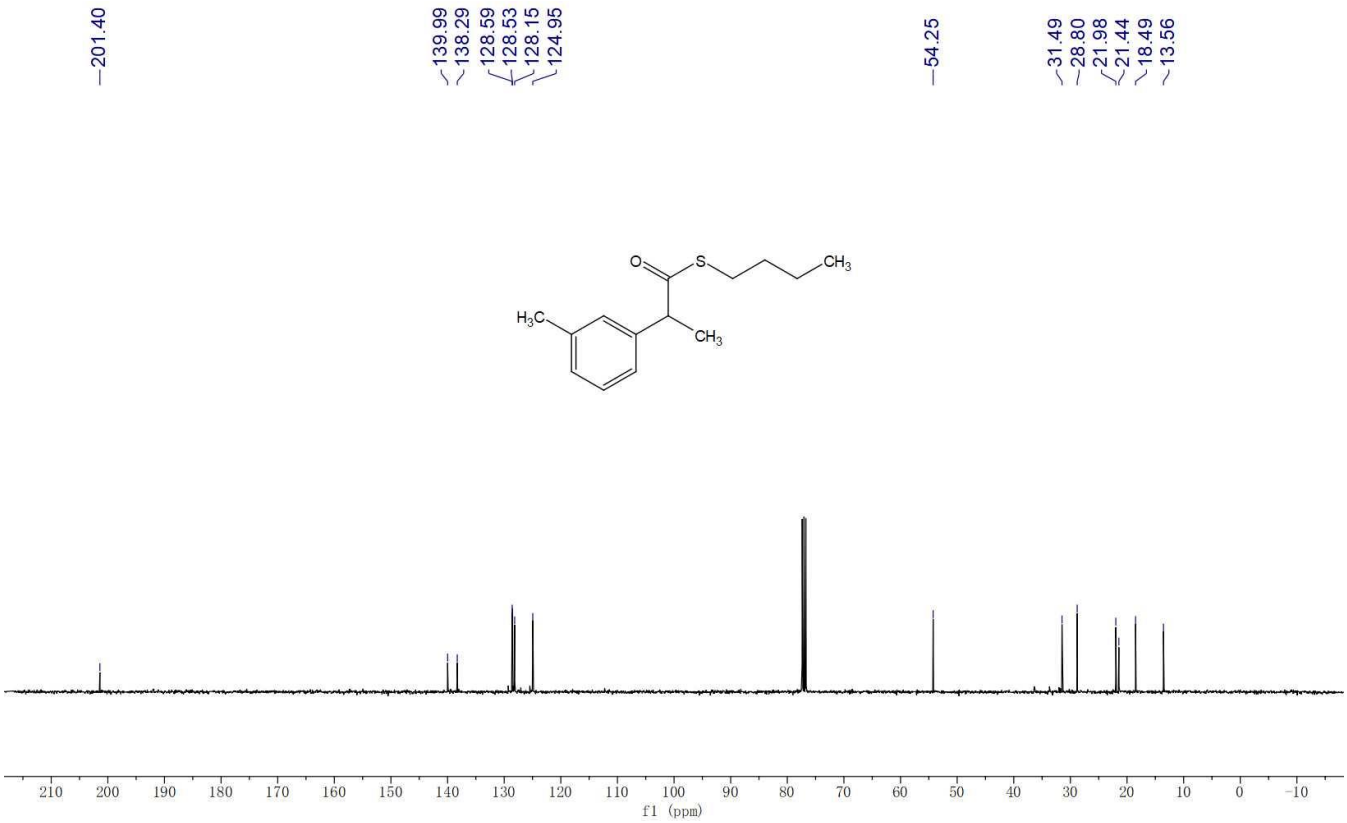


^{1}H and ^{13}C NMR spectra of **3a**

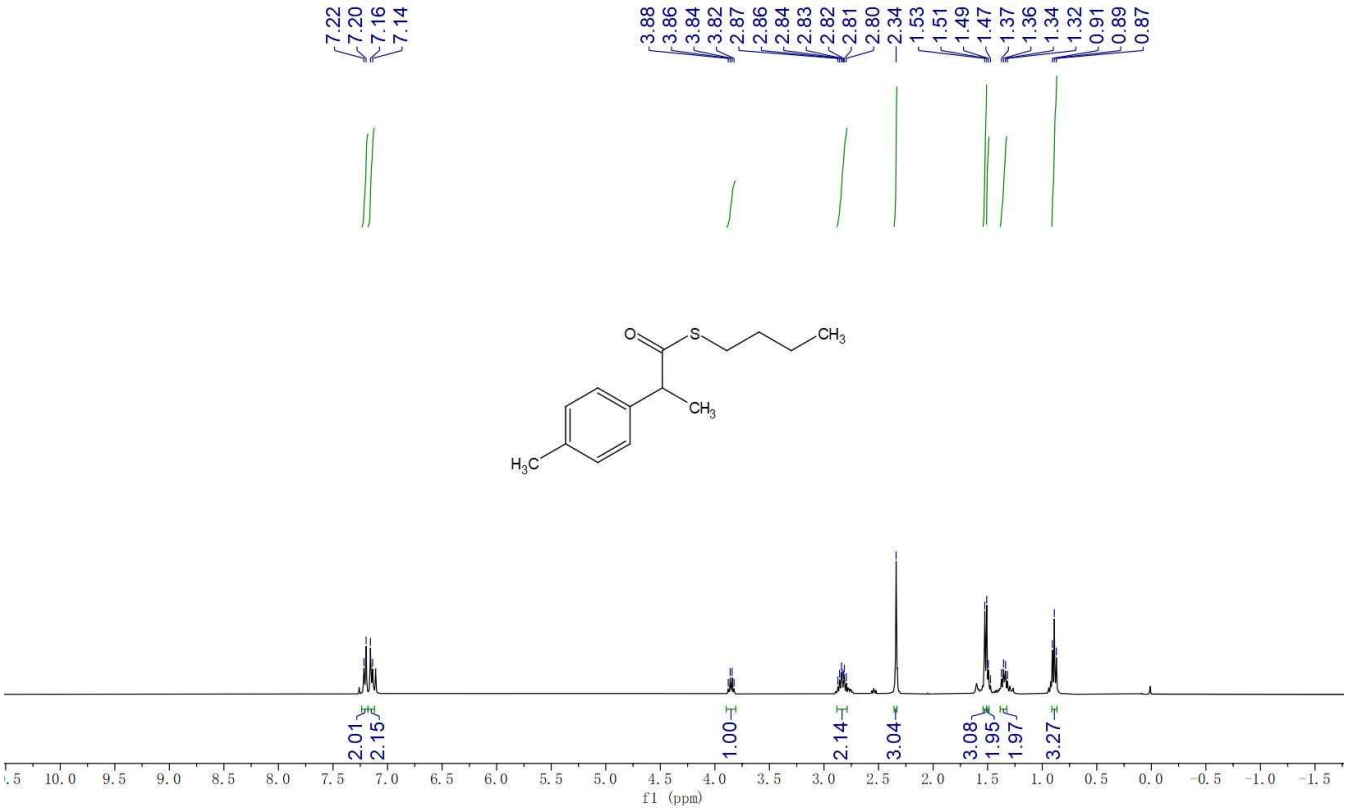


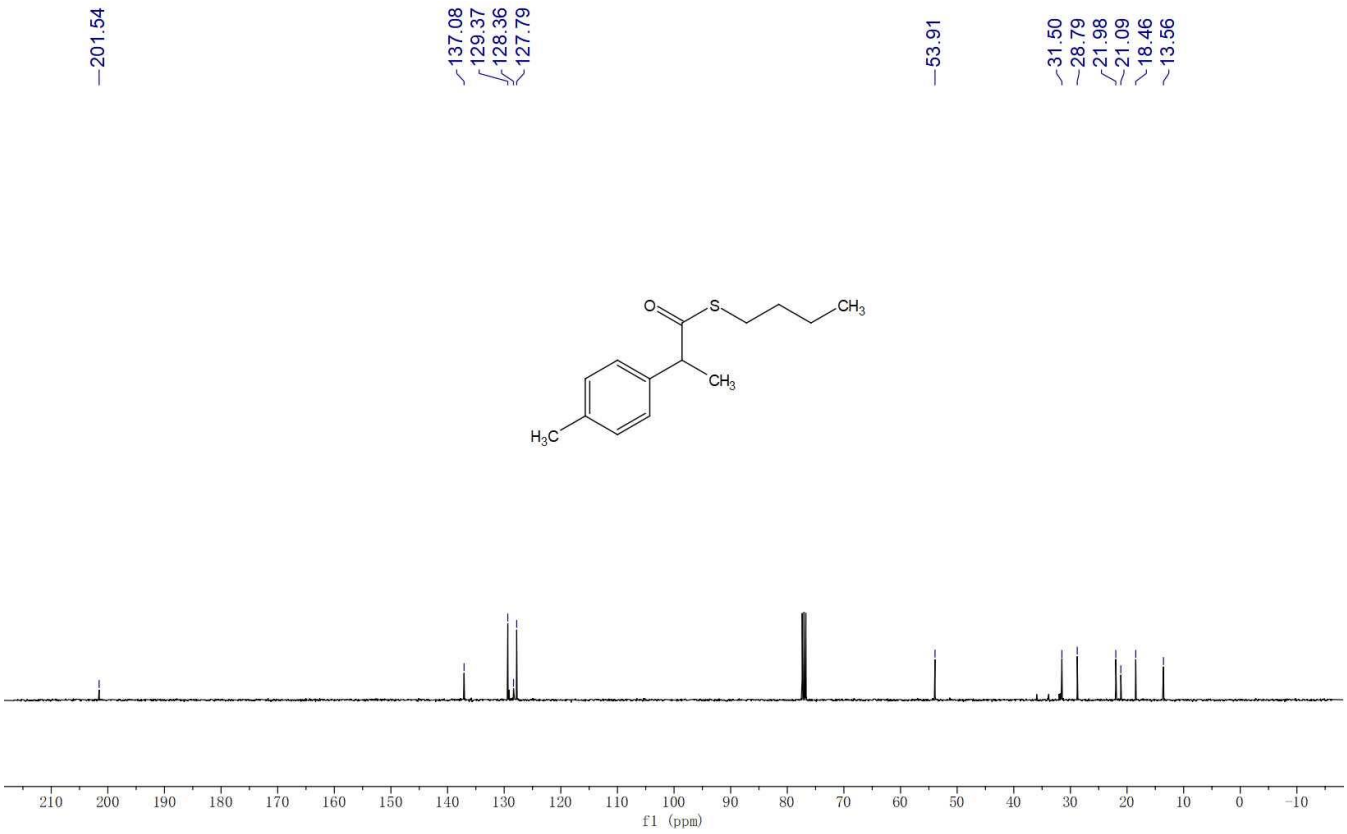


^{1}H and ^{13}C NMR spectra of **3b**

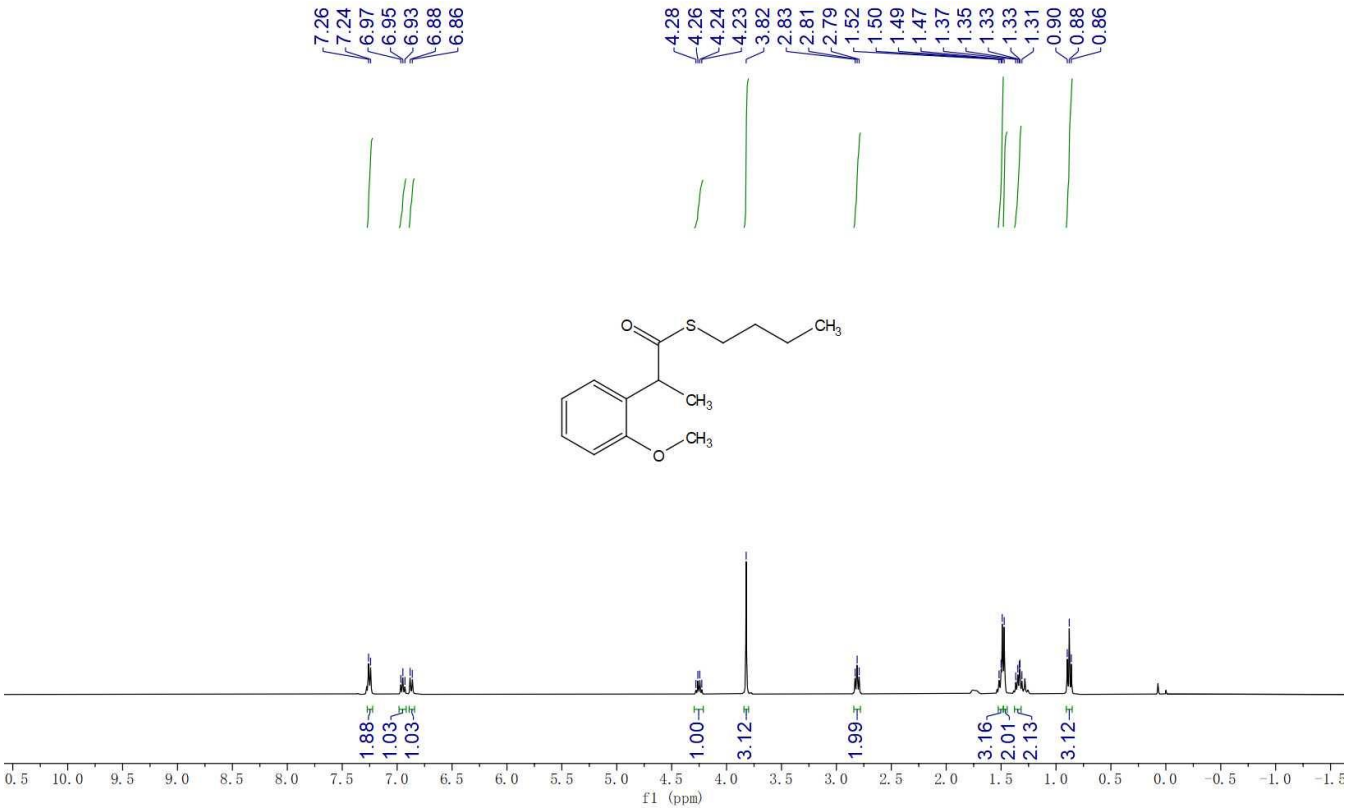


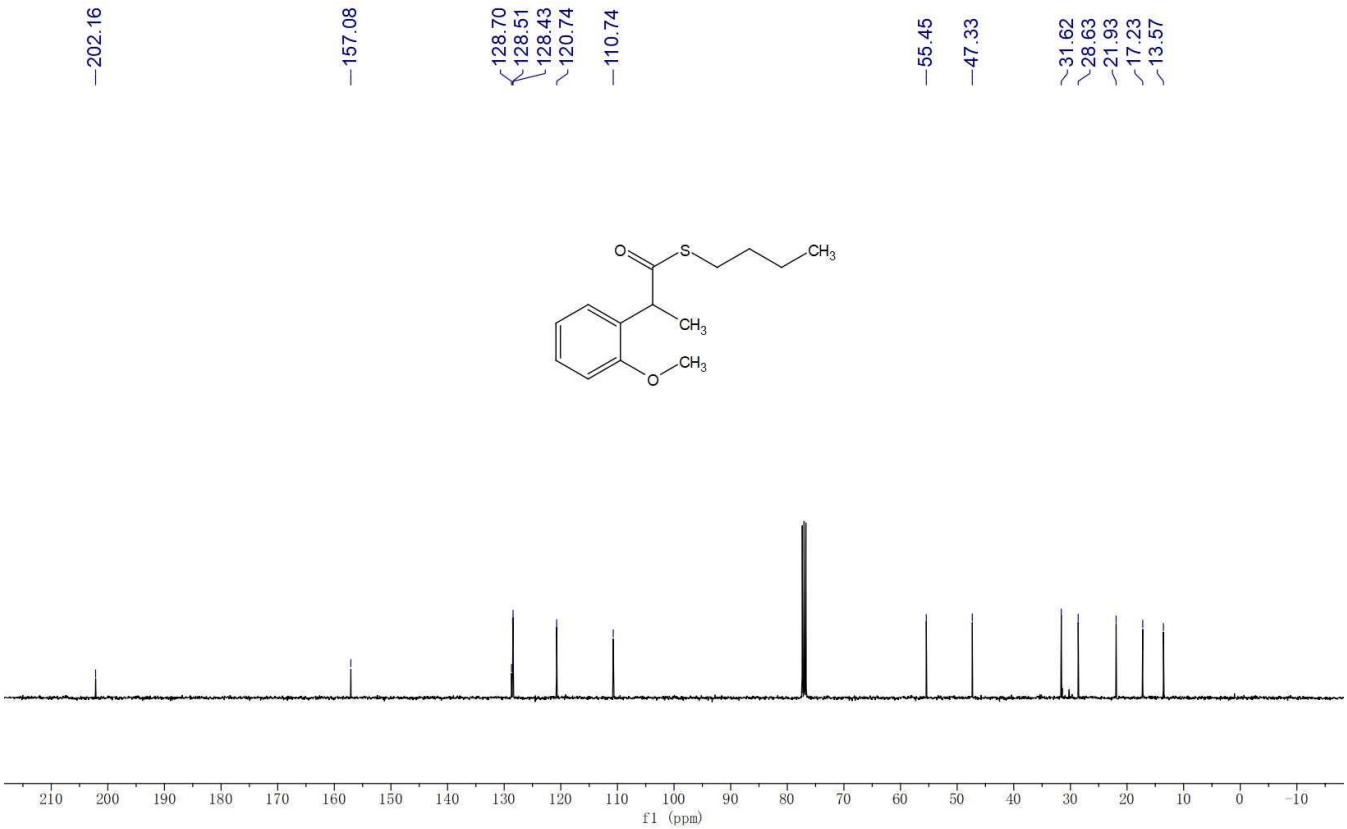
^{1}H and ^{13}C NMR spectra of **3c**



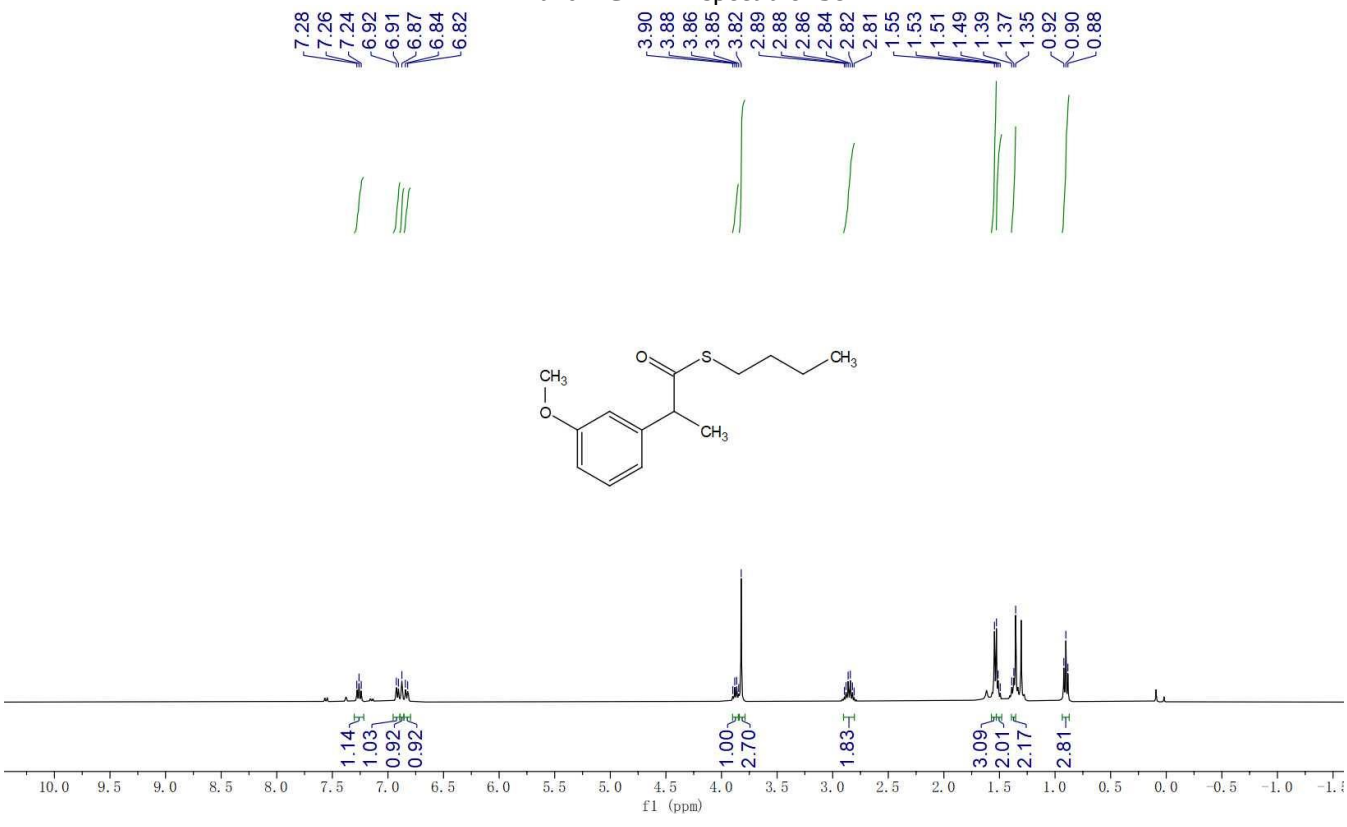


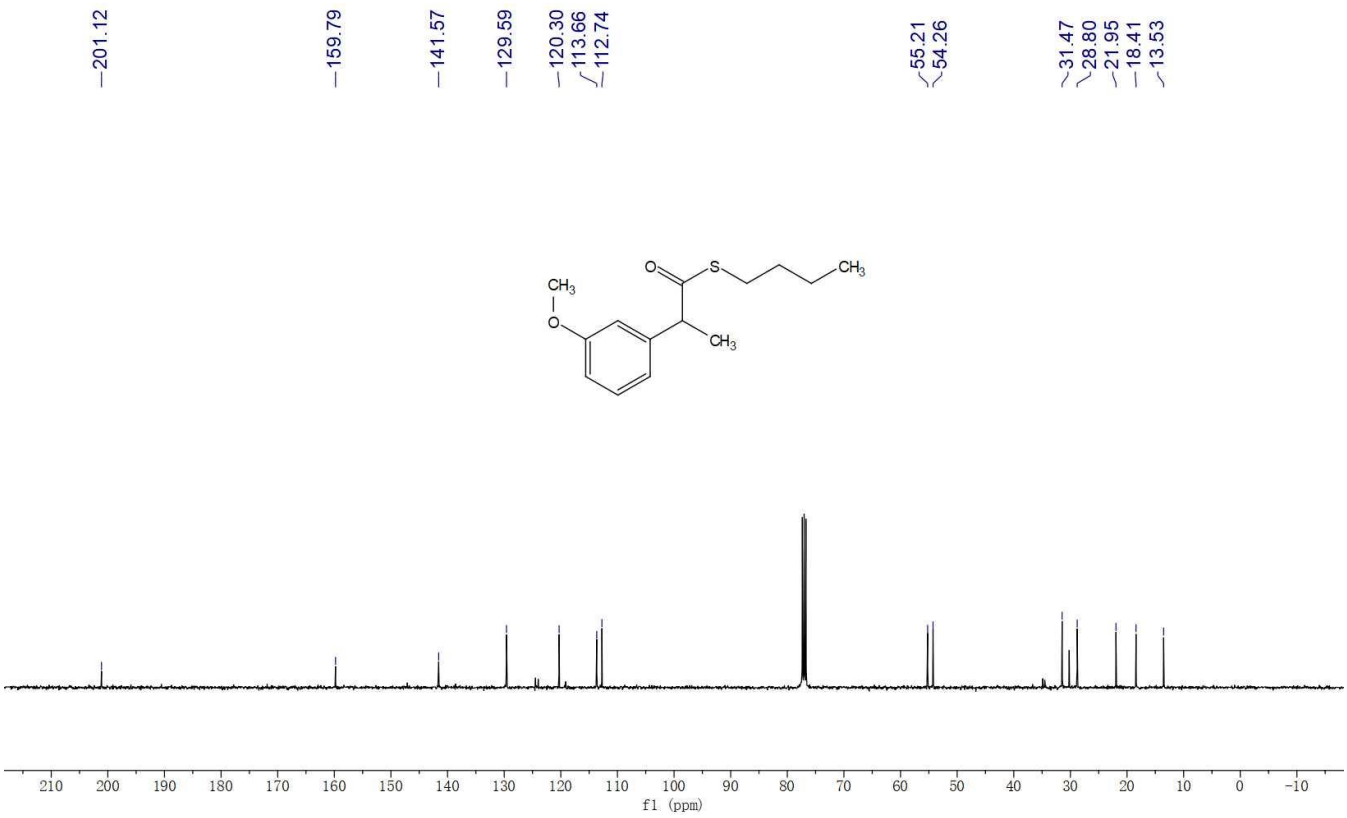
^{1}H and ^{13}C NMR spectra of **3d**



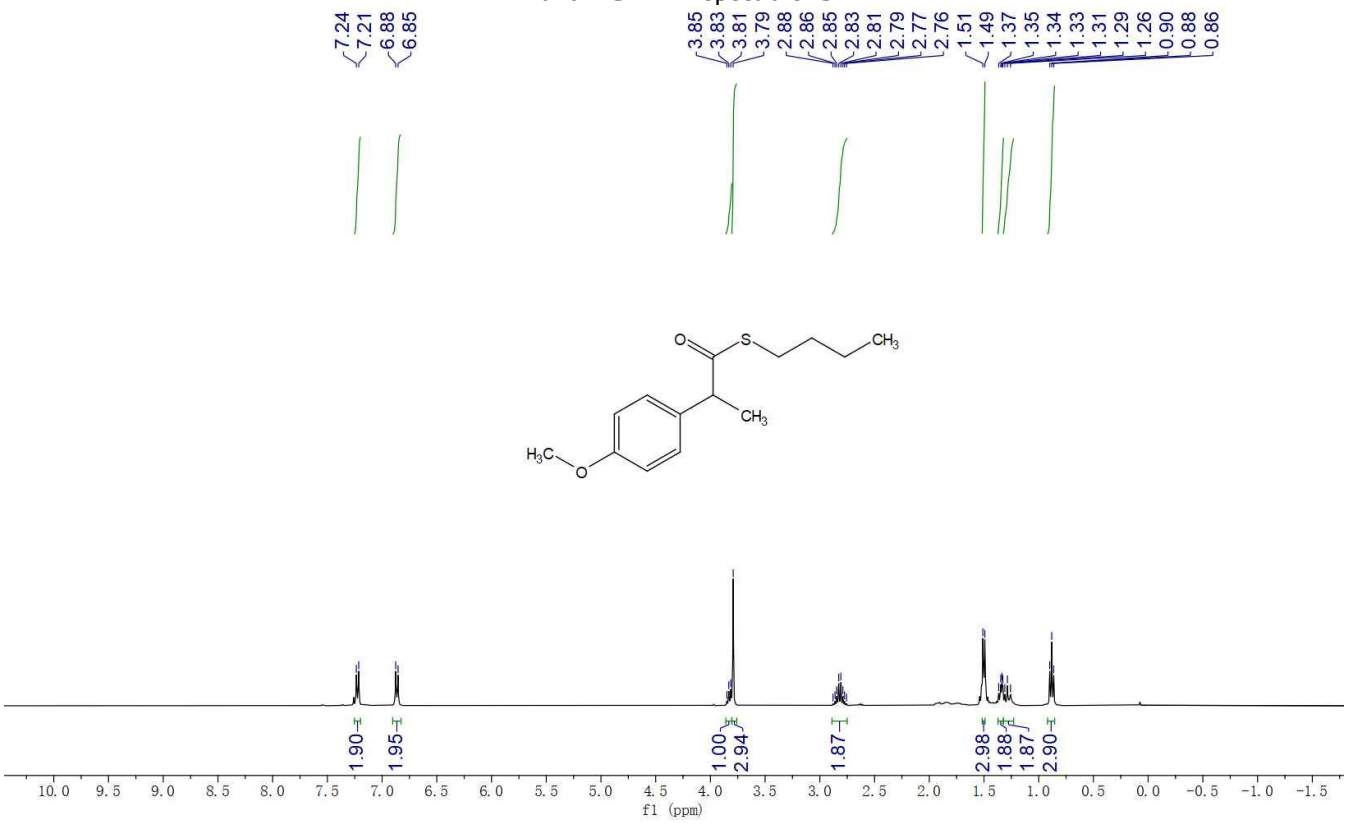


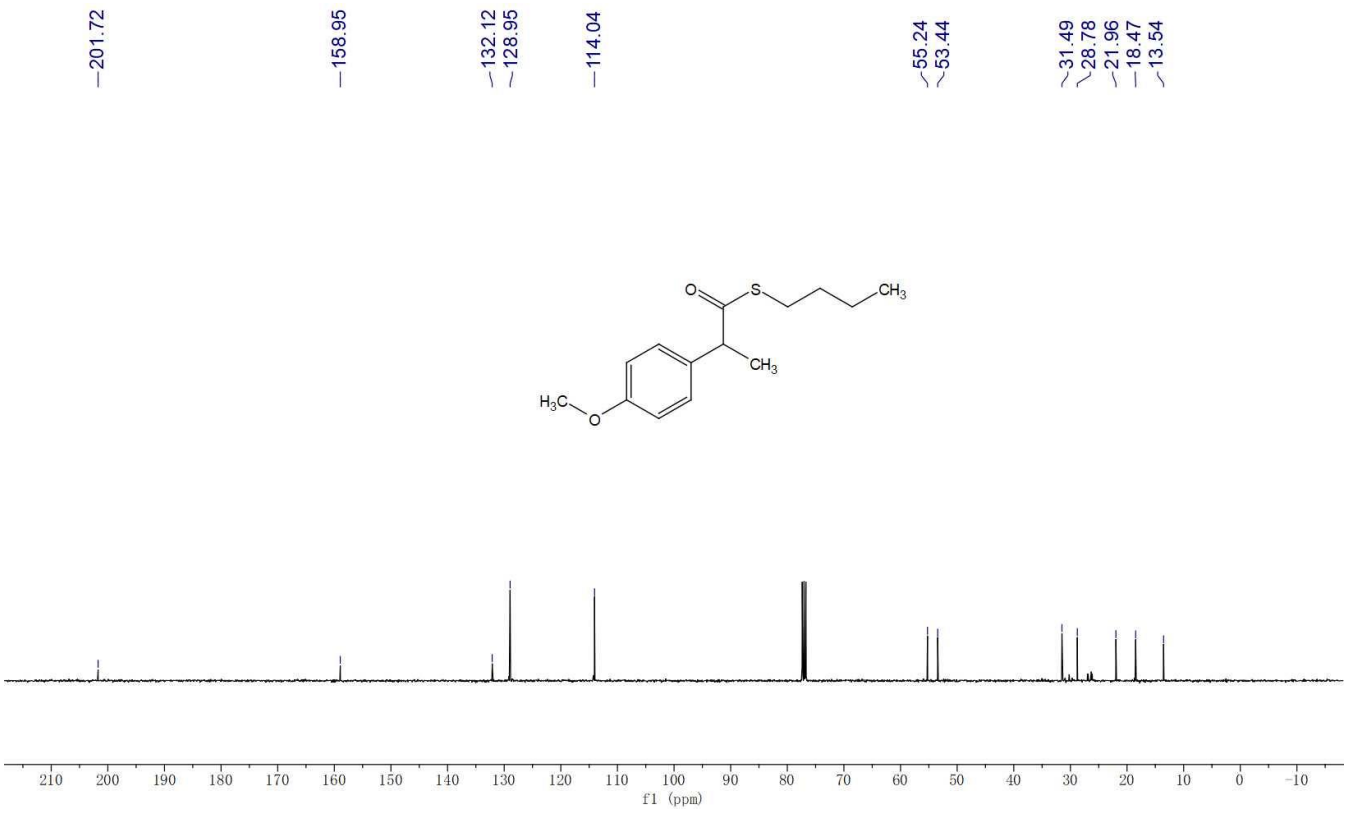
^{1}H and ^{13}C NMR spectra of **3e**



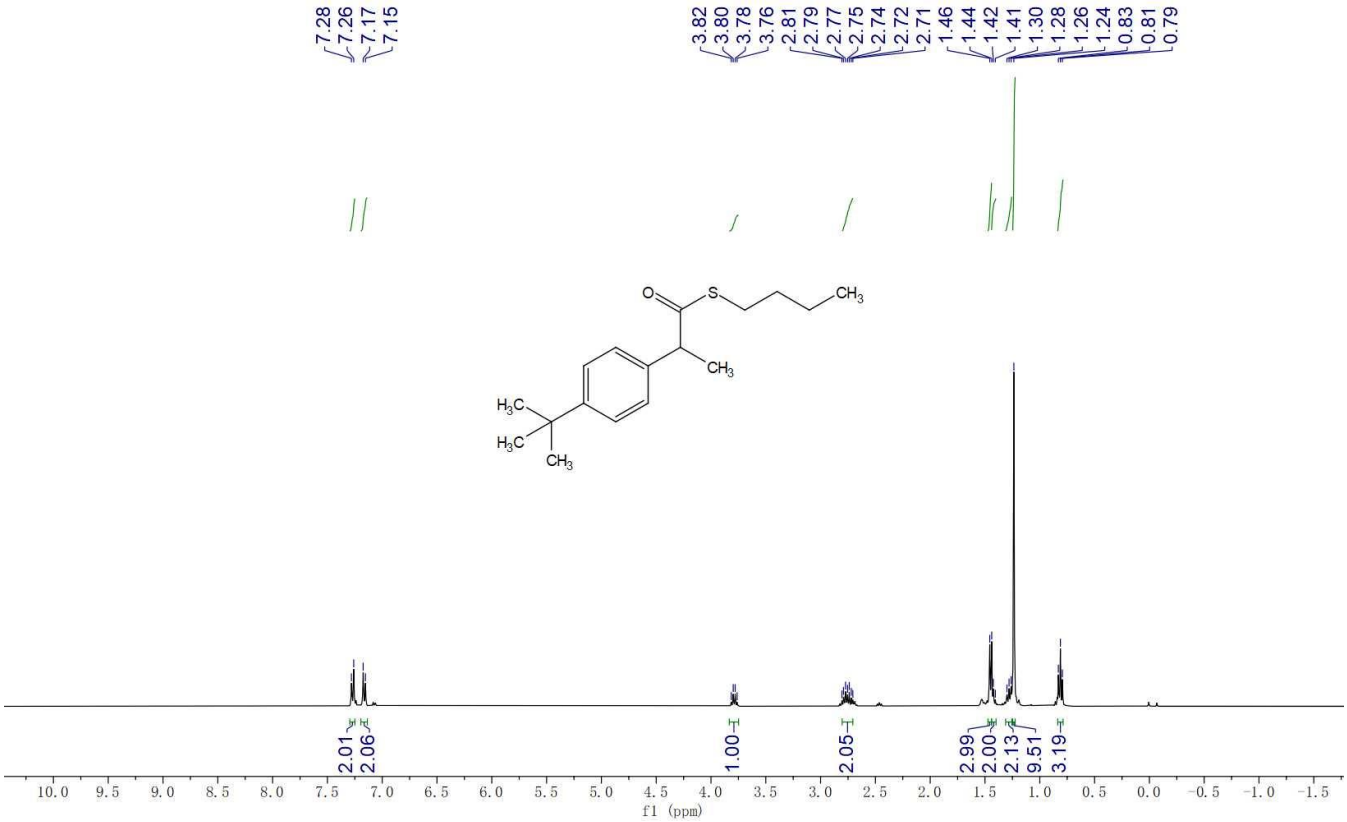


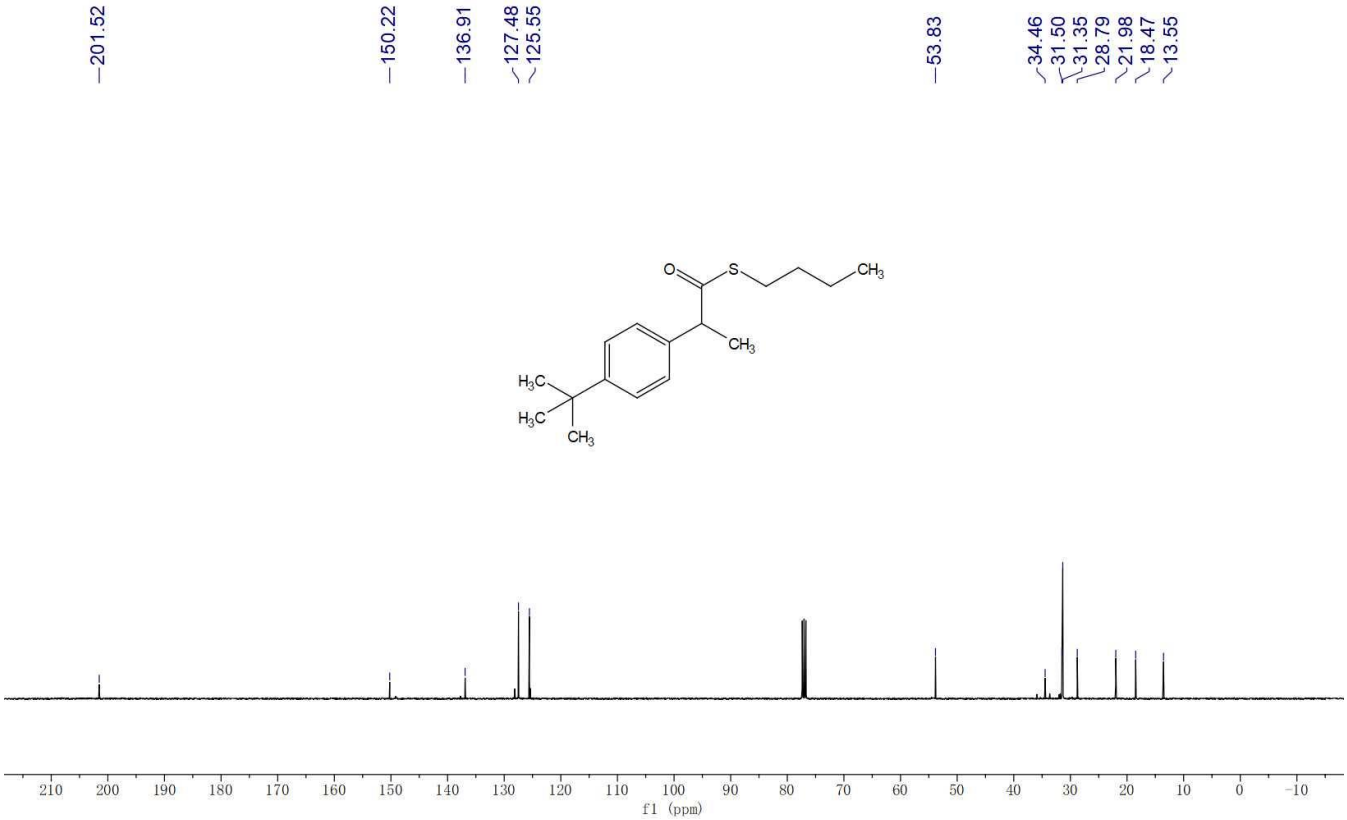
