

Visible Light-Induced Deaminative Thioesterification of Amino Acid-Derived Katritzky Salts via Electron-Donor Acceptor Complex Formation

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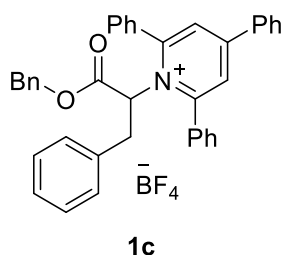
1. General Methods

Unless stated otherwise, all reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished by flash chromatography on silica gel. The product spots on the thin layer chromatography (TLC) was identified/visualized by fluorescence quenching or potassium permanganate stains. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz and 100 MHz) or a Bruker Avance 500 (500 MHz and 126 MHz) instrument, and are internally referenced to solvent residual signals (note: CDCl_3 referenced at 7.26 and 77.00 ppm respectively). Data for ^1H NMR were reported as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in ppm with the internal chloroform signal at 77.00 ppm as a standard. High resolution mass spectra were recorded on Waters Micromass GCT Premier (EI) and Exactive Plus LC-MS (ESI) mass spectrometers. GC measurements were performed on a GCMS-QP2010SE from SHIMADZU.

2. Synthesis of Katritzky Salts

Katritzky salts **1a**,¹ **1b**,³ **1d**,² **1h**,¹ **1j**,⁴ **1o**,¹ **1p**,² **1q**,² **1r**³ were prepared according to previous reported procedures.¹ Unknown Katritzky salts **1c**, **1e**, **1f**, **1g**, **1i**, **1k**, **1l**, **1m**, **1n** were prepared according to literature procedures¹ as described as follows:

The corresponding amino acid ester hydrochloride (1.2 equiv) was weighed into a reaction tube then EtOH (1.0 M) and Et₃N (1.2 equiv) were added successively. The reaction mixture was stirred at room temperature for 30 min and then triphenylpyrylium tetrafluoroborate (1 g, 1.0 equiv) was added and heated to 90 °C. After 4 h cooled to room temperature, diethyl ether was added to the reaction mixture and the resulting suspension was stirred at rt for at least 1 h to complete the precipitation process. The solid was collected by filtration and washed with H₂O (to remove Et₃N·HX salts) and Et₂O. The solid was then dried under reduced pressure to give the pyridinium salts without further purification. If precipitation did not take place, the solvent was removed under reduced pressure. The crude product was then dissolved in CH₂Cl₂ (1 M), washed with isopyknic H₂O (3 times) and concentrated under reduced pressure. The crude product was then purified by column chromatography with a gradient of acetone in CH₂Cl₂ eluting to afford the pyridinium salt product.



1-(1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1c**), recrystallized from hot EtOH/Et₂O (v/v 1:4), white solid, 81% yield.

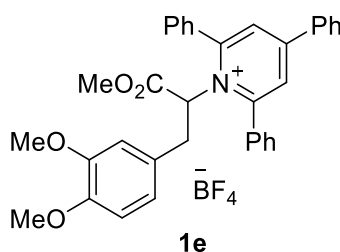
¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.95 (s, 2H), 7.85 – 7.66 (m, 4H), 7.58 – 7.37 (m, 14H), 7.18 (d, *J* = 6.8 Hz, 2H), 7.10 – 7.00 (m, 3H), 6.72 (d, *J* = 7.2 Hz, 2H), 5.68

– 5.67 (m, 1H), 5.12 (d, $J = 11.6$ Hz, 1H), 5.02 (d, $J = 11.6$ Hz, 1H), 3.51 – 3.47 (m, 1H), 2.75 (dd, $J = 14.4, 8.4$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 167.4, 156.9, 156.8, 136.0, 133.5, 133.5, 132.4, 132.2, 131.4, 129.6, 129.3, 129.1, 128.9, 128.7, 128.5, 128.4, 127.7, 127.1, 70.4, 69.0, 37.3.

^{19}F NMR (376 MHz, CDCl_3): δ (ppm): -152.68, -152.73.

HRMS (EI): m/z calculated for $\text{C}_{39}\text{H}_{32}\text{NO}_2$ (M-BF_4) $^+$: 546.2428, found 546.2430.



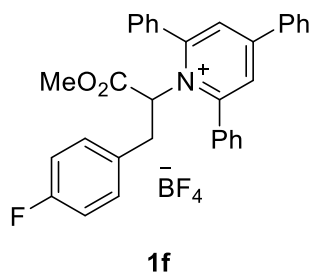
1-(3-(3,4-dimethoxyphenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1e**), recrystallized from EtOH/Et₂O (v/v 1:4), white solid, 86% yield.

^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.94 (s, 2H), 7.84 – 7.78 (m, 4H), 7.59 – 7.48 (m, 11H), 6.57 (d, $J = 8.0$ Hz, 1H), 6.41 (s, 1H), 6.34 (d, $J = 8.0$ Hz, 1H), 5.64 (dd, $J = 6.8, 4.0$ Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.67 (s, 3H), 3.35 (dd, $J = 14.4, 4.0$ Hz, 1H), 2.86 (dd, $J = 14.4, 7.2$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 168.0, 156.8, 148.8, 148.0, 133.6, 132.4, 132.3, 131.5, 129.7, 129.4, 129.1, 128.6, 128.4, 127.8, 121.0, 112.1, 110.9, 70.5, 55.84, 55.76, 53.7, 37.4.

^{19}F NMR (376 MHz, CDCl_3): δ (ppm): -152.63, -152.68.

HRMS (EI): m/z calculated for $\text{C}_{35}\text{H}_{32}\text{NO}_4$ (M-BF_4) $^+$: 530.2326, found 530.2330.



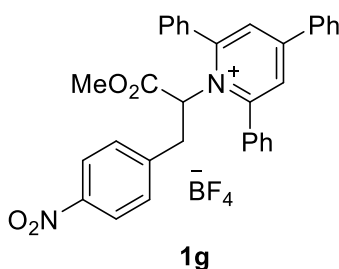
1-(3-(4-fluorophenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1f**), recrystallized from EtOH/Et₂O (v/v 1:4), white solid, 82% yield.

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.92 (s, 2H), 7.82 – 7.80 (m, 4H), 7.59 – 7.47 (m, 11H), 6.81 – 6.72 (m, 4H), 5.56 (d, *J* = 7.6 Hz, 1H), 3.69 (s, 3H), 3.47 (d, *J* = 13.6 Hz, 1H), 2.87 (dd, *J* = 14.0, 8.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 167.8, 161.8 (d, *J* = 245.0 Hz, 1C), 157.0, 156.7, 133.7, 132.4, 132.3 (d, *J* = 3.0 Hz, 1C), 132.2, 131.5, 130.6 (d, *J* = 8.0 Hz, 1C), 129.6, 129.3, 129.1, 128.5, 127.8, 115.3 (d, *J* = 21.0 Hz, 1C), 70.0, 53.7, 36.9.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -115.18, -152.51, -152.56.

HRMS (EI): *m/z* calculated for C₃₃H₂₇FNO₂ (M-BF₄)⁺: 488.2020, found 488.2021.



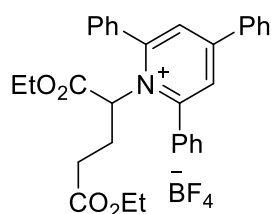
1-(1-methoxy-3-(4-nitrophenyl)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1g**), recrystallized from EtOH/Et₂O (v/v 1:4), brown solid, 74% yield.

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.95 (s, 2H), 7.88 – 7.59 (m, 10H), 7.57 – 7.47 (m, 7H), 7.02 (d, *J* = 8.4 Hz, 2H), 5.59 (d, *J* = 8.8 Hz, 1H), 3.73 – 3.69 (m, 1H), 3.69 (s, 3H), 2.92 (dd, *J* = 14.4, 9.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 167.5, 157.2, 156.5, 146.8, 144.6, 133.7, 132.4, 132.1, 131.7, 130.1, 129.6, 129.2, 128.4, 127.8, 123.5, 69.1, 53.9, 37.4.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -152.23, -152.28.

HRMS (EI): *m/z* calculated for C₃₃H₂₇N₂O₄ (M-BF₄)⁺: 515.1965, found 515.1969.



1i

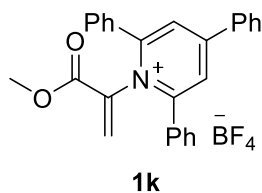
1-(1,5-diethoxy-1,5-dioxopent-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1i**), recrystallized from EtOH/Et₂O (v/v 1:4), white solid, 82% yield.

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.95 (s, 2H), 7.85 – 7.74 (m, 4H), 7.67 – 7.49 (m, 11H), 5.61 – 5.60 (m, 1H), 4.22 – 4.10 (m, 2H), 3.91 (q, *J* = 7.2 Hz, 2H), 2.26 – 2.19 (m, 2H), 2.04 – 1.96 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 171.6, 168.0, 157.0, 156.9, 133.7, 132.4, 132.4, 131.4, 129.6, 129.2, 128.5, 127.9, 67.8, 63.5, 60.6, 31.0, 26.8, 13.9, 13.7.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -153.04, -153.09.

HRMS (EI): *m/z* calculated for C₃₂H₃₂NO₄ (M-BF₄)⁺: 494.2326, found 494.2328.



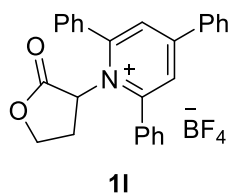
1-(3-methoxy-3-oxoprop-1-en-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1k**), purified by flash chromatography on silica gel (dichloromethane/acetone = 80:1), yellow solid, 70% yield.

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.99 (s, 2H), 7.84 – 7.83 (m, 2H), 7.56 – 7.45 (m, 13H), 6.64 (s, 1H), 6.45 (s, 1H), 3.60 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 161.8, 158.3, 156.4, 136.5, 134.2, 134.0, 132.3, 132.2, 130.8, 129.7, 129.5, 128.8, 128.4, 126.0, 53.4.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -152.94, -152.99.

HRMS (EI): *m/z* calculated for C₂₇H₂₂NO₂ (M-BF₄)⁺: 392.1645, found 392.1647.



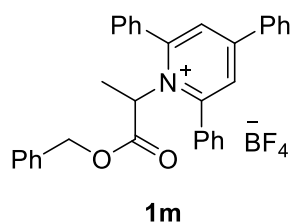
1-(1-carboxy-3-hydroxypropyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1l**), purified by flash chromatography on silica gel (dichloromethane/acetone = 70:1), yellow solid, 77% yield.

¹H NMR (400 MHz, CDCl₃): δ (ppm): 8.09 – 8.03 (m, 3H), 7.91 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.71 – 7.49 (m, 11H), 5.66 (dd, *J* = 11.2, 9.2 Hz, 1H), 3.98 (q, *J* = 8.4 Hz, 1H), 3.38 – 3.32 (m, 1H), 3.03 – 2.93 (m, 1H), 2.78 – 2.68 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 172.1, 159.2, 157.1, 156.2, 133.6, 132.8, 132.6, 131.8, 131.6, 131.4, 131.3, 130.3, 130.1, 129.9, 129.7, 129.6, 129.2, 128.8, 128.7, 128.4, 126.8, 66.6, 63.6, 27.3.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -152.84, -152.89.

HRMS (EI): m/z calculated for C₂₇H₂₂NO₂ (M-BF₄)⁺: 392.1645, found 392.1646.



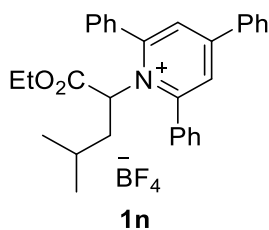
1-(1-(benzyloxy)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1m**), recrystallized from EtOH/Et₂O (v/v 1:4), white solid, 80% yield.

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.89 (s, 2H), 7.79 (d, J = 7.6 Hz, 2H), 7.67 – 7.35 (m, 16H), 7.22 (d, J = 6.0 Hz, 2H), 5.58 (q, J = 7.2 Hz, 1H), 5.15 (d, J = 12.0 Hz, 1H), 5.06 (d, J = 12.0 Hz, 1H), 1.42 (d, J = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 168.7, 156.9, 156.7, 133.9, 132.7, 132.2, 131.2, 129.6, 129.0, 128.8, 128.7, 128.43, 128.36, 127.7, 127.5, 126.9, 68.7, 64.8, 16.9.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -153.10, -153.16.

HRMS (EI): m/z calculated for C₃₃H₂₈NO₂ (M-BF₄)⁺: 470.2115, found 470.2116.



1-(1-ethoxy-4-methyl-1-oxopentan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1n**), recrystallized from EtOH/Et₂O (v/v 1:4), white solid, 81% yield.

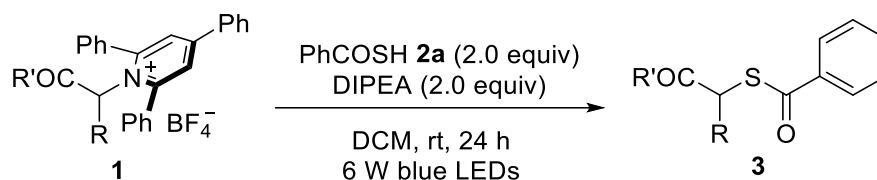
¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.93 (s, 2H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.73 – 7.49 (m, 13H), 5.45 (d, *J* = 5.2 Hz, 1H), 4.18 (dd, *J* = 12.4, 6.4 Hz, 2H), 1.78 – 1.76 (m, 1H), 1.51 – 1.44 (m, 1H), 1.37 – 1.29 (m, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.58 (d, *J* = 6.4 Hz, 3H), 0.46 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 168.9, 156.8, 156.7, 133.8, 133.8, 132.7, 132.2, 131.4, 129.6, 129.0, 128.5, 128.0, 67.7, 63.3, 40.2, 26.3, 22.3, 20.7, 13.8.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -152.98, -153.00, -153.03, -153.05.

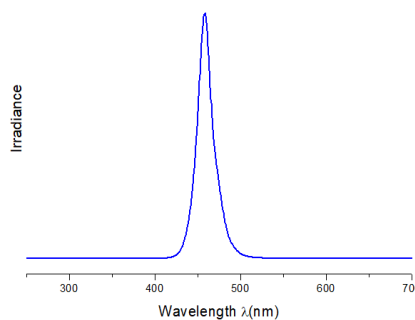
HRMS (EI): *m/z* calculated for C₃₁H₃₂NO₂ (M-BF₄)⁺: 450.2428, found 450.2429.

3. General Procedure for the Photoinduced Deaminative Thioesterification

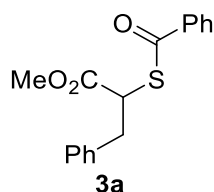


A mixture of amino acid Katritzky salts **1** (0.20 mmol), thiobenzoic acid **2a** (0.40 mmol), DIPEA (0.40 mmol) and DCM (2.0 mL) was stirred at room temperature with 6 W Blue LEDs for 24 h. After quenching the reaction, the mixture was purified by flash chromatography on silica gel to give the products **3**.

Reaction Setup: Reactions were conducted in a 6 W photo-reactor (Model: H106062, GEAO CHEMICAL, Wuhan, China) as shown below. One place/hole with three 1W blue LED beads ($\lambda_{\text{max}} = 458 \text{ nm}$) on both side, and the distance between the Schlenk tube and LED beads is ca. 2 cm.



Methyl 2-(benzoylthio)-3-phenylpropanoate (3a)



Prepared according to the general procedure using 1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (114.4 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 to 10:1) delivered **3a** as a liquid in 96% yield (57.6 mg).

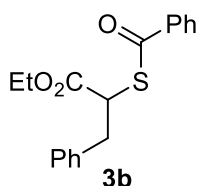
Asymmetric induction was investigated with enantiomerically pure amino ester-derived Katritzky salt **1a** under the standard conditions. The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-H column (*n*-hexane/2-propanol 95:5, 1 mL/min), UV 254 nm, t_r = 4.36 min and 4.69 min (1.3% ee). Reaction was also performed in toluene, and the enantiomeric excess was determined to be 2%.

^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.92 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.32 – 7.21 (m, 5H), 4.65 (t, J = 7.6 Hz, 1H), 3.68 (s, 3H), 3.34 (dd, J = 14.0, 8.4 Hz, 1H), 3.14 (dd, J = 14.0, 8.4 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 189.7, 171.6, 137.2, 136.1, 133.8, 129.1, 128.7, 128.5, 127.4, 127.1, 52.6, 47.1, 38.1.

HRMS (EI): m/z calculated for $\text{C}_{17}\text{H}_{16}\text{O}_3\text{S}+\text{H}^+$: 301.0893, found 301.0887.

Ethyl 2-(benzoylthio)-3-phenylpropanoate (3b)



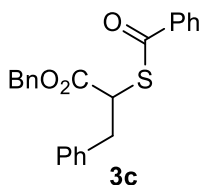
Prepared according to the general procedure using 1-(1-ethoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (114.2 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 to 10:1) delivered **3b** as a liquid in 94% yield (59.0 mg).

^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.91 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H), 7.29 – 7.21 (m, 5H), 4.61 (t, J = 7.2 Hz, 1H), 4.12 (q, J = 7.2 Hz, 2H), 3.31 (dd, J = 13.6, 9.2 Hz, 1H), 3.13 (dd, J = 13.6, 6.4 Hz, 1H), 1.15 (t, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 189.8, 171.0, 137.3, 136.3, 133.7, 129.2, 128.7, 128.4, 127.4, 127.0, 61.7, 47.4, 38.2, 14.0.

HRMS (EI): m/z calculated for $\text{C}_{18}\text{H}_{18}\text{O}_3\text{S}+\text{H}^+$: 315.1049, found 315.1042.

Benzyl 2-(benzoylthio)-3-phenylpropanoate (3c)



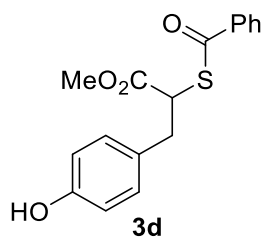
Prepared according to the general procedure using 1-(1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (126.6 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 12:1 to 10:1) delivered **3c** as a liquid in 86% yield (64.6 mg).

^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.91 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.28 – 7.21 (m, 10H), 5.11 (s, 2H), 4.69 (t, J = 8.0 Hz, 1H), 3.33 (dd, J = 13.6, 8.8 Hz, 1H), 3.16 (dd, J = 14.0, 6.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 189.7, 170.9, 137.1, 136.2, 135.3, 133.7, 129.2, 128.7, 128.5, 128.4, 128.2, 128.1, 127.4, 127.0, 67.3, 47.4, 38.2.

HRMS (EI): *m/z* calculated for C₂₃H₂₀O₃S+H⁺: 377.1211, found 377.1201.

Methyl 2-(benzoylthio)-3-(4-hydroxyphenyl)propanoate (3d)



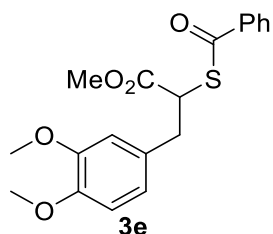
Prepared according to the general procedure using 1-(3-(4-hydroxyphenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (114.6 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μl, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μl, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1 to 4:1) delivered **3d** as a liquid in 89% yield (56.2 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.93 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.76 (d, *J* = 7.2 Hz, 2H), 4.61 (t, *J* = 7.6 Hz, 1H), 3.69 (s, 3H), 3.26 (dd, *J* = 14.0, 8.8 Hz, 1H), 3.08 (dd, *J* = 14.0, 6.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 190.1, 171.9, 154.8, 136.1, 133.8, 130.3, 129.2, 128.7, 127.4, 115.4, 52.7, 47.4, 37.3.

HRMS (EI): *m/z* calculated for C₁₇H₁₆O₄S+Na⁺: 339.0662, found 339.0654.

Methyl 2-(benzoylthio)-3-(3,4-dimethoxyphenyl)propanoate (3e)



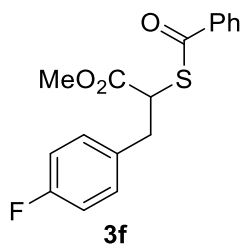
Prepared according to the general procedure using 1-(3-(3,4-dimethoxyphenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (123.4 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1 to 4:1) delivered **3e** as a liquid in 99% yield (71.3 mg).

^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.92 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.82 – 6.77 (m, 3H), 4.63 (t, J = 8.0 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.70 (s, 3H), 3.29 (dd, J = 14.0, 8.4 Hz, 1H), 3.09 (dd, J = 14.0, 6.8 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 189.8, 171.7, 148.8, 148.0, 136.1, 133.8, 129.7, 128.7, 127.3, 121.2, 112.1, 111.0, 55.8, 55.8, 52.6, 47.2, 37.8.

HRMS (EI): m/z calculated for $\text{C}_{19}\text{H}_{20}\text{O}_5\text{S}+\text{H}^+$: 361.1100, found 361.1098.

Methyl 2-(benzoylthio)-3-(4-fluorophenyl)propanoate (3f)



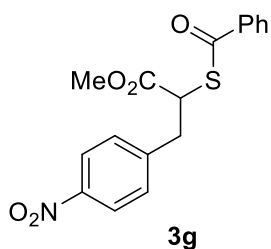
Prepared according to the general procedure using 1-(3-(4-fluorophenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (115.0 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 12:1 to 10:1) delivered **3f** as a liquid in 76% yield (48.4 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.92 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.25 – 7.22 (m, 2H), 6.98 (t, J = 8.8 Hz, 2H), 4.61 (t, J = 7.6 Hz, 1H), 3.69 (s, 3H), 3.31 (dd, J = 14.0, 8.4 Hz, 1H), 3.11 (dd, J = 14.0, 7.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 189.6, 171.4, 161.9 (d, J = 243.7 Hz, 1C), 136.1, 133.9, 132.9 (d, J = 3.2 Hz, 1C), 130.7 (d, J = 8.0 Hz, 1C), 128.7, 127.4, 115.3 (d, J = 21.2 Hz, 1C), 52.7, 47.0, 37.4.

HRMS (EI): m/z calculated for C₁₇H₁₅FO₃S+H⁺: 319.0799, found 319.0792.