^{1}H and ^{13}C NMR spectra of **3f**



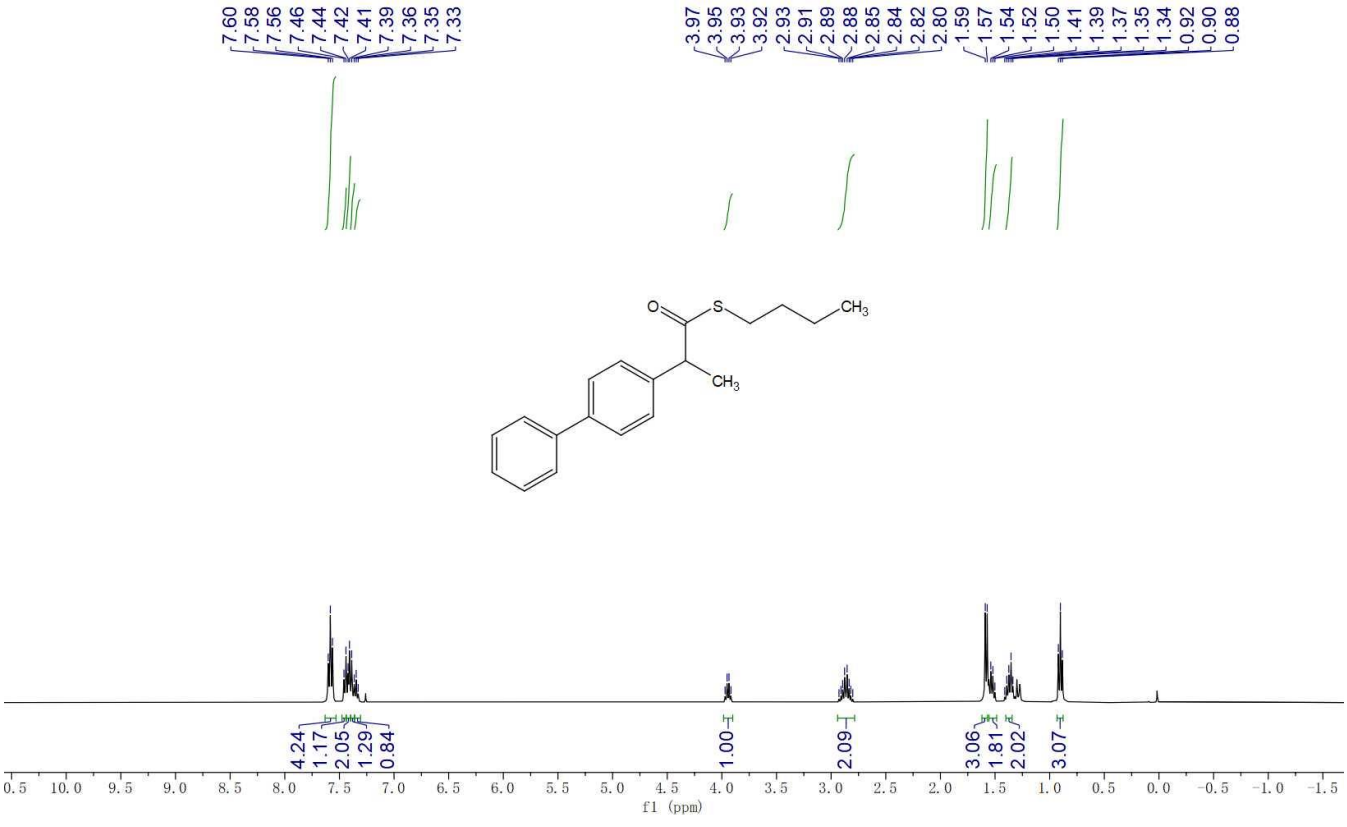


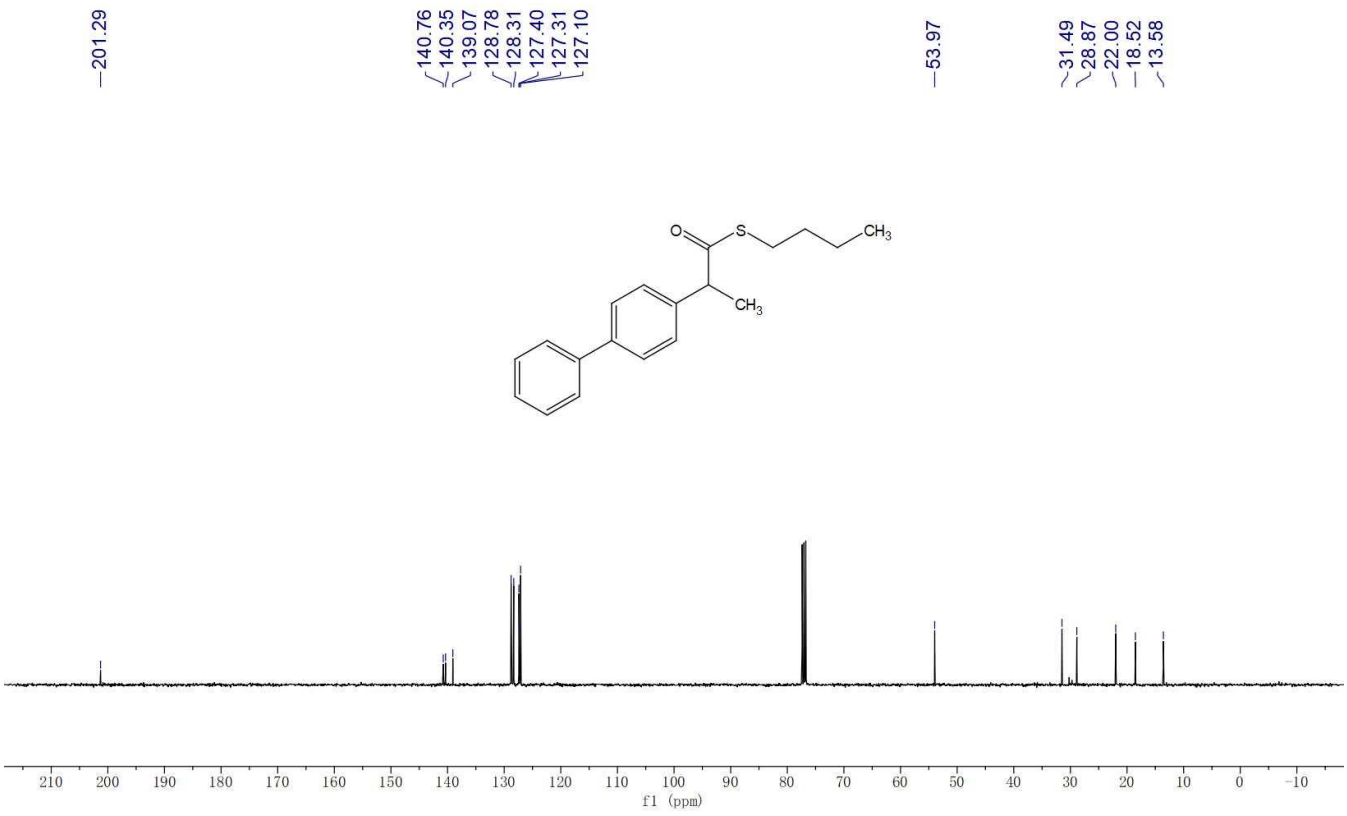
^{1}H and ^{13}C NMR spectra of **3g**



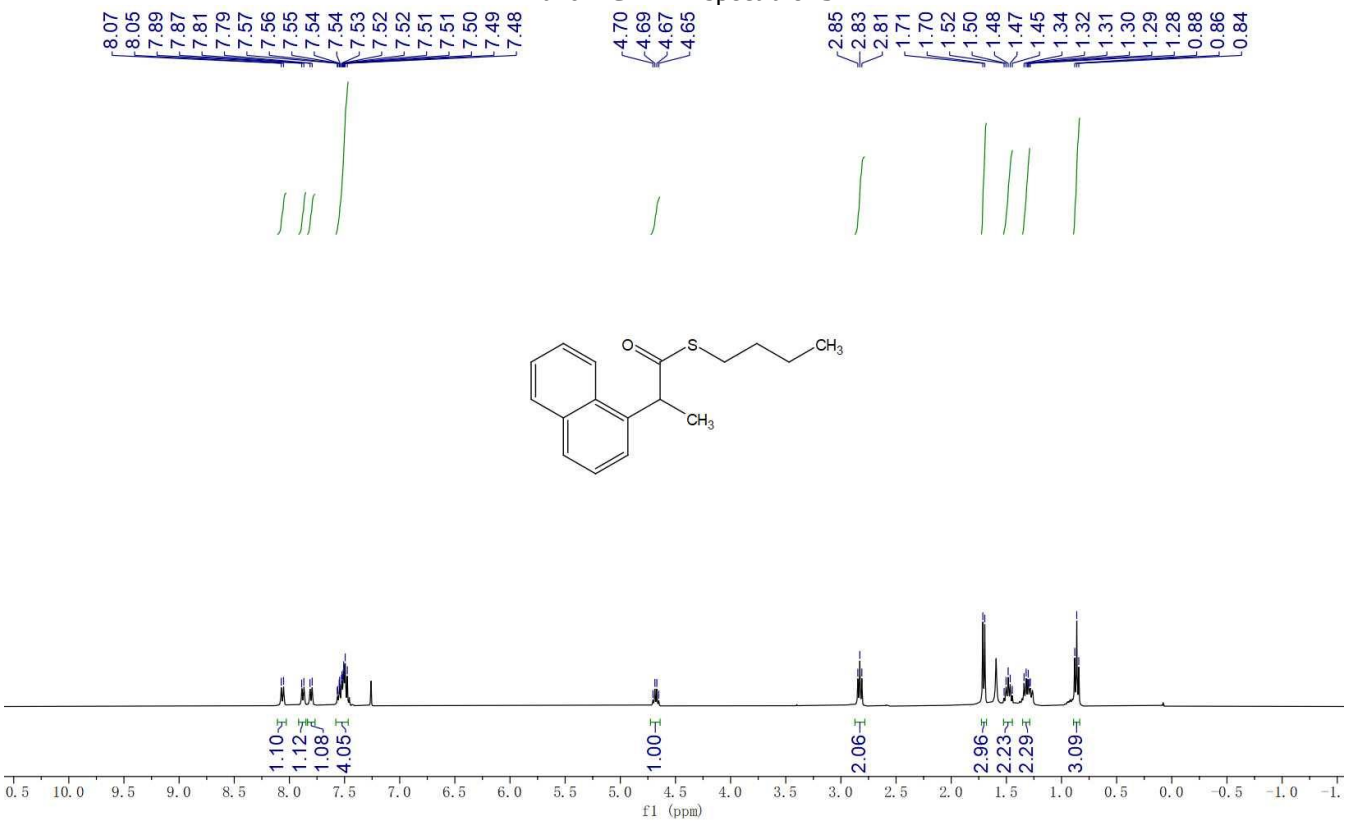


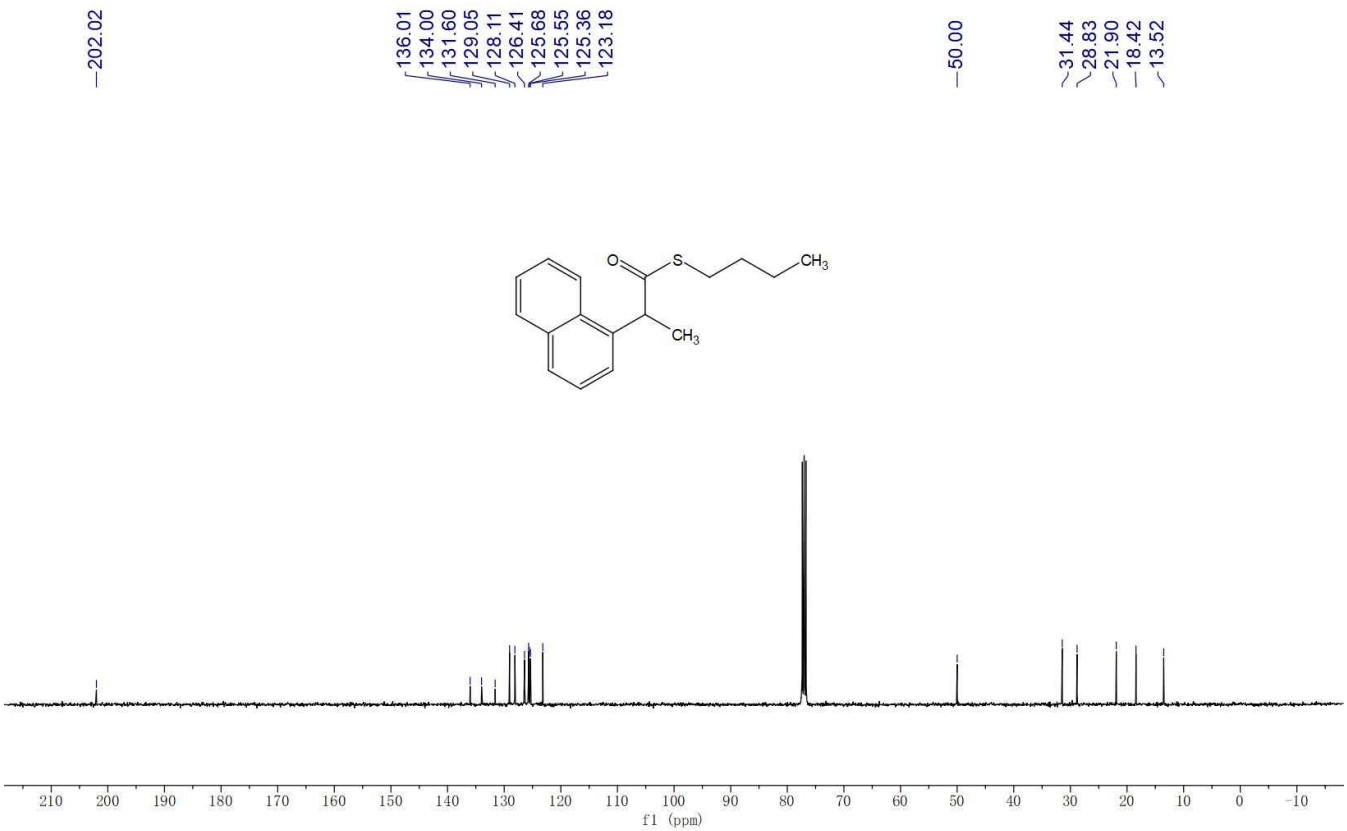
^{1}H and ^{13}C NMR spectra of **3h**



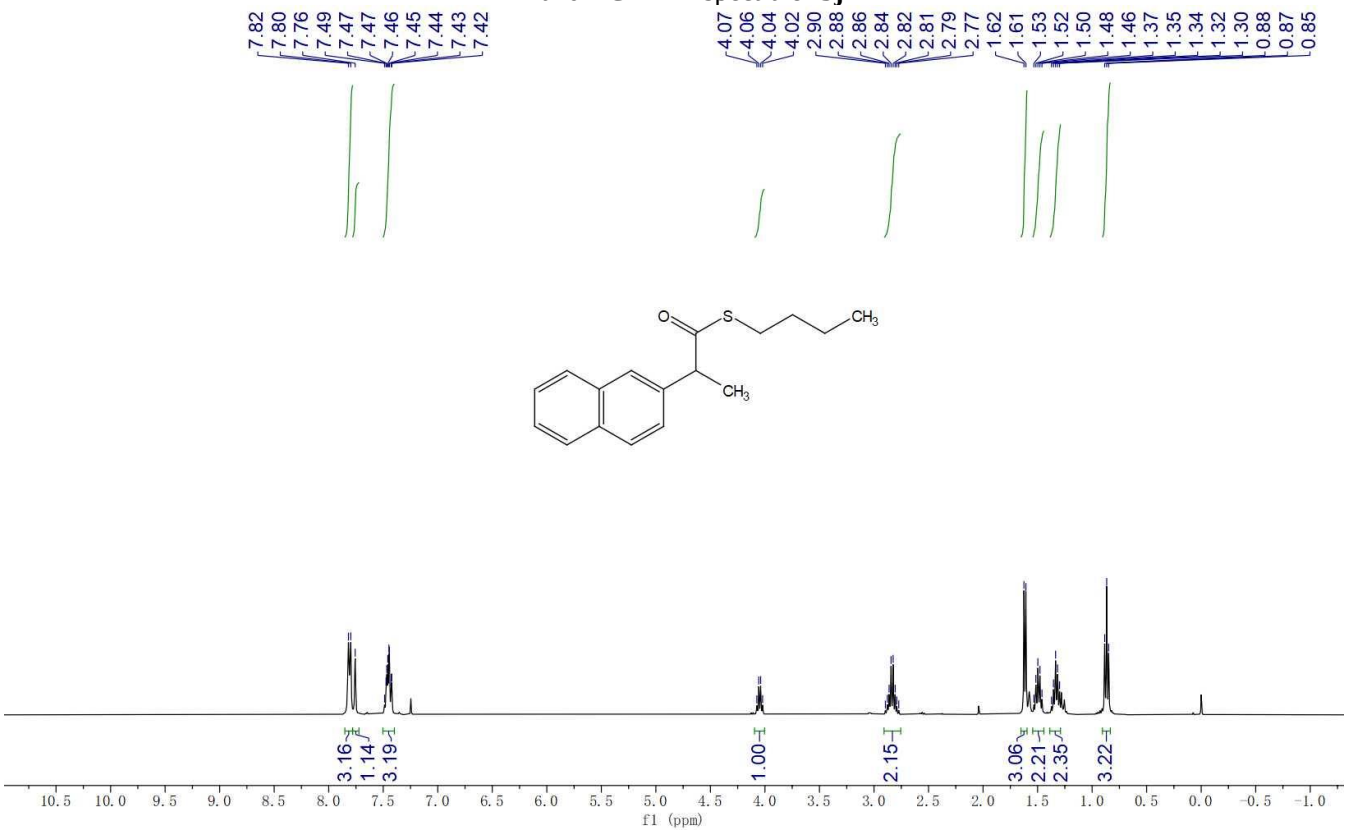


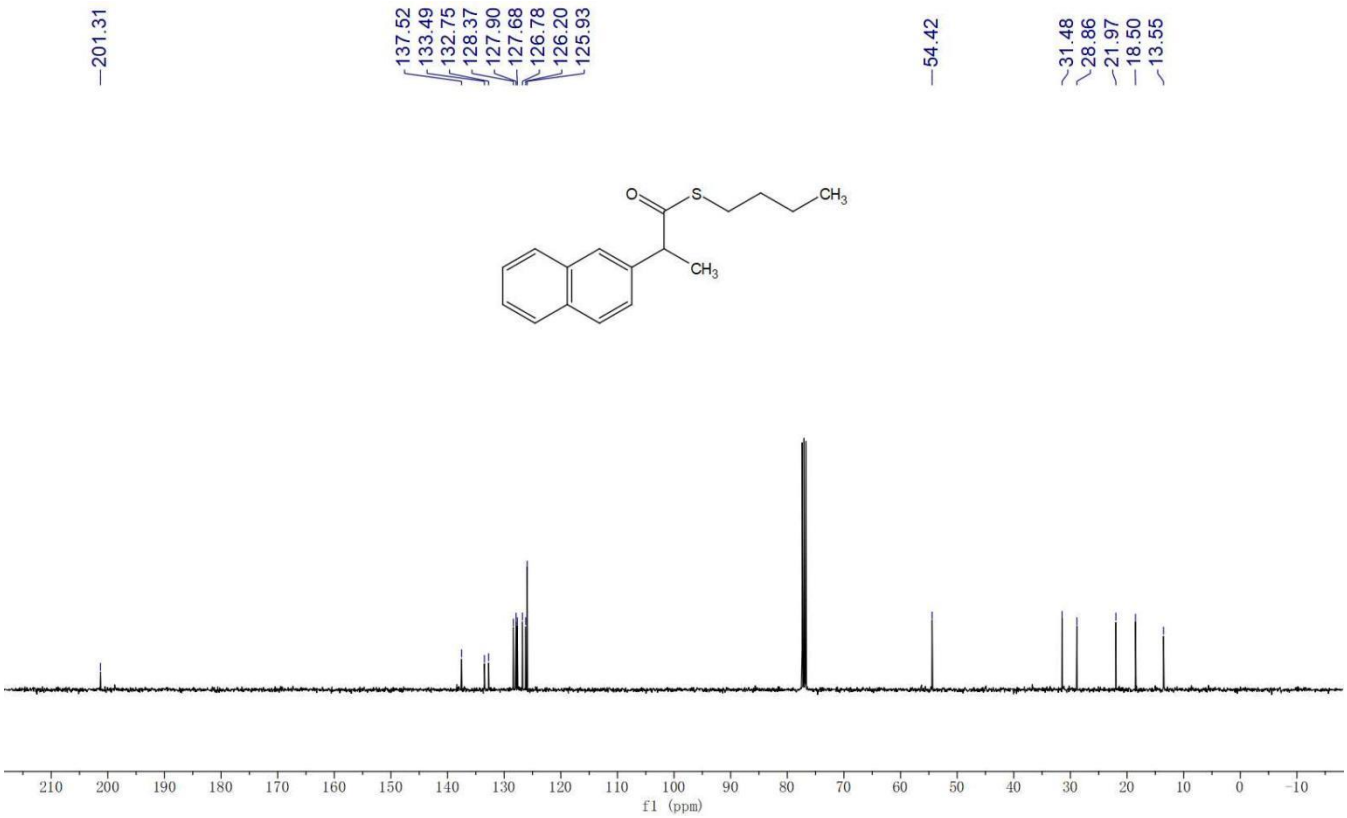
^{1}H and ^{13}C NMR spectra of **3i**



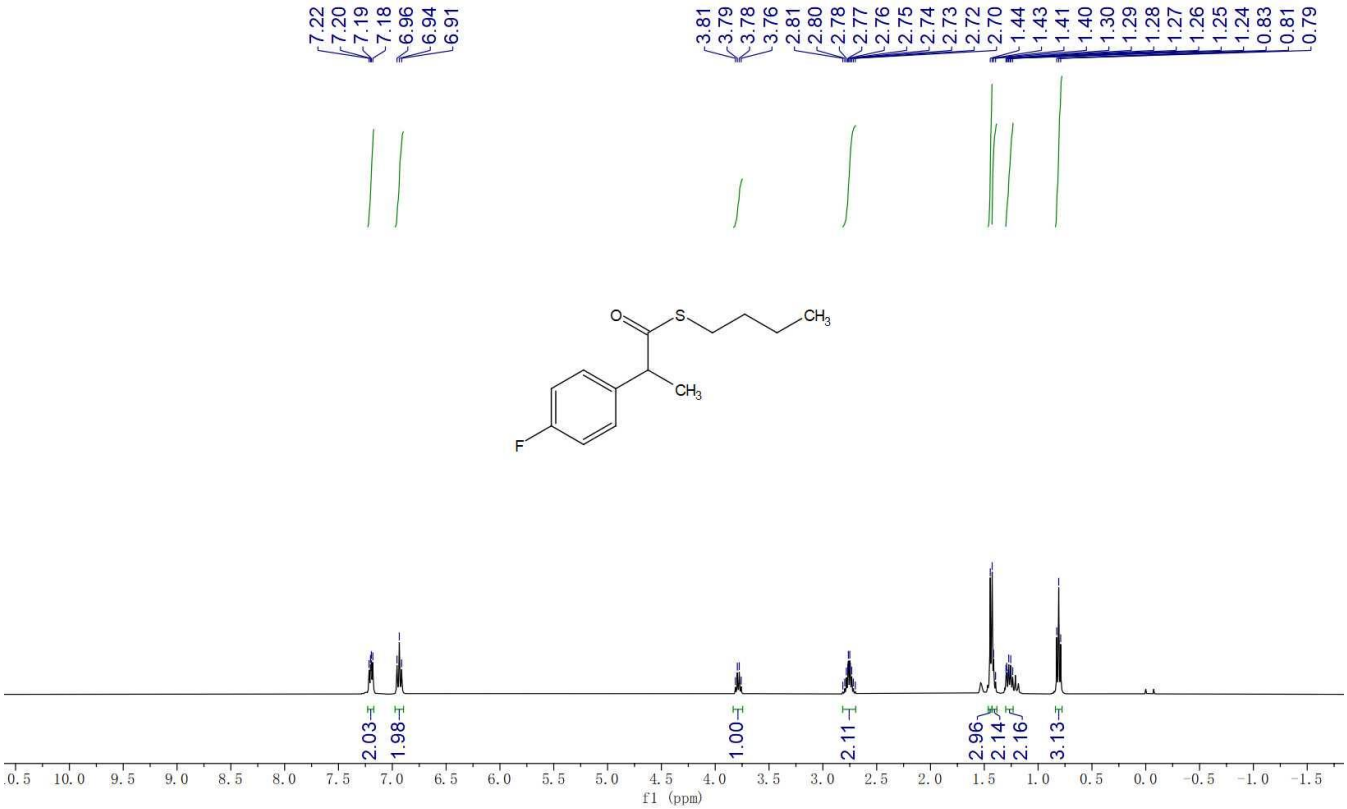


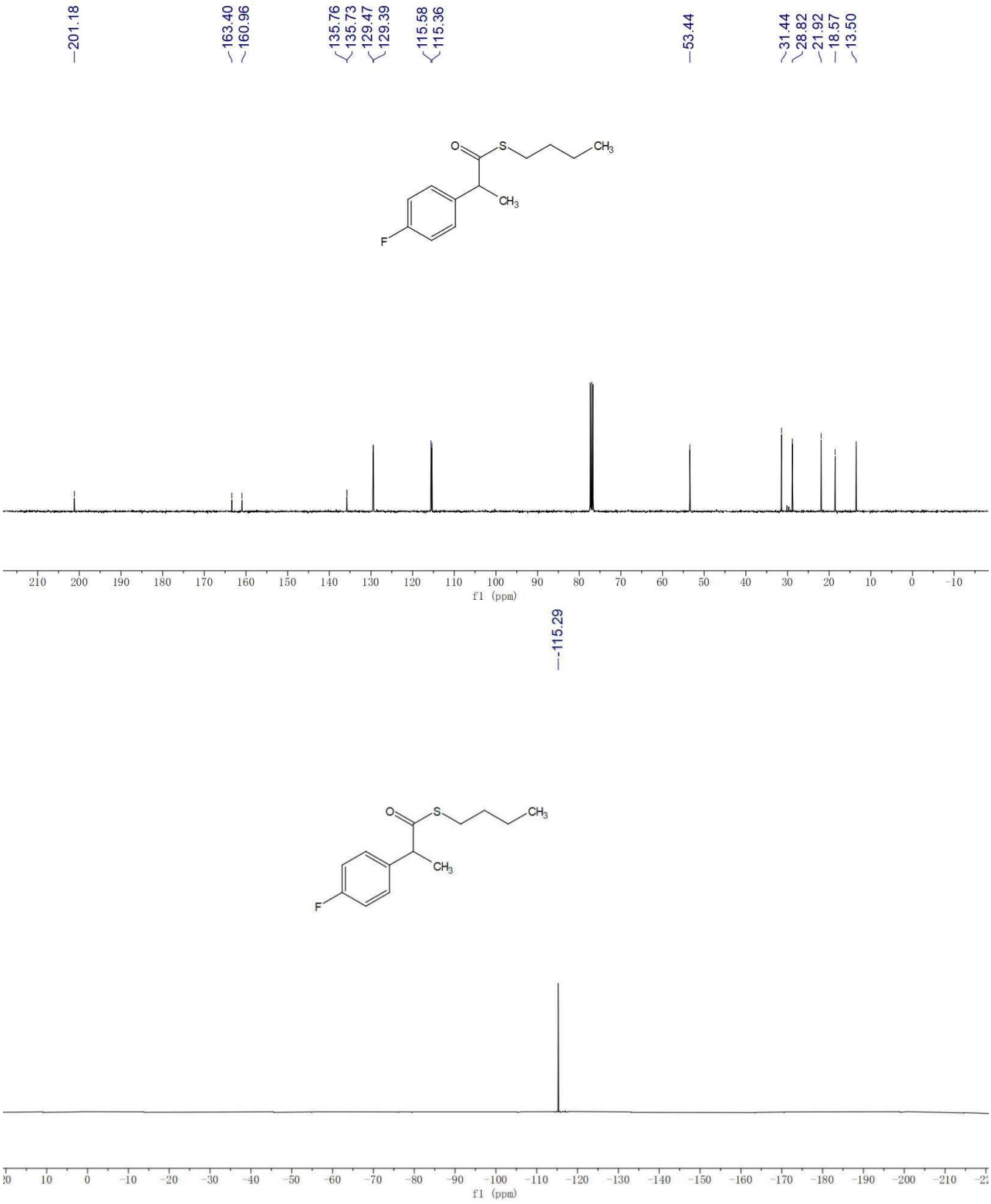
^{1}H and ^{13}C NMR spectra of **3j**



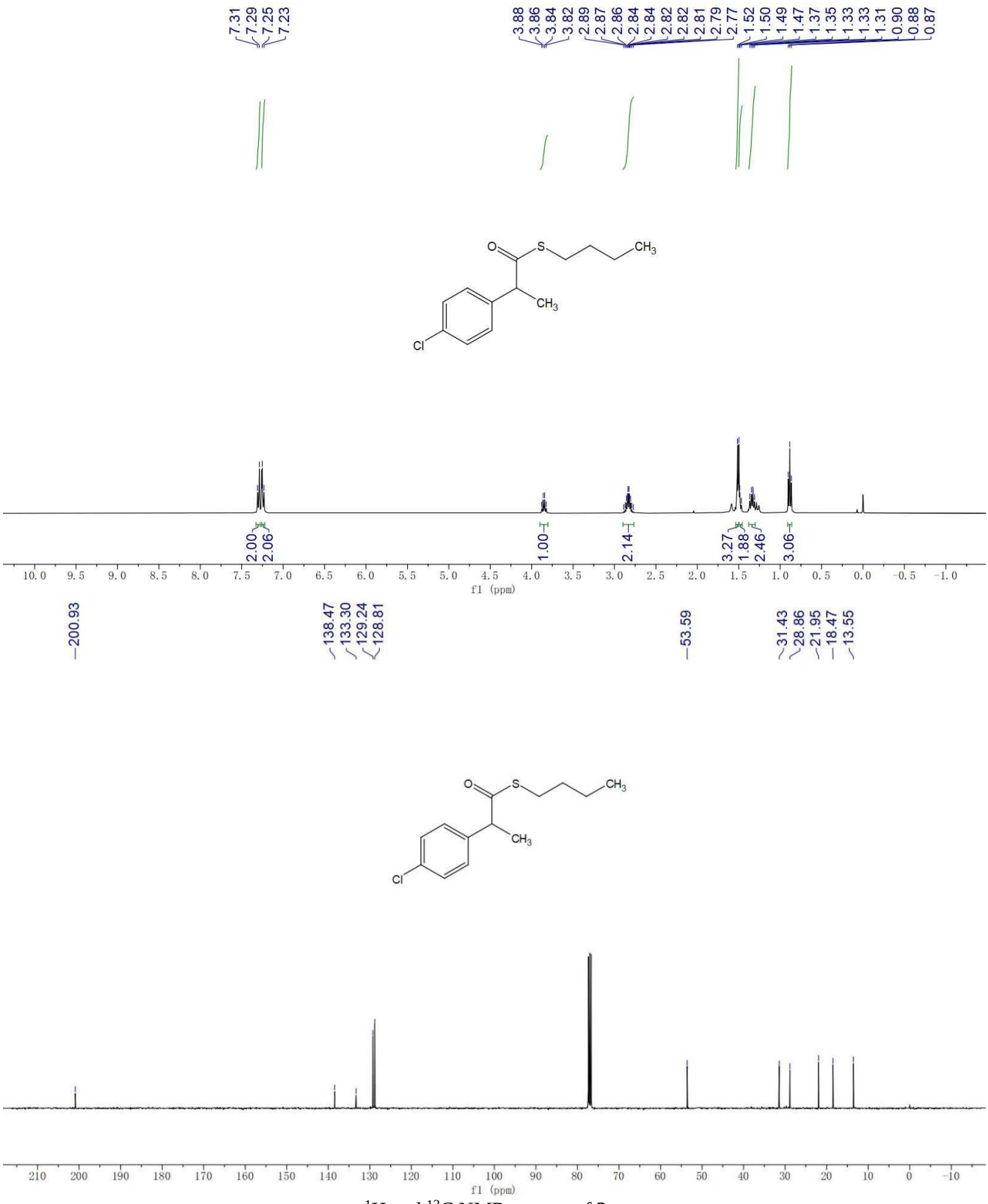


^{1}H and ^{13}C NMR spectra of **3k**

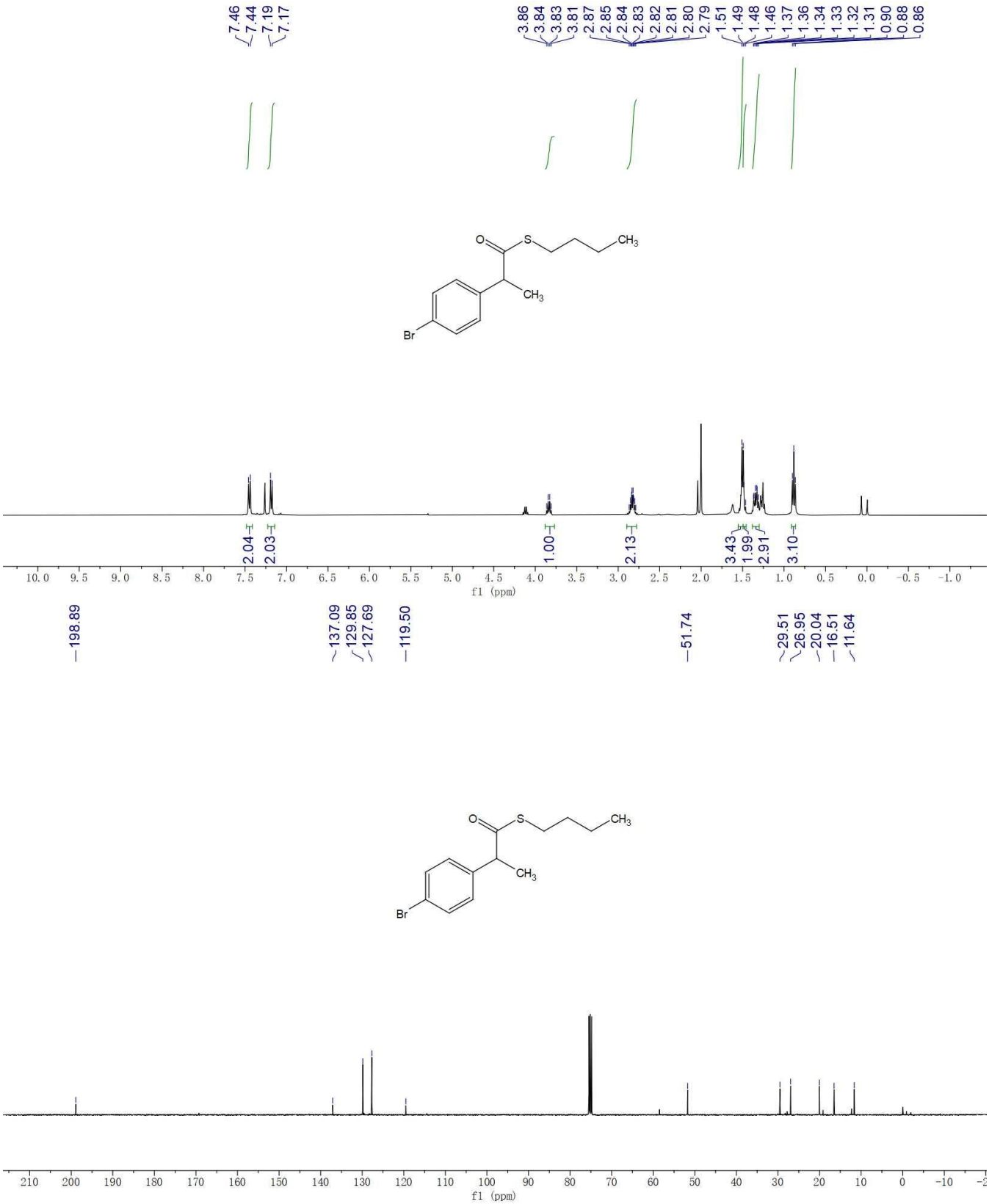




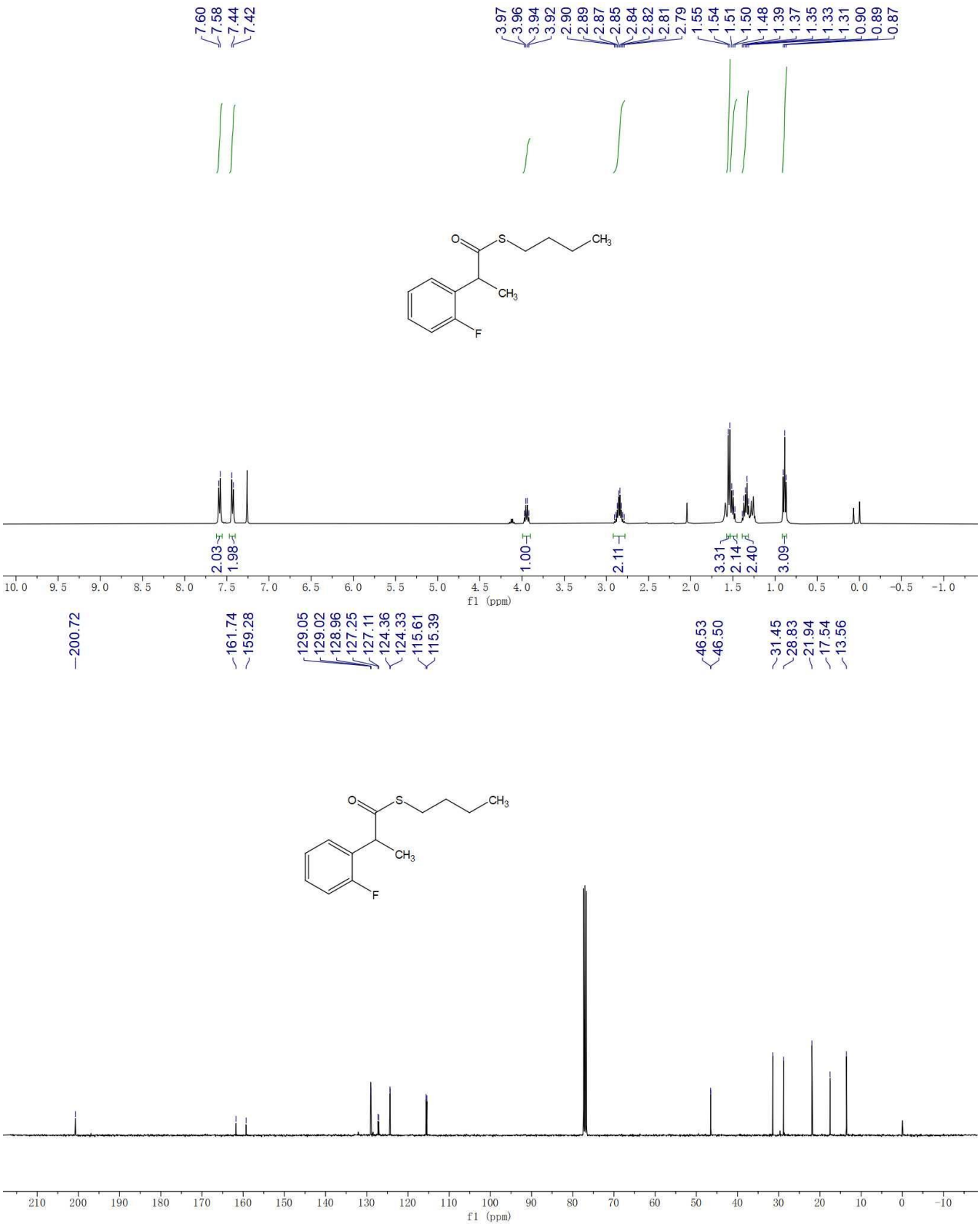
^{1}H, ^{13}C and ^{19}F NMR spectra of **3l**



^{1}H and ^{13}C NMR spectra of **3m**



^{1}H and ^{13}C NMR spectra of **3n**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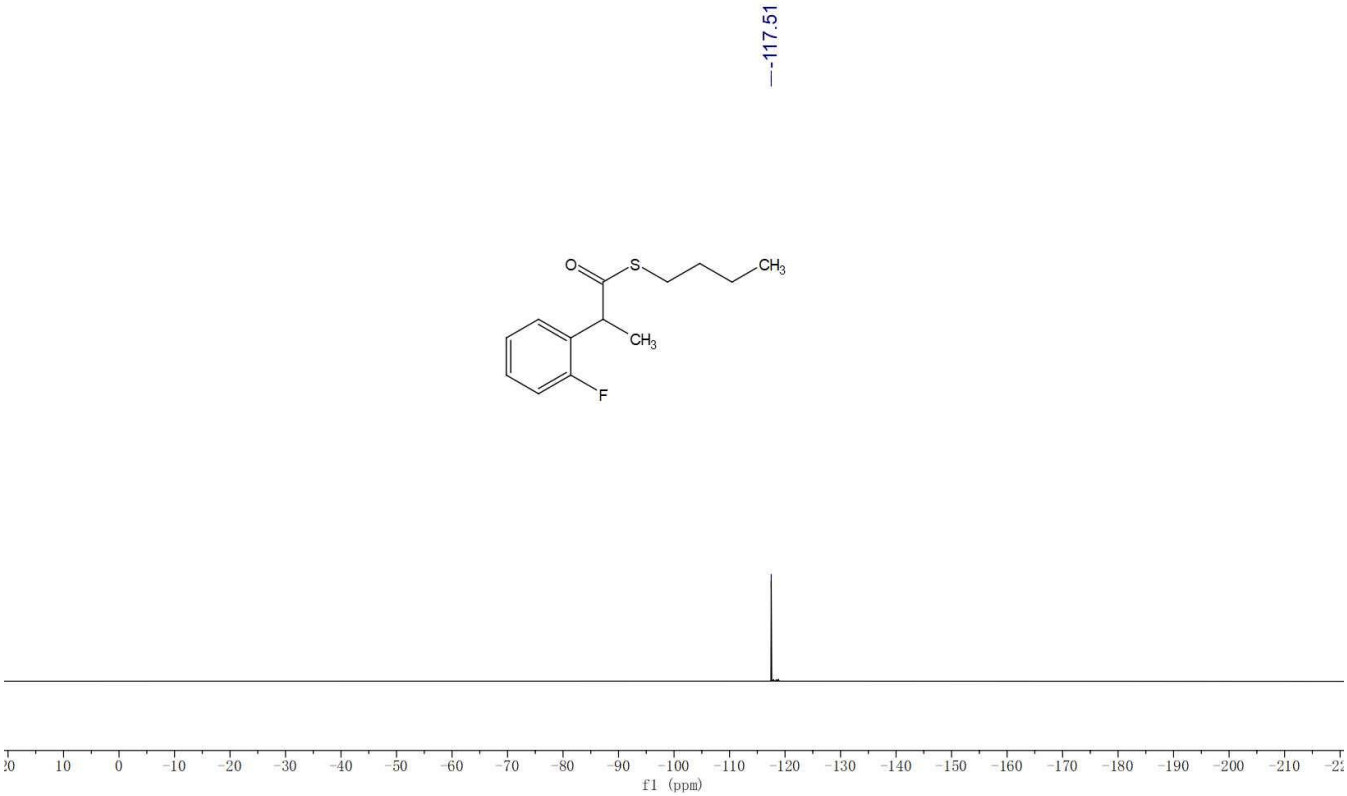
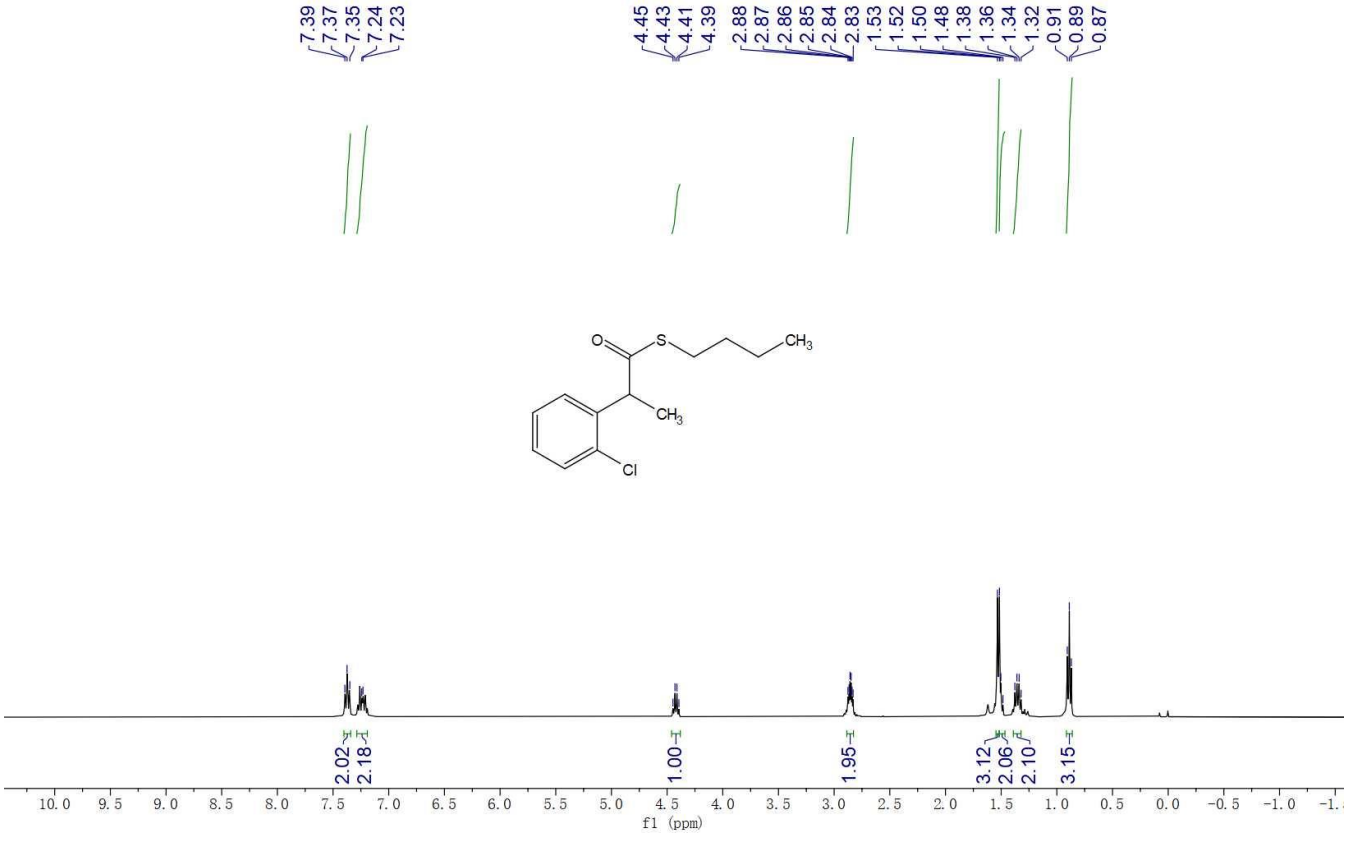
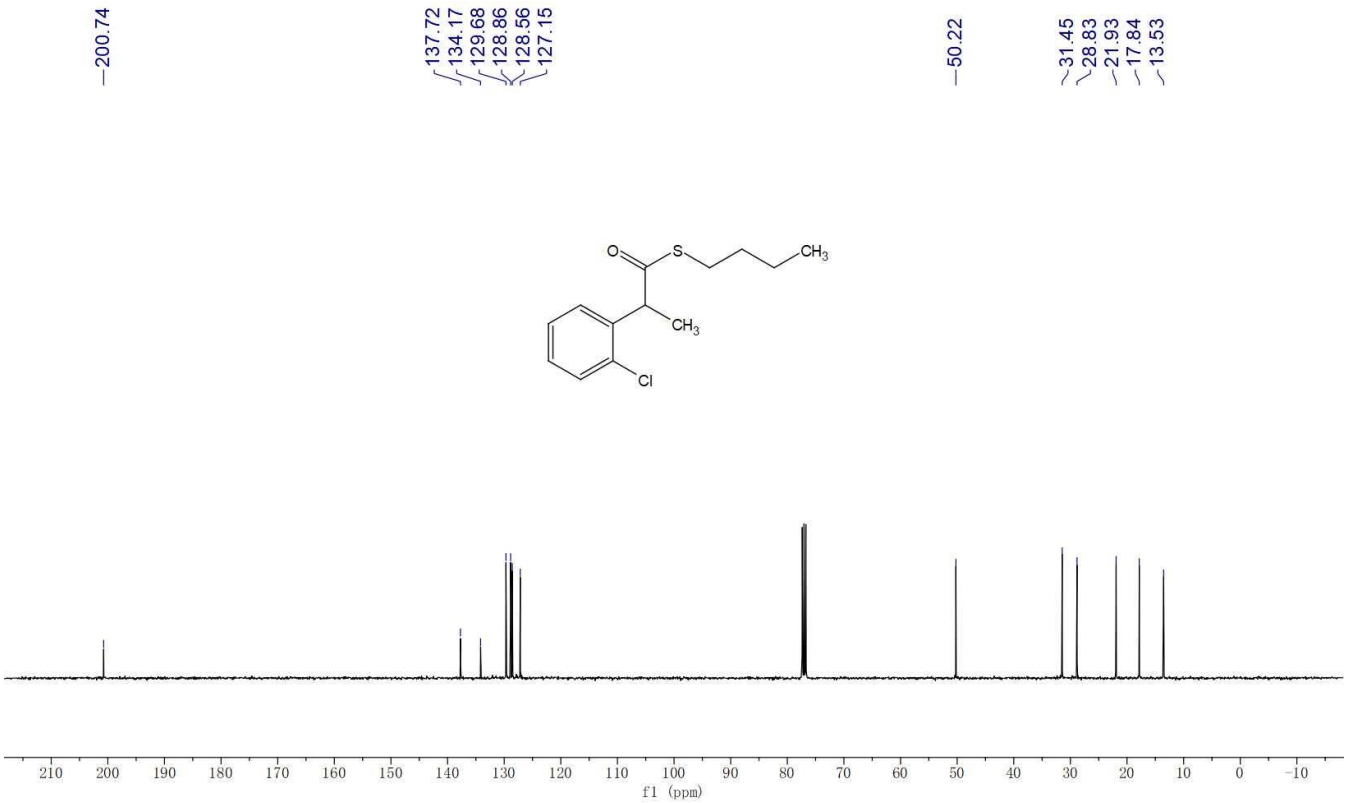
7.58
7.44
7.42
3.97
3.96
3.94
3.92
2.90
2.89
2.87
2.85
2.84
2.82
2.81
2.79
1.55
1.54
1.51
1.50
1.48
1.39
1.37
1.35
1.33
1.31
0.90
0.89
0.87
O
S
CH3
CH3
F
2.03
1.98
1.00
2.11
3.31
2.14
2.40
3.09
f1 (ppm)
200.72
161.74
159.28
129.05
129.02
128.96
127.25
127.11
124.36
124.33
115.61
115.39
46.53
46.50
31.45
28.83
21.94
17.54
13.56
f1 (ppm)