Methyl 2-(benzoylthio)-3-(4-nitrophenyl)propanoate (3g)



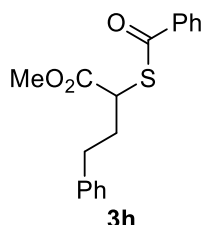
Prepared according to the general procedure using 1-(1-methoxy-3-(4-nitrophenyl)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (120.4 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) delivered **3g** as a liquid in 47% yield (32.4 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 8.16 (d, J = 7.2 Hz, 2H), 7.91 (d, J = 7.2 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.47 – 7.46 (m, 4H), 4.69 (t, J = 7.2 Hz, 1H), 3.71 (s, 3H), 3.46 (dd, J = 13.6, 8.8 Hz, 1H), 3.24 (dd, J = 13.6, 6.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 189.1, 171.0, 147.1, 145.0, 135.9, 134.1, 130.2, 128.8, 127.4, 123.7, 52.9, 46.2, 38.0.

HRMS (EI): m/z calculated for C₁₇H₁₅NO₅S+Na⁺: 368.0563, found 368.0558.

Methyl 2-(benzoylthio)-4-phenylbutanoate (3h)



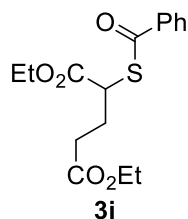
Prepared according to the general procedure using 1-(1-methoxy-1-oxo-4-phenylbutan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (114.2 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) delivered **3h** as a liquid in 75% yield (47.0 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.96 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.2 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.20 – 7.18 (m, 3H), 4.44 (t, J = 6.9 Hz, 1H), 3.74 (s, 3H), 2.83 – 2.69 (m, 2H), 2.40 – 2.31 (m, 1H), 2.23 – 2.11 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 189.8, 172.0, 140.4, 136.2, 133.8, 128.7, 128.5, 128.4, 127.4, 126.2, 52.7, 45.4, 33.5, 33.3.

HRMS (EI): *m/z* calculated for C₁₈H₁₈O₃S+H⁺: 315.1049, found 315.1041.

Diethyl 2-(benzoylthio)pentanedioate (3i)



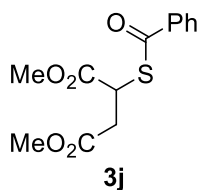
Prepared according to the general procedure using 1-(1,5-diethoxy-1,5-dioxopentan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (116.2 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μl, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μl, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) delivered **3i** as a liquid in 80% yield (51.8 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.95 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 4.46 (t, *J* = 6.4 Hz, 1H), 4.22 (q, *J* = 6.4 Hz, 2H), 4.14 (q, *J* = 6.4 Hz, 2H), 2.50 – 2.46 (m, 2H), 2.42 – 2.35 (m, 1H), 2.24 – 2.15 (m, 1H), 1.30 – 1.24 (m, 6H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 189.6, 172.2, 171.1, 136.2, 133.8, 128.7, 127.4, 61.8, 60.6, 45.2, 31.6, 27.2, 14.2, 14.1.

HRMS (EI): *m/z* calculated for C₁₆H₂₀O₅S+H⁺: 325.1100, found 325.1095.

Dimethyl 2-(benzoylthio)succinate (3j)



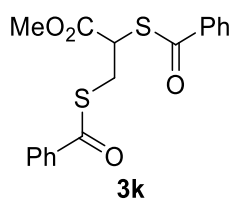
Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) delivered **3j** as a liquid in 70% yield (39.5 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.95 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 4.80 – 4.77 (m, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.11 (dd, J = 16.8, 7.6 Hz, 1H), 2.98 (dd, J = 17.2, 5.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 189.2, 170.9, 170.9, 135.9, 134.0, 128.8, 127.5, 53.1, 52.1, 40.8, 36.7.

HRMS (EI): m/z calculated for C₁₃H₁₄O₅S+H⁺: 283.0635, found 283.0629.

Methyl 2,3-bis(benzoylthio)propanoate (3k)



Prepared according to the general procedure using 1-(3-methoxy-3-oxoprop-1-en-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (95.8 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (93.6 μ l, 0.80 mmol, 4.0 equiv) and DIPEA (128.0 μ l, 0.80 mmol, 4.0 equiv). After quenching the reaction, purification of

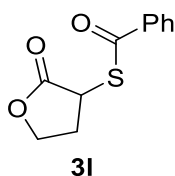
the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 5:1) delivered **3k** as a liquid in 58% yield (41.8 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.97 – 7.96 (m, 4H), 7.62 – 7.56 (m, 2H), 7.48 – 7.43 (m, 4H), 4.72 (t, J = 7.2 Hz, 1H), 3.79 (s, 3H), 3.72 (dd, J = 13.6, 8.0 Hz, 1H), 3.63 (dd, J = 13.6, 6.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 190.4, 188.8, 170.7, 136.5, 135.9, 134.0, 133.6, 128.8, 128.6, 127.6, 127.4, 53.0, 45.2, 30.5.

HRMS (EI): m/z calculated for C₁₈H₁₆O₄S₂+Na⁺: 383.0382, found 383.0379.

Methyl 2-(benzoylthio)-4-hydroxybutanoate (3l)



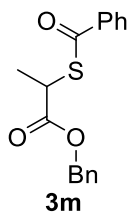
Prepared according to the general procedure using 1-(4-hydroxy-1-methoxy-1-oxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (102.2 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 5:1) delivered **3l** as a liquid in 54% yield (23.8 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.95 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 4.57 – 4.52 (m, 1H), 4.47 – 4.37 (m, 2H), 2.91 – 2.83 (m, 1H), 2.46 – 2.36 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 189.5, 174.5, 135.7, 134.2, 128.8, 127.5, 66.8, 40.2, 30.5.

HRMS (EI): m/z calculated for C₁₁H₁₀O₃S+Na⁺: 245.0243, found 245.0241.

Benzyl 2-(benzoylthio)propanoate (3m)



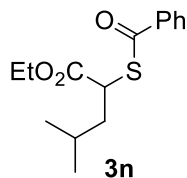
Prepared according to the general procedure using 1-(1-(benzyloxy)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (101.4 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 8:1) delivered **3m** as a liquid in 74% yield (44.4 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.94 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 7.35 – 7.33 (m, 5H), 5.21 (s, 2H), 4.50 (q, J = 6.8 Hz, 1H), 1.63 (d, J = 6.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 190.0, 171.9, 136.3, 135.5, 133.7, 128.7, 128.5, 128.2, 128.0, 127.3, 67.3, 41.0, 17.7.

HRMS (EI): m/z calculated for C₁₇H₁₆O₃S+Na⁺: 323.0712, found 323.0704.

Ethyl 2-(benzoylthio)-4-methylpentanoate (3n)



Prepared according to the general procedure using 1-(1-ethoxy-4-methyl-1-oxopentan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (107.4 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification

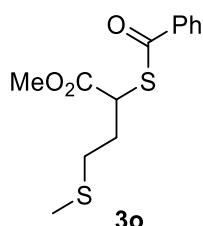
of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 12:1) delivered **3n** as a liquid in 82% yield (46.0 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.96 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.43 (t, *J* = 7.6 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.96 – 1.89 (m, 1H), 1.79 – 1.67 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.00 (d, *J* = 6.0 Hz, 3H), 0.95 (d, *J* = 6.0 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 190.2, 172.1, 136.4, 133.7, 128.7, 127.4, 61.6, 44.5, 40.8, 26.3, 22.3, 22.3, 14.1.

HRMS (EI): *m/z* calculated for C₁₅H₂₀O₃S+H⁺: 281.1206, found 281.1201.

Methyl 2-(benzoylthio)-4-(methylthio)butanoate (3o)



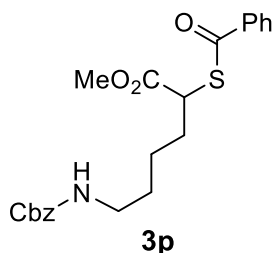
Prepared according to the general procedure using 1-(1-methoxy-4-(methylthio)-1-oxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (108.2 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μl, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μl, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) delivered **3o** as a liquid in 92% yield (52.2 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.96 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.57 (t, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 2.68 – 2.56 (m, 2H), 2.39 – 2.29 (m, 1H), 2.20 – 2.14 (m, 1H), 2.11 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 189.6, 171.76, 136.1, 133.8, 128.7, 127.4, 52.8, 44.6, 31.3, 31.3, 15.4.

HRMS (EI): *m/z* calculated for C₁₃H₁₆O₃S₂+Na⁺: 307.0433, found 307.0430.

Methyl 2-(benzoylthio)-6-(((benzyloxy)carbonyl)amino)hexanoate (3p)



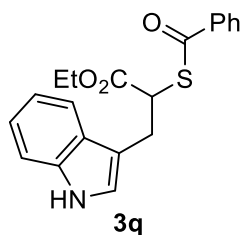
Prepared according to the general procedure using 1-(6-(((benzyloxy)carbonyl)amino)-1-methoxy-1-oxohexan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (134.4 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1 to 4:1) delivered **3p** as a liquid in 76% yield (63.0 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.95 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.34 – 7.31 (m, 5H), 5.08 (s, 2H), 4.80 (s, 1H), 4.41 (t, J = 6.8 Hz, 1H), 3.75 (s, 3H), 3.20 – 3.19 (m, 2H), 2.08 – 2.01 (m, 1H), 1.92 – 1.87 (m, 1H), 1.58 – 1.54 (m, 1H), 1.47 – 1.46 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 190.0, 172.0, 156.3, 136.6, 136.2, 133.8, 128.7, 128.5, 128.0, 127.4, 66.6, 52.7, 45.5, 40.7, 31.5, 29.4, 24.2.

HRMS (EI): m/z calculated for C₂₂H₂₅NO₅S+Na⁺: 438.1346, found 438.1338.

Ethyl 2-(benzoylthio)-3-(1H-indol-3-yl)propanoate (3q)



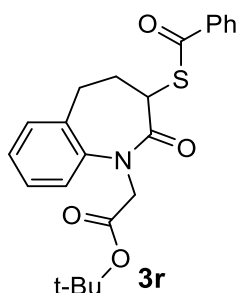
Prepared according to the general procedure using 1-(1-ethoxy-3-(1H-indol-3-yl)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (122.0 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1 to 4:1) delivered **3q** as a liquid in 58% yield (41.0 mg).

^1H NMR (400 MHz, CDCl_3): δ (ppm): 8.06 (s, 1H), 7.96 (d, J = 7.2 Hz, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.58 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 7.35 (d, J = 7.6 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.11 (s, 1H), 4.75 (t, J = 6.8 Hz, 1H), 4.12 (q, J = 6.8 Hz, 2H), 3.51 (dd, J = 14.4, 9.2 Hz, 1H), 3.35 (dd, J = 14.4, 6.4 Hz, 1H), 1.15 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 190.2, 171.5, 136.4, 136.0, 133.7, 128.7, 127.4, 127.3, 122.9, 122.1, 119.6, 118.9, 111.9, 111.1, 61.6, 46.9, 28.3, 13.9.

HRMS (EI): m/z calculated for $\text{C}_{20}\text{H}_{19}\text{NO}_3\text{S}+\text{H}^+$: 354.1158, found 354.1151.

tert-Butyl-2-(3-(benzoylthio)-2-oxo-2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)acetate (3r)



Prepared according to the general procedure using 1-(1-(2-(*tert*-butoxy)-2-oxoethyl)-2-oxo-2,3,4,5-tetrahydro-1H-benzo[b]azepin-3-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (133.6 mg, 0.20 mmol, 1.0 equiv), thiobenzoic acid (46.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column

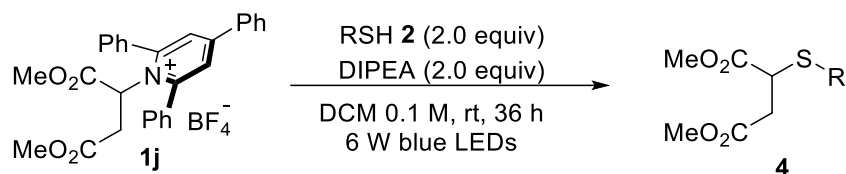
chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) delivered **3r** as a liquid in 49% yield (40.2 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.90 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.28 – 7.21 (m, 3H), 4.73 (d, J = 16.8 Hz, 1H), 4.51 – 4.46 (m, 1H), 4.25 (d, J = 17.2 Hz, 1H), 3.53 – 3.46 (m, 1H), 2.74 – 2.70 (m, 1H), 2.55 – 2.42 (m, 2H), 1.41 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 190.8, 170.0, 167.6, 141.5, 136.5, 135.3, 133.5, 129.7, 128.6, 128.1, 127.2, 127.1, 122.6, 82.0, 51.4, 45.8, 35.9, 29.7, 28.0.

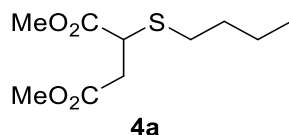
HRMS (EI): m/z calculated for C₂₃H₂₅NO₄S+H⁺: 412.1577, found 412.1576.

4. General Procedure for the Photoinduced Deaminative Thiolation



A mixture of asparagine amino acid Katritzky salts **1** (0.20 mmol), thiols **2** (0.40 mmol), DIPEA (0.40 mmol) and DCM (2.0 mL) was stirred at room temperature with 6 W Blue LEDs for 36 h. After quenching the reaction, the mixture was purified by flash chromatography on silica gel to give the products **4**.

Dimethyl 2-(butylthio)succinate (**4a**)



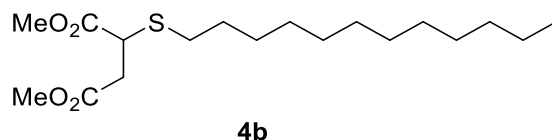
Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), butanethiol (43.2 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 12:1) delivered **4a** as a liquid in 80% yield (37.4 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 3.76 (s, 3H), 3.69 (s, 3H), 3.67 – 3.65 (m, 1H), 3.00 (dd, J =17.2, 10.0 Hz, 1H), 2.70 – 2.59 (m, 3H), 1.59 – 1.50 (m, 2H), 1.43 – 1.34 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 172.3, 171.2, 52.5, 52.0, 41.4, 36.3, 31.2 (2C), 21.9, 13.6.

HRMS (EI): m/z calculated for C₁₀H₁₈O₄S+Na⁺: 257.0818, found 257.0812.

Dimethyl 2-(dodecylthio)succinate (**4b**)



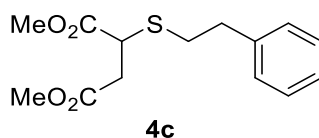
Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), dodecyl mercaptan (95.6 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 12:1) delivered **4b** as oil liquid in 85% yield (58.8 mg).

^1H NMR (400 MHz, CDCl_3): δ (ppm): 3.76 (s, 3H), 3.69 (s, 3H), 3.69 – 3.65 (m, 1H), 3.00 (dd, J = 17.2, 10.0 Hz, 1H), 2.71 – 2.58 (m, 3H), 1.58 – 1.50 (m, 2H), 1.35 – 1.25 (m, 18H), 0.87 (t, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 172.3, 171.2, 52.5, 52.0, 41.4, 36.4, 31.9, 31.5, 29.62, 29.60, 29.56, 29.5, 29.3, 29.17, 29.14, 28.8, 22.7, 14.1.

HRMS (EI): m/z calculated for $\text{C}_{18}\text{H}_{34}\text{O}_4\text{S}+\text{Na}^+$:369.2070, found 369.2071.

Dimethyl 2-(phenethylthio)succinate (4c)



Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), 2-phenylethanethiol (53.4 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 9:1) delivered **4c** as a liquid in 73% yield (41.2 mg).

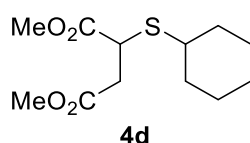
^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.30 (t, J = 7.2 Hz, 2H), 7.24 – 7.19 (m, 3H), 3.76 (s, 3H), 3.72 – 3.69 (m, 1H), 3.69 (s, 3H), 3.01 (dd, J = 16.8, 10.0 Hz, 1H), 2.96

– 2.84 (m, 4H), 2.67 (dd, $J = 17.2, 5.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 172.1, 171.1, 139.9, 128.5, 126.5, 52.5, 52.0, 41.5, 36.3, 35.7, 33.0.

HRMS (EI): m/z calculated for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{S}+\text{H}^+$: 283.0999, found 283.0994.

Dimethyl 2-(cyclohexylthio)succinate (4d)



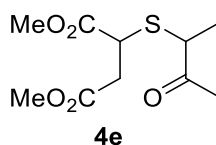
Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), cyclohexyl mercaptan (48.8 μl , 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μl , 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) delivered **4d** as a liquid in 81% yield (42.0 mg).

^1H NMR (400 MHz, CDCl_3): δ (ppm): 3.75 (s, 3H), 3.75 – 3.71 (m, 1H), 3.68 (s, 3H), 2.99 (dd, $J = 16.8, 10.0$ Hz, 1H), 2.93 – 2.81 (m, 1H), 2.66 (dd, $J = 16.8, 5.6$ Hz, 1H), 2.04 – 1.92 (m, 2H), 1.75 – 1.73 (m, 2H), 1.61 – 1.58 (m, 1H), 1.37 – 1.21 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 172.7, 171.2, 52.4, 52.0, 44.3, 40.3, 36.9, 33.6, 33.4, 26.0, 25.8, 25.6.

HRMS (EI): m/z calculated for $\text{C}_{12}\text{H}_{20}\text{O}_4\text{S}+\text{Na}^+$: 283.0975, found 283.0971.

Dimethyl 2-((3-oxobutan-2-yl)thio)succinate (4e)



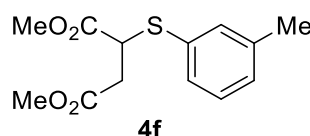
Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), 3-mercapto-2-butanone (40.0 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) delivered **4e** as a liquid in 58% yield (28.8 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 3.75 (s, 3H), 3.69 (s, 3H), 3.71 – 3.60 (m, 2H), 3.00 – 2.93 (m, 1H), 2.72 – 2.64 (m, 1H), 2.26 (s, 3H), 1.42 (d, J = 7.2 Hz, 1.5 H), 1.40 (d, J = 7.2 Hz, 1.5 H).

¹³C NMR (100 MHz, CDCl₃): 205.5 (205.3), 171.9 (171.8), 170.7 (170.6), 52.6 (52.1), 49.7 (48.8), 45.5, 41.5 (41.0), 36.7 (36.3), 26.1 (25.7), 16.7 (16.4).

HRMS (EI): m/z calculated for C₁₀H₁₆O₅S+Na⁺: 271.0611, found 271.0606.

Dimethyl 2-(*m*-tolylthio)succinate (4f)



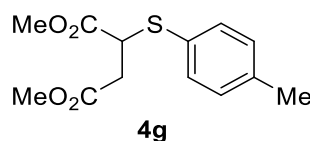
Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), 3-methylbenzenethiol (47.6 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 14:1) delivered **4f** as a liquid in 79% yield (42.4 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.28 (d, J = 7.2 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 4.03 – 3.99 (m, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 2.96 (dd, J = 16.8, 9.6 Hz, 1H), 2.74 (dd, J = 17.2, 5.6 Hz, 1H), 2.34 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): 171.6, 171.1, 138.9, 134.7, 131.3, 131.1, 129.6, 128.9, 52.5, 52.0, 45.6, 36.4, 21.2.

HRMS (EI): m/z calculated for C₁₃H₁₆O₄S+Na⁺: 291.0662, found 291.0656.

Dimethyl 2-(p-tolylthio)succinate (4g)



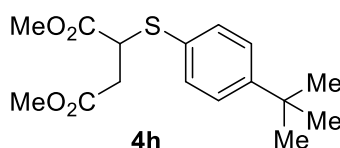
Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), *p*-toluenethiol (49.6 mg, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 14:1) delivered **4g** as a liquid in 81% yield (43.4 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.36 (d, J = 7.6 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 3.95 (dd, J = 9.6, 5.6 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 2.92 (dd, J = 17.2, 9.6 Hz, 1H), 2.72 (dd, J = 16.8, 5.6 Hz, 1H), 2.35 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 171.5, 171.1, 139.3, 134.8, 129.9, 127.6, 52.5, 52.0, 45.7, 36.3, 21.2.

HRMS (EI): m/z calculated for C₁₃H₁₆O₄S+H⁺: 269.0842, found 269.0838.

Dimethyl 2-((4-(tert-butyl)phenyl)thio)succinate (4h)



Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), 4-*tert*-butylthiophenol (68.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 14:1) delivered **4h** as a liquid in 74% yield (45.8 mg).

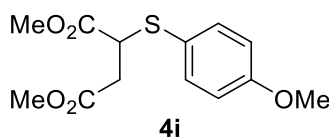
¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.40 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 7.2 Hz,

2H), 3.98 – 3.95 (m, 1H), 3.71 (s, 3H), 3.67 (s, 3H), 2.94 (dd, $J=16.8$, 9.6 Hz, 1H), 2.73 (dd, $J=17.2$, 5.2 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 171.6, 171.1, 152.3, 134.3, 127.8, 126.2, 52.5, 52.0, 45.7, 36.4, 34.7, 31.2.

HRMS (EI): m/z calculated for $\text{C}_{16}\text{H}_{22}\text{O}_4\text{S}+\text{Na}^+$: 333.1131, found 333.1127.

Dimethyl 2-((4-methoxyphenyl)thio)succinate (4i)



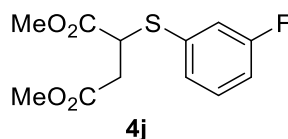
Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), 4-methoxybenzenethiol (49.2 μl , 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μl , 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) delivered **4i** as a liquid in 80% yield (45.4 mg).

^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.40 (d, $J=7.6$ Hz, 2H), 6.85 (d, $J=7.6$ Hz, 2H), 3.90 – 3.86 (m, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 2.89 (dd, $J=16.8$, 9.6 Hz, 1H), 2.70 (dd, $J=16.8$, 5.6 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 171.5, 171.1, 160.7, 137.1, 121.4, 114.6, 55.3, 52.4, 52.0, 46.0, 36.2.

HRMS (EI): m/z calculated for $\text{C}_{13}\text{H}_{16}\text{O}_5\text{S}+\text{Na}^+$: 307.0611, found 307.0606.

Dimethyl 2-((3-fluorophenyl)thio)succinate (4j)



Prepared according to the general procedure using

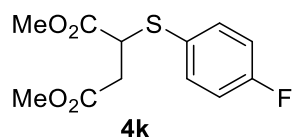
1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), 3-fluorothiophenol (33.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 14:1) delivered **4j** as a liquid in 62% yield (33.8 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.33 – 7.20 (m, 3H), 7.03 (t, J = 8.0 Hz, 1H), 4.07 – 4.03 (m, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 2.98 (dd, J = 17.2, 9.6 Hz, 1H), 2.76 (dd, J = 17.2, 5.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 171.3, 170.8, 162.50 (d, J = 247.9 Hz, 1C), 134.11 (d, J = 7.9 Hz, 1C), 130.33 (d, J = 8.3 Hz, 1C), 129.04 (d, J = 3.0 Hz, 1C), 120.20 (d, J = 22.1 Hz, 1C), 115.71 (d, J = 20.9 Hz, 1C), 52.6, 52.1, 45.5, 36.3.

HRMS (EI): m/z calculated for C₁₂H₁₃FO₄S+Na⁺: 295.0416, found 295.0408.

Dimethyl 2-((4-fluorophenyl)thio)succinate (4k)



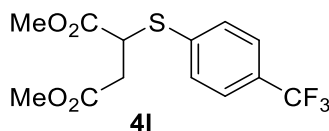
Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), 4-fluorothiophenol (42.6 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 14:1) delivered **4k** as a liquid in 58% yield (31.6 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.47 (t, J = 6.0 Hz, 2H), 7.03 (t, J = 8.0 Hz, 2H), 3.95 – 3.92 (m, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 2.92 (dd, J = 16.8, 9.6 Hz, 1H), 2.71 (dd, J = 16.8, 5.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 171.3, 170.9, 163.42 (d, J = 248.4 Hz, 1C), 137.01 (d, J = 8.4 Hz, 1C), 126.46 (d, J = 3.4 Hz, 1C), 116.27 (d, J = 21.8 Hz, 1C), 52.5, 52.1, 46.0, 36.2.

HRMS (EI): m/z calculated for $C_{12}H_{13}FO_4S+Na^+$: 295.0416, found 295.0408.

Dimethyl 2-((4-(trifluoromethyl)phenyl)thio)succinate (4I)



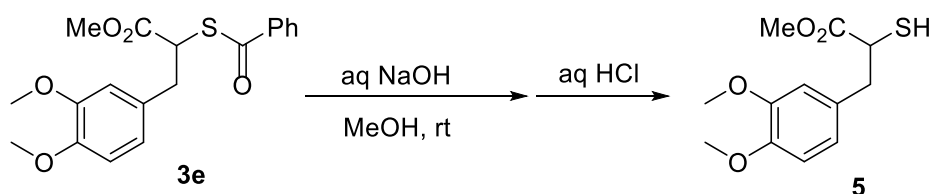
Prepared according to the general procedure using 1-(1,4-dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (107.8 mg, 0.20 mmol, 1.0 equiv), 4-(trifluoromethyl) thiophenol (54.8 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 12:1) delivered **4I** as a liquid in 91% yield (58.6 mg).

1H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.57 (s, 4H), 4.13 (dd, J = 9.2, 6.0 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.01 (dd, J = 17.2, 9.2 Hz, 1H), 2.77 (dd, J = 17.2, 6.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 171.2, 170.7, 132.4, 130.0, 128.8 (q, J = 270.4 Hz, 1C), 125.9 (q, J = 3.7 Hz, 1C), 52.8, 52.2, 45.0, 36.2.

HRMS (EI): m/z calculated for $C_{13}H_{13}F_3O_4S+H^+$: 323.0559, found 323.0554.

5. Scale-up Reaction and Deprotection to Free Thiol



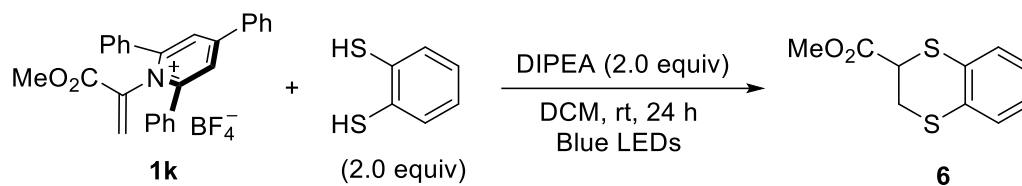
A scaled-up reaction was conducted with **1e** (2 mmol, 1.23 g) under the standard conditions. The isolated yield of **3e** was 99%. A mixture of the obtained product **3e**, aq. NaOH (1.0 M, 3 mL) and MeOH (30 mL) was degassed for three times and then stirred at room temperature under argon for 24 h. The reaction was then acidified with 15 mL of aq. HCl (0.2 M), extracted with degassed DCM, and washed with saturated sodium chloride solution. Concentration and further purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8:1 to 4:1) gave the products **5** in 93 % yield (474 mg).

¹H NMR (400 MHz, CDCl₃): δ (ppm): 6.79 - 6.77 (m, 1H), 6.73 - 6.70 (m, 2H), 3.84 (s, 6H), 3.68 (s, 3H), 3.59 – 3.53 (m, 1H), 3.17 (dd, J = 14.0, 8.8 Hz, 1H), 2.95 (dd, J = 14.0, 6.8 Hz, 1H), 2.10 (d, J = 8.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm): 173.2, 148.8, 148.0, 130.1, 121.1, 112.1, 111.1, 55.8 (2C), 52.4, 42.4, 41.4.

HRMS (EI): m/z calculated for C₁₂H₁₆O₄S+Na⁺: 279.0667, found 279.0667.

6. Tandem Reaction with Benzenedithiol



Prepared according to the general procedure using 1-(3-methoxy-3-oxoprop-1-en-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1k**, 95.8 mg, 0.20 mmol, 1.0 equiv), 1,2-benzenedithiol (46.0 μ l, 0.40 mmol, 2.0 equiv) and DIPEA (64.0 μ l, 0.40 mmol, 2.0 equiv). After quenching the reaction, purification of the crude product via column chromatography on silica gel (petroleum ether/ethyl acetate = 12:1) delivered **6** as a solid in 54% yield (24.4 mg).

^1H NMR (400 MHz, CDCl_3): δ (ppm): 7.33 – 7.26 (m, 2H), 7.09 – 7.07 (m, 2H), 4.33 (t, J = 6.0 Hz, 1H), 3.79 (s, 3H), 3.33 (d, J = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm): 170.1, 133.1, 131.7, 129.4, 129.0, 126.2, 125.9, 53.0, 46.8, 31.3.

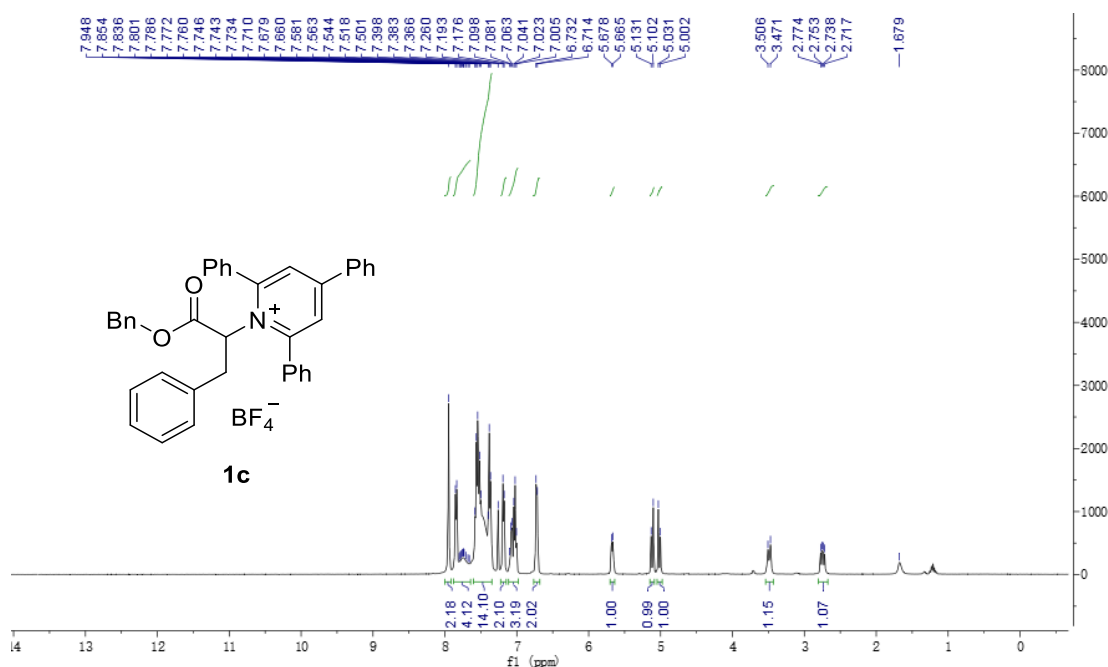
HRMS (EI): m/z calculated for $\text{C}_{10}\text{H}_{10}\text{O}_2\text{S}_2+\text{Na}^+$: 249.0020, found 249.0014.

7. References

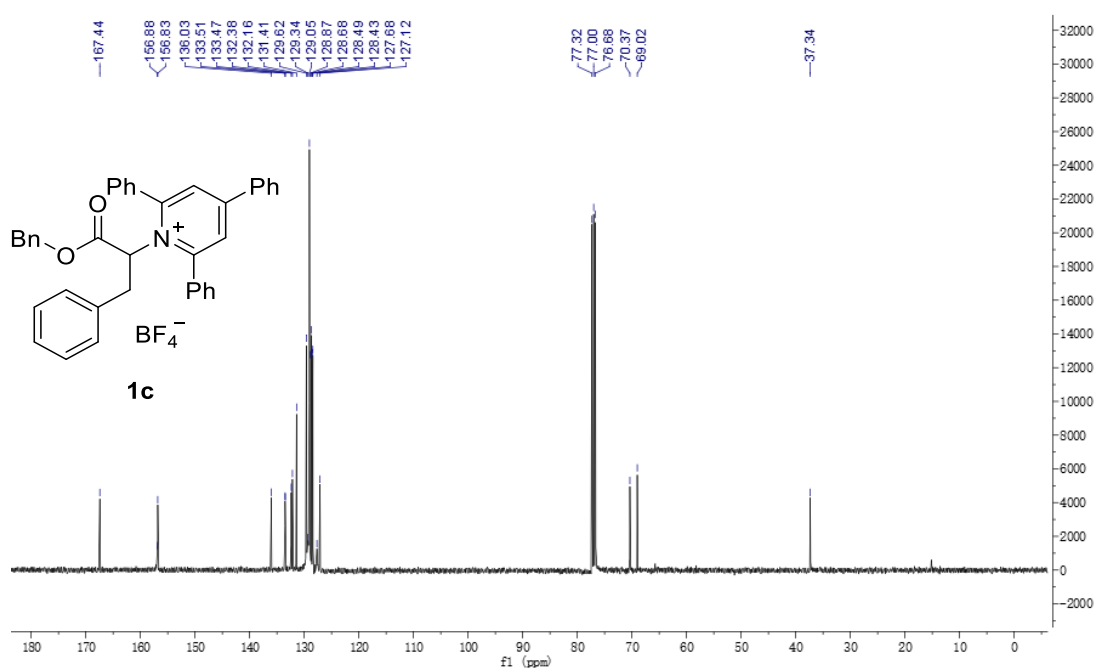
- (1) Klauck, F. J. R.; James, M. J.; Glorius, F. Deaminative Strategy for the Visible-Light-Mediated Generation of Alkyl Radicals. *Angew. Chem., Int. Ed.* **2017**, *56*, 12336-12339.
- (2) James, M. J.; Strieth-Kalthoff, F.; Sandfort, F.; Klauck, F. J. R.; Wagener, F.; Glorius, F. Visible-Light-Mediated Charge Transfer Enables C–C Bond Formation with Traceless Acceptor Groups. *Chem. Eur. J.* **2019**, *25*, 8240-8244.
- (3) Jiang, X.; Zhang, M.-M.; Xiong, W.; Lu, L.-Q.; Xiao, W.-J. Deaminative (Carbonylative) Alkyl-Heck-type Reactions Enabled by Photocatalytic C–N Bond Activation. *Angew. Chem., Int. Ed.* **2019**, *58*, 2402-2406.
- (4) Zhang, M.-M.; Liu, F. Visible-Light-Mediated Allylation of Alkyl Radicals with Allylic Sulfones via a Deaminative Strategy. *Org. Chem. Front.* **2018**, *5*, 3443-3446.

8. NMR Spectra

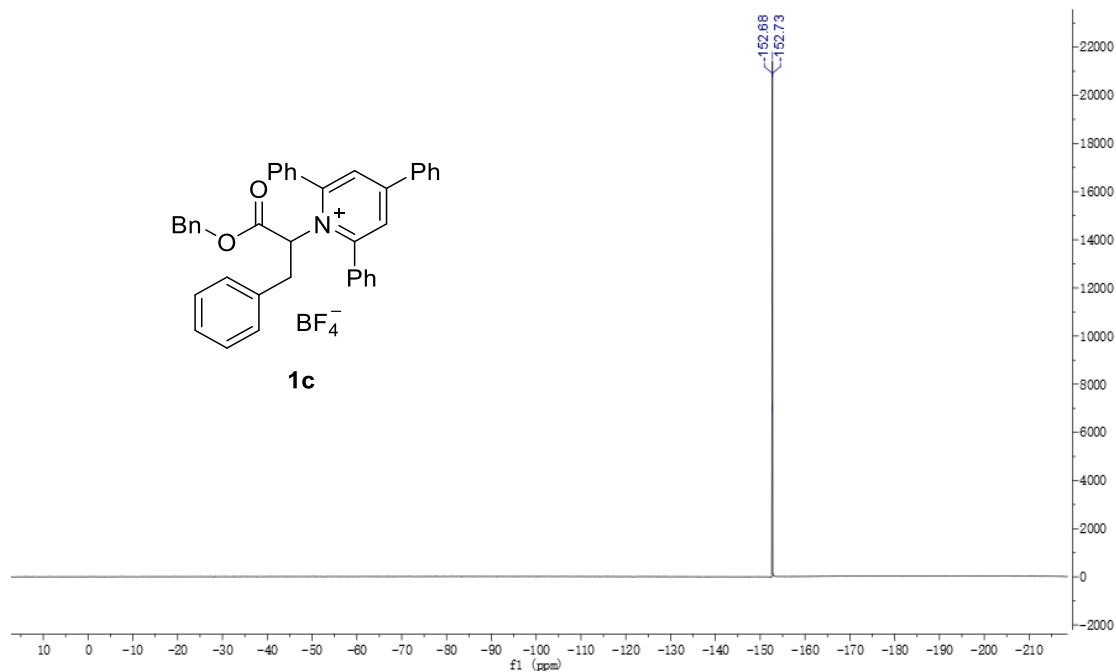
^1H NMR (400 MHz, CDCl_3) spectrum of product **1c**



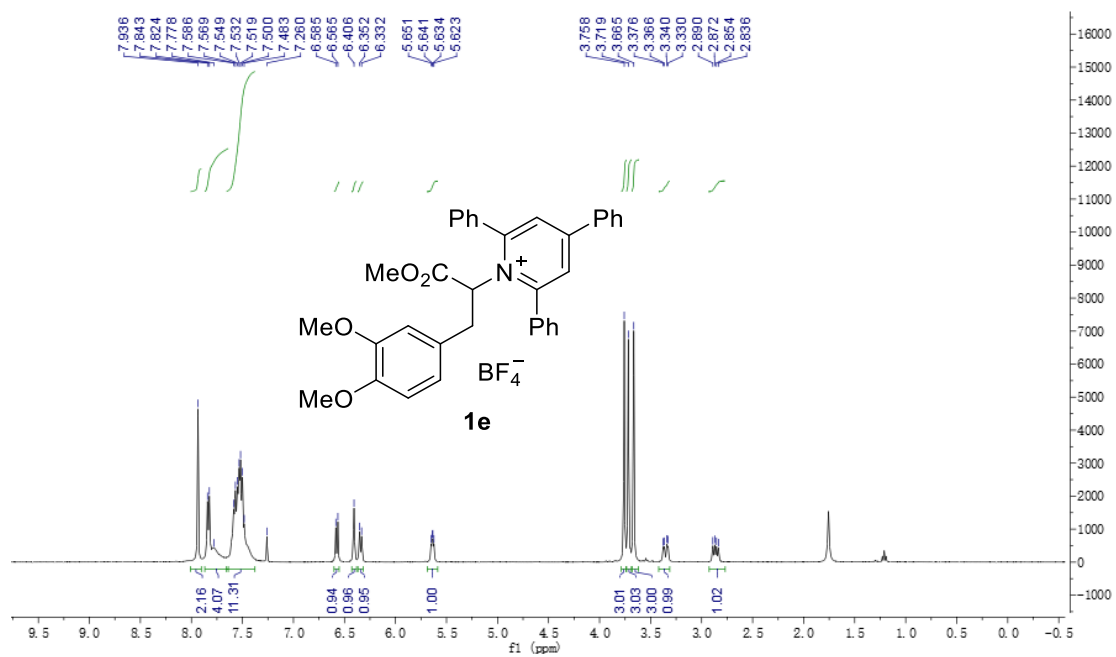
^{13}C NMR (100 MHz, CDCl_3) spectrum of product **1c**



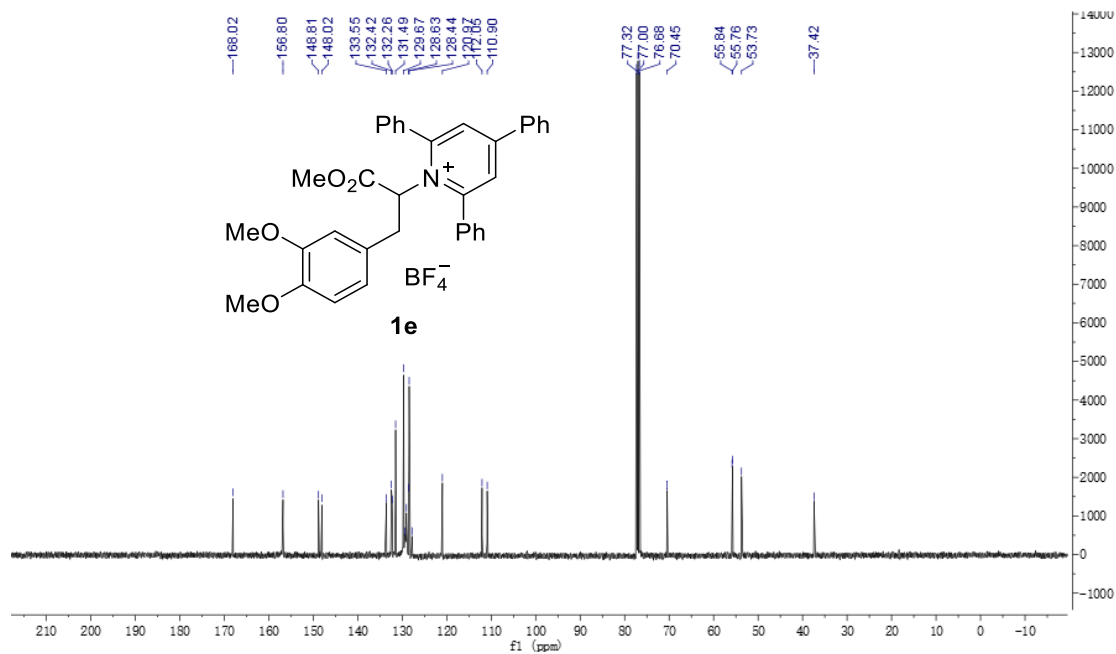
^{19}F NMR (376 MHz, CDCl_3) spectrum of product 1c



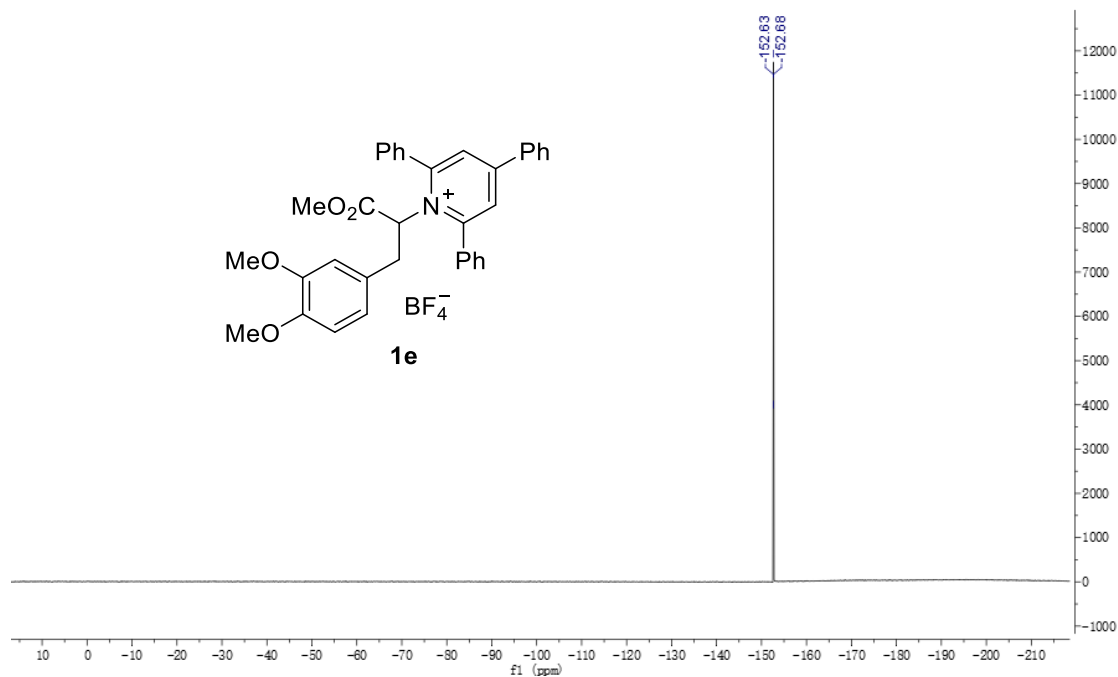
^1H NMR (400 MHz, CDCl_3) spectrum of product 1e