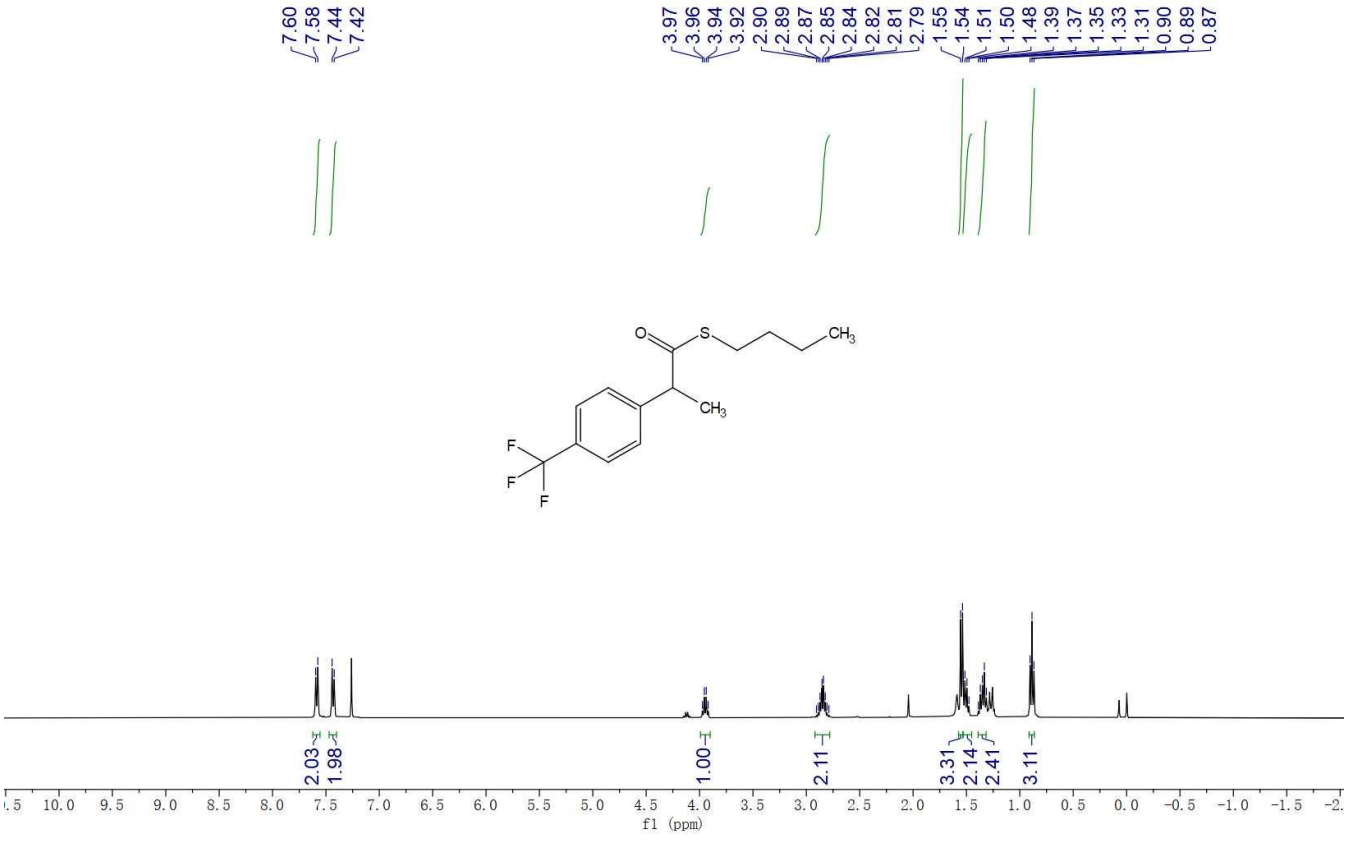


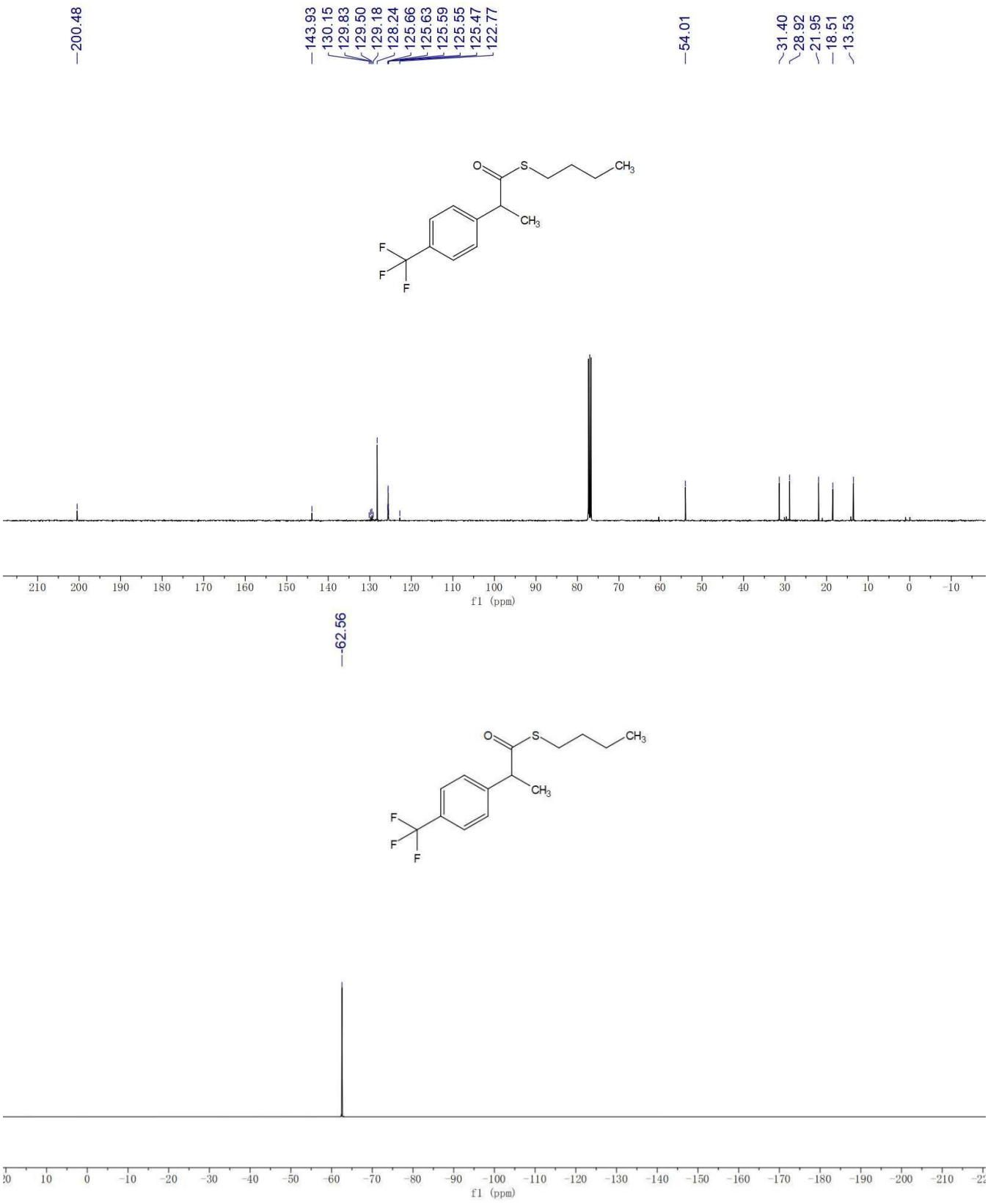
^{1}H, ^{13}C and ^{19}F NMR spectra of **3o**



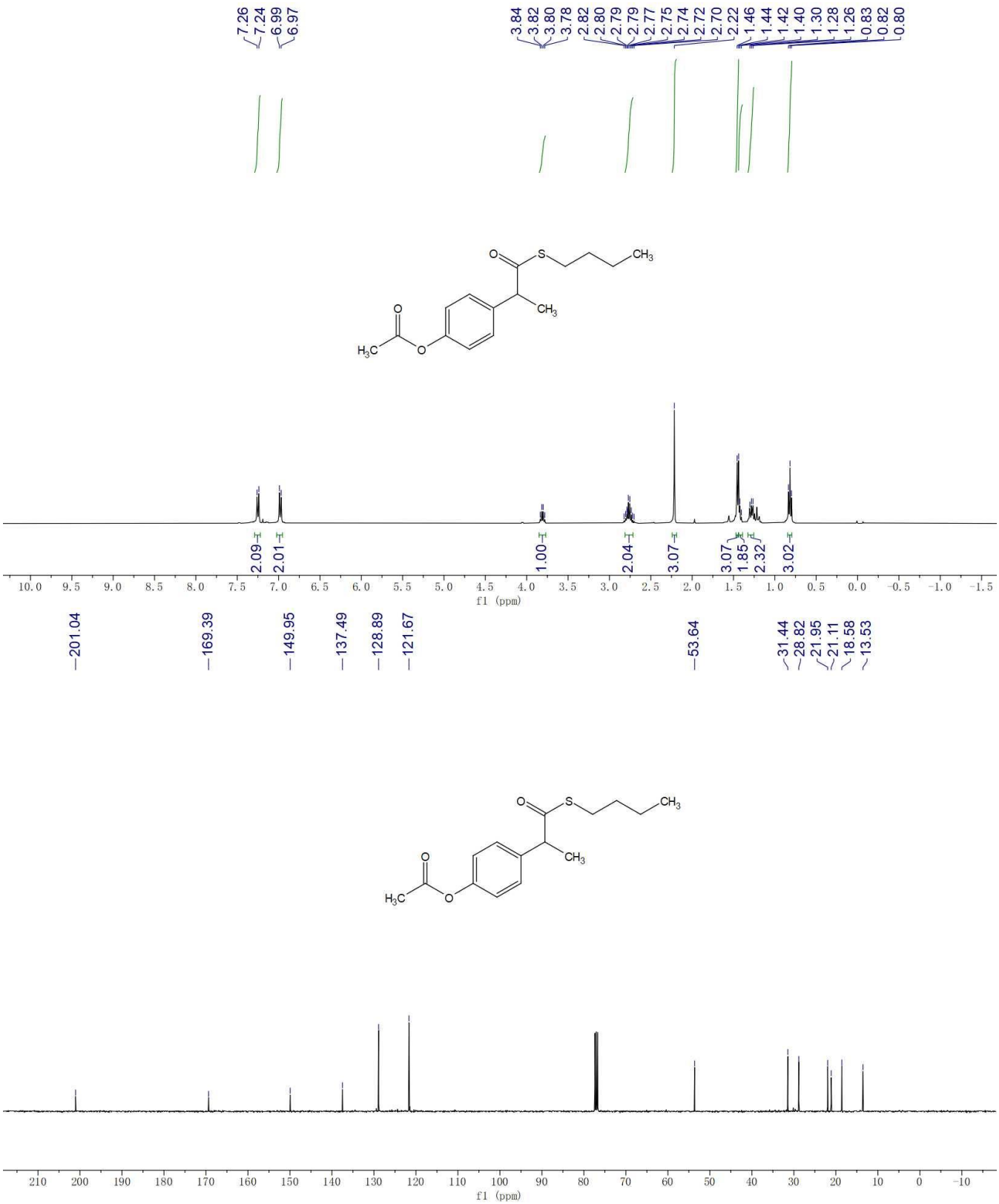


^{1}H and ^{13}C NMR spectra of **3p**

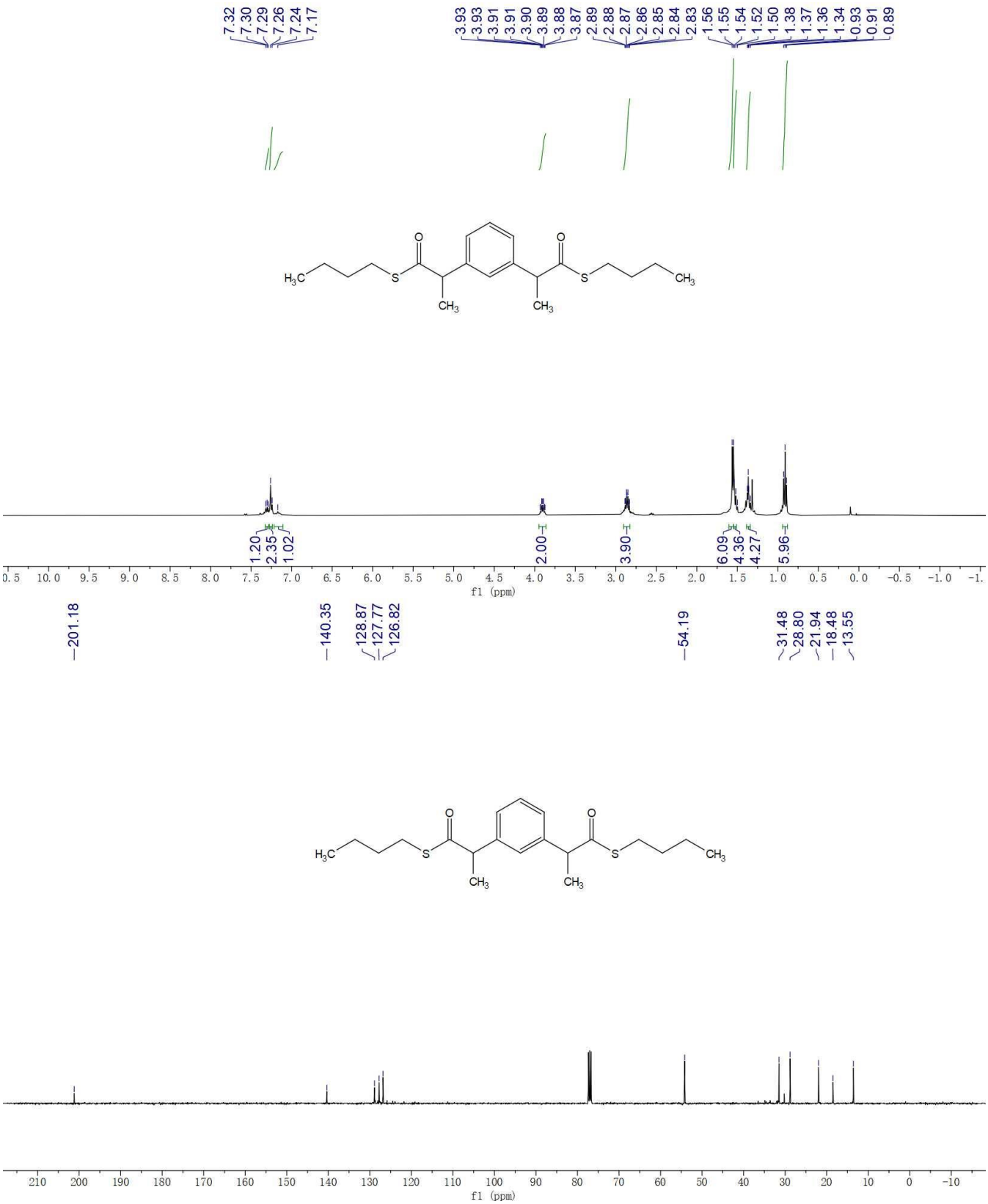




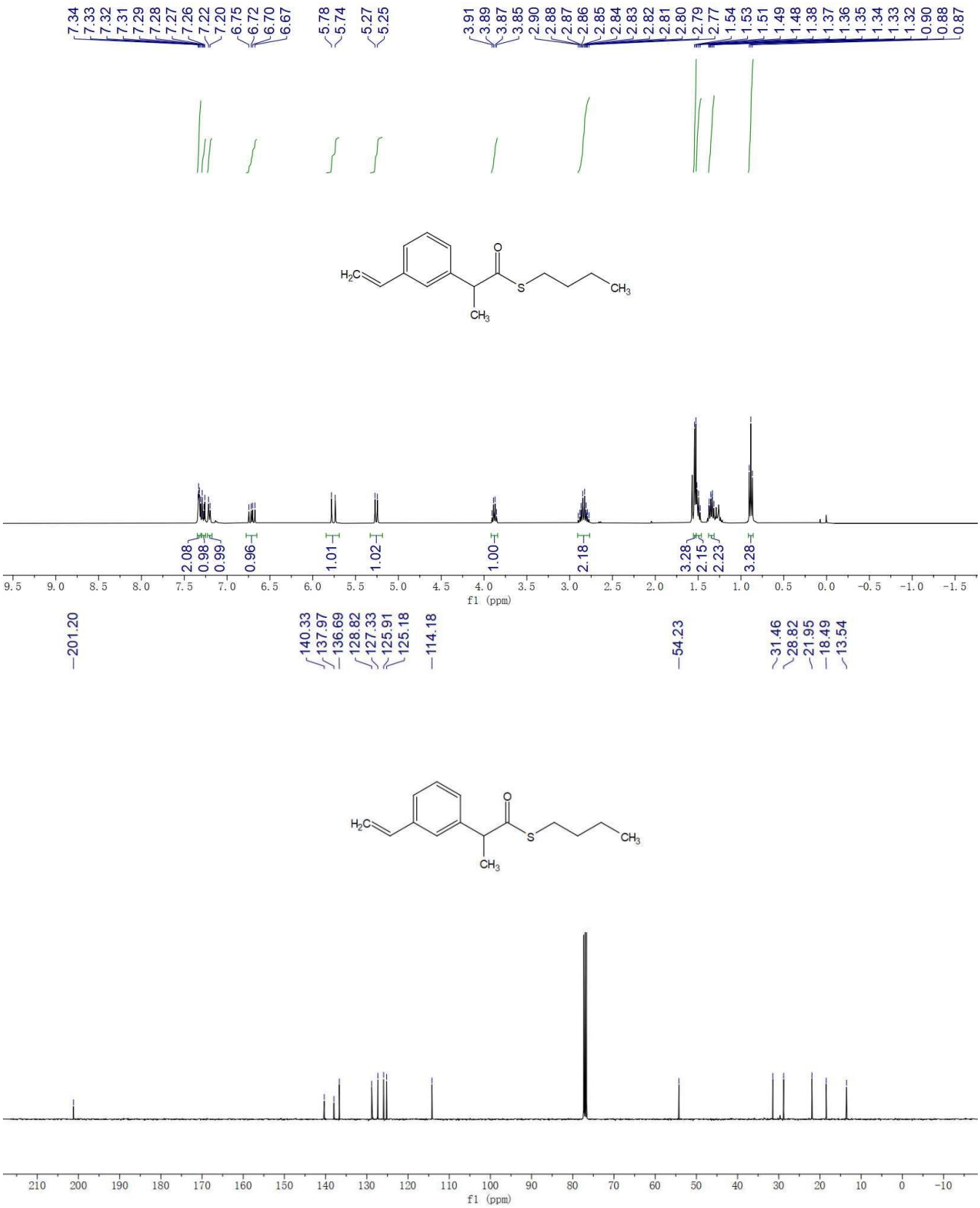
^{1}H, ^{13}C NMR and ^{19}F spectra of **3q**