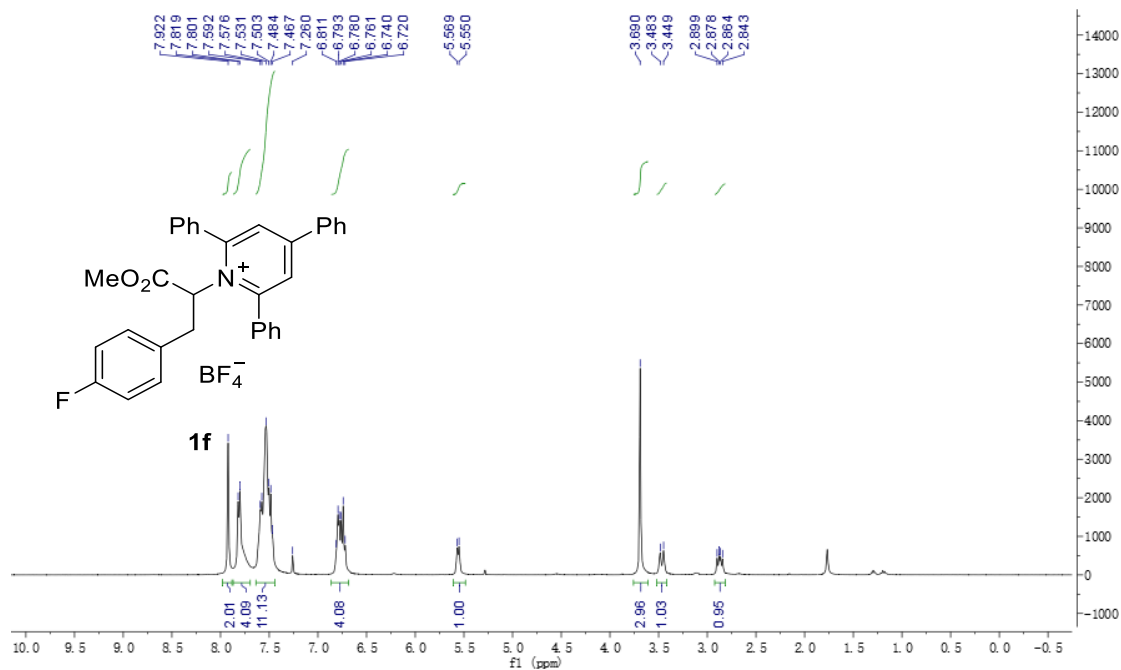
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 1e



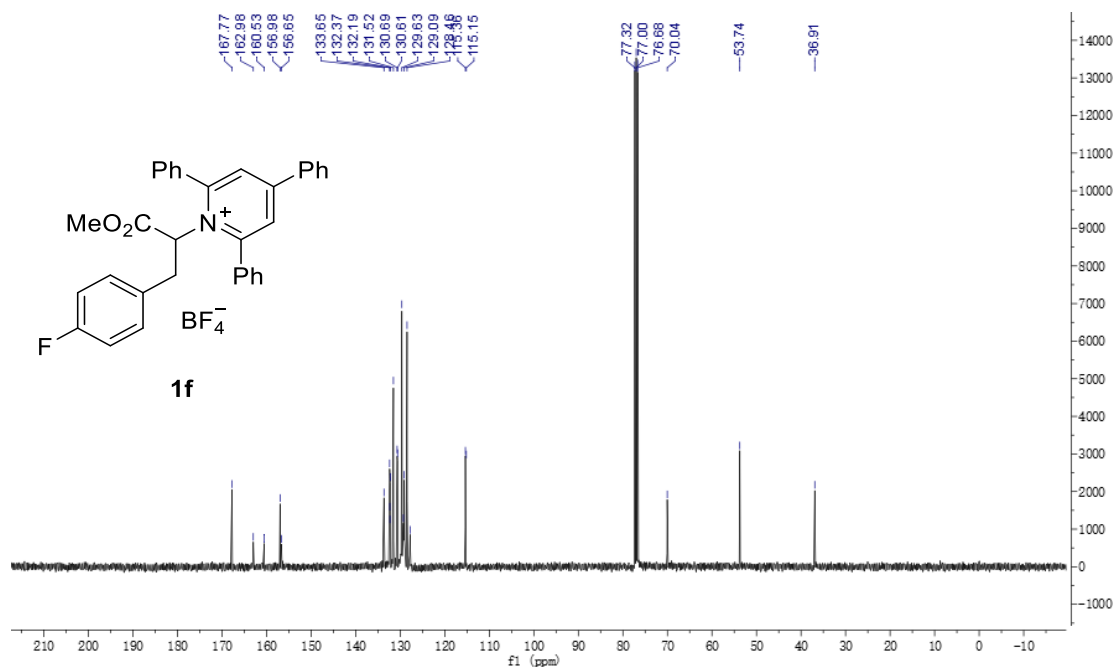
^{19}F NMR (376 MHz, CDCl_3) spectrum of product 1e



¹H NMR (400 MHz, CDCl₃) spectrum of product 1f



¹³C NMR (100 MHz, CDCl₃) spectrum of product 1f



1f

Chemical structure of **1f** is shown. The structure is a 4-fluorophenyl group attached to a 2-(4,6-diphenyl-1,3,5-triazol-2-yl)ethyl ester. The spectrum shows peaks at 152.51, 152.56, and 115.18 ppm.

1g

Chemical structure of **1g** is shown as an inset. It is a 4-nitrobenzyl 2,4,6-phenyl-1,1-diphenyl-1H-imidazol-3-ylidene-1-carboxylate salt, with a BF_4^- counterion.

^1H NMR spectrum (CDCl_3) of **1g**. The x-axis represents the chemical shift in ppm (δ), ranging from 10.0 to -0.5. The y-axis represents the intensity in arbitrary units, ranging from -1000 to 16000. The spectrum shows several peaks corresponding to the structure of **1g**.

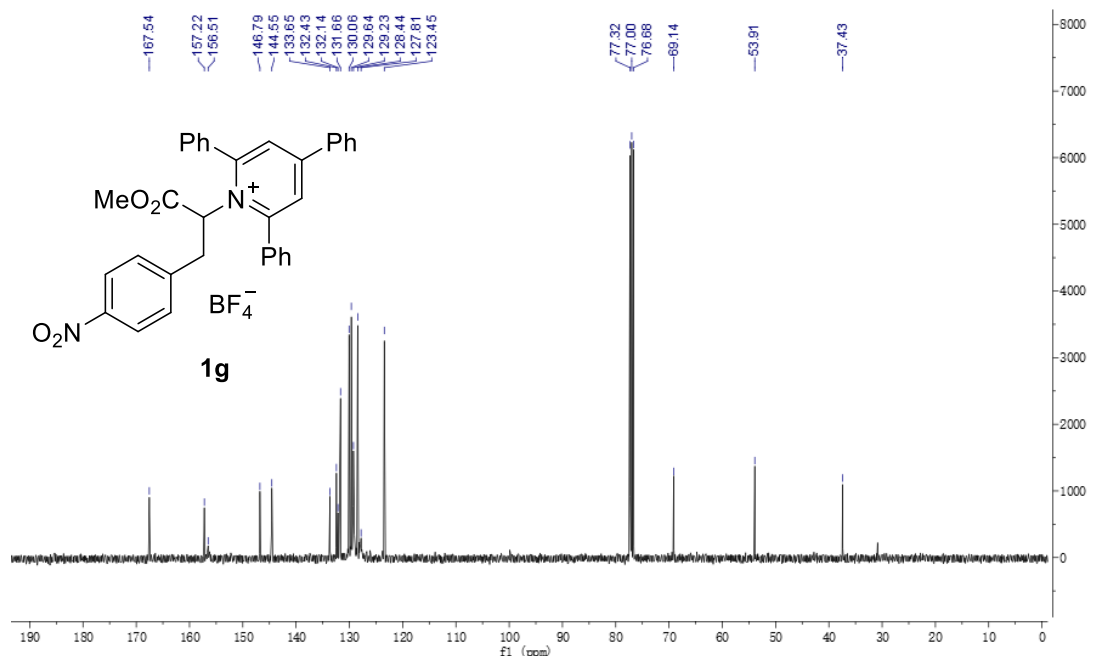
Key peaks and integrations:

- Aromatic protons (7.0-8.0 ppm): Integration values of 2.15, 10.02, 7.26, and 1.99 are shown below the peaks.
- Methoxy protons (3.7-3.9 ppm): Integration values of 0.93 and 3.19 are shown below the peaks.
- Methyl protons (2.9 ppm): Integration value of 0.93 is shown below the peak.

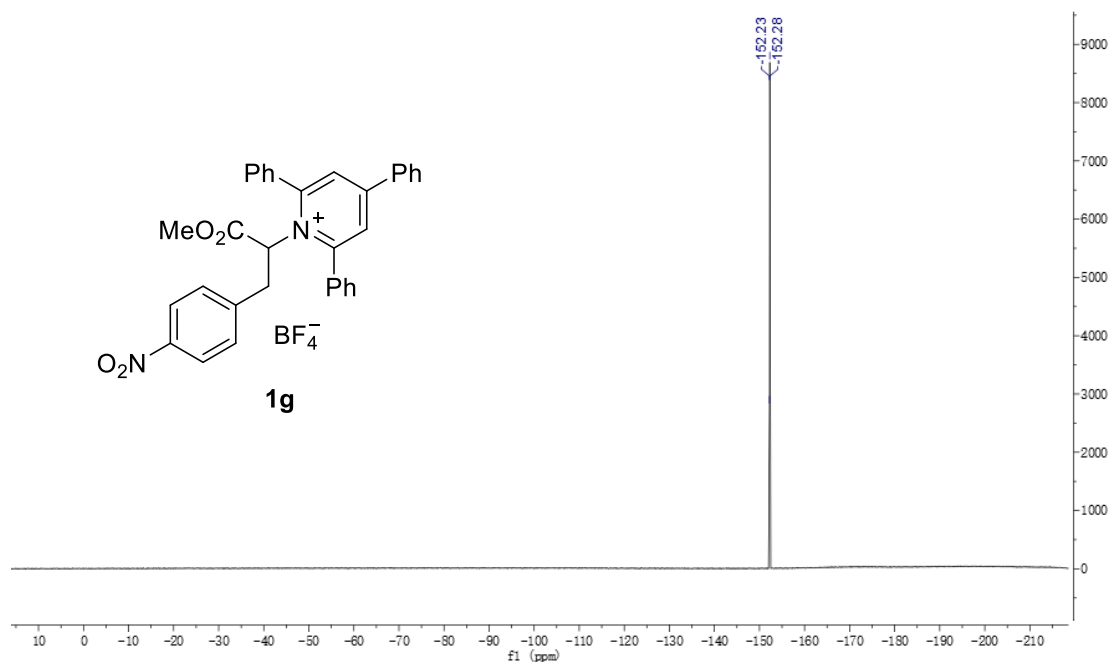
Chemical shift values (ppm) are listed above the peaks:

- 7.953, 7.880, 7.860, 7.819, 7.800, 7.593, 7.611, 7.588, 7.550, 7.533, 7.506, 7.488, 7.470, 7.260, 7.030, 7.009
- 5.597, 5.575
- 3.726, 3.694
- 2.964, 2.931, 2.918, 2.896

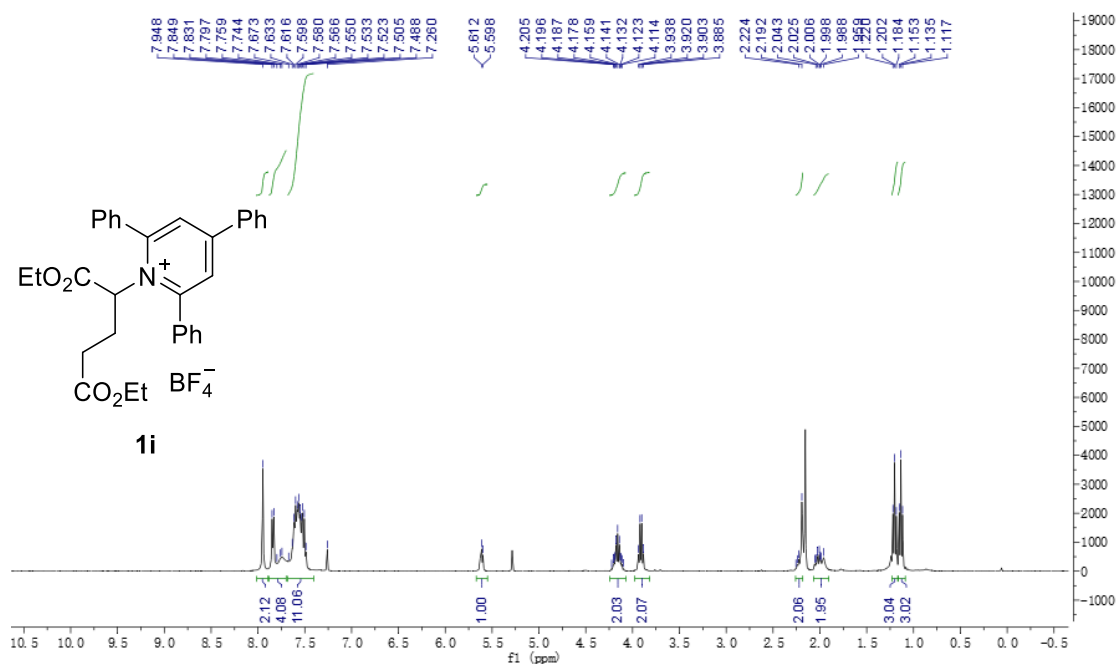
^{13}C NMR (100 MHz, CDCl_3) spectrum of product **1g**



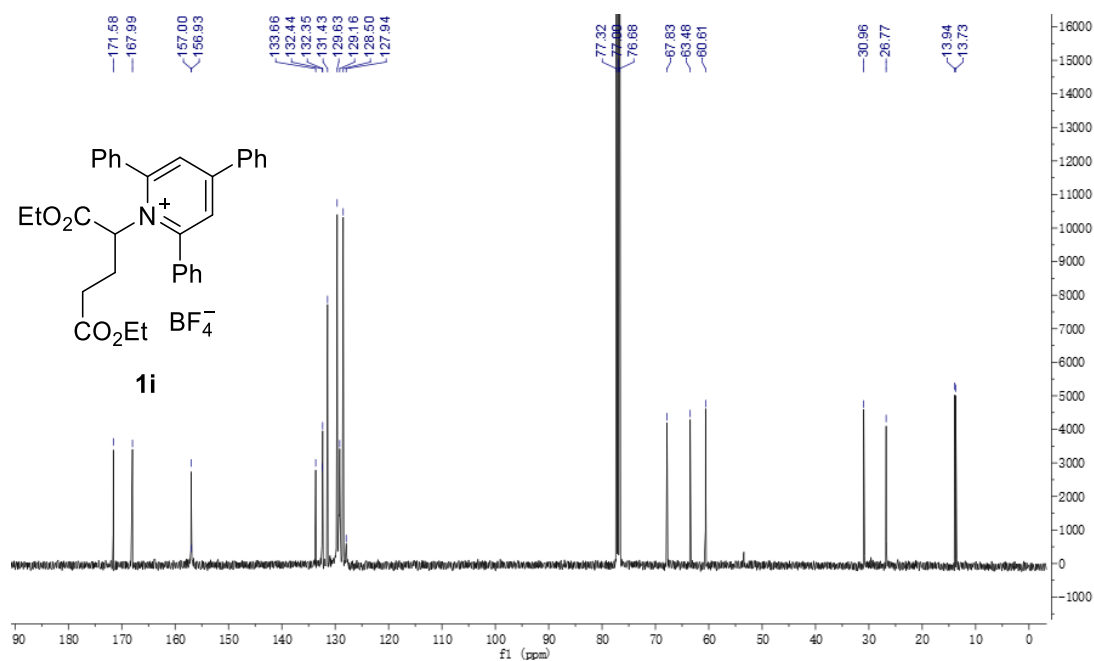
^{19}F NMR (376 MHz, CDCl_3) spectrum of product **1g**



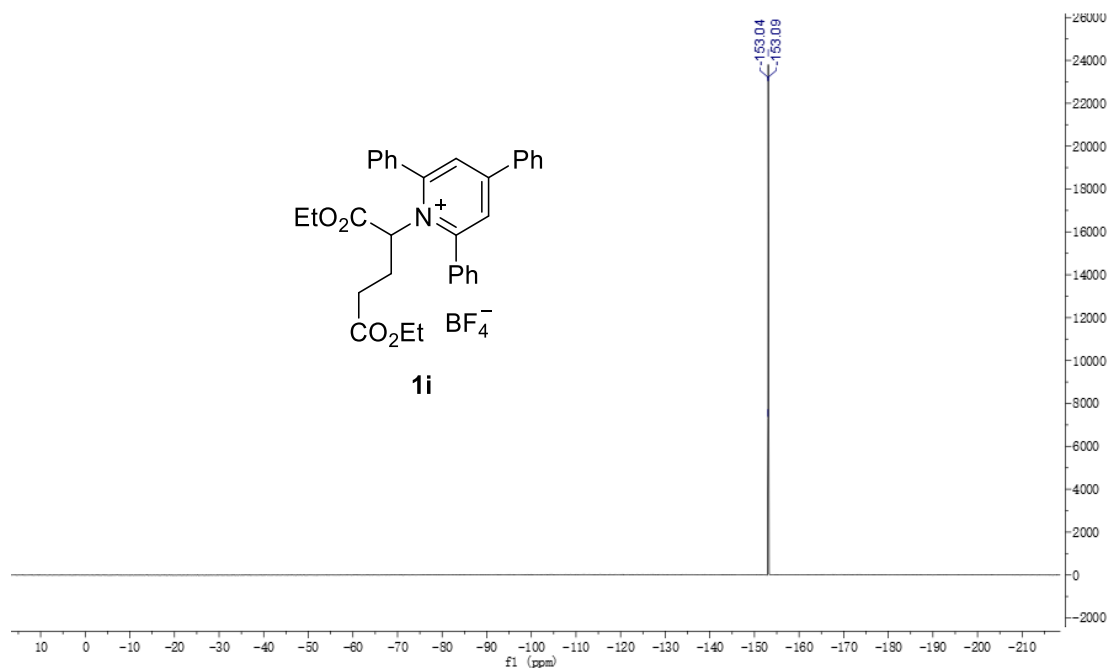
¹H NMR (400 MHz, CDCl₃) spectrum of product 1i



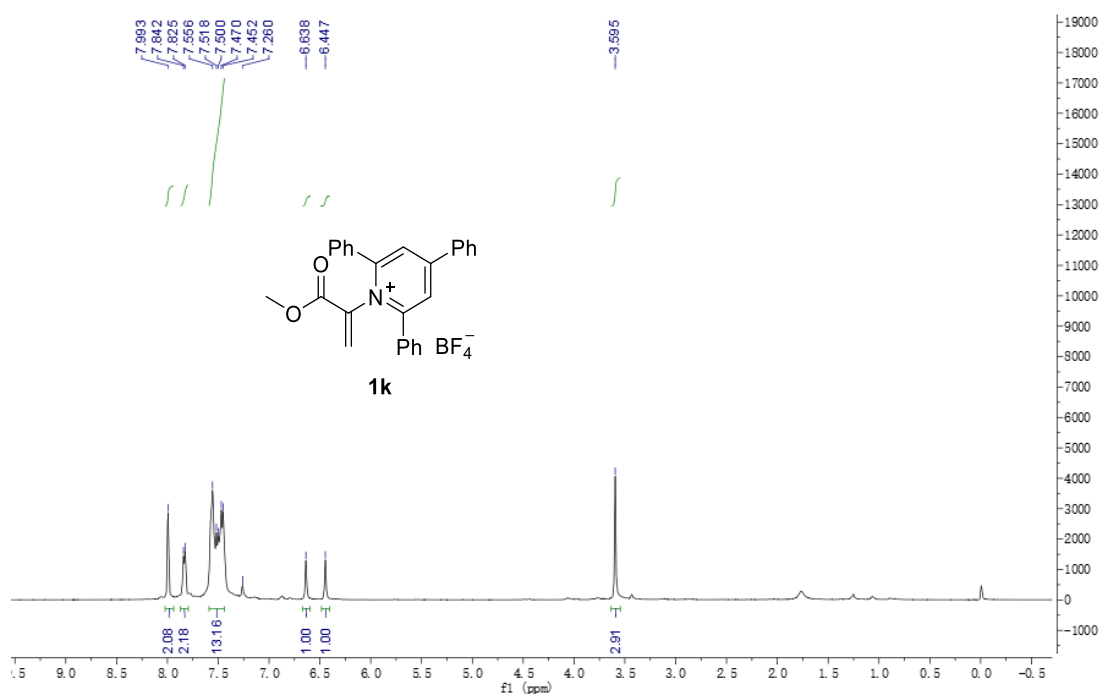
¹³C NMR (100 MHz, CDCl₃) spectrum of product 1i



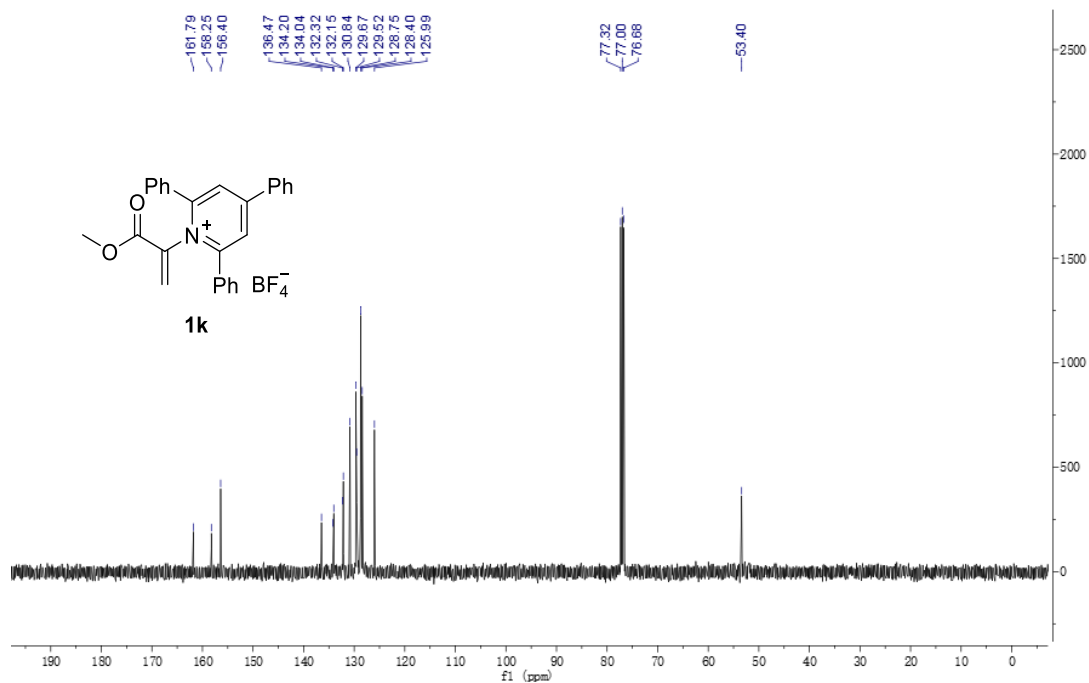
^{19}F NMR (376 MHz, CDCl_3) spectrum of product **1i**



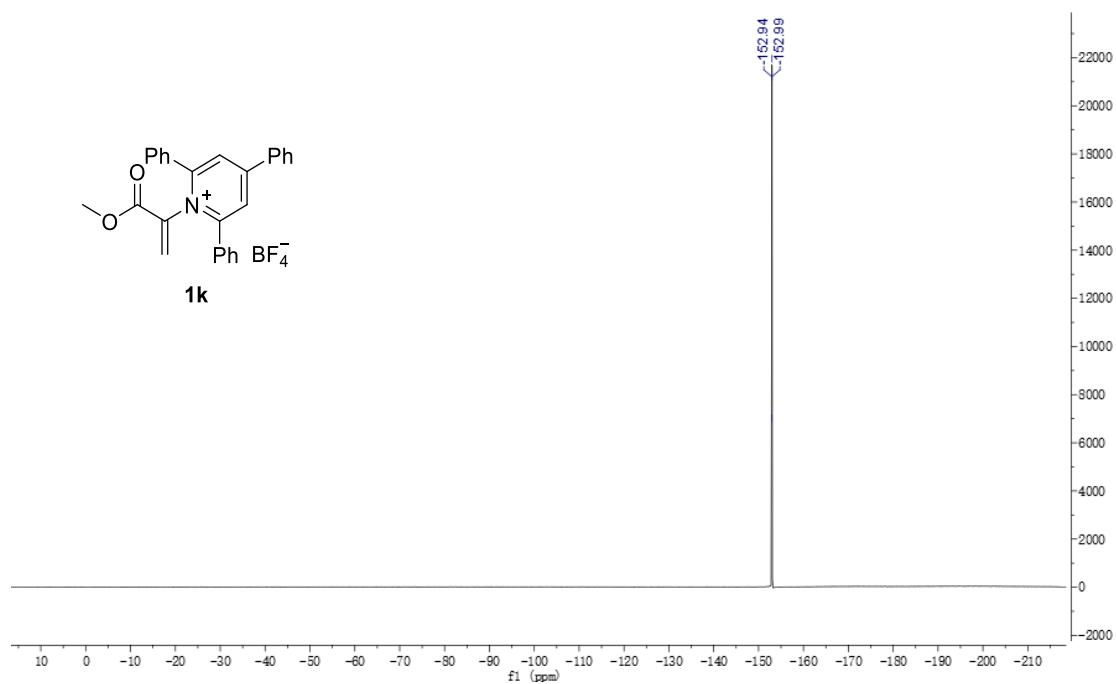
^1H NMR (400 MHz, CDCl_3) spectrum of product **1k**



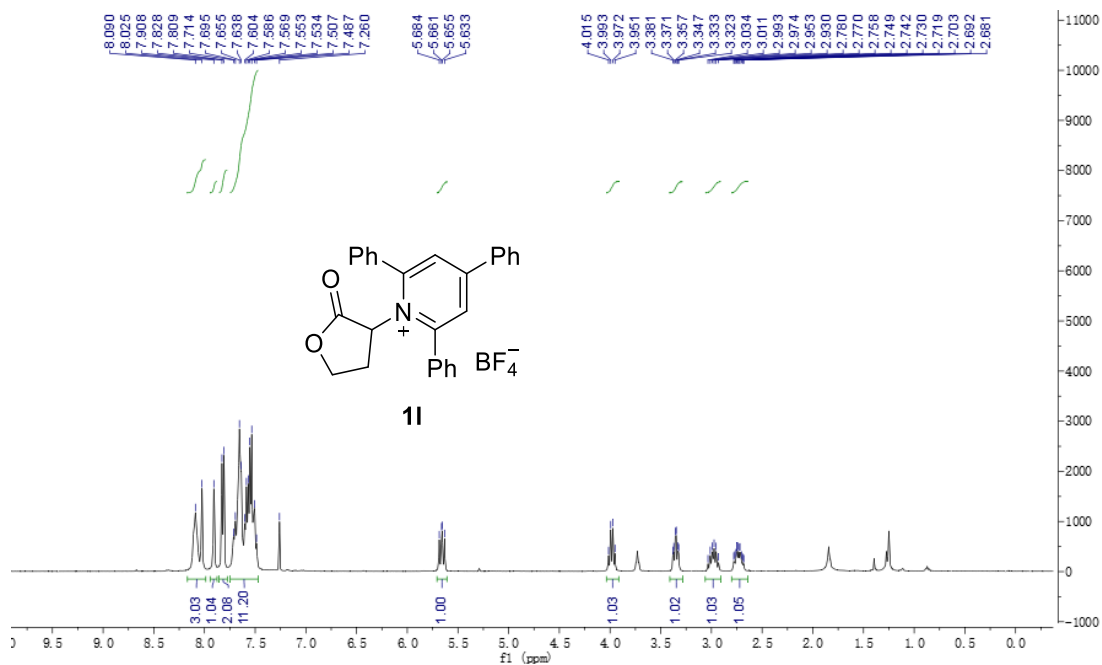
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 1k



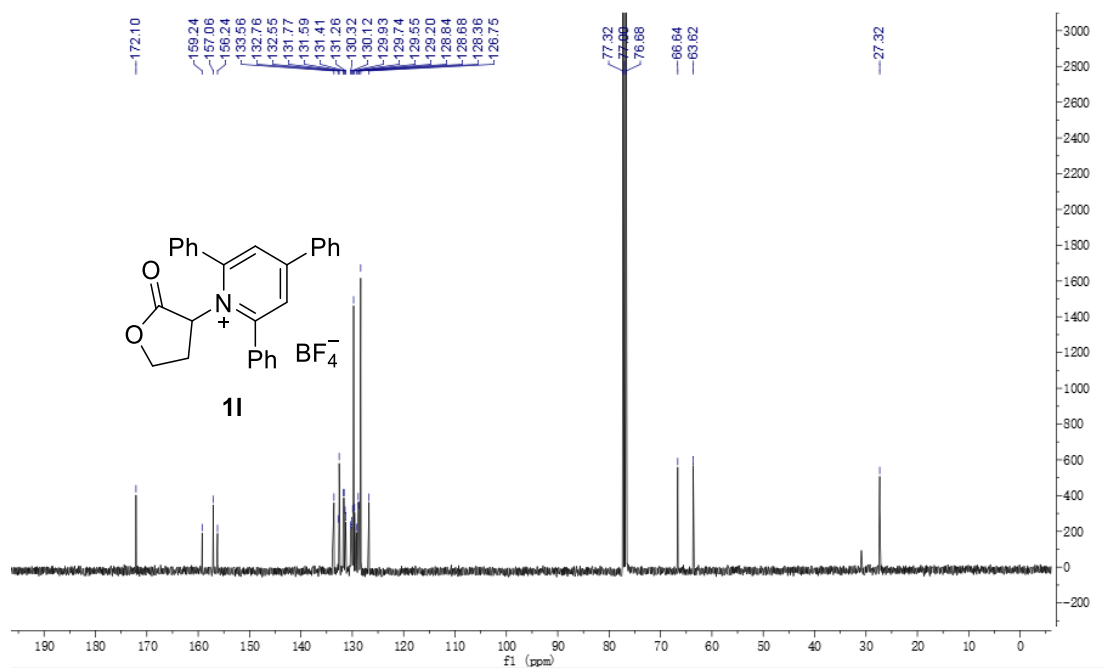
^{19}F NMR (376 MHz, CDCl_3) spectrum of product 1k



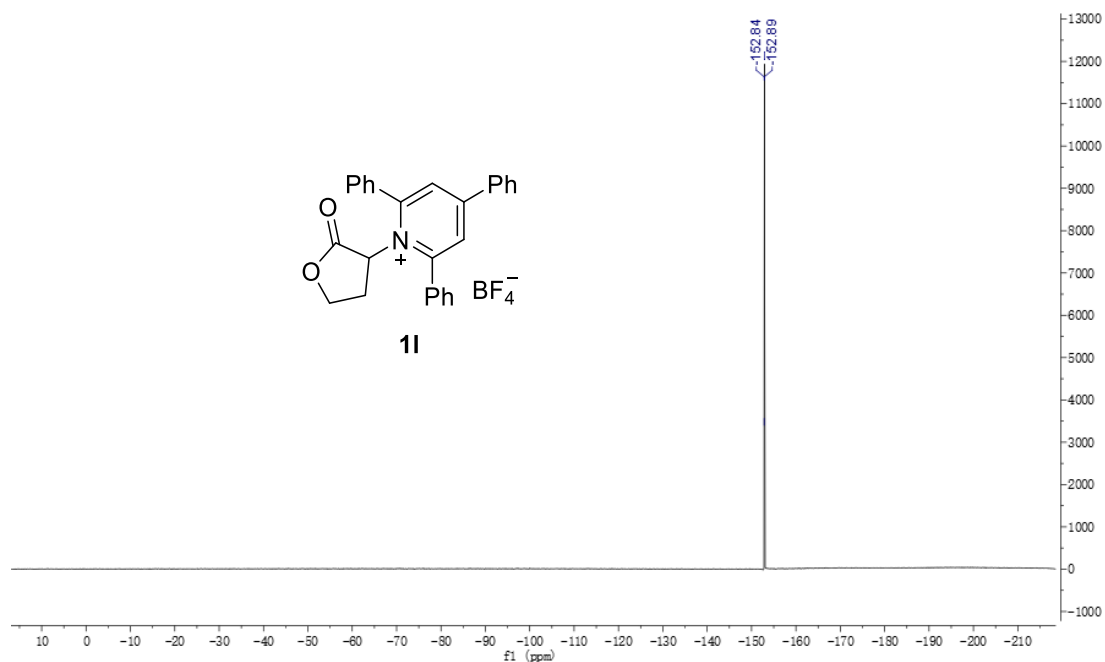
¹H NMR (400 MHz, CDCl₃) spectrum of product 11



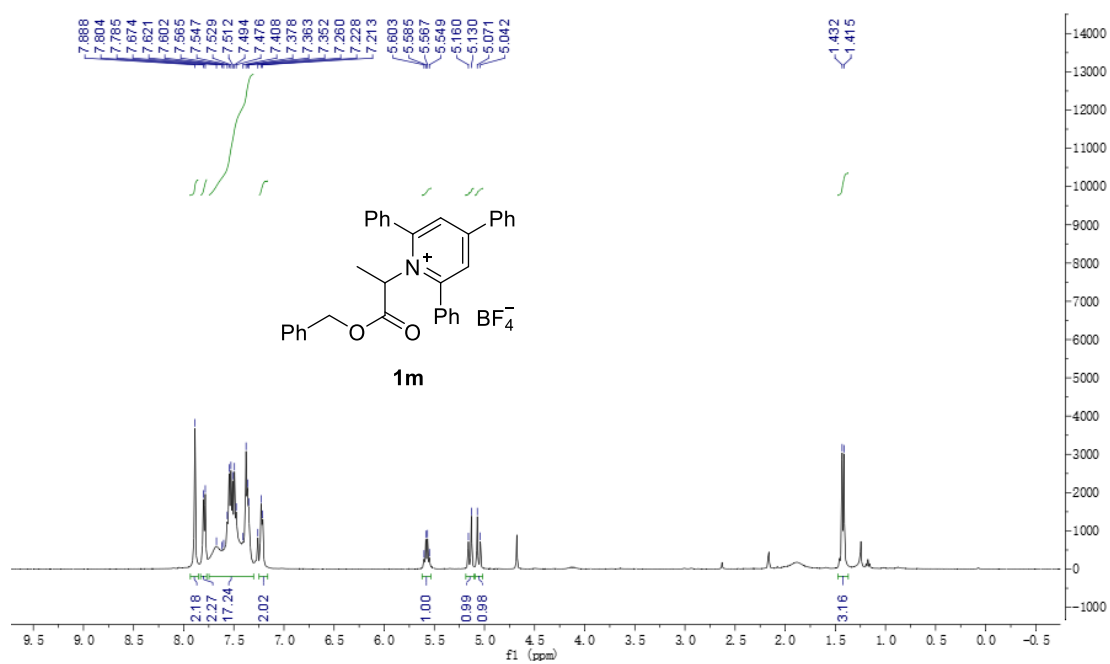
¹³C NMR (100 MHz, CDCl₃) spectrum of product 11



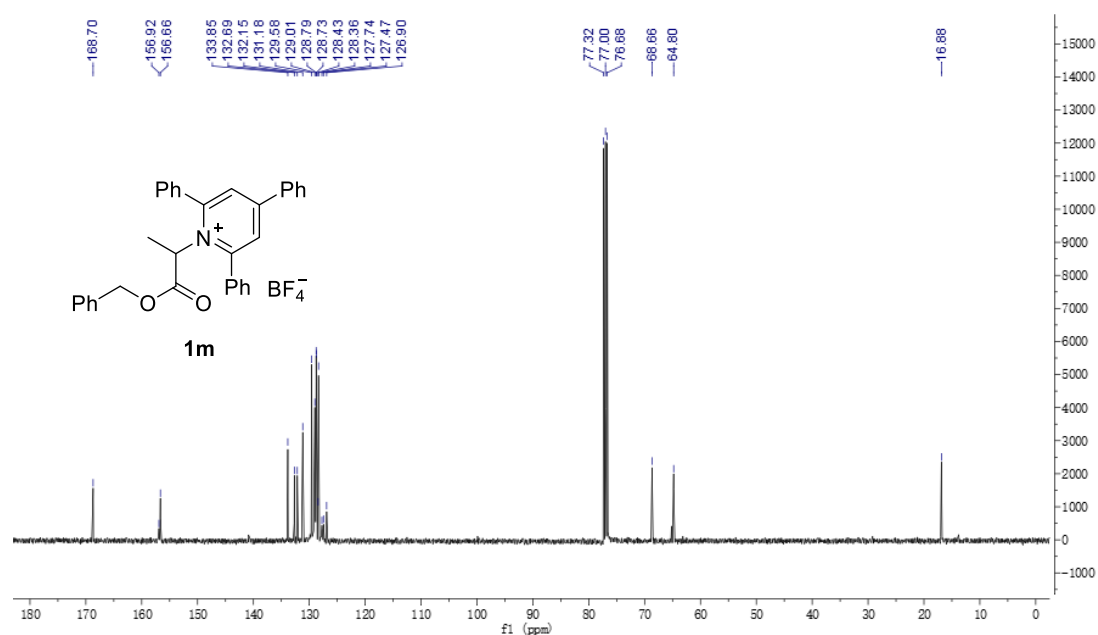
^{19}F NMR (376 MHz, CDCl_3) spectrum of product 1l



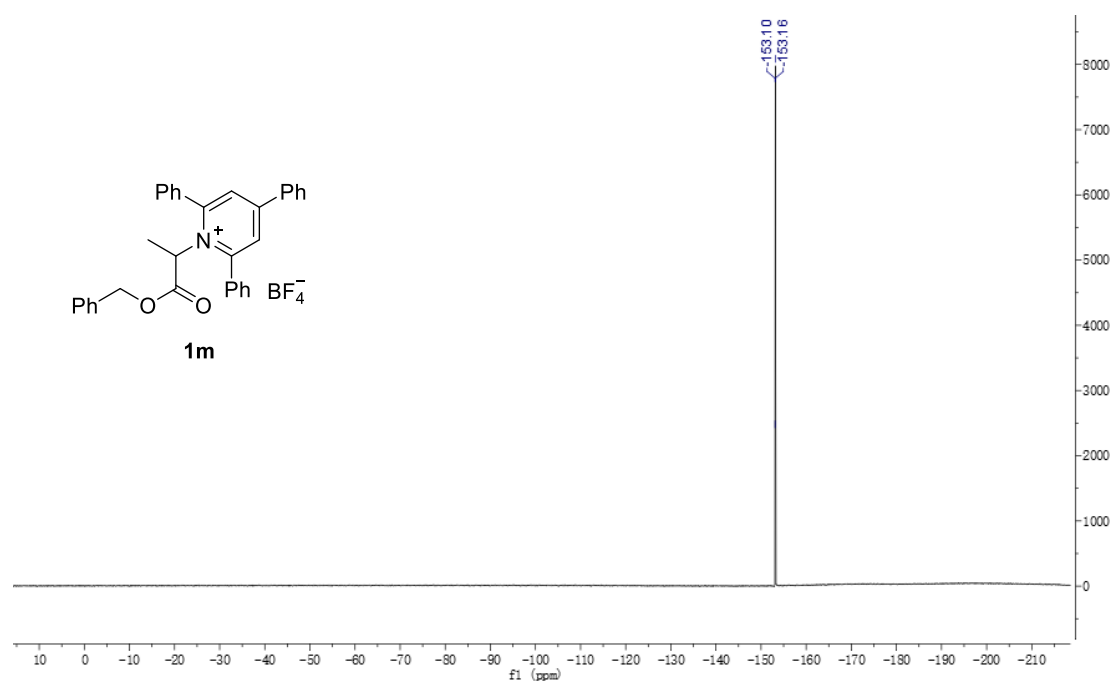
^1H NMR (400 MHz, CDCl_3) spectrum of product 1m



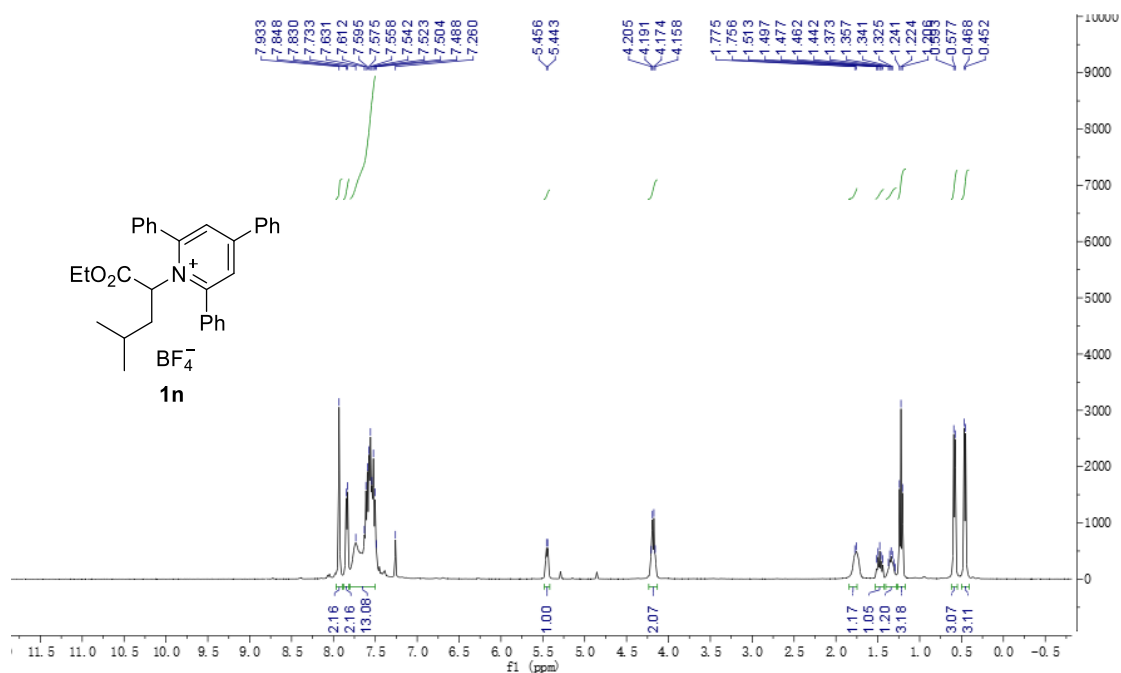
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 1m