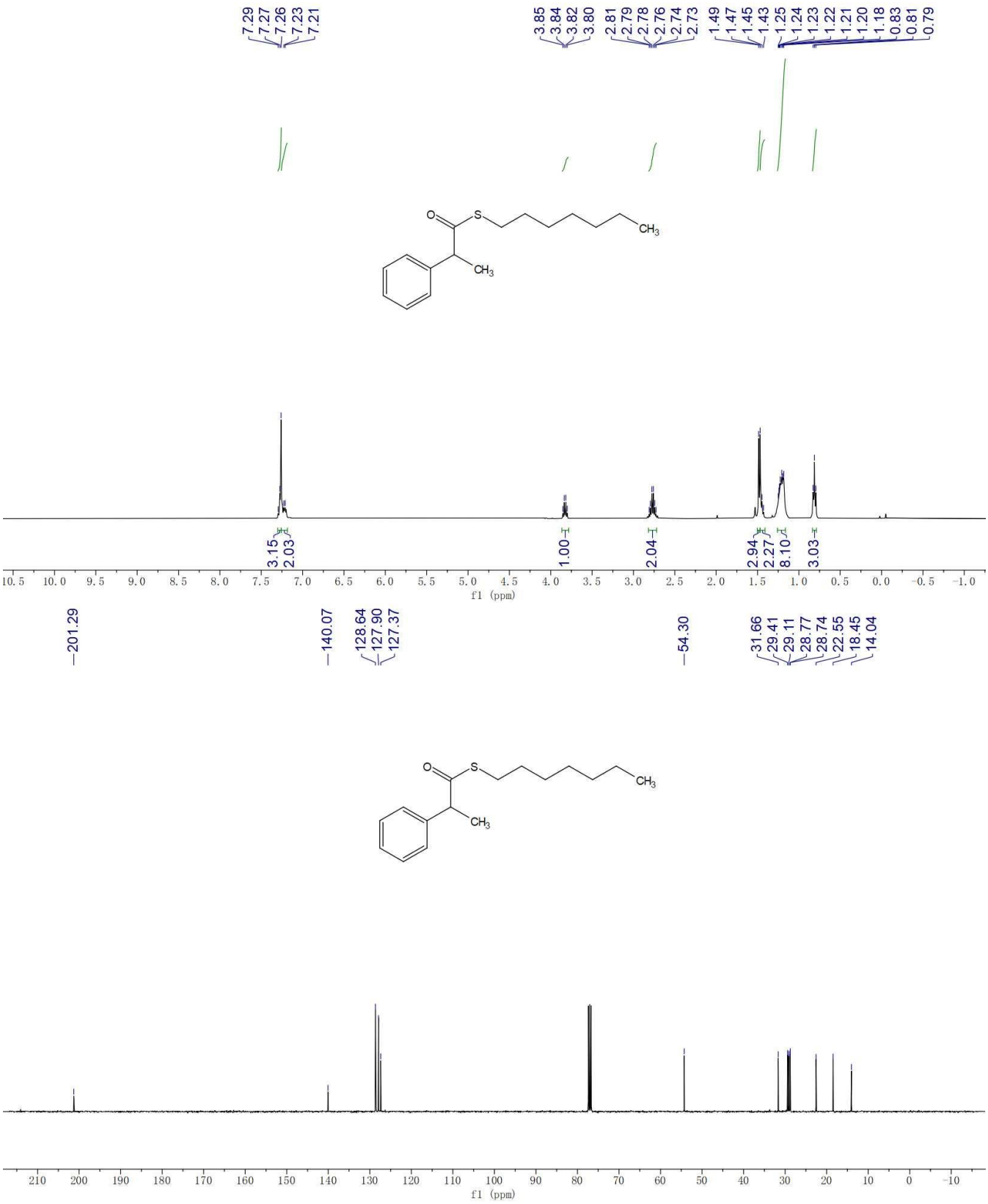
^{1}H and ^{13}C NMR spectra of **3r**



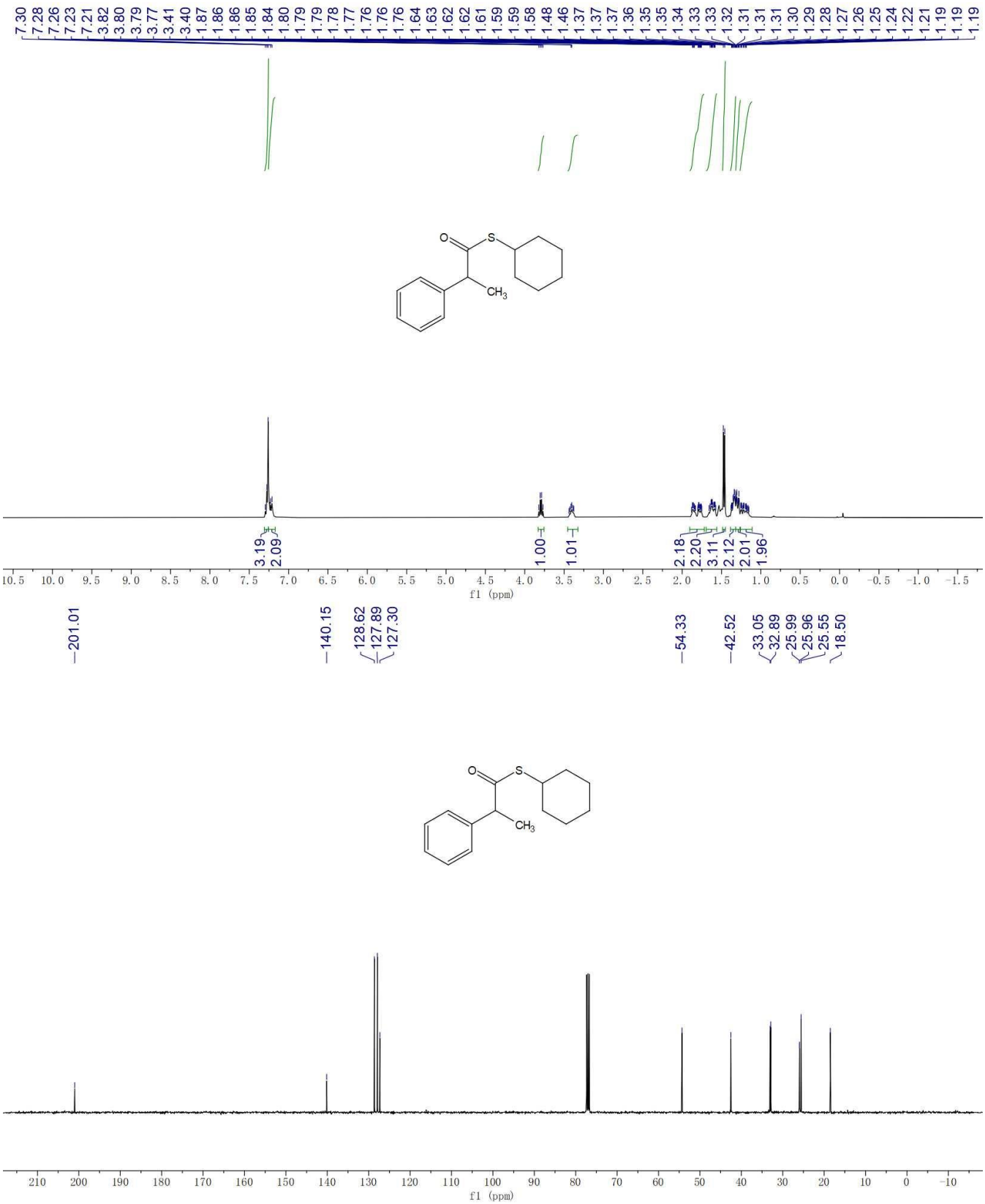
^{1}H and ^{13}C NMR spectra of **3s**



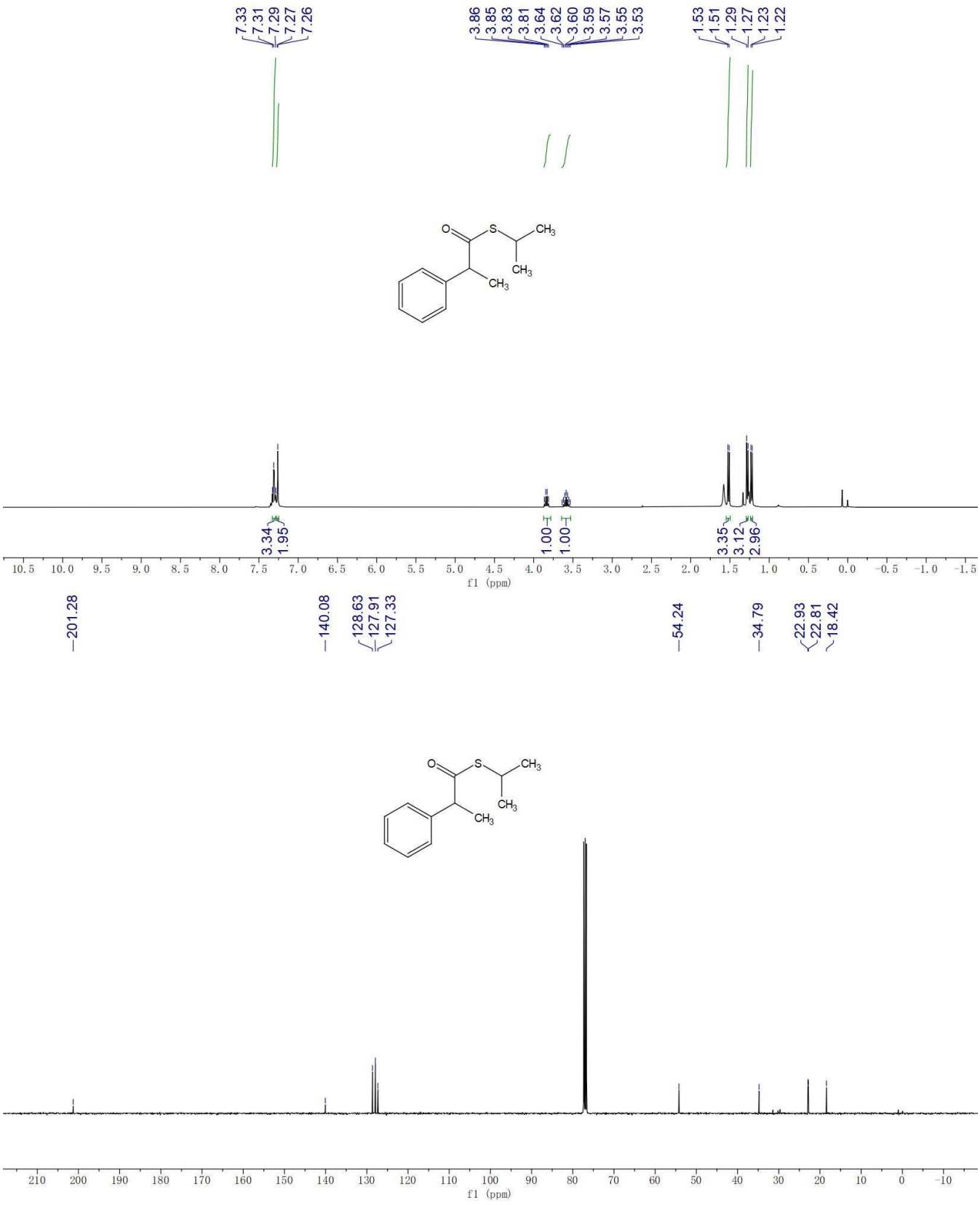
^{1}H and ^{13}C NMR spectra of **3t**



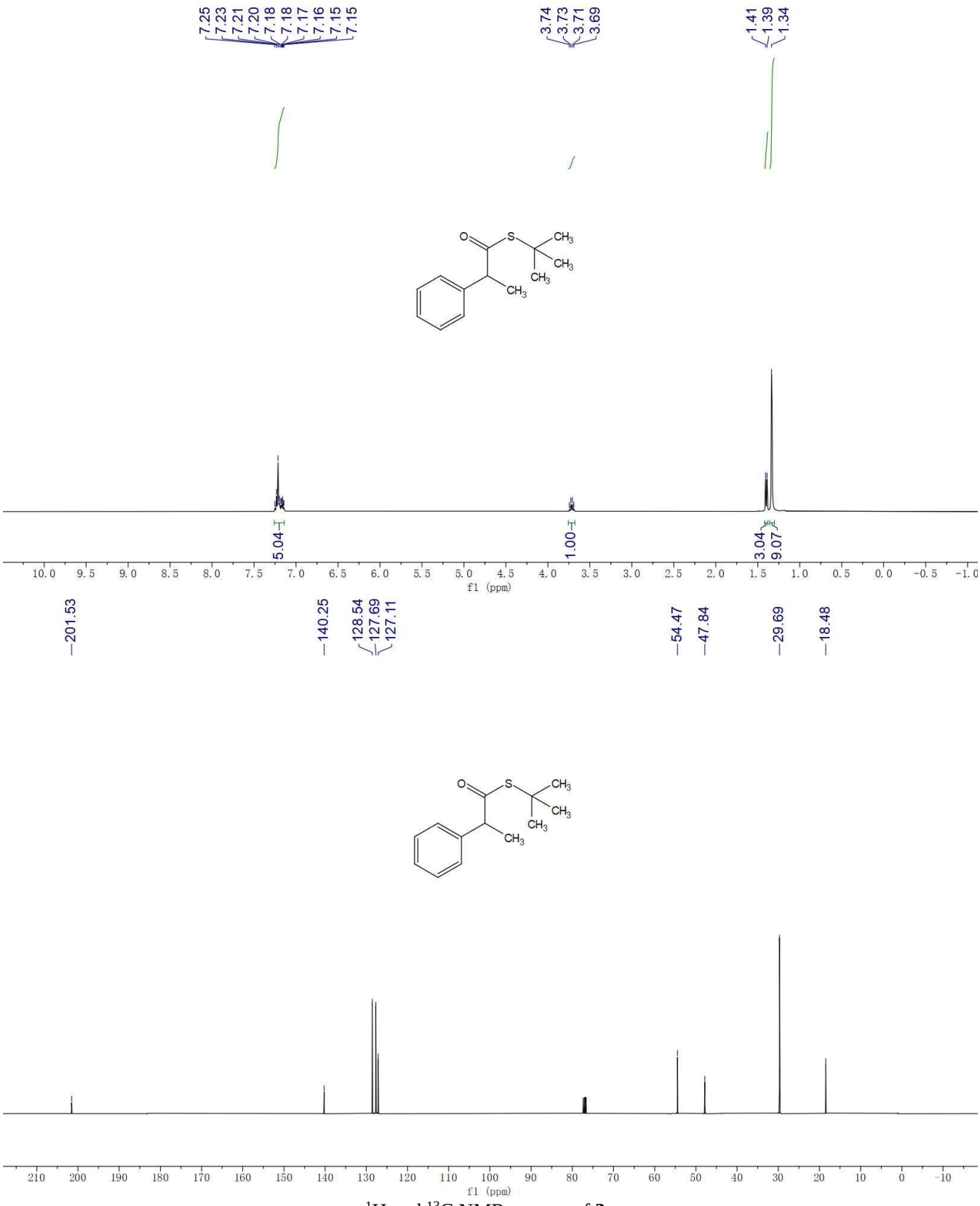
^{1}H and ^{13}C NMR spectra of **3v**



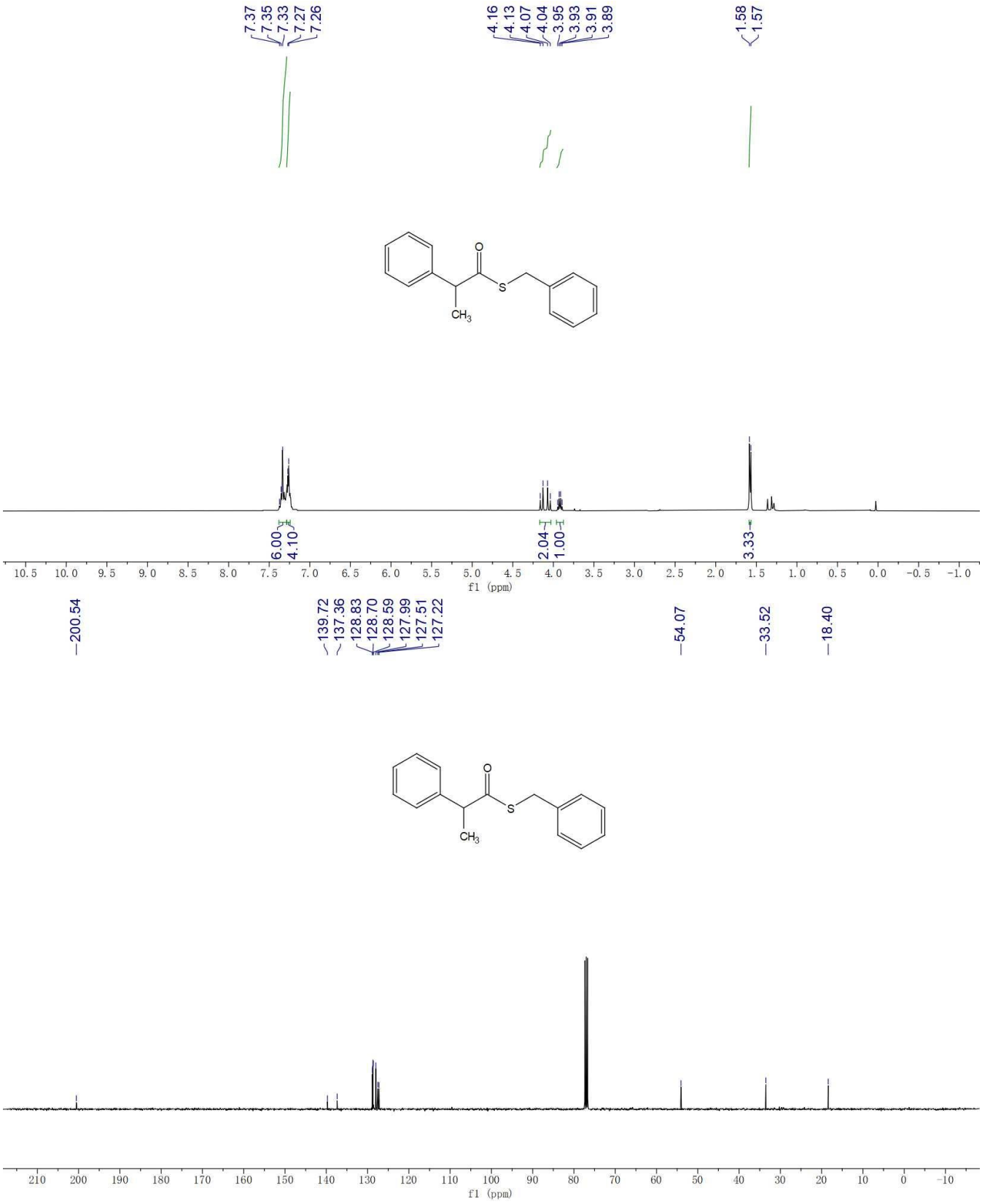
^{1}H and ^{13}C NMR spectra of **3w**



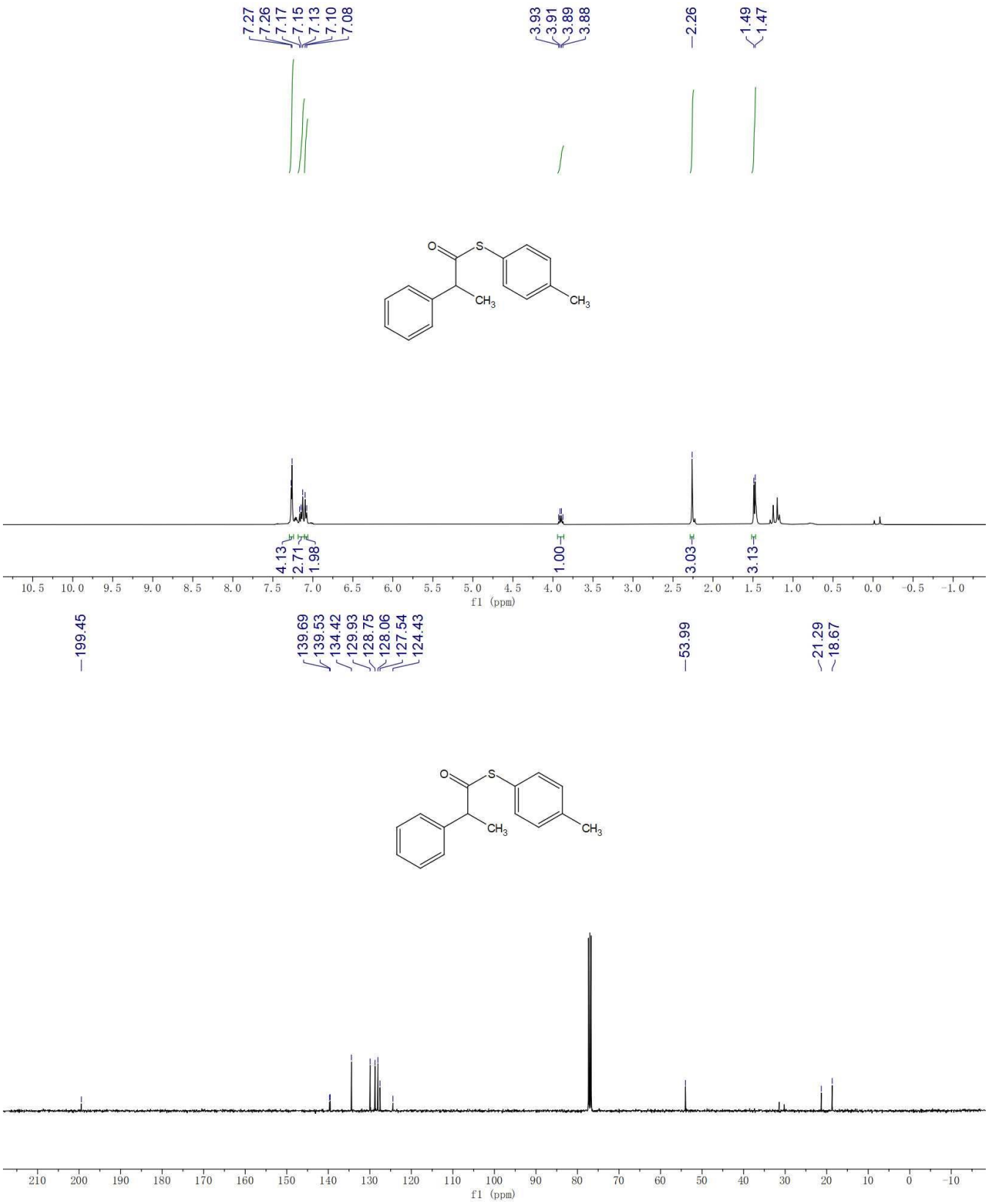
^{1}H and ^{13}C NMR spectra of **3x**



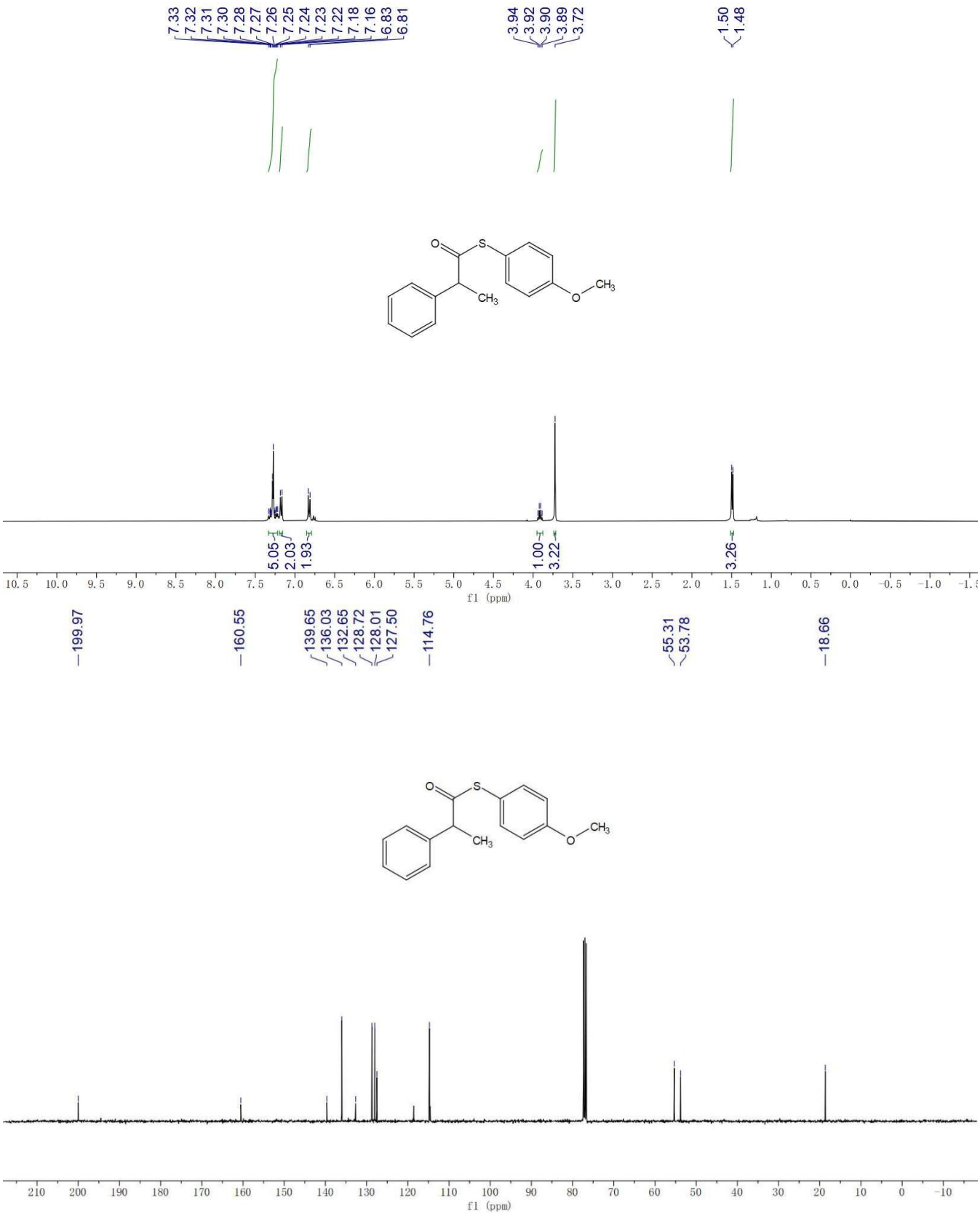
^{1}H and ^{13}C NMR spectra of **3y**



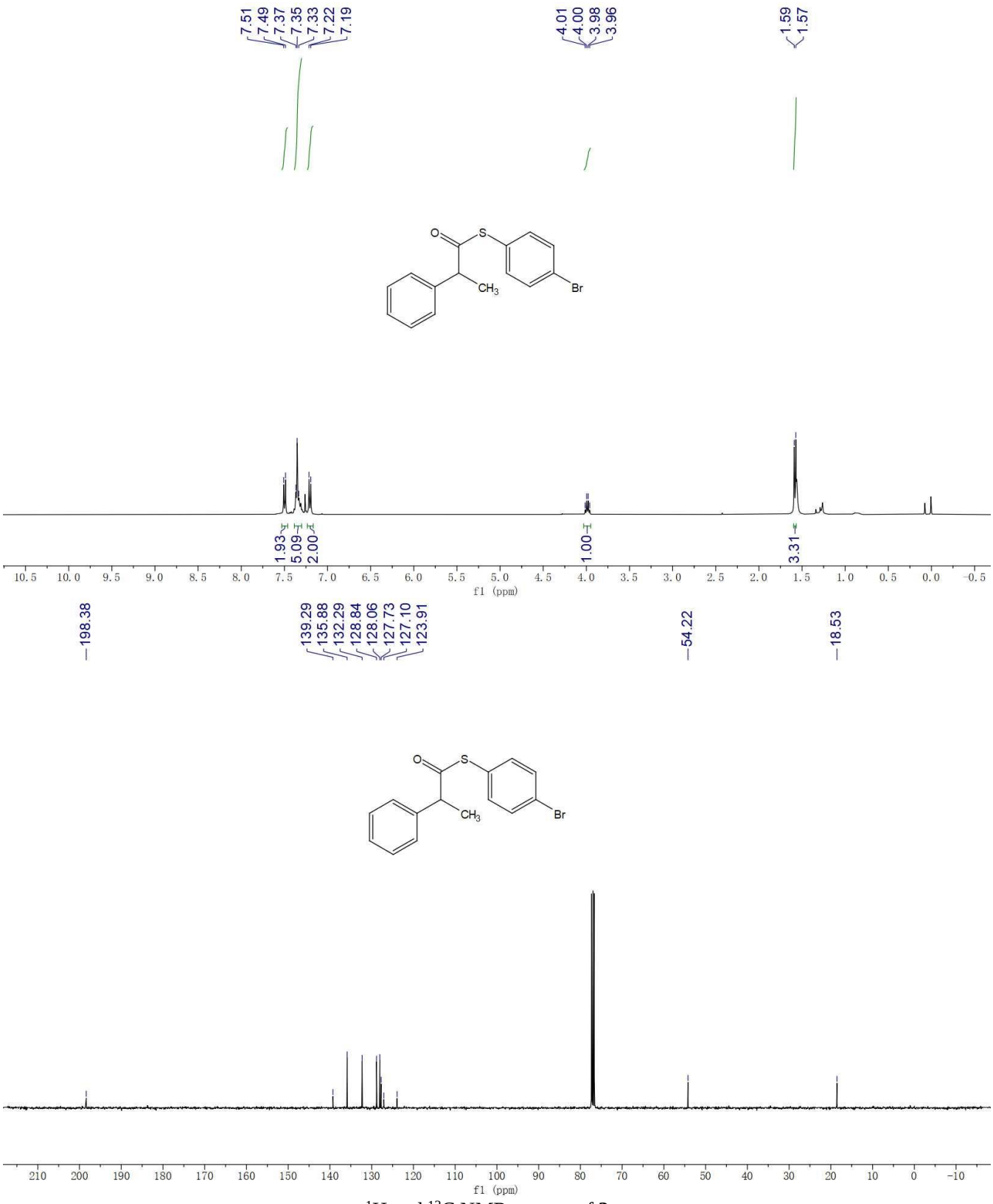
^{1}H and ^{13}C NMR spectra of **3z**



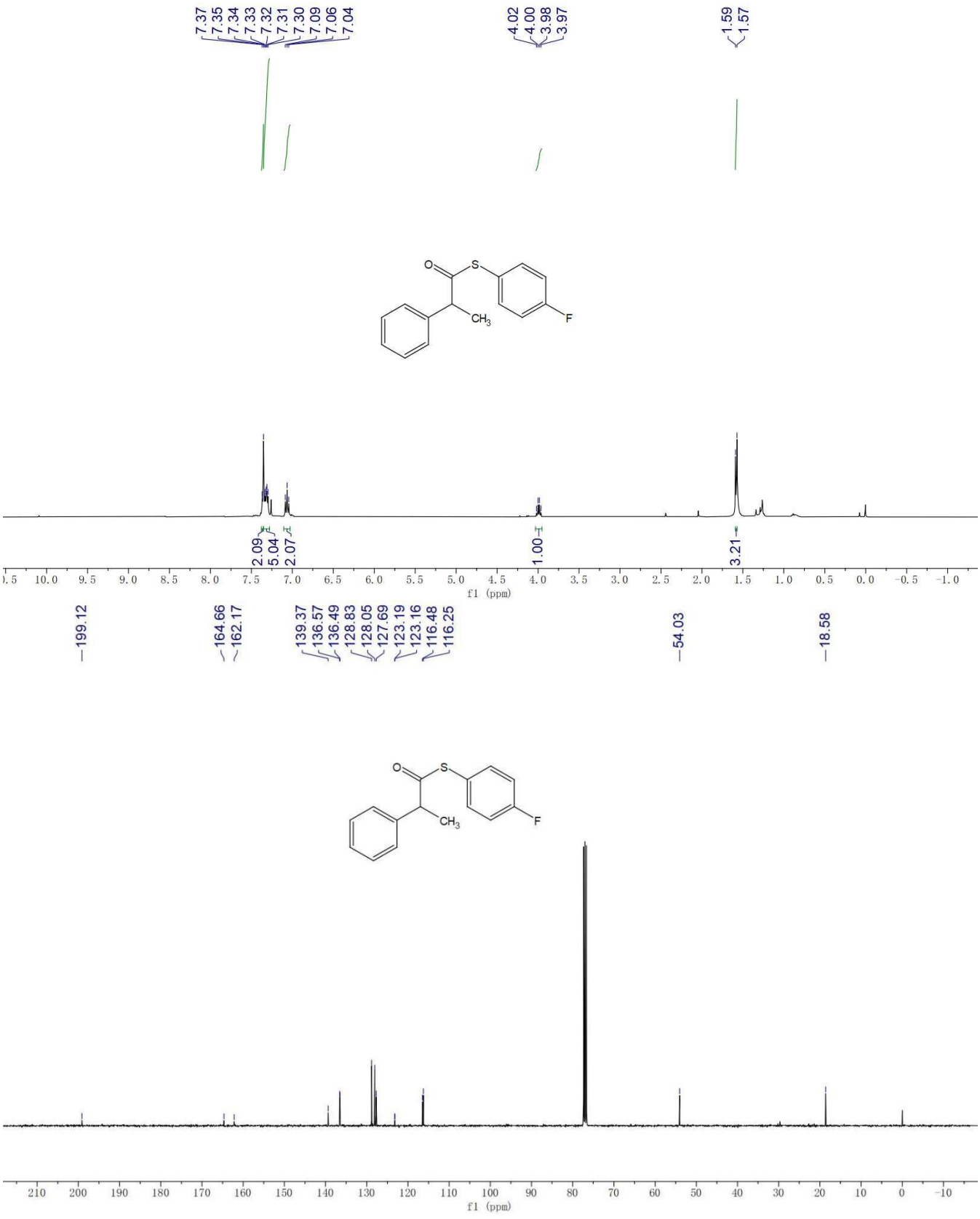
^{1}H and ^{13}C NMR spectra of **3aa**

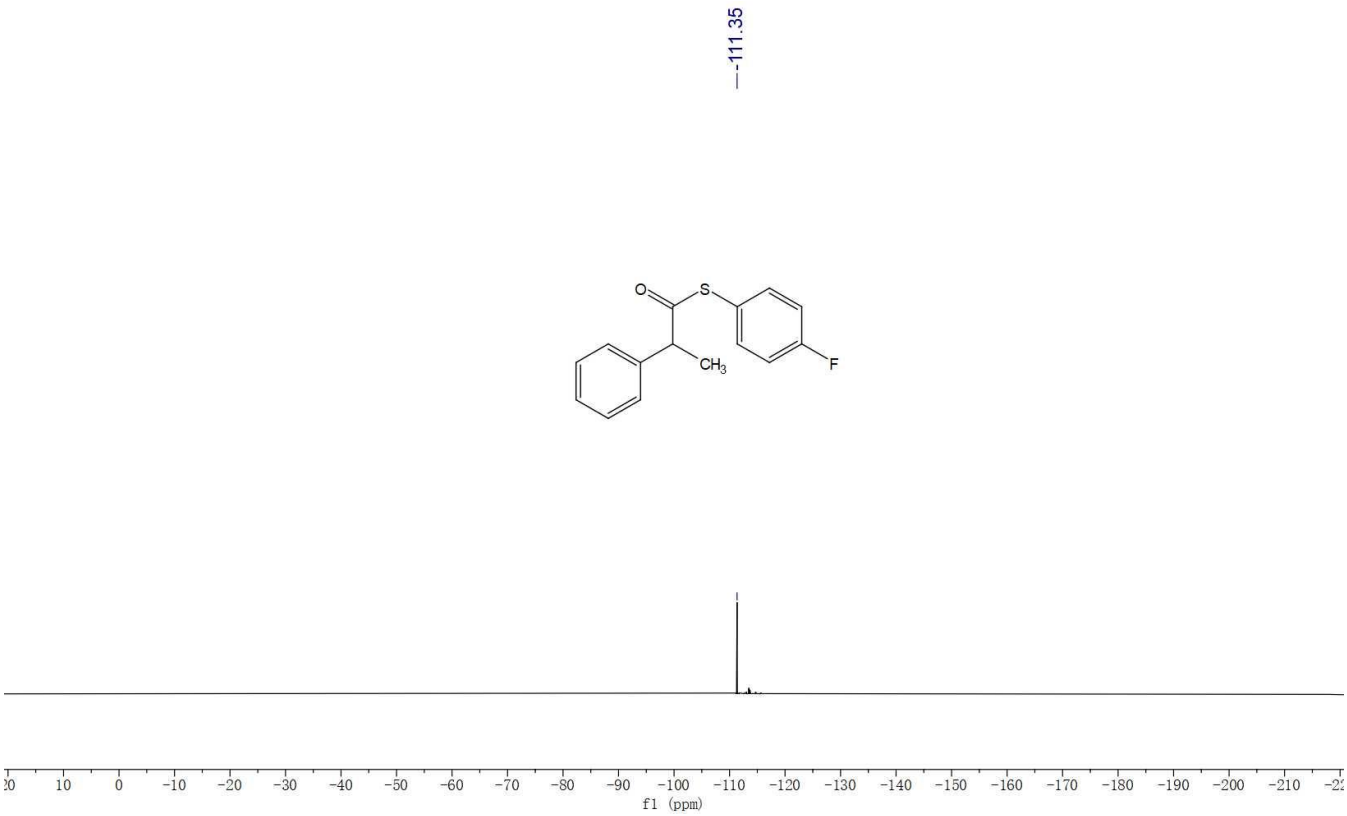


^{1}H and ^{13}C NMR spectra of **3ab**

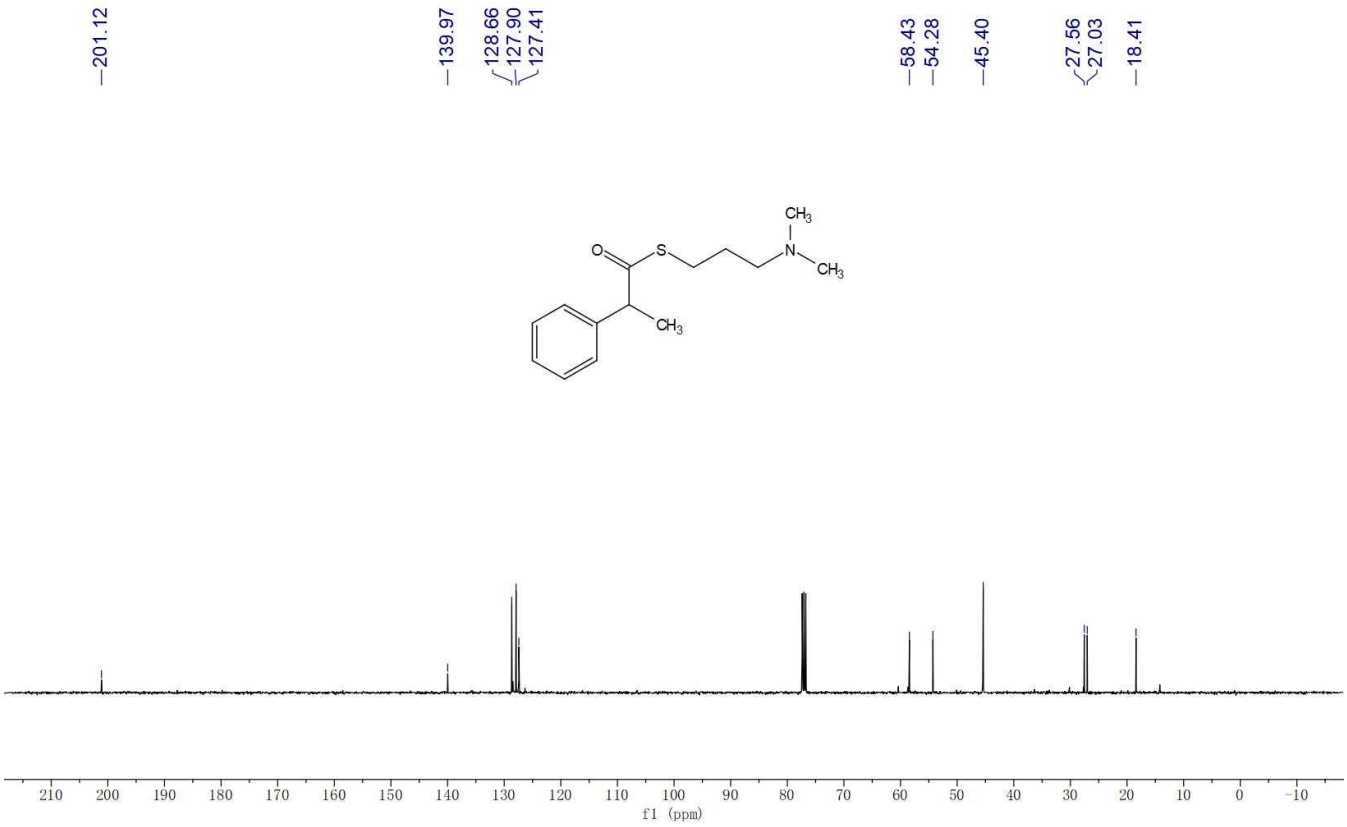


^{1}H and ^{13}C NMR spectra of **3ac**

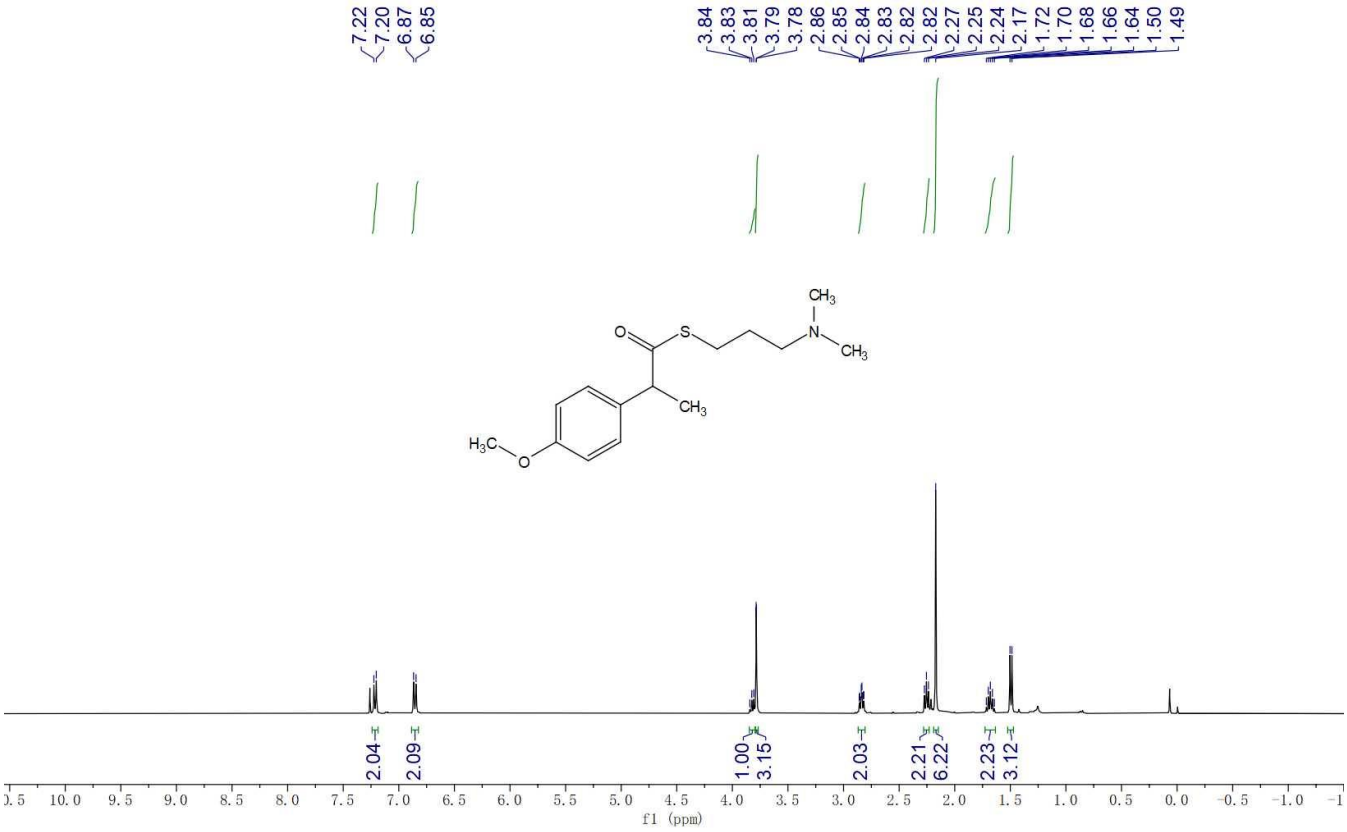

7.37
7.35
7.34
7.33
7.32
7.31
7.30
7.09
7.06
7.04
4.02
4.00
3.98
3.97
1.59
1.57
O
S
CH3
F
2.09
5.04
2.07
1.00
3.21
f1 (ppm)
199.12
164.66
162.17
139.37
136.57
136.49
128.83
128.05
127.69
123.19
123.16
116.48
116.25
54.03
18.58
O
S
CH3
F
f1 (ppm)