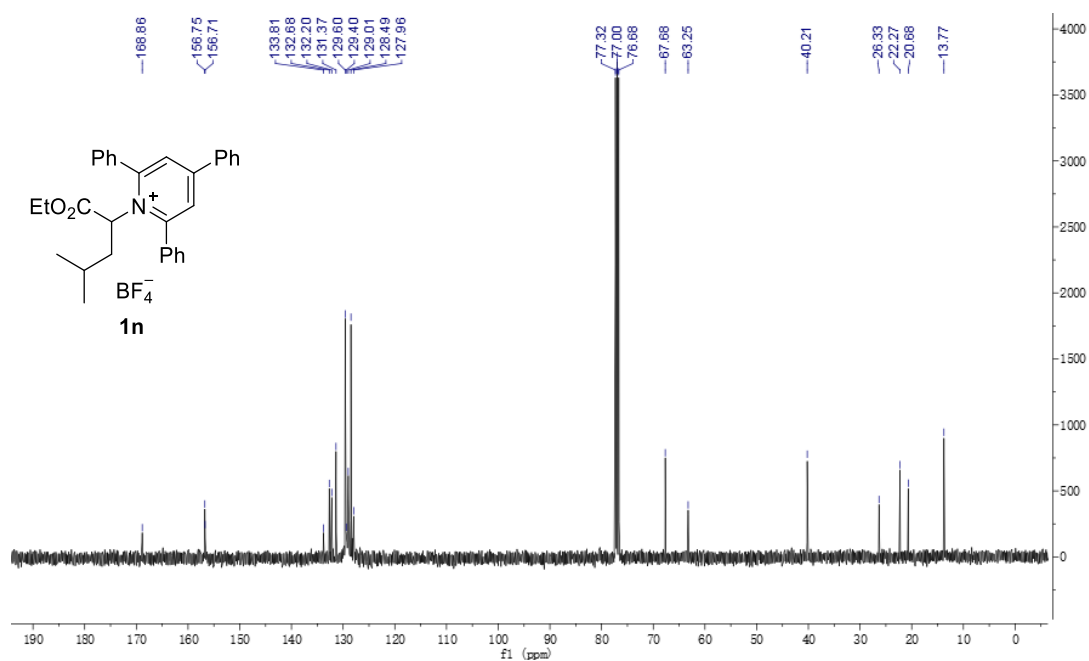
^{19}F NMR (376 MHz, CDCl_3) spectrum of product 1m



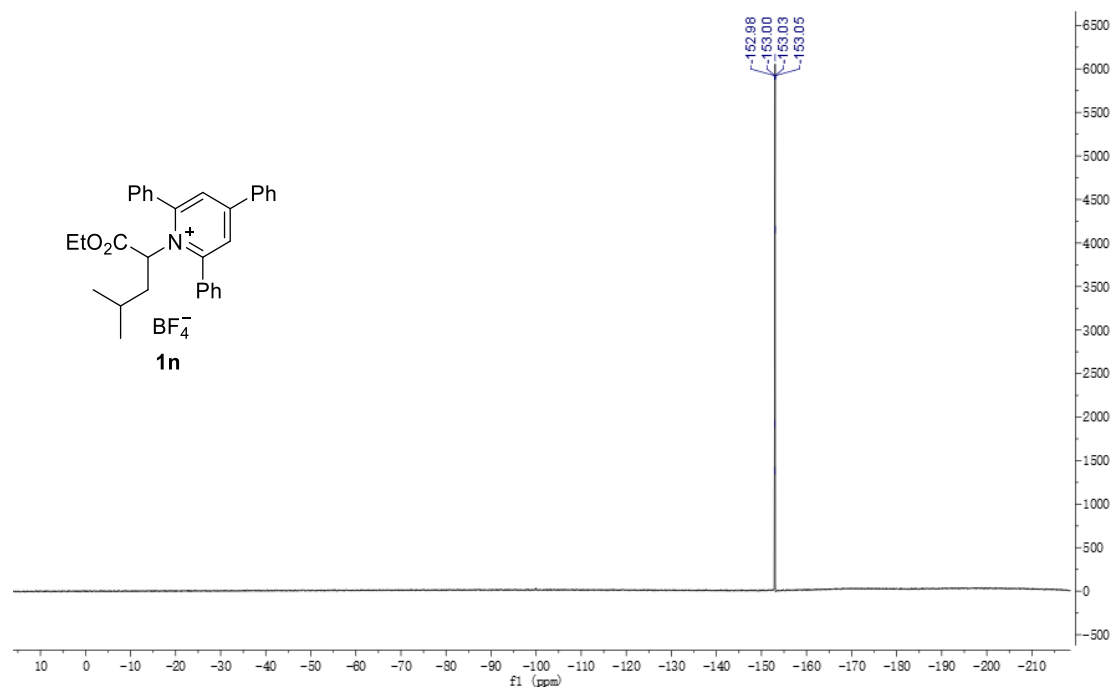
¹H NMR (400 MHz, CDCl₃) spectrum of product 1n



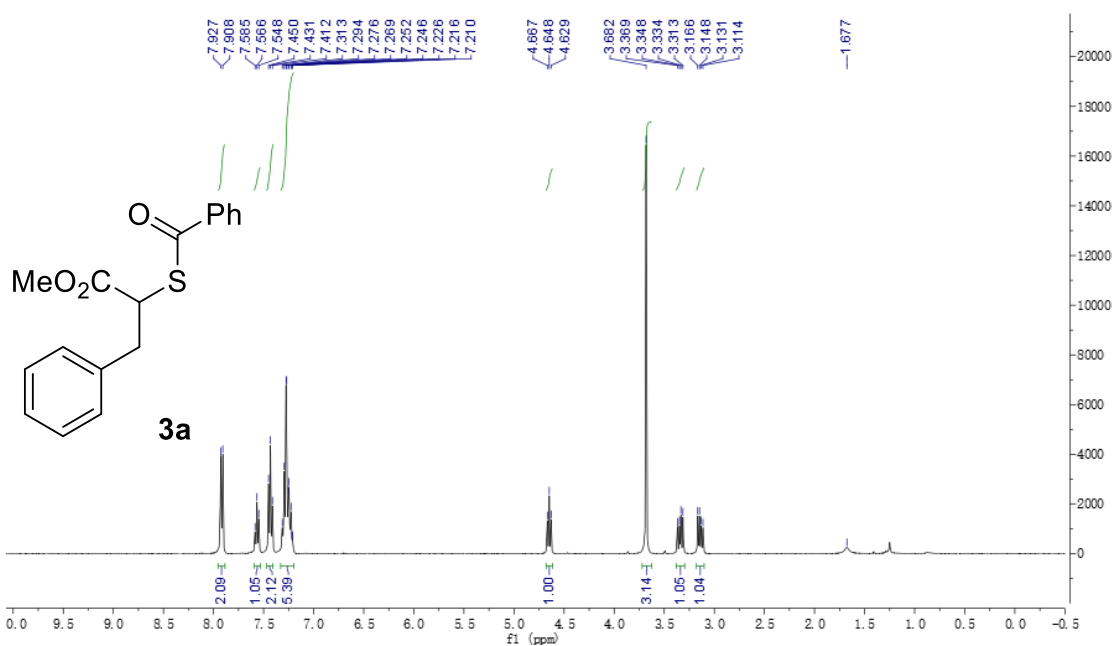
¹³C NMR (100 MHz, CDCl₃) spectrum of product 1n



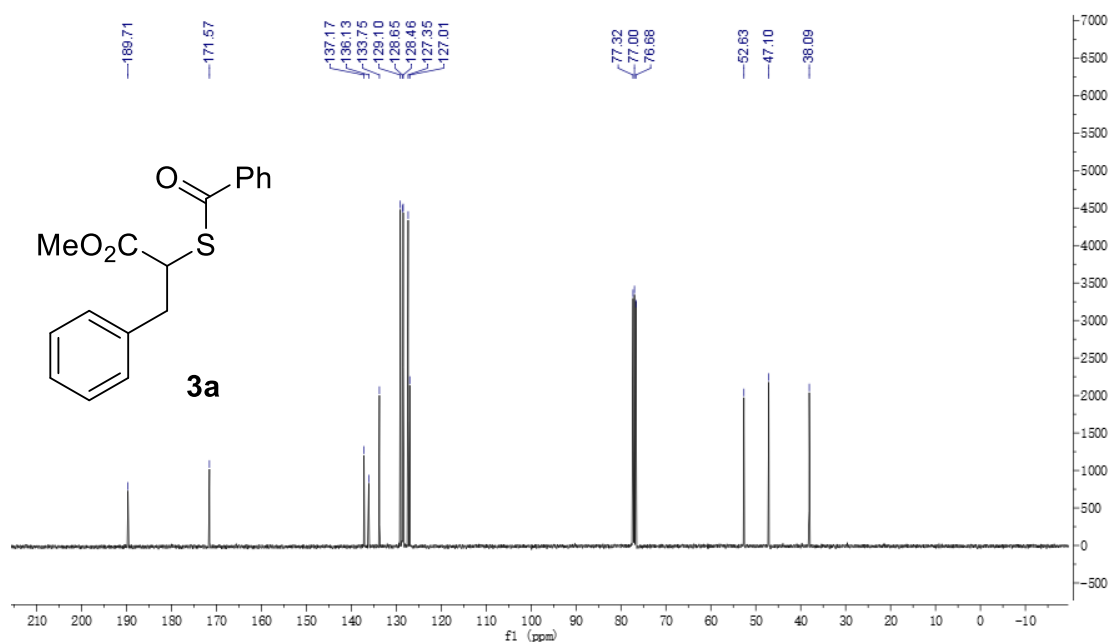
^{19}F NMR (376 MHz, CDCl_3) spectrum of product **1n**



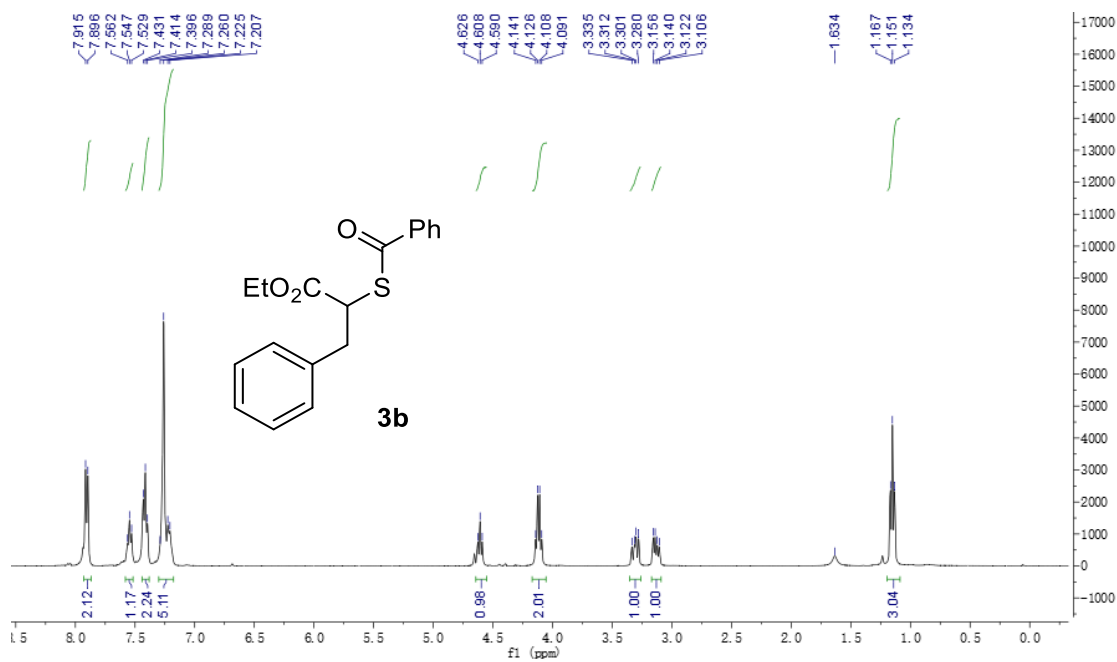
¹H NMR (400 MHz, CDCl₃) spectrum of product 3a



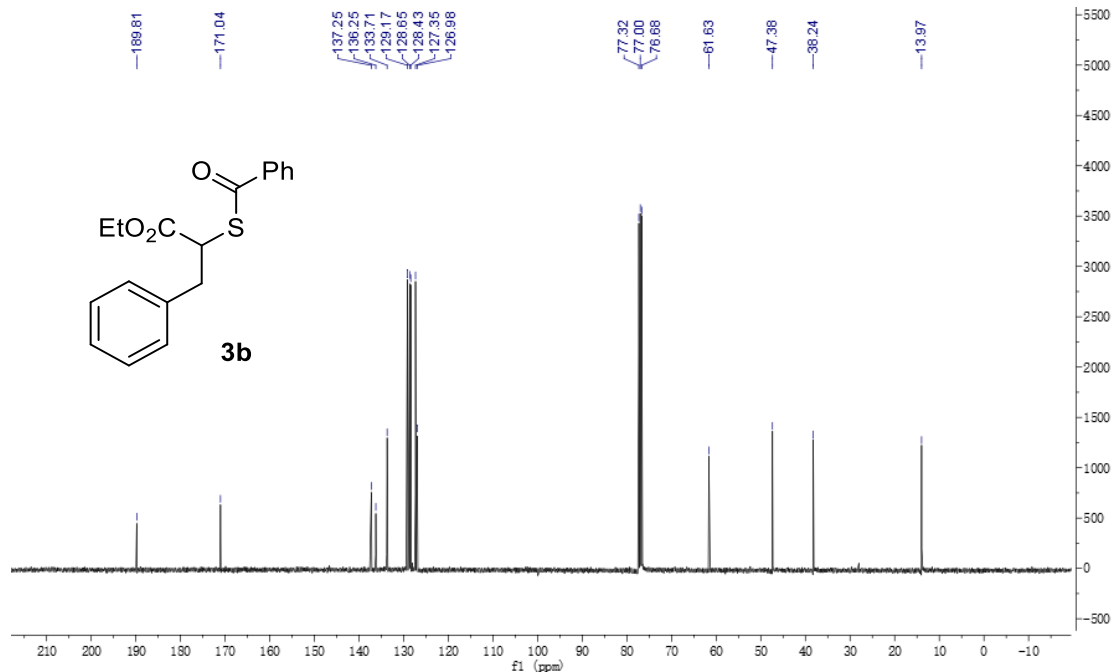
¹³C NMR (100 MHz, CDCl₃) spectrum of product 3a



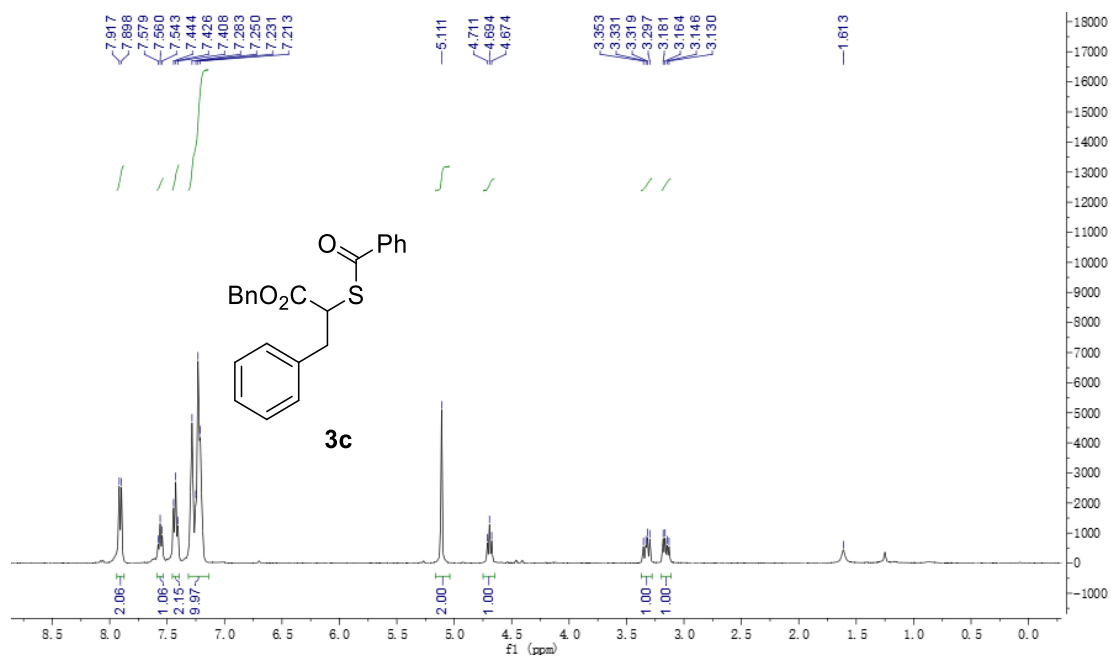
¹H NMR (400 MHz, CDCl₃) spectrum of product 3b



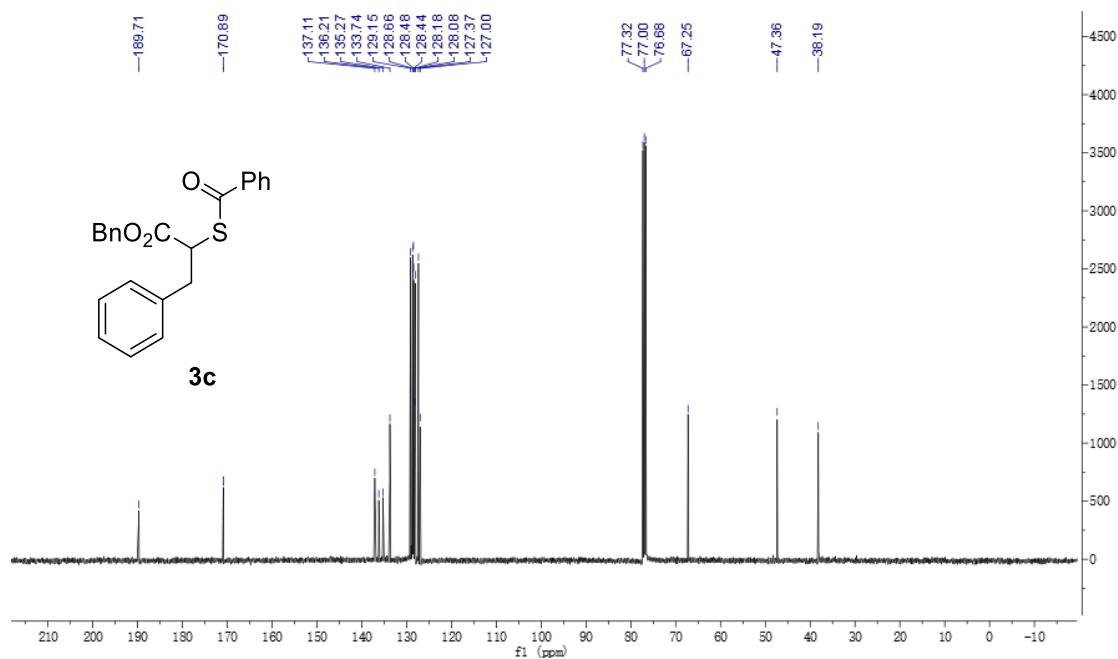
¹³C NMR (100 MHz, CDCl₃) spectrum of product 3b



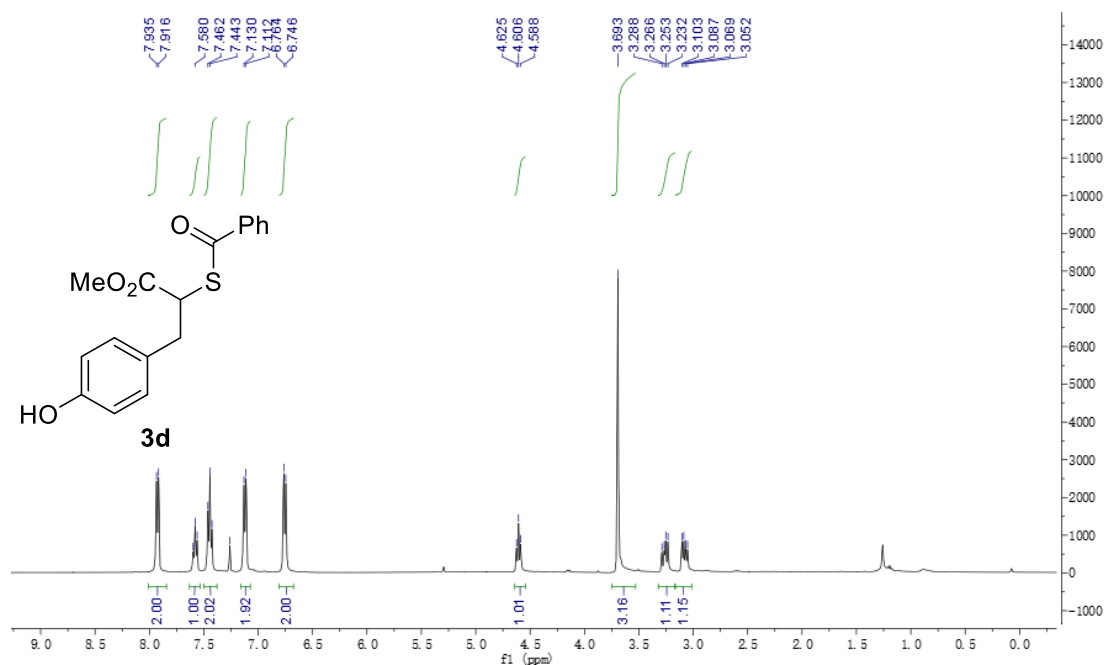
¹H NMR (400 MHz, CDCl₃) spectrum of product 3c