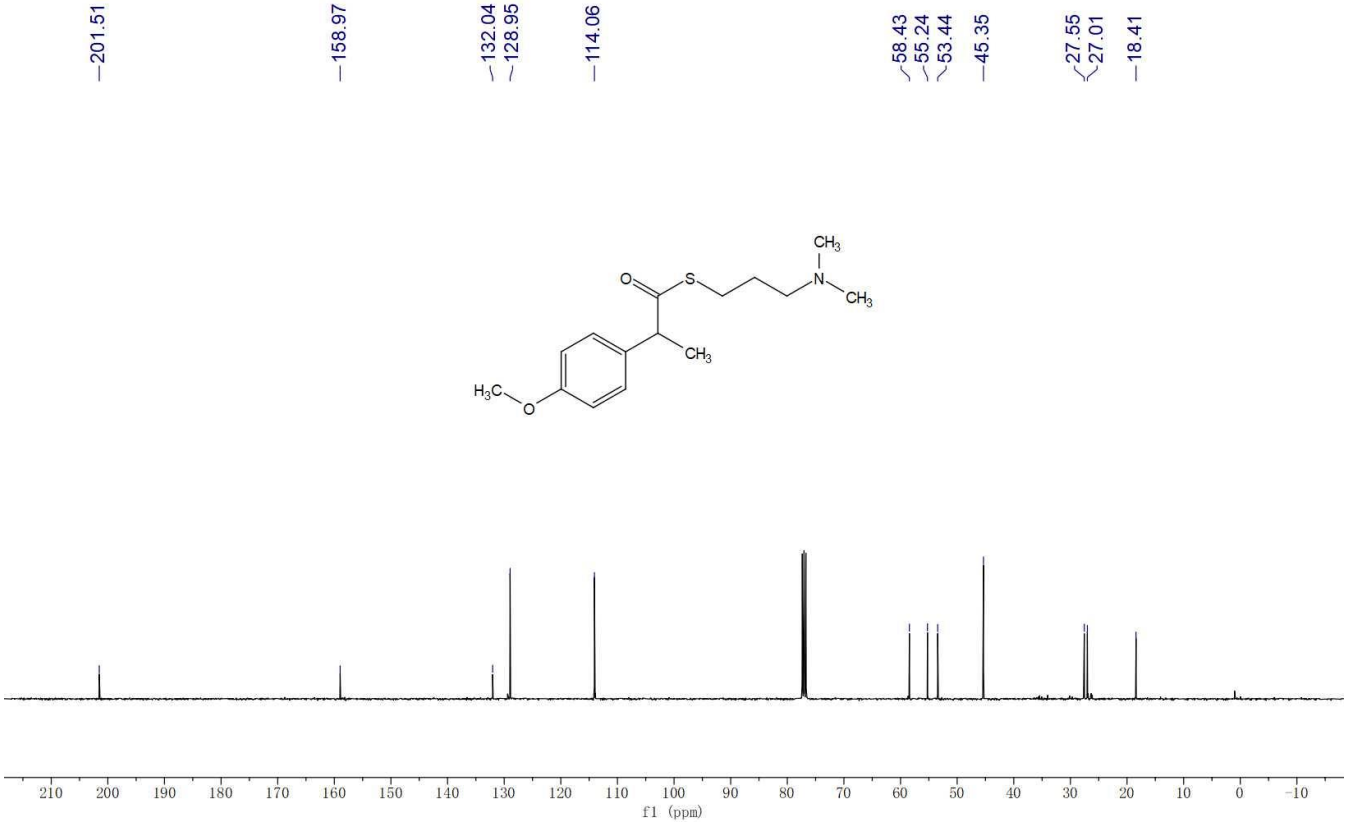


^{1}H, ^{13}C and ^{19}F NMR spectra of **3ad**

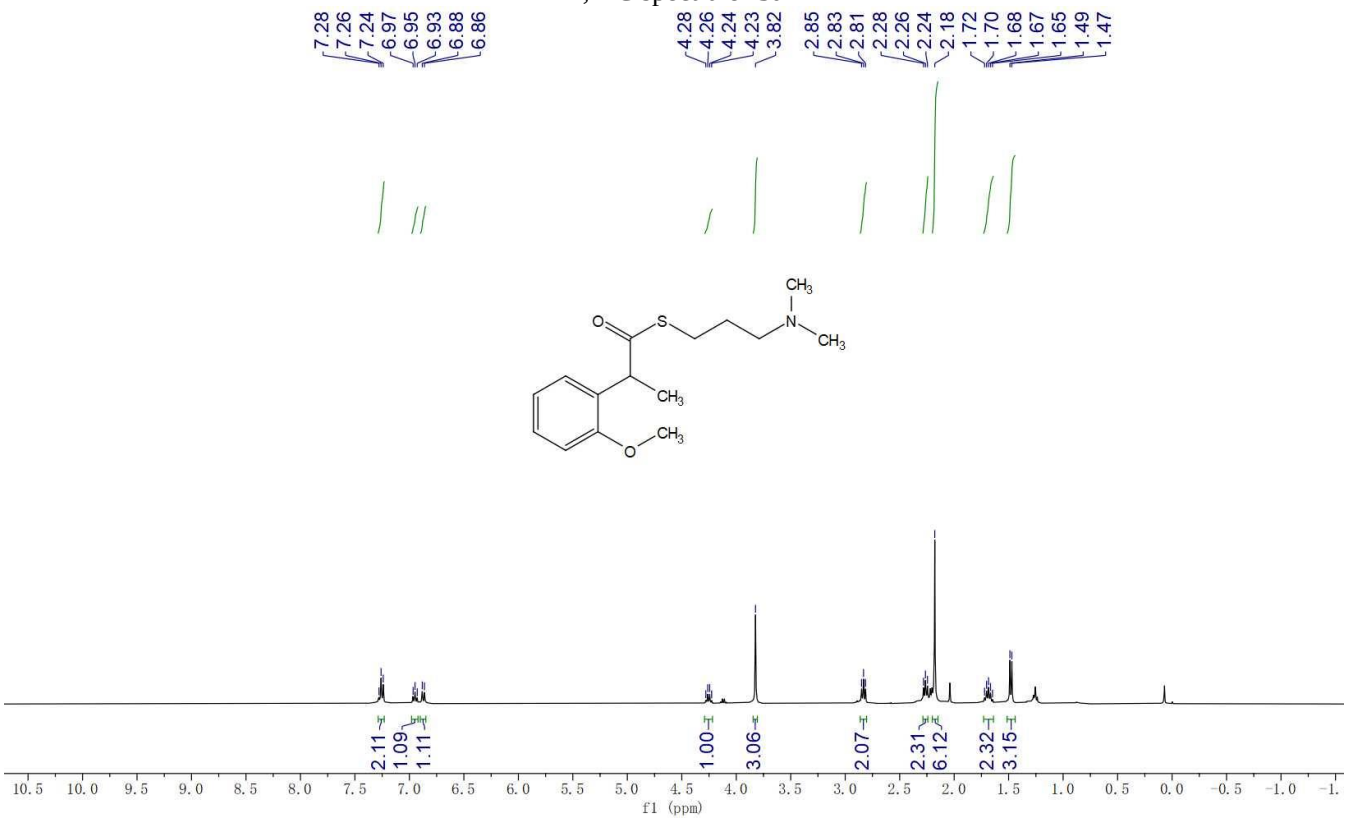


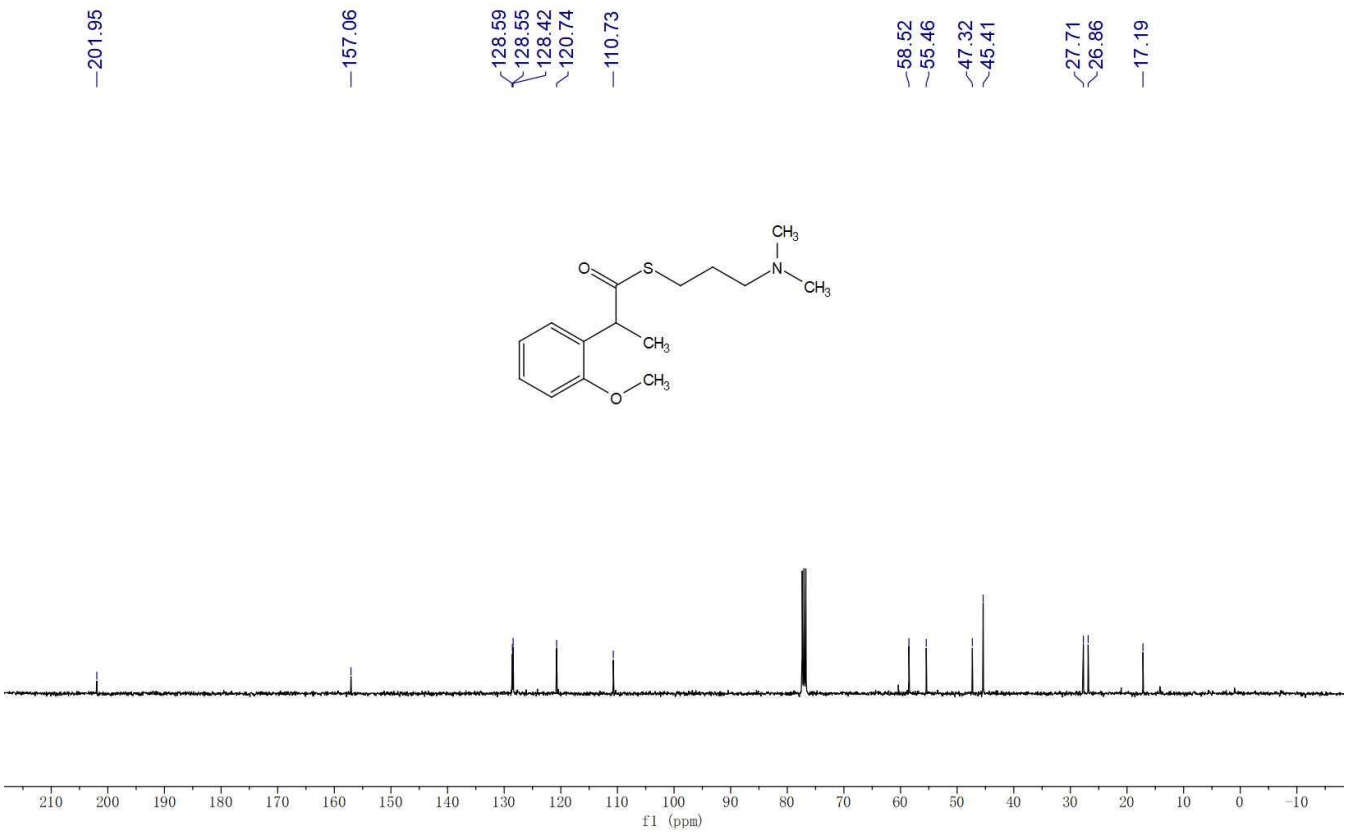
^{1}H, ^{13}C spectra of **3ae**



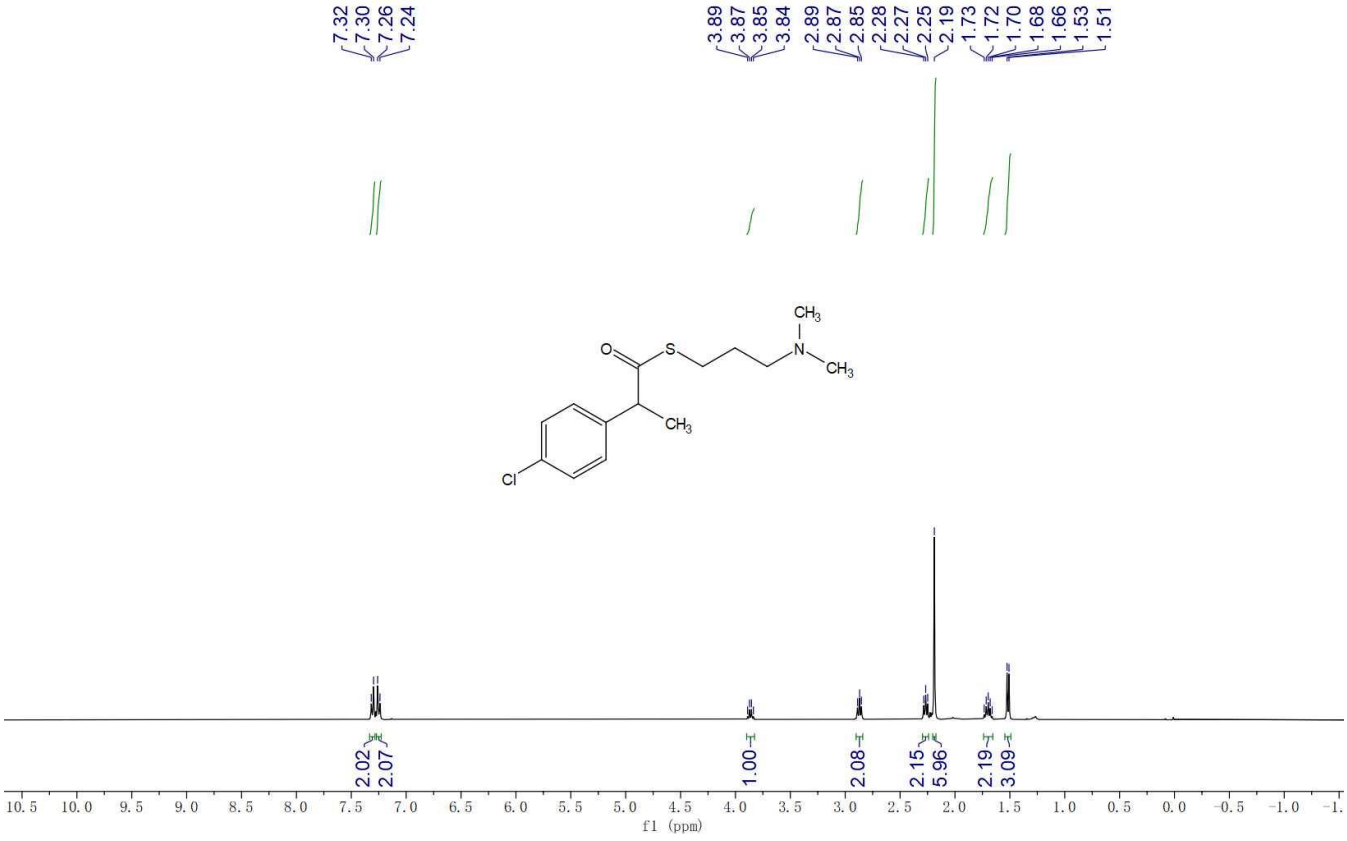


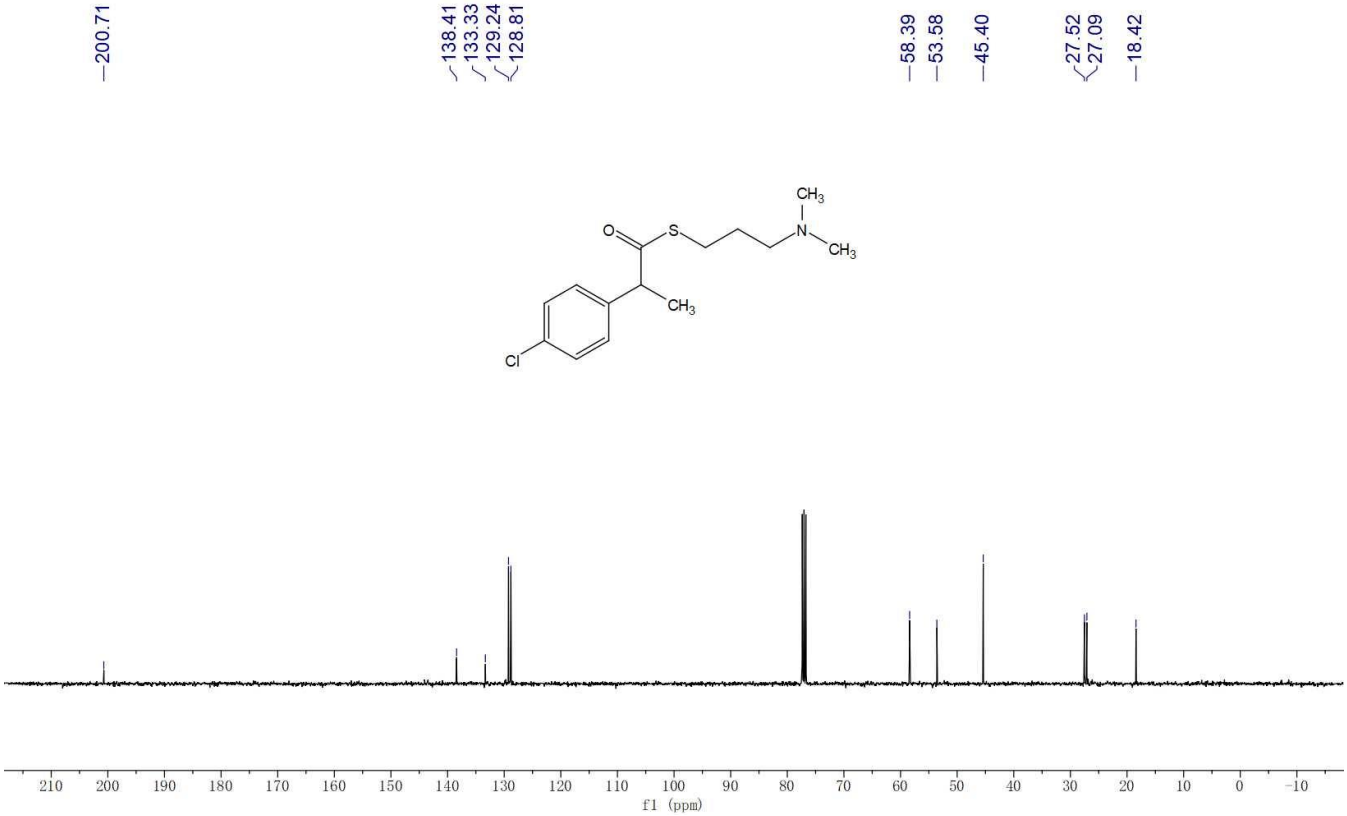
^{1}H, ^{13}C spectra of **3af**



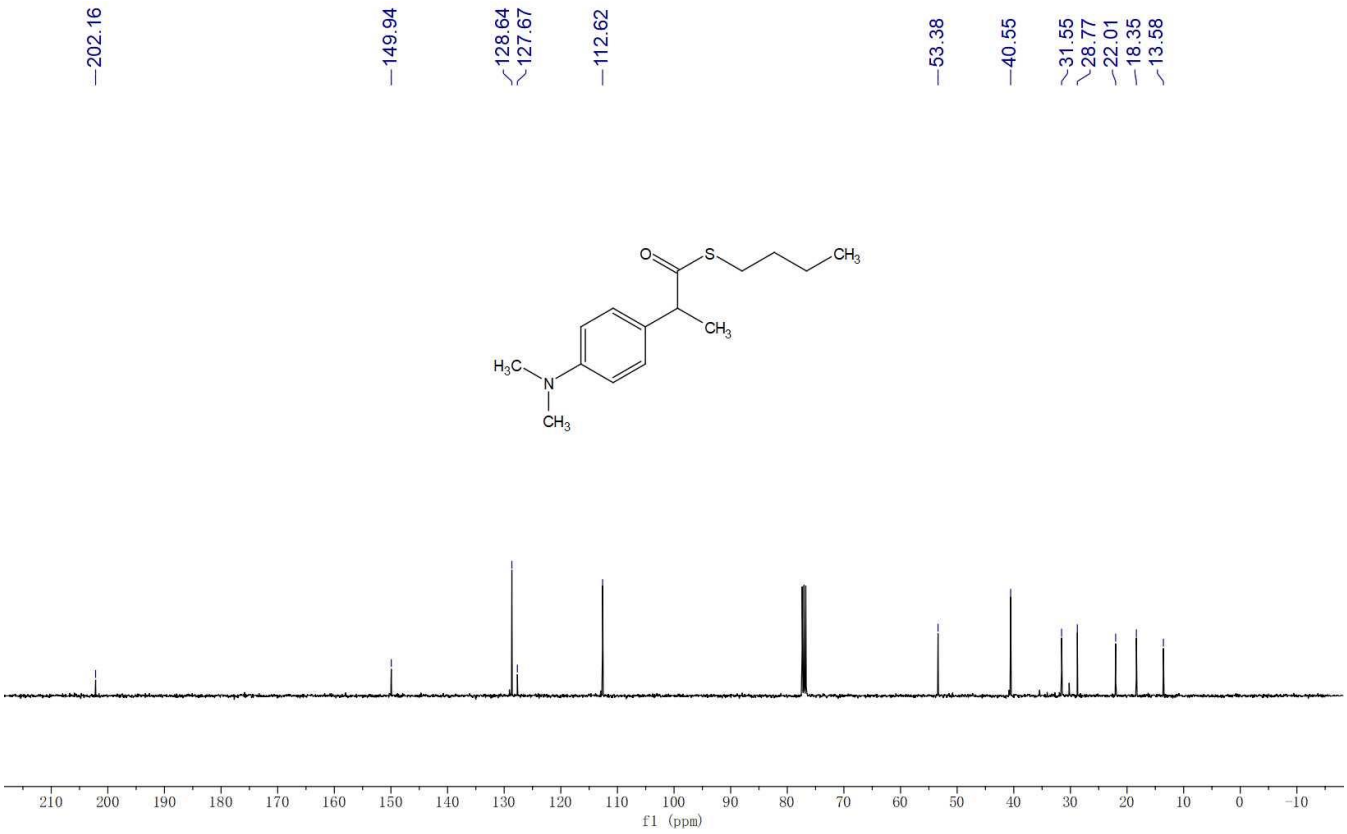


^{1}H, ^{13}C spectra of **3ag**

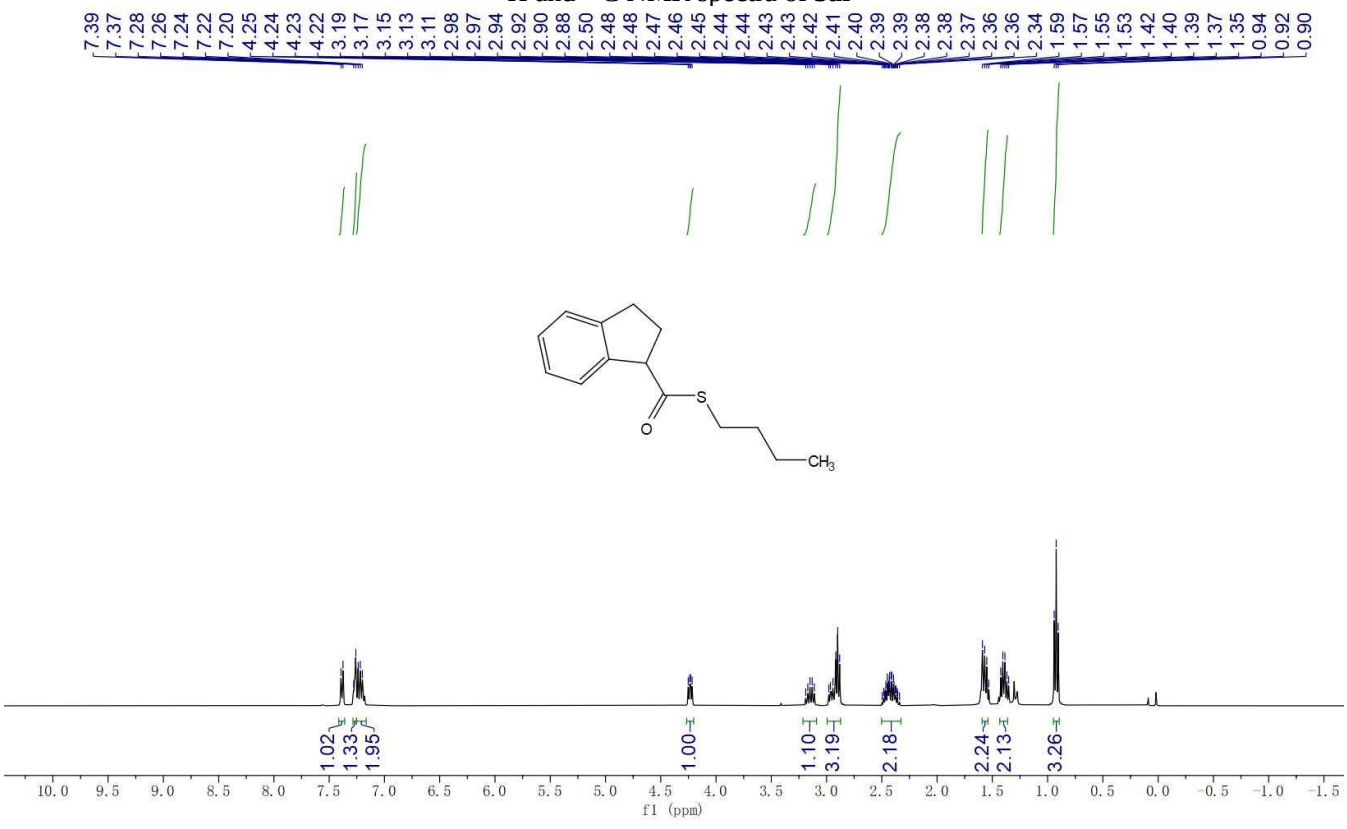


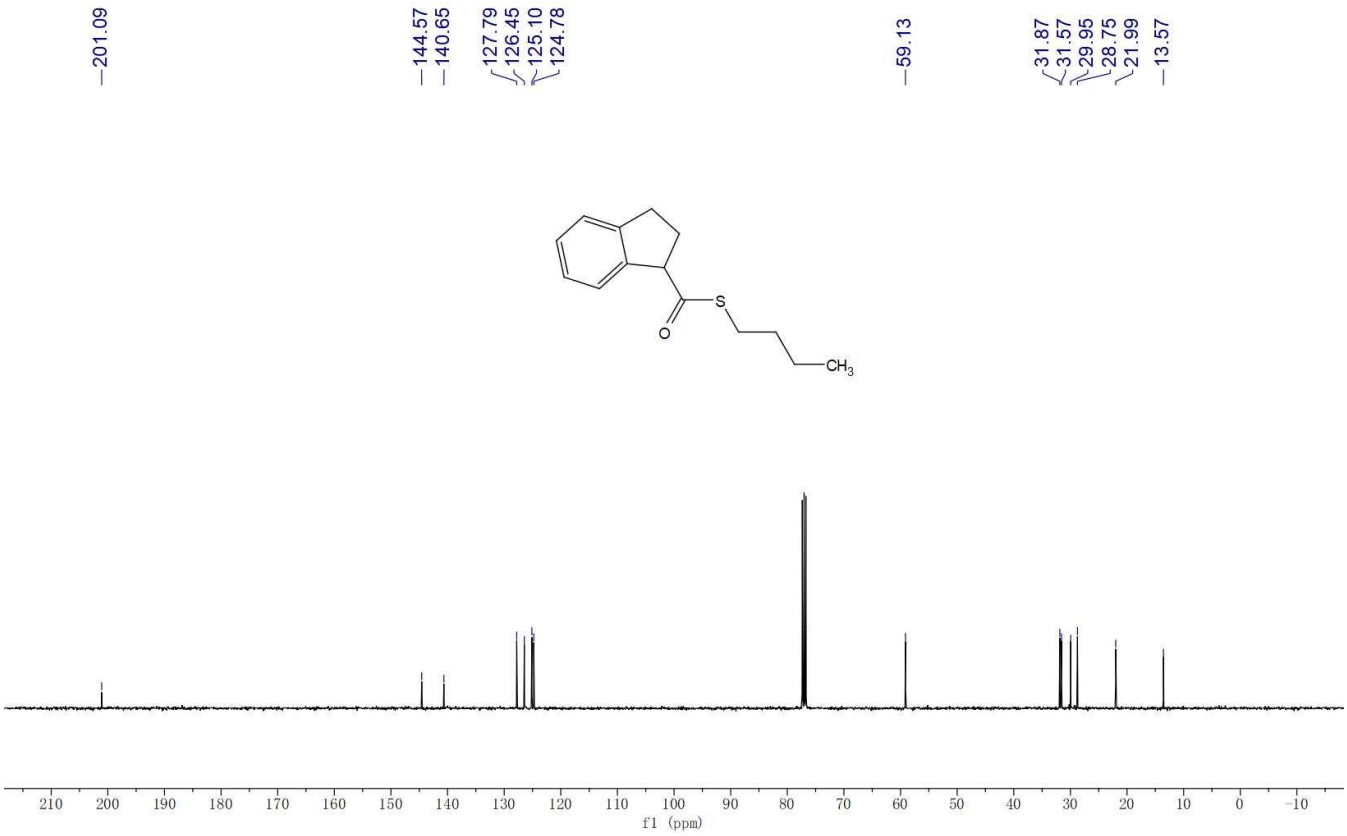


^{1}H, ^{13}C spectra of **3ah**

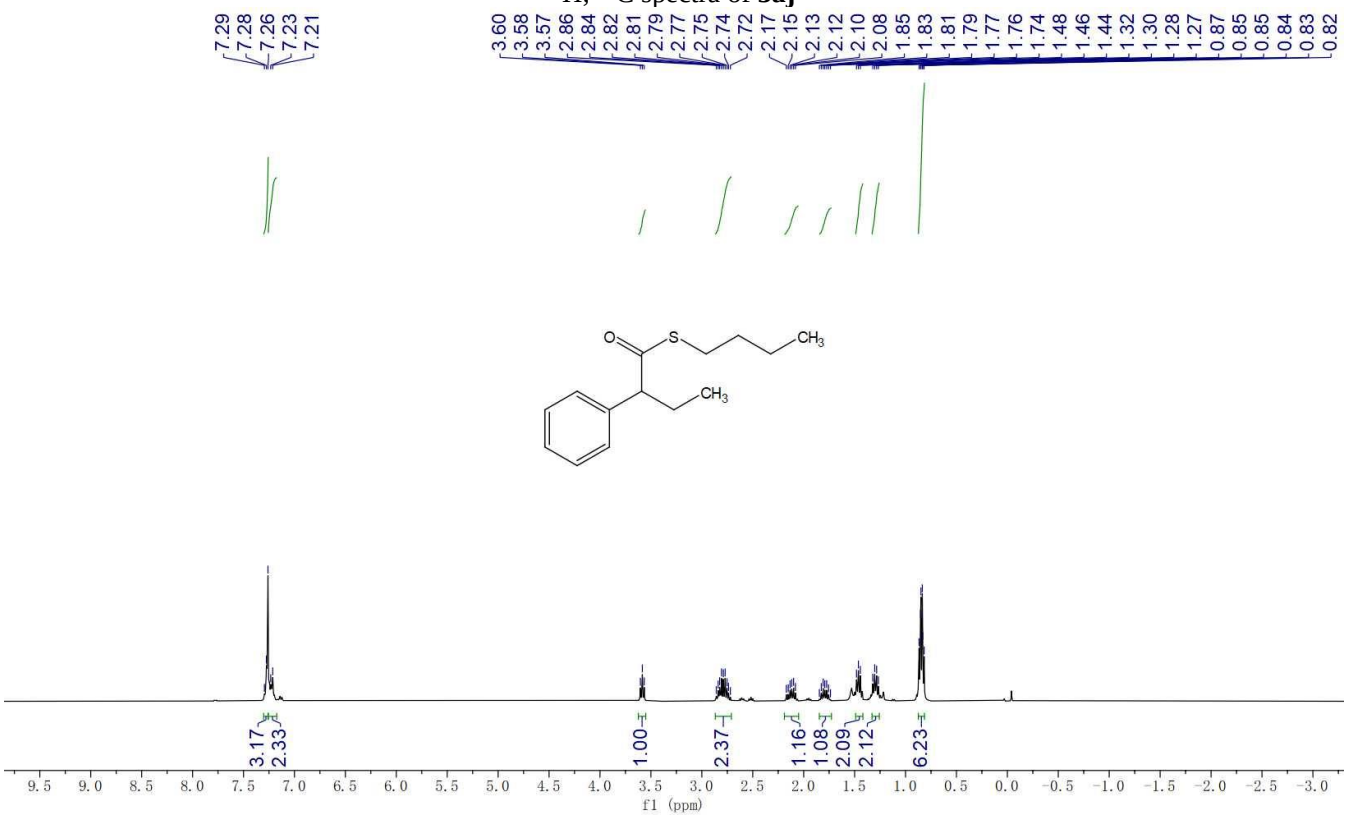


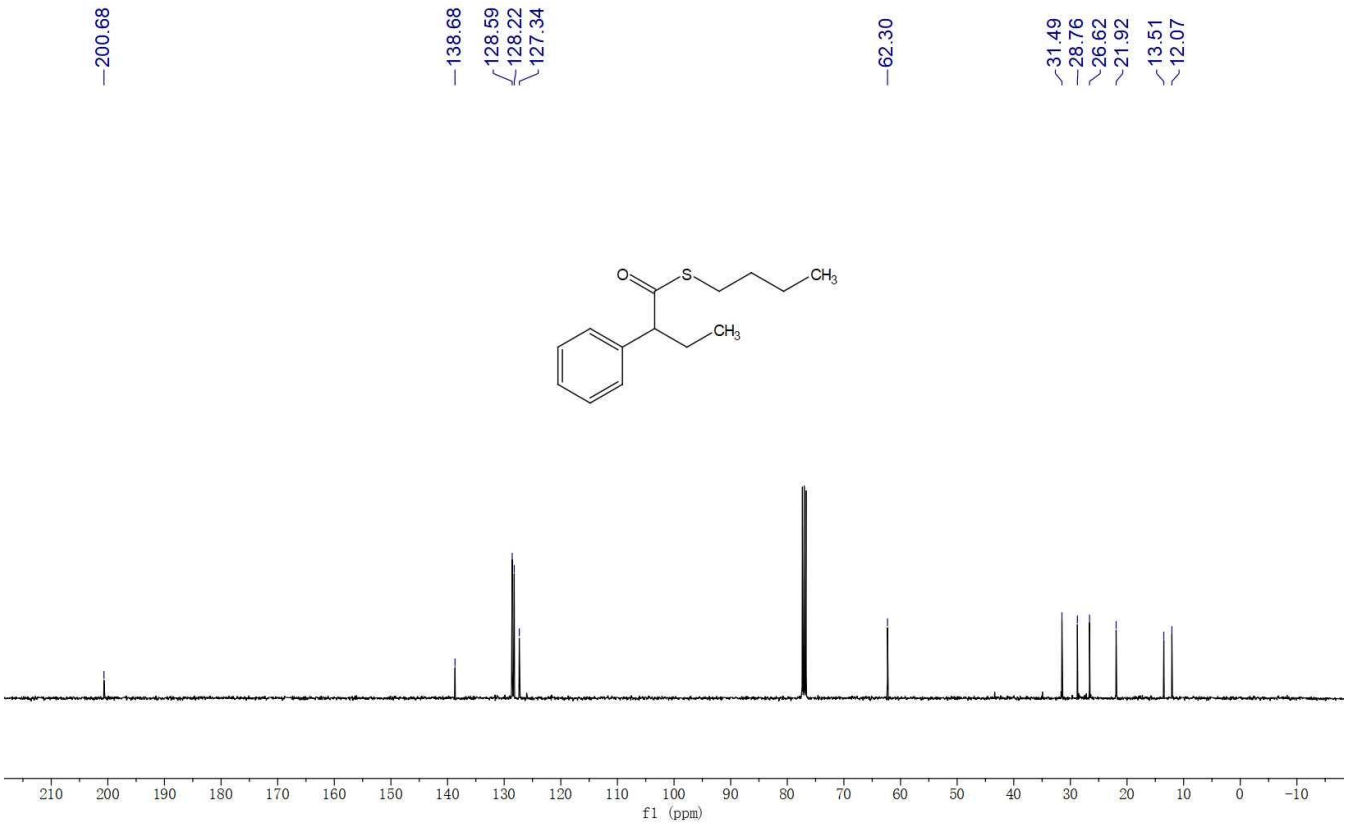
^{1}H and ^{13}C NMR spectra of **3ai**



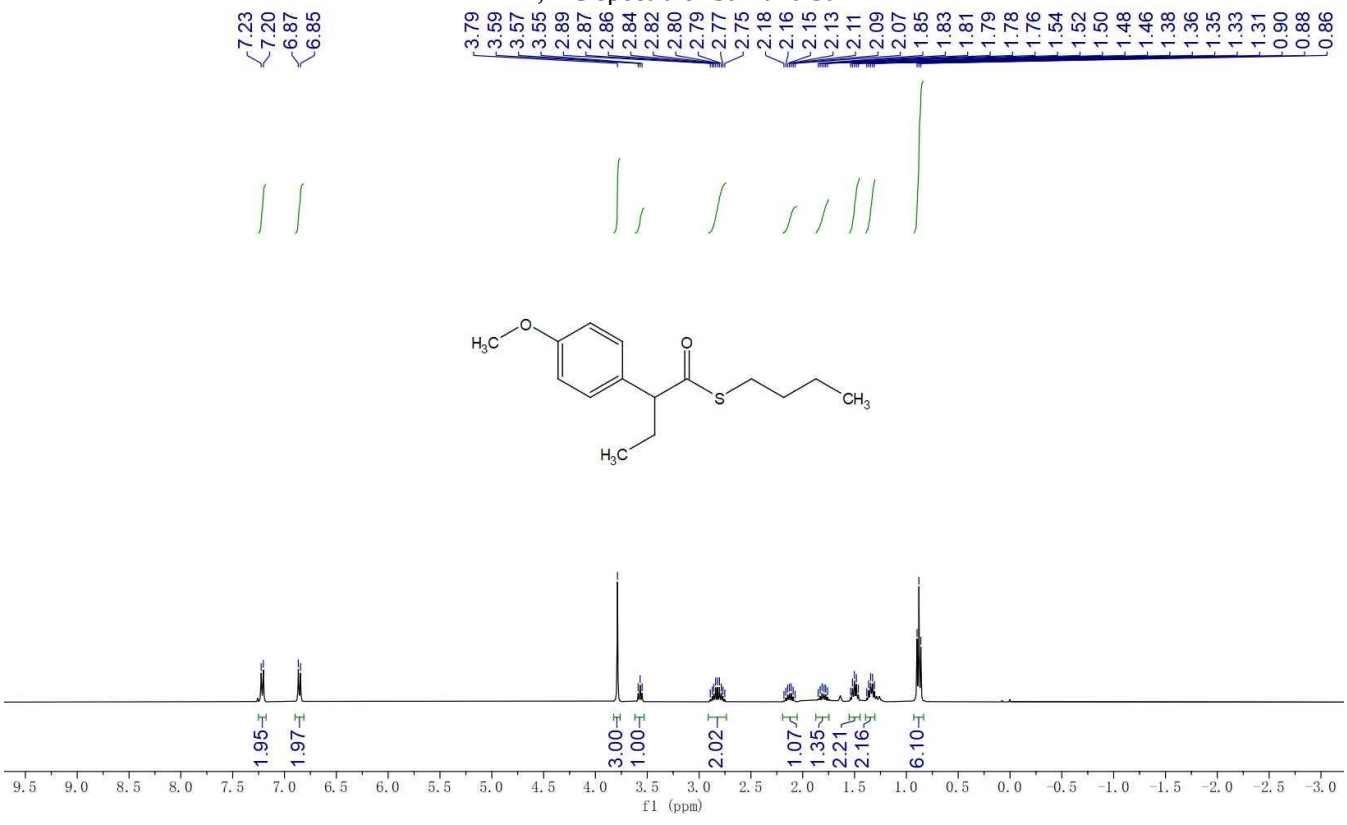


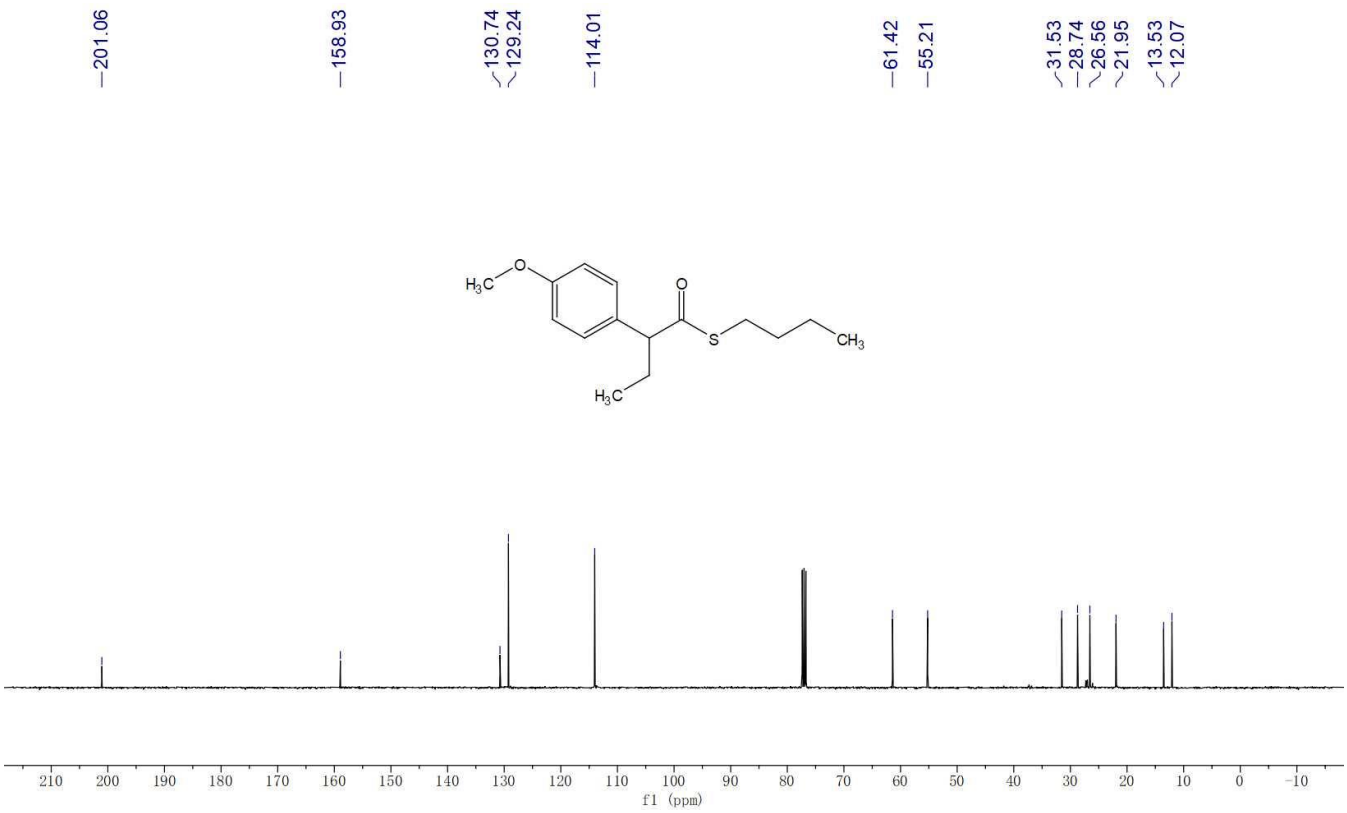
^{1}H, ^{13}C spectra of **3aj**



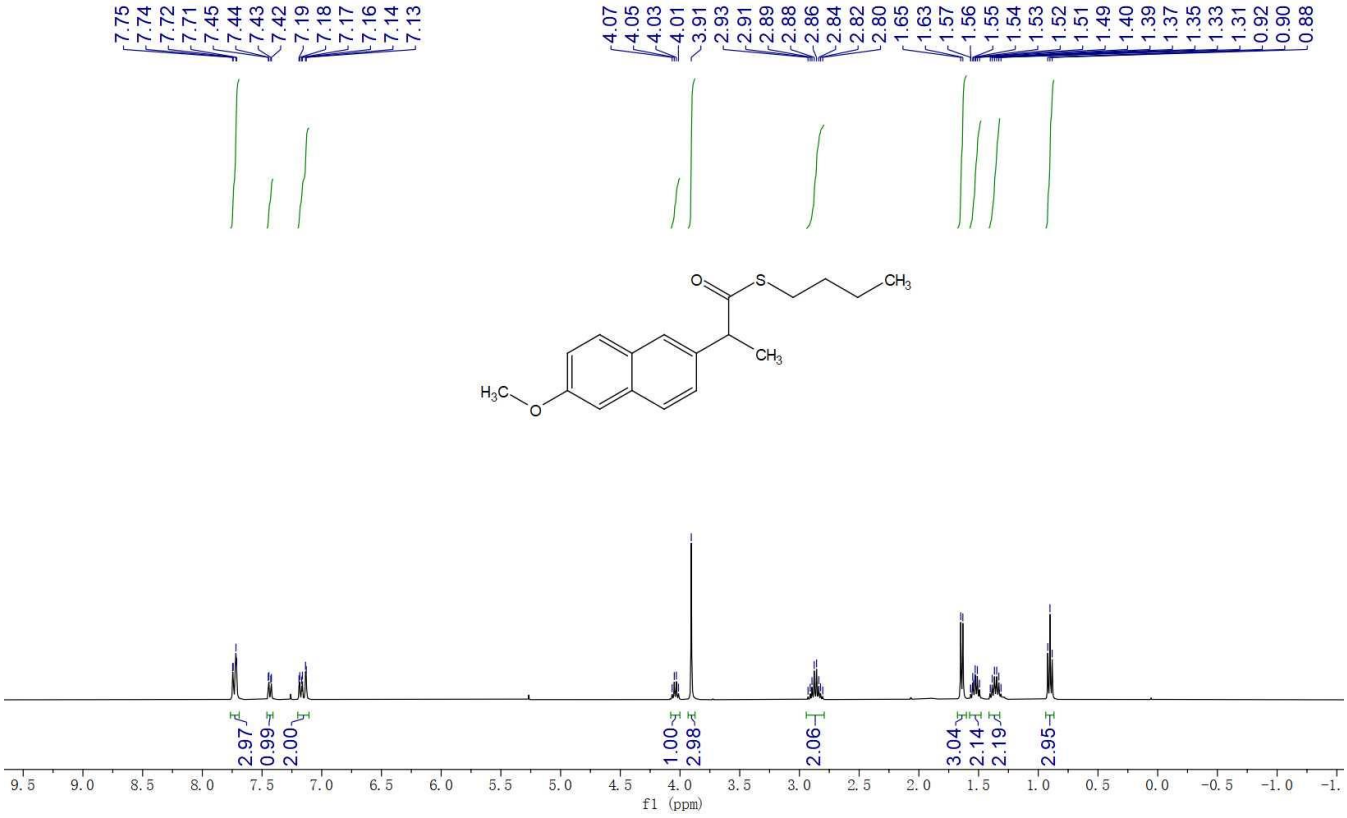


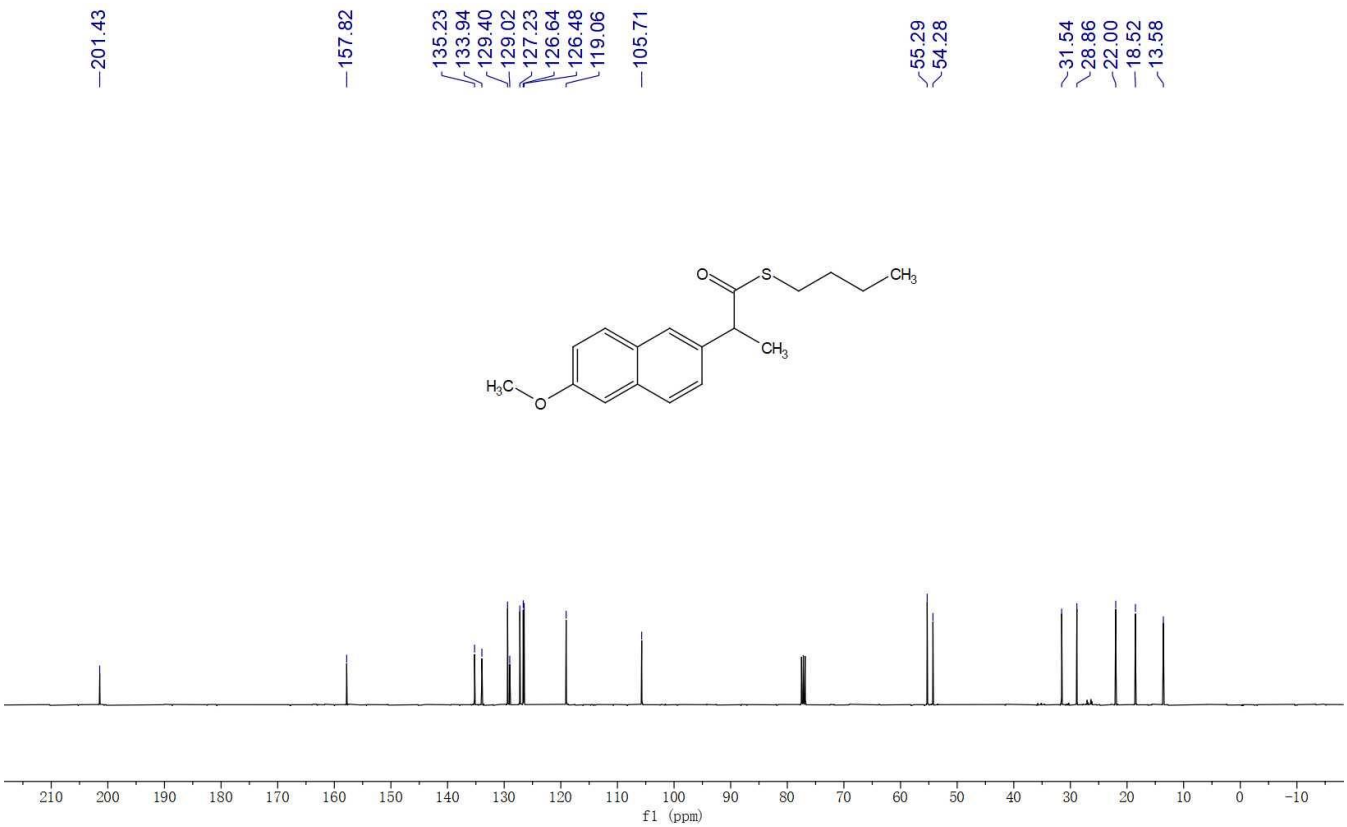
^{1}H, ^{13}C spectra of **3ak** and **3u**