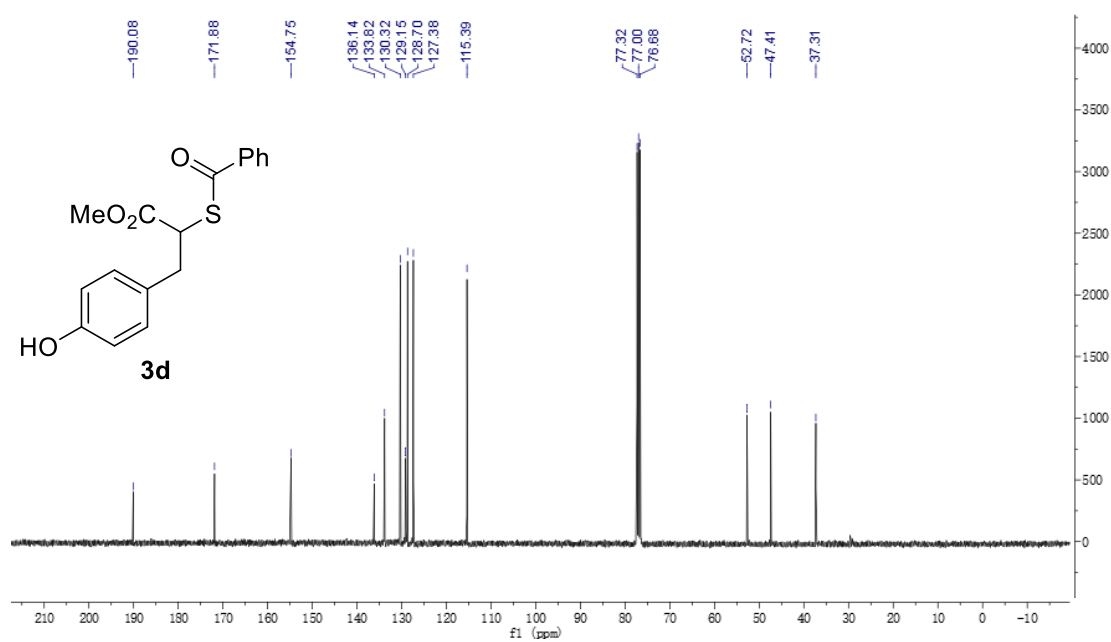
¹³C NMR (100 MHz, CDCl₃) spectrum of product 3c



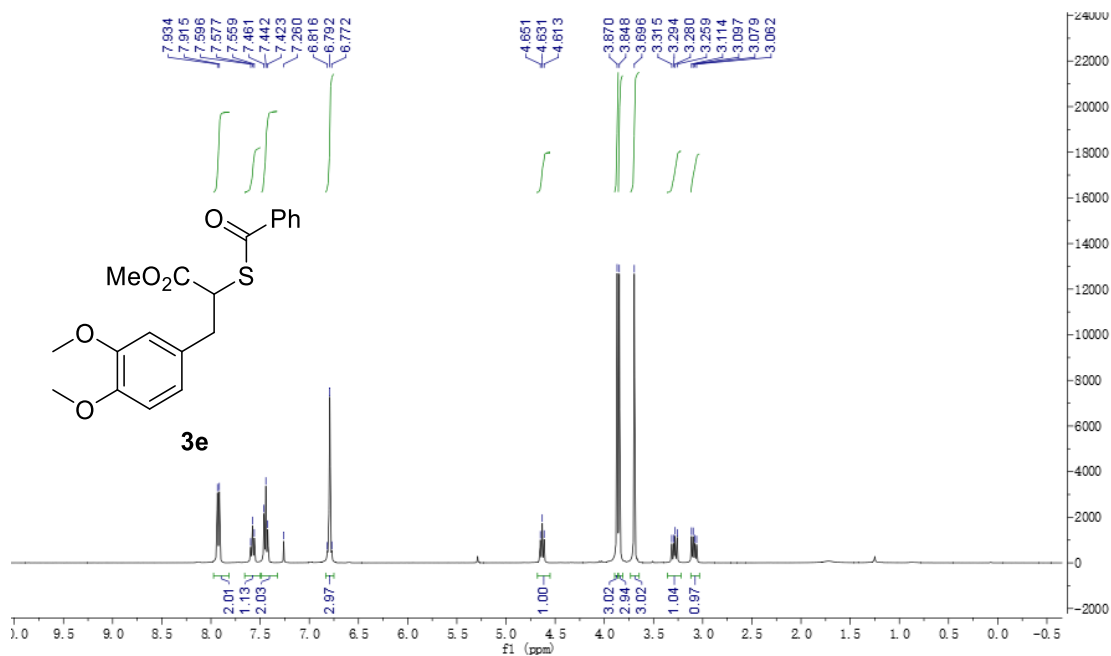
^1H NMR (400 MHz, CDCl_3) spectrum of product 3d



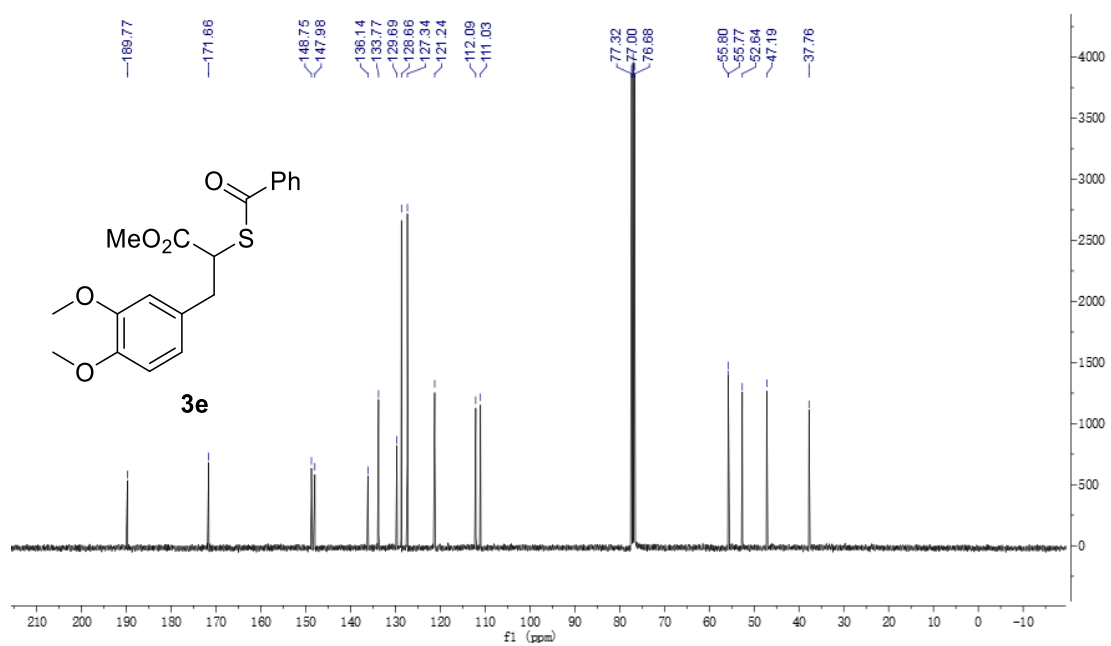
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3d



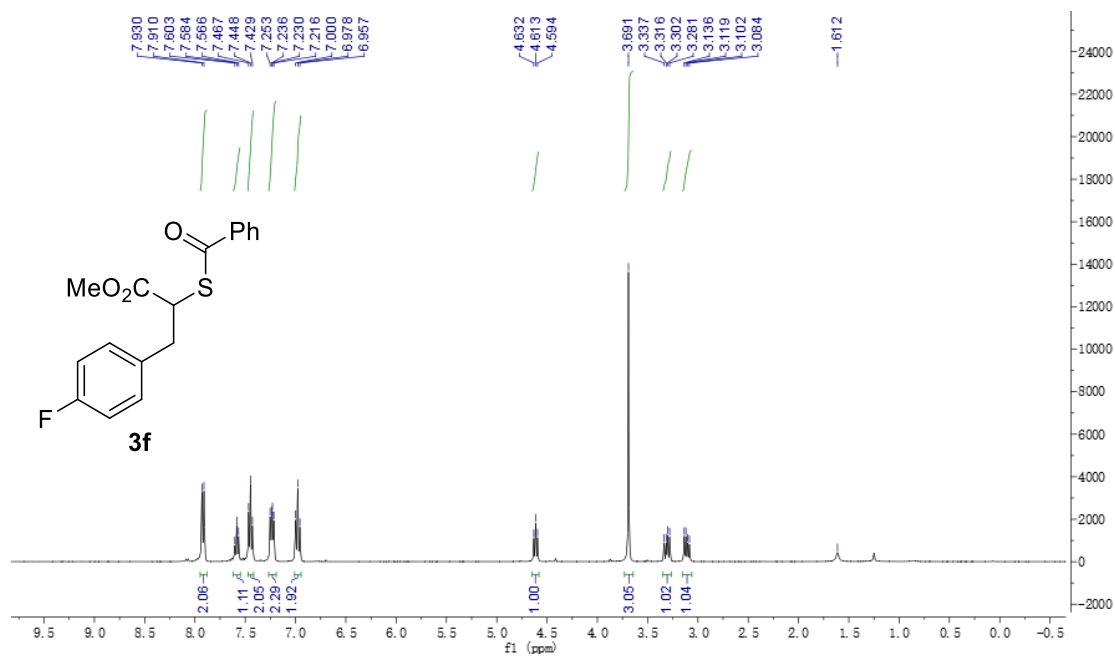
¹H NMR (400 MHz, CDCl₃) spectrum of product 3e



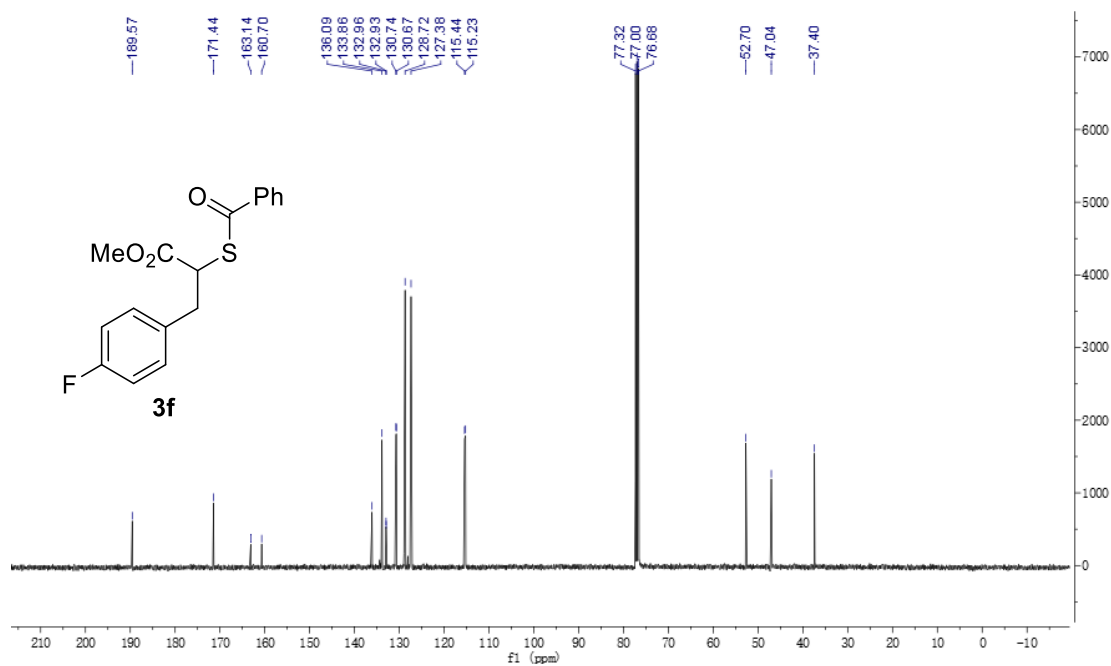
¹³C NMR (100 MHz, CDCl₃) spectrum of product 3e



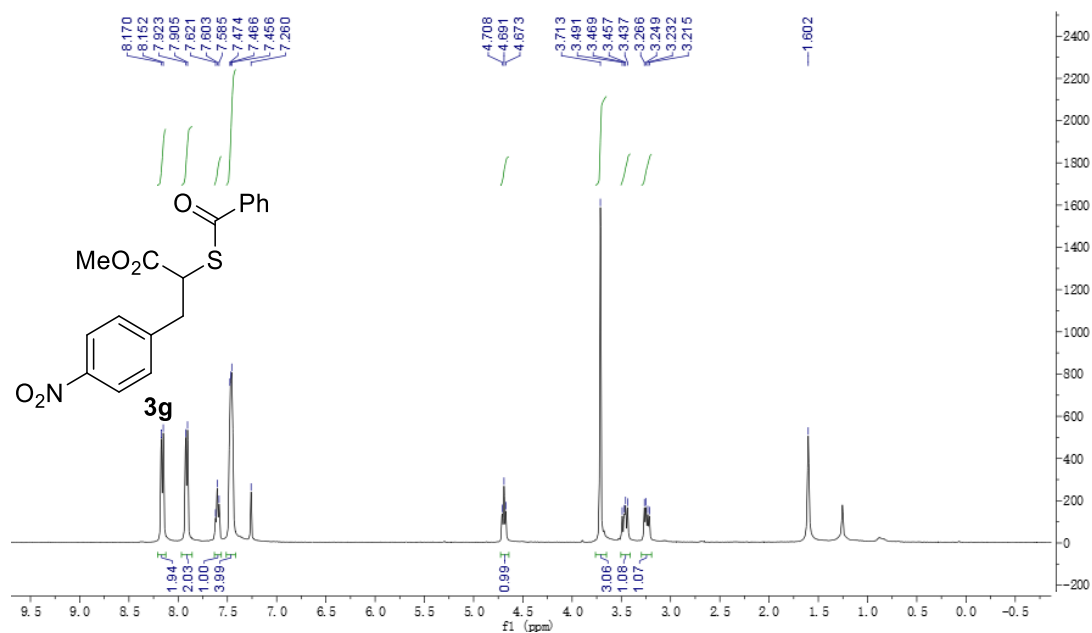
¹H NMR (400 MHz, CDCl₃) spectrum of product 3f



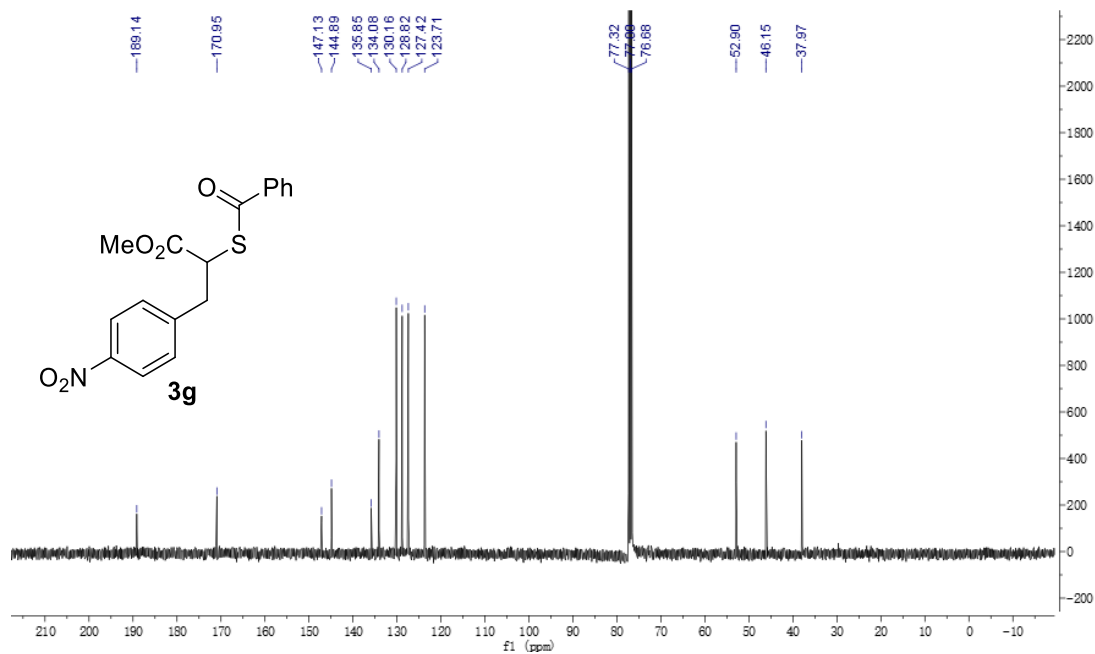
¹³C NMR (100 MHz, CDCl₃) spectrum of product 3f



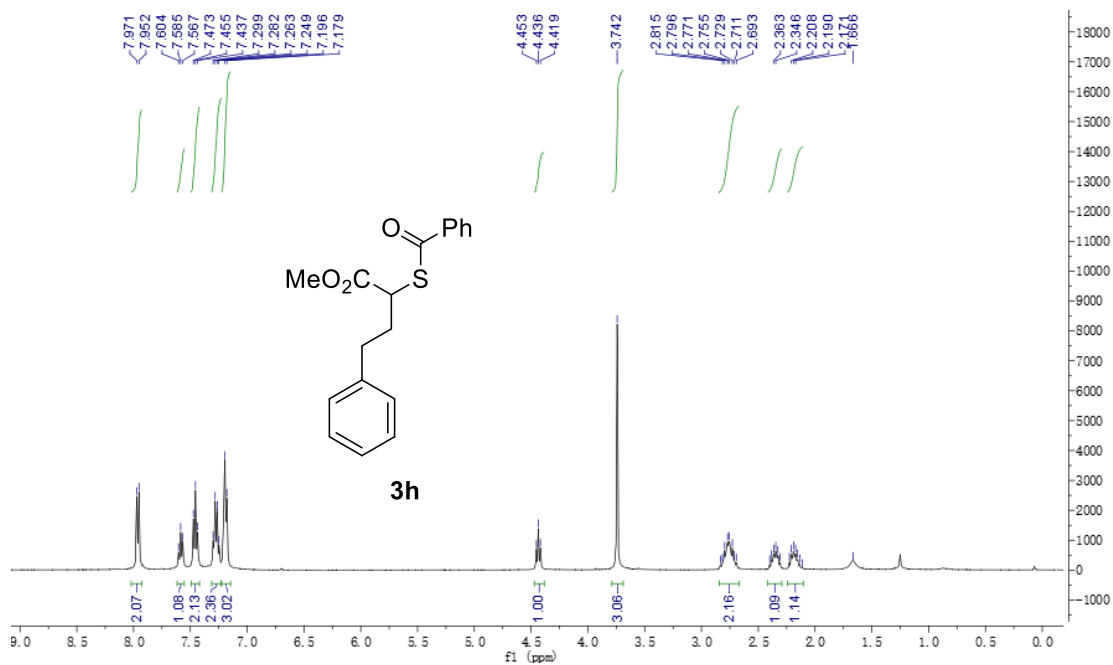
¹H NMR (400 MHz, CDCl₃) spectrum of product 3g



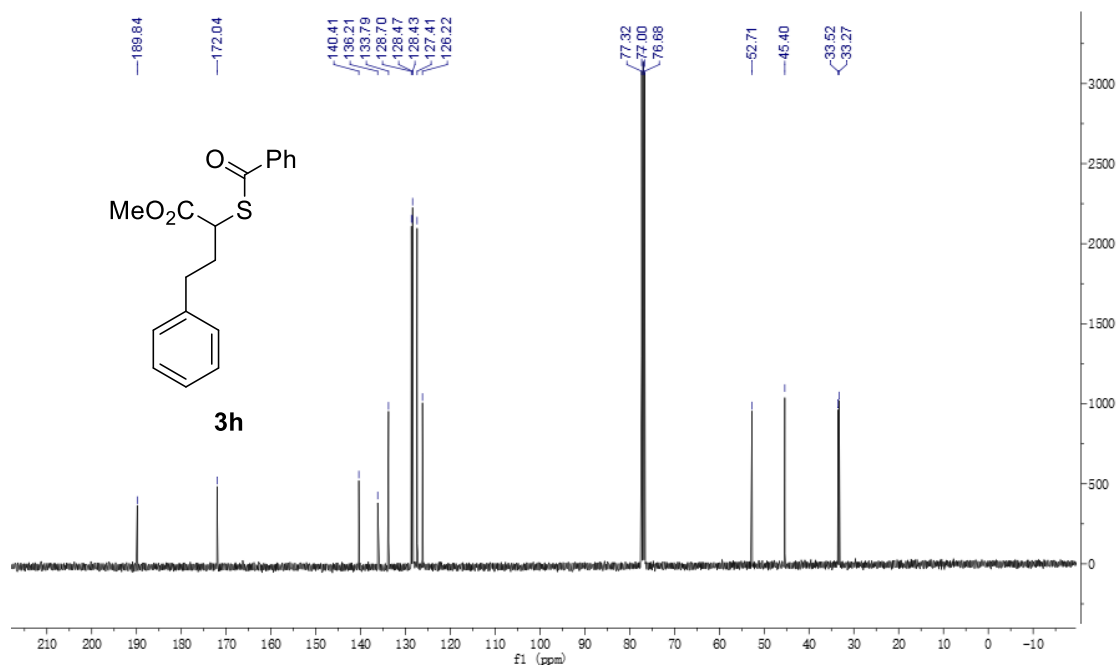
¹³C NMR (100 MHz, CDCl₃) spectrum of product 3g



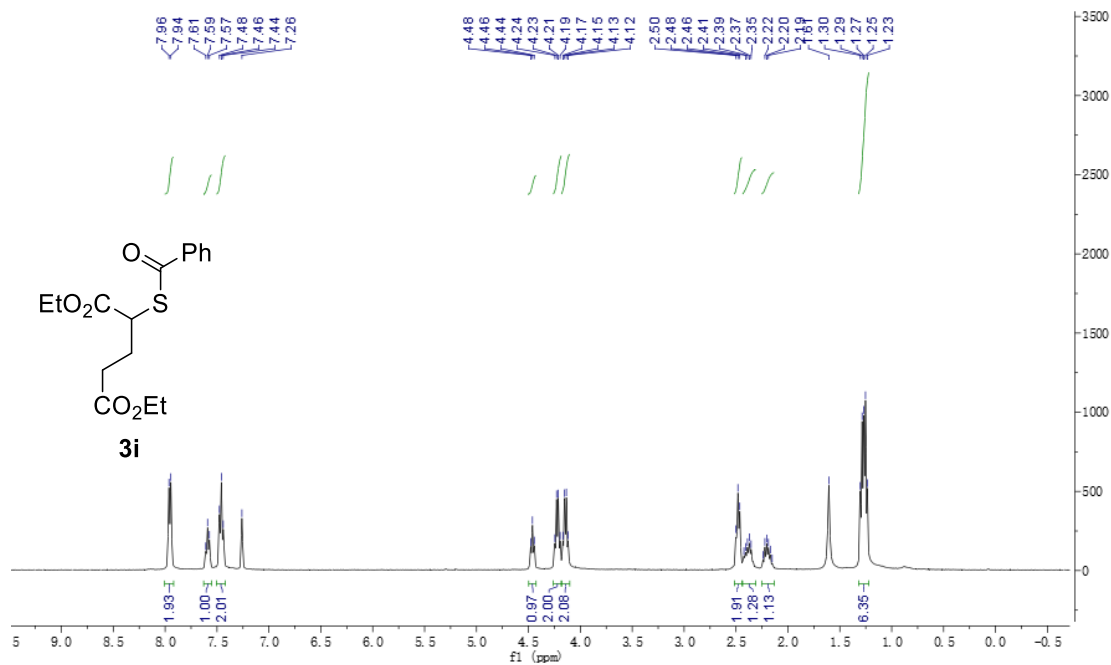
^1H NMR (400 MHz, CDCl_3) spectrum of product 3h