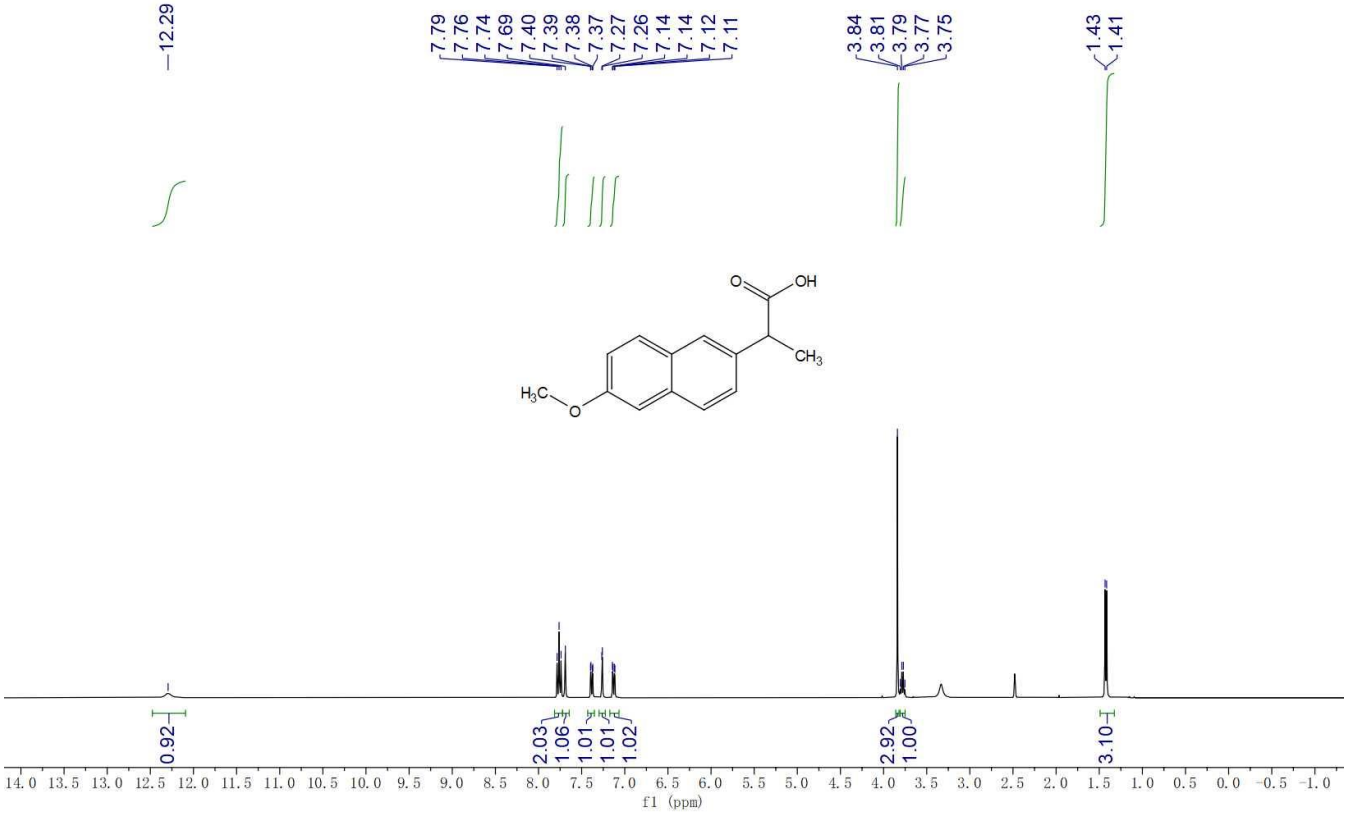


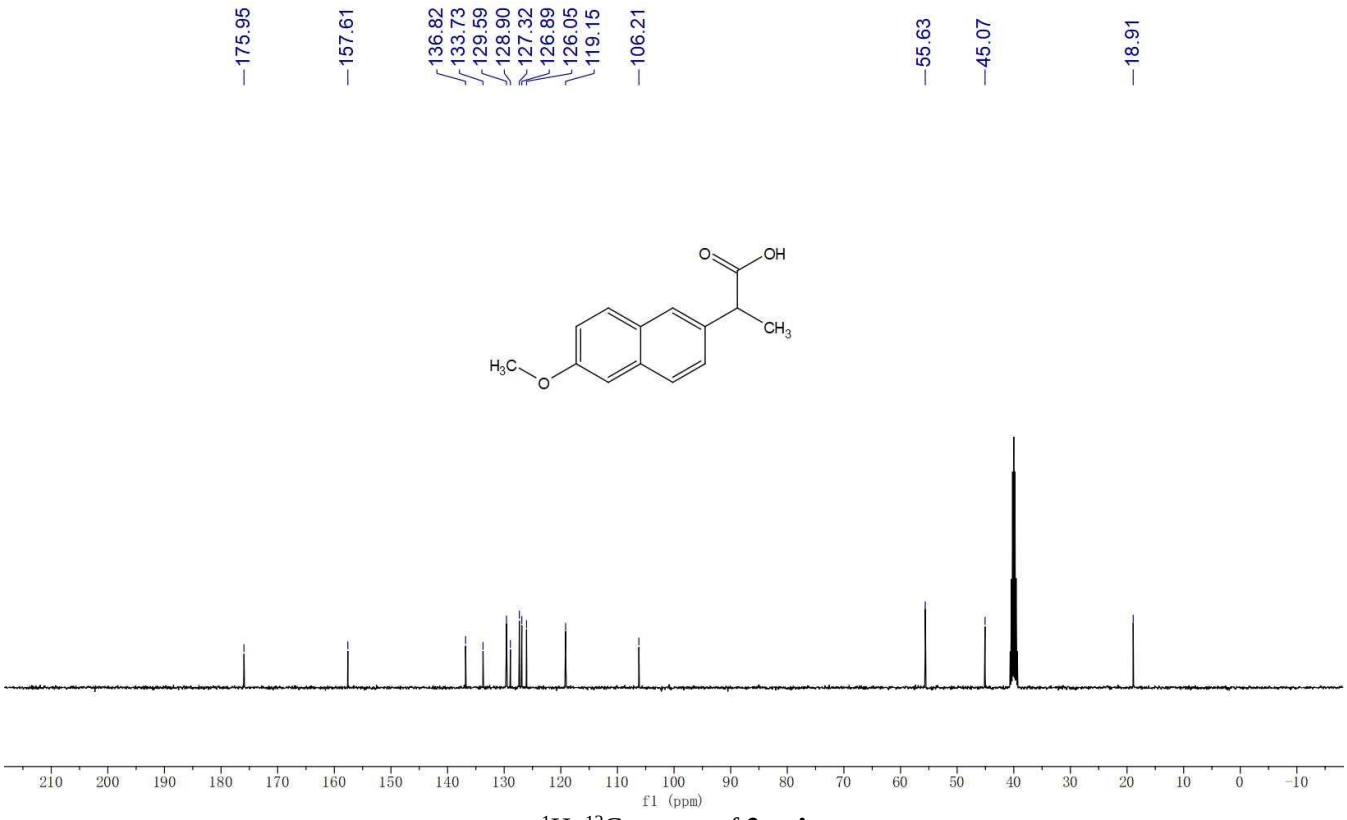
^{1}H, ^{13}C spectra of **3al**



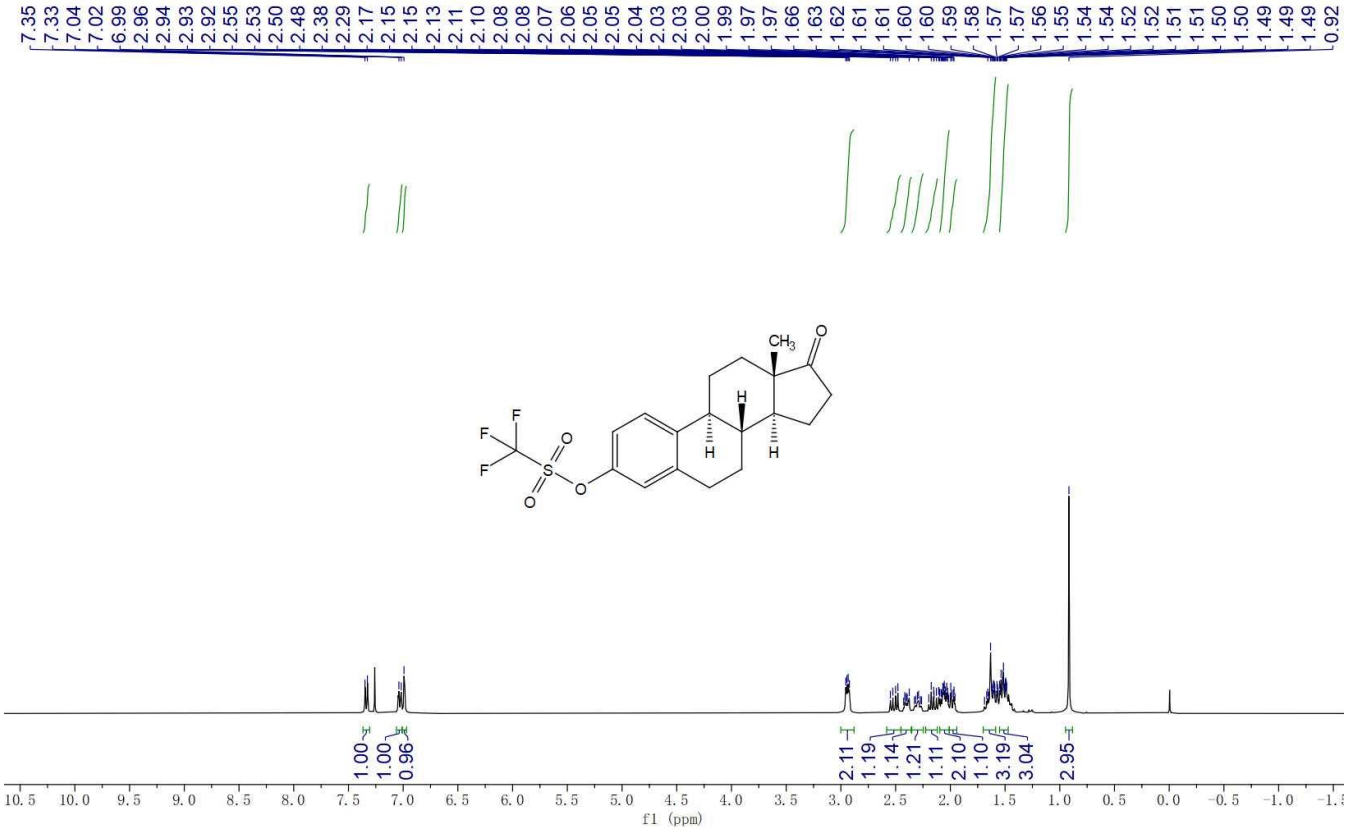


^{1}H, ^{13}C spectra of **3am**

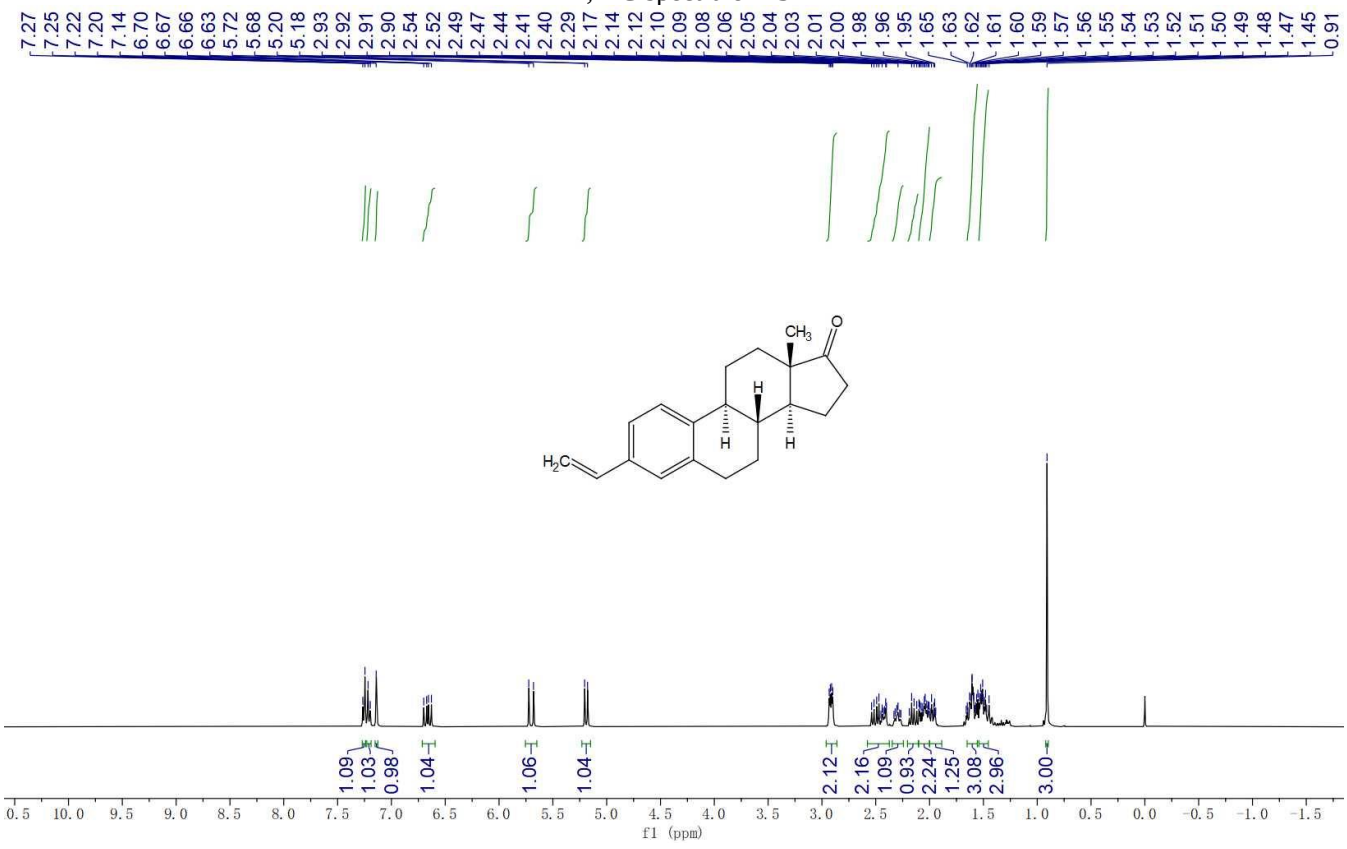


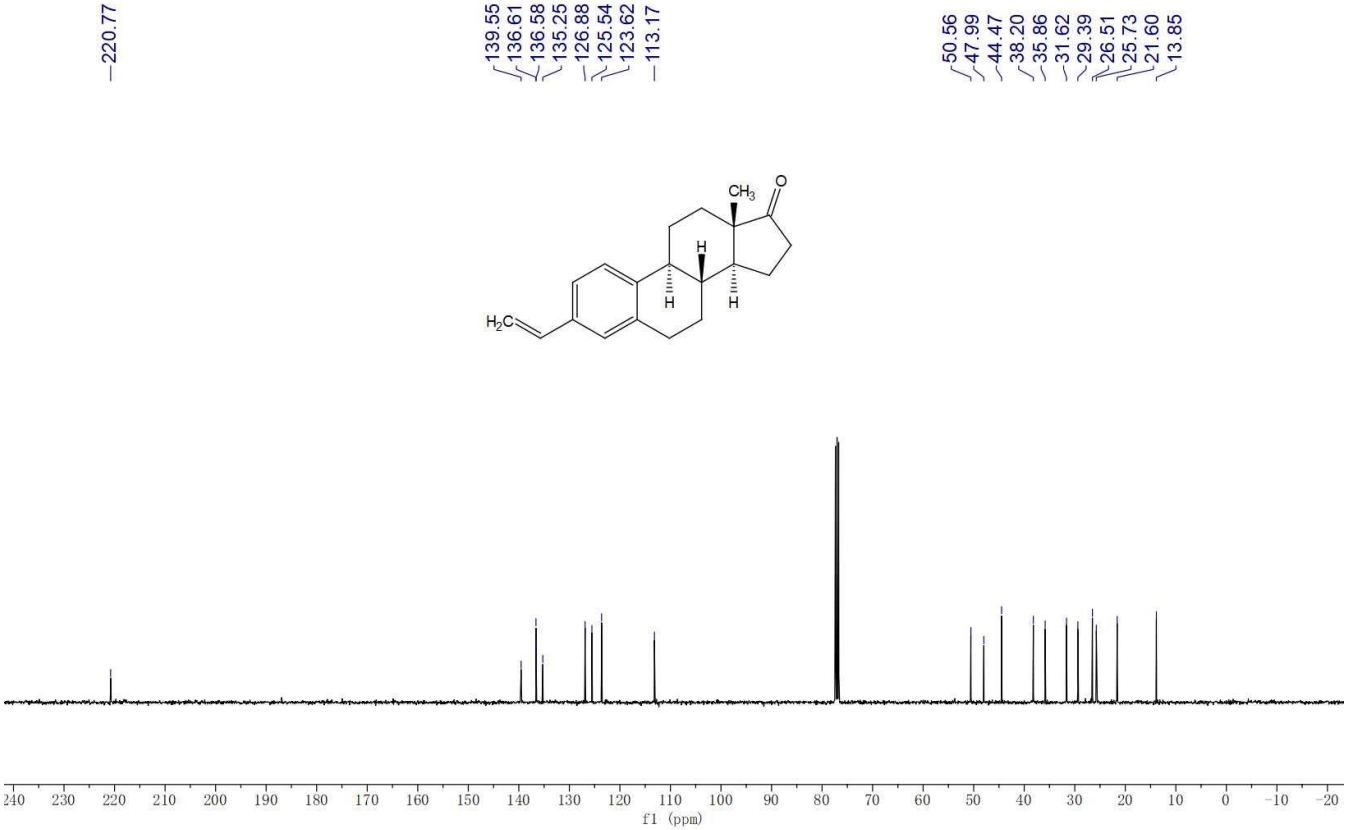


^{1}H, ^{13}C spectra of **3am'**

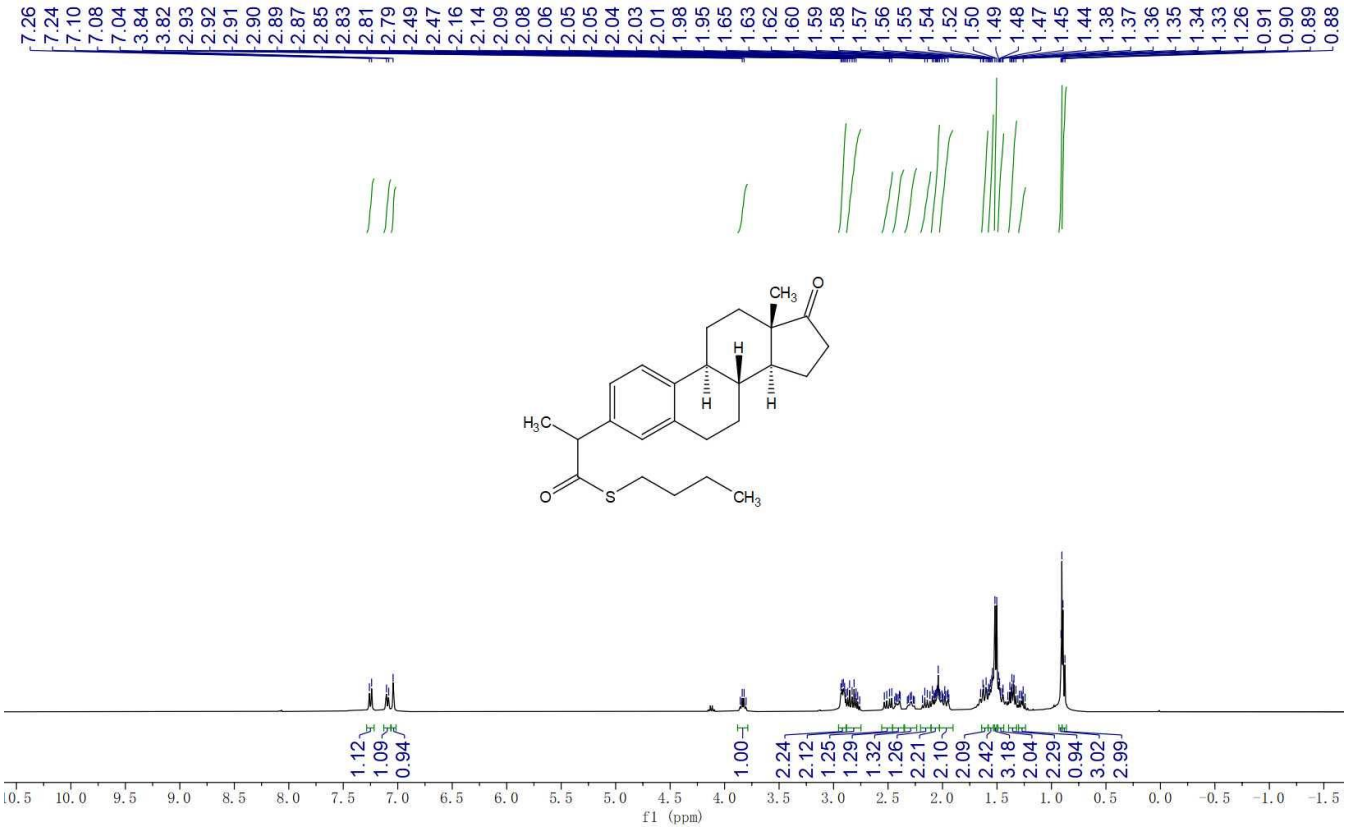


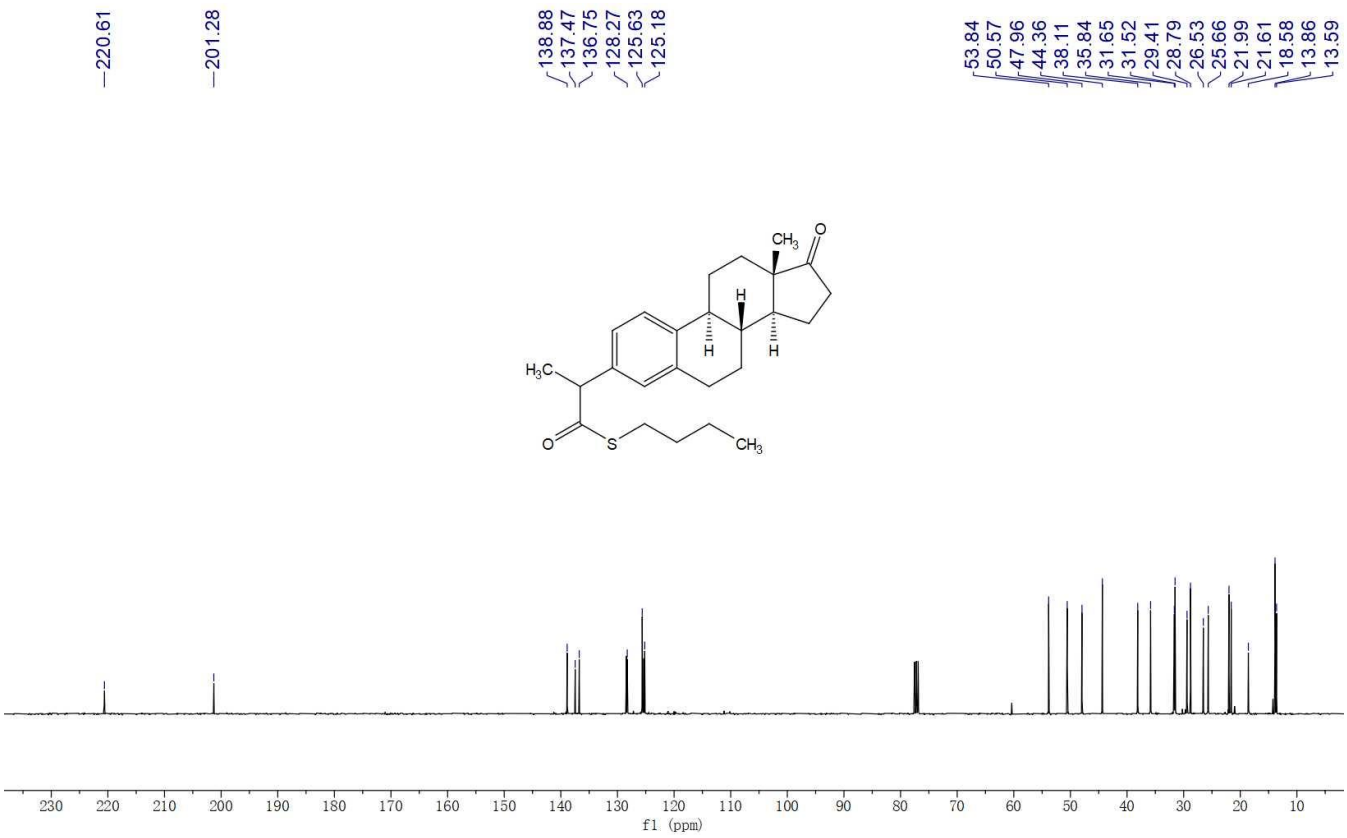
^{1}H, ^{13}C spectra of **1S**





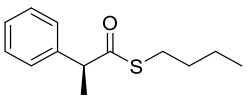
^{1}H, ^{13}C spectra of **1an**





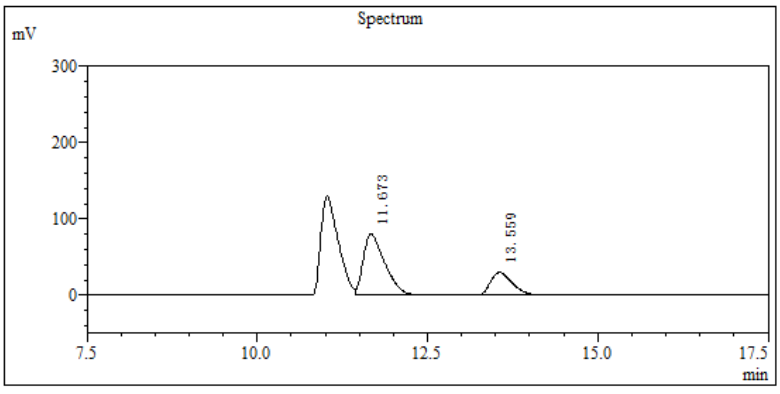
^{1}H, ^{13}C spectra of **3an**

14. Chiral HPLC chromatogram



***S*-butyl (*S*)-2-phenylpropanethioate (3aaa)**[16]

Yellow liquid; Yield = 38%, b/l > 99/1, ee = 46%, HPLC analysis: Daicel Chiralpak OJ-H, *n*-hexane/*i*-propanol = 500:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.67 min (major) and 13.56 (minor). $[\alpha]_D^{20}$ = +30.0 (c = 0.50, $CHCl_3$).



检测器A 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	11.673	80404	1765909	72.649
2	13.559	29907	664818	27.351
总计				100.000