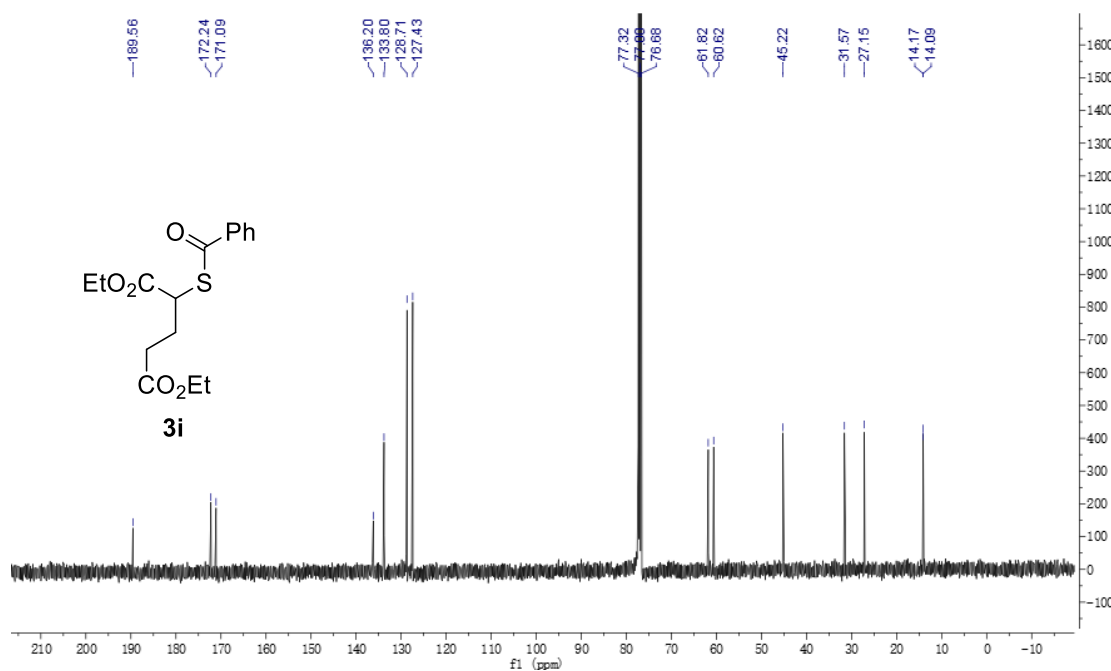
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3h



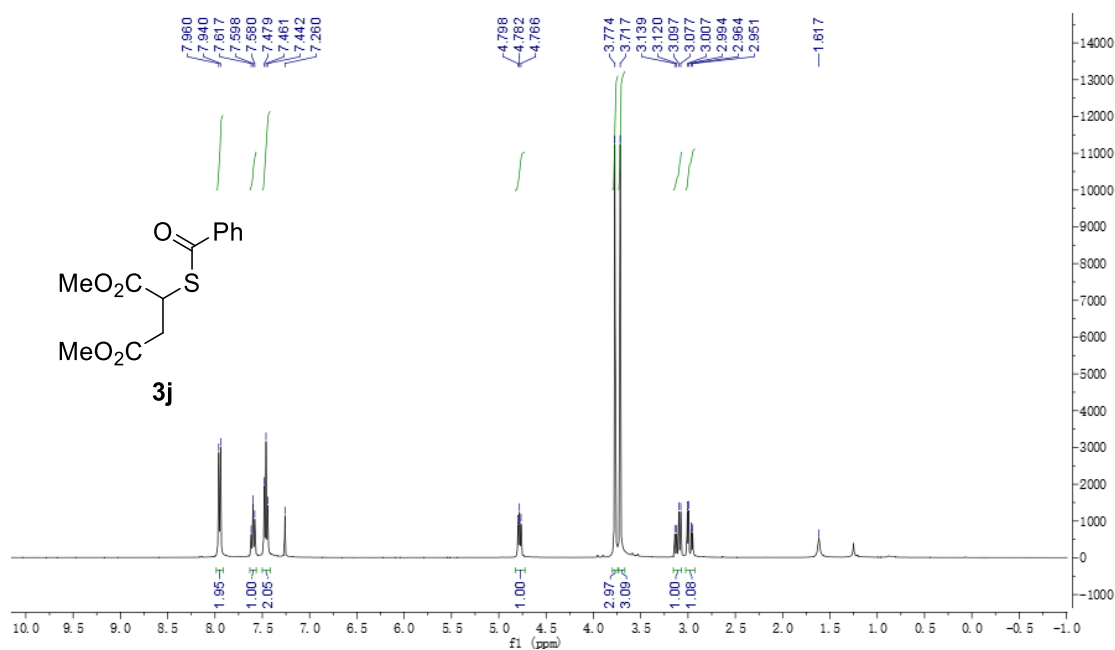
^1H NMR (400 MHz, CDCl_3) spectrum of product 3i



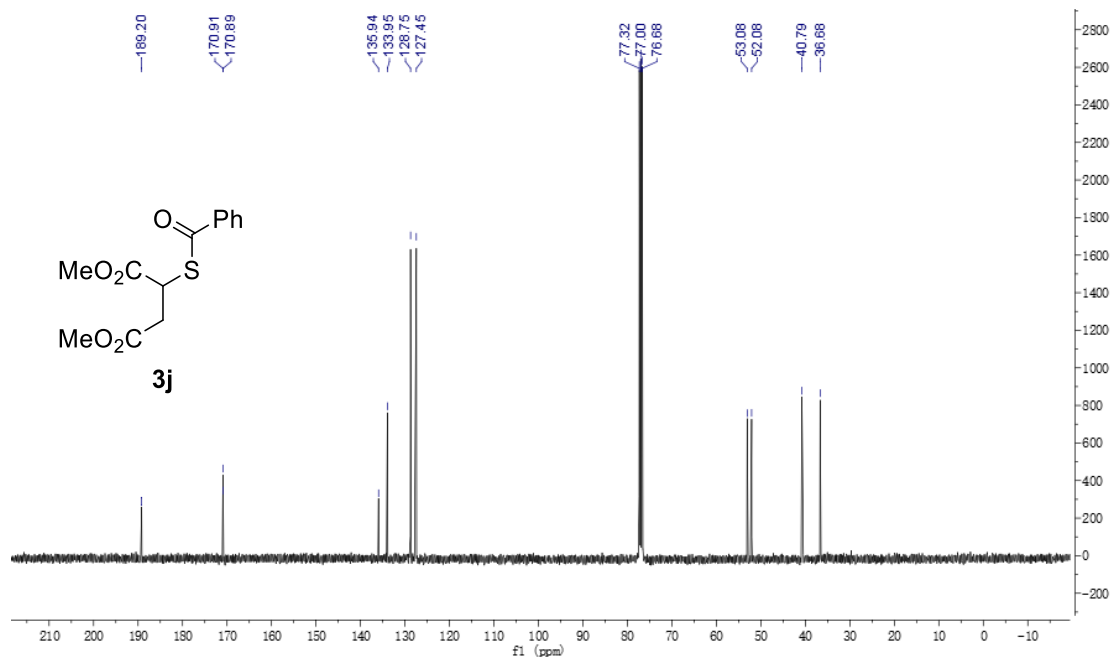
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3i



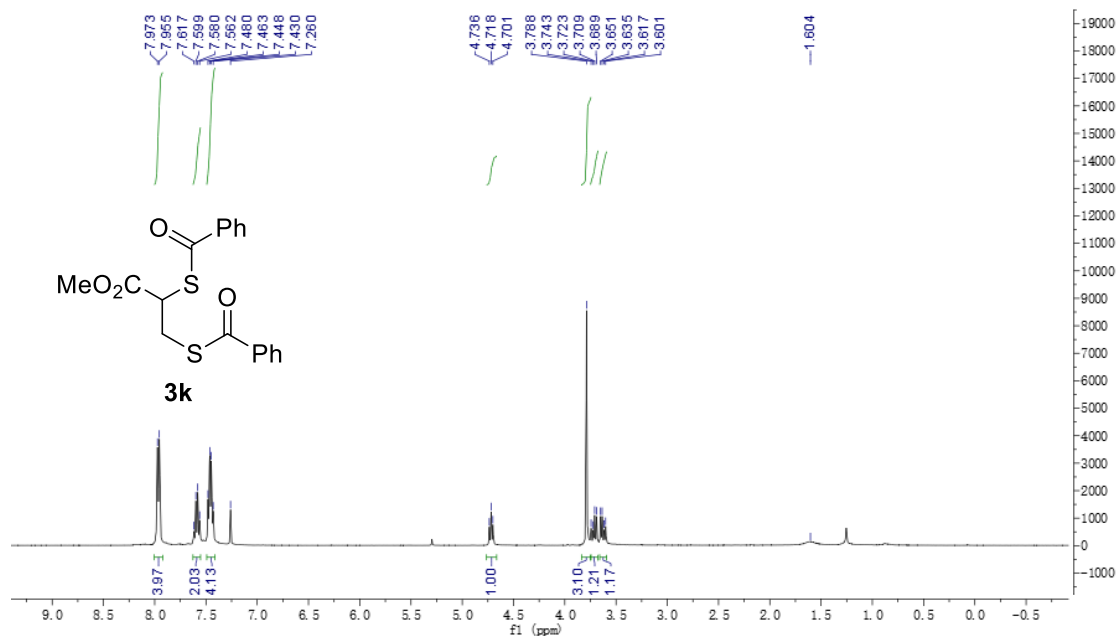
¹H NMR (400 MHz, CDCl₃) spectrum of product 3j



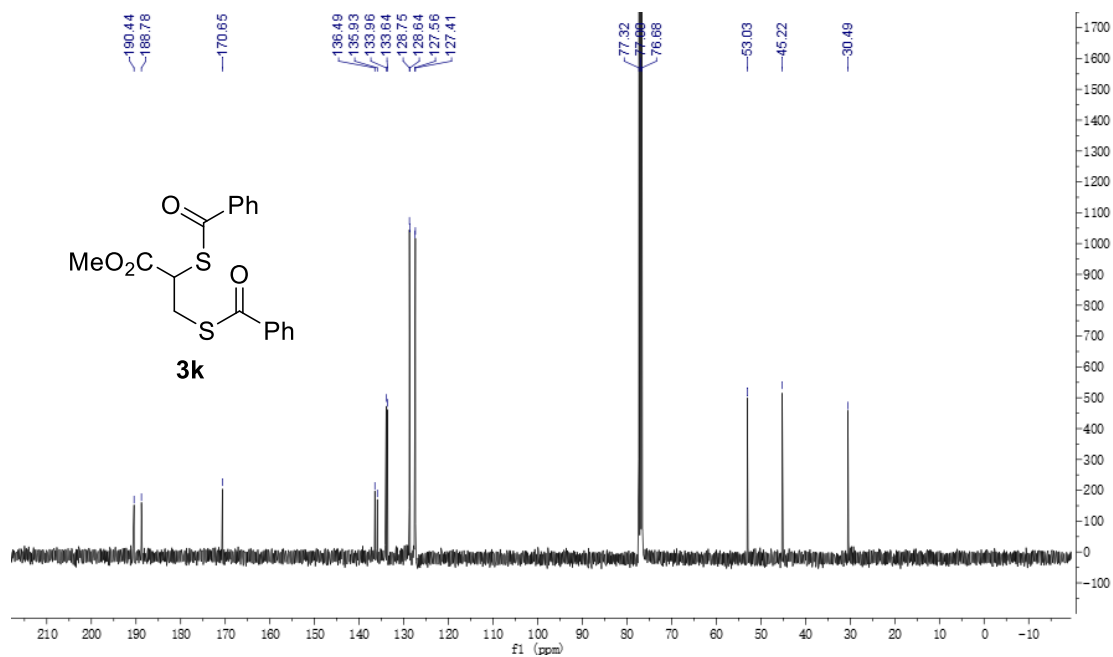
¹³C NMR (100 MHz, CDCl₃) spectrum of product 3j



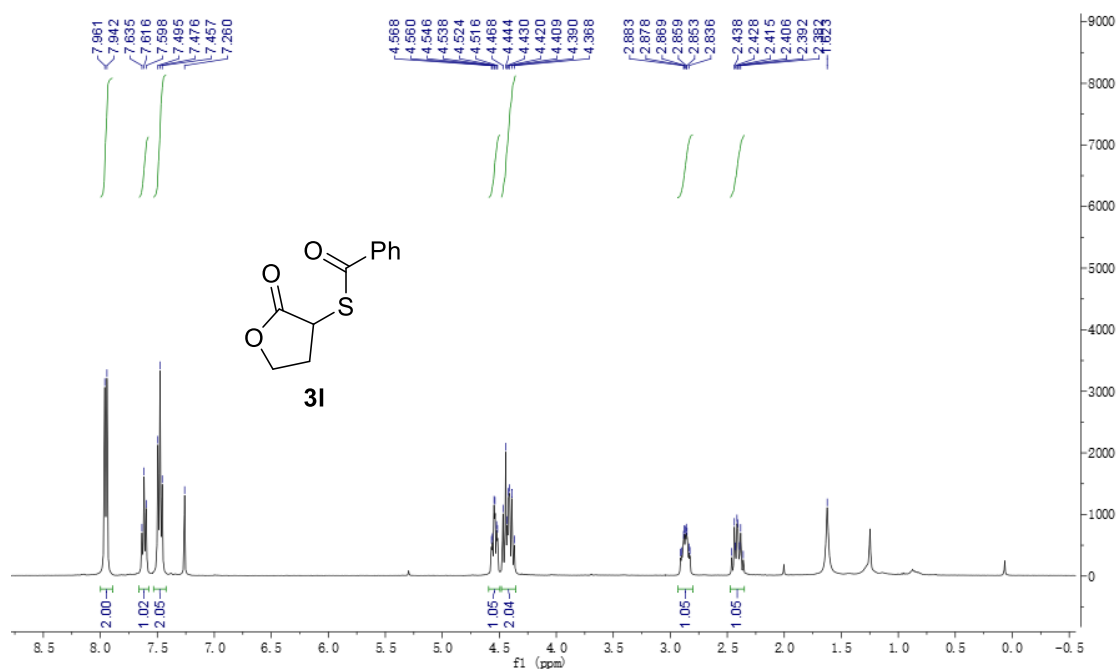
^1H NMR (400 MHz, CDCl_3) spectrum of product 3k



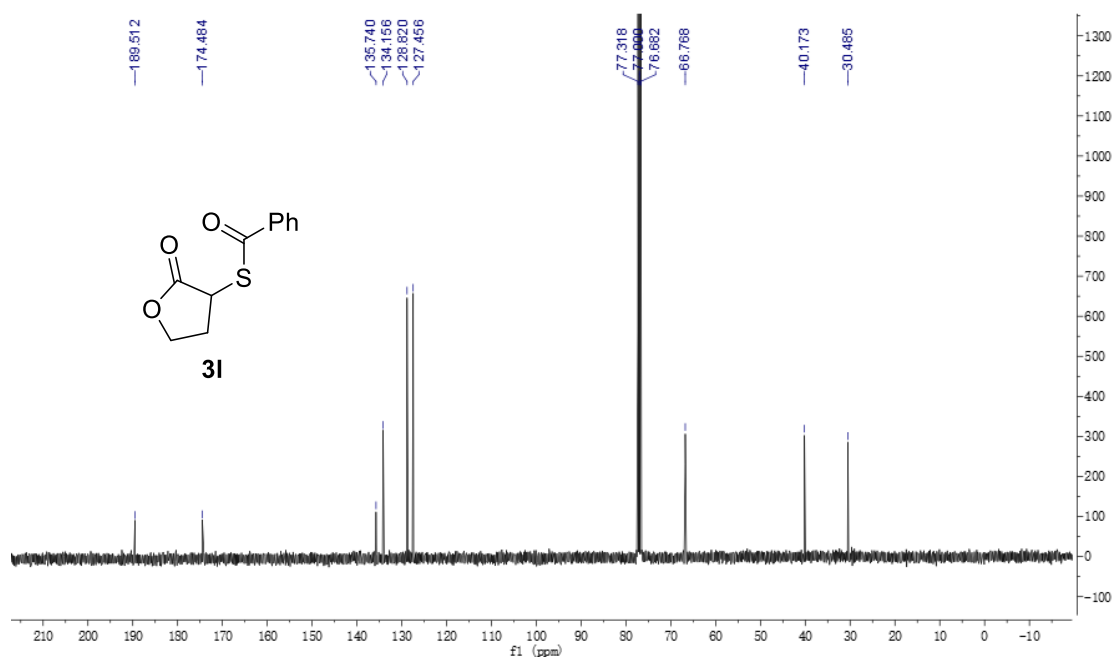
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3k



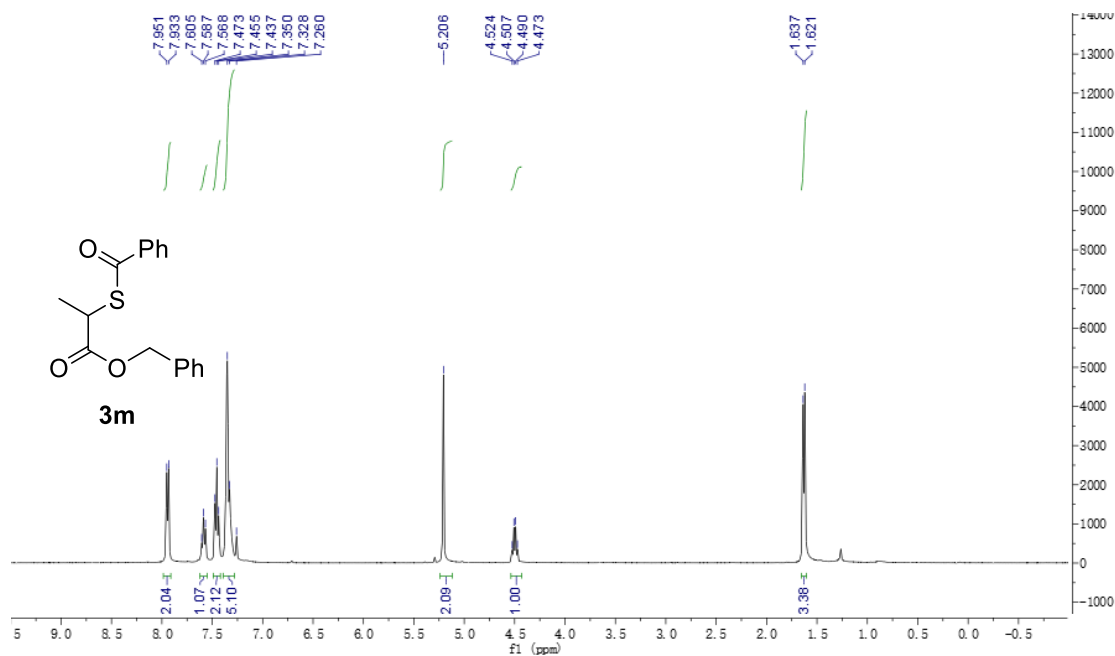
^1H NMR (400 MHz, CDCl_3) spectrum of product 3I



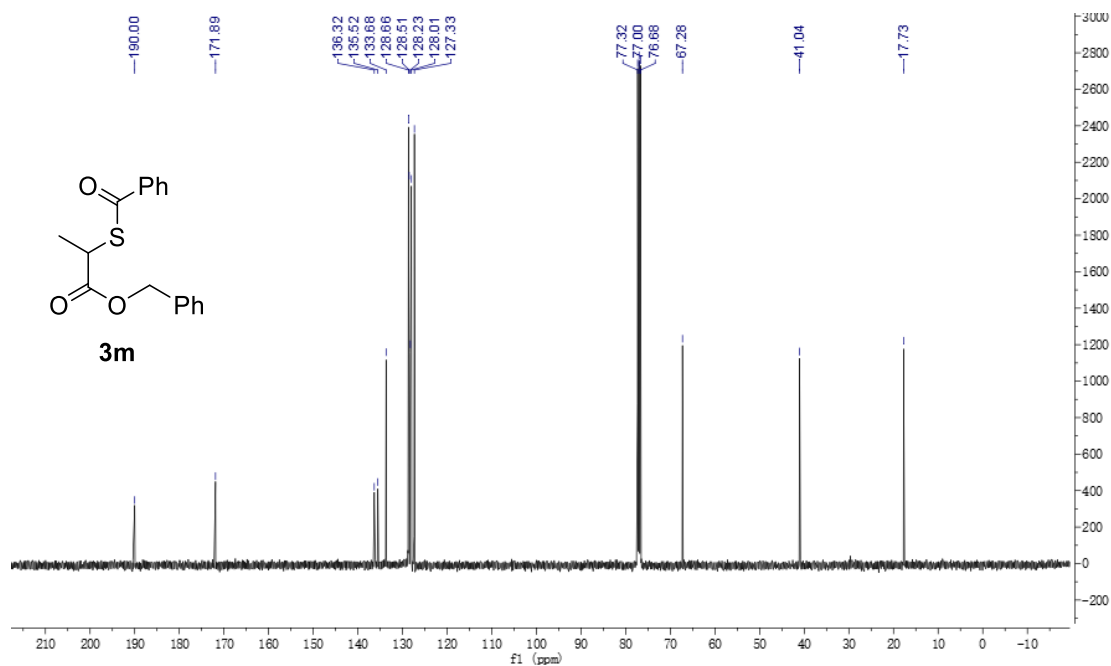
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3I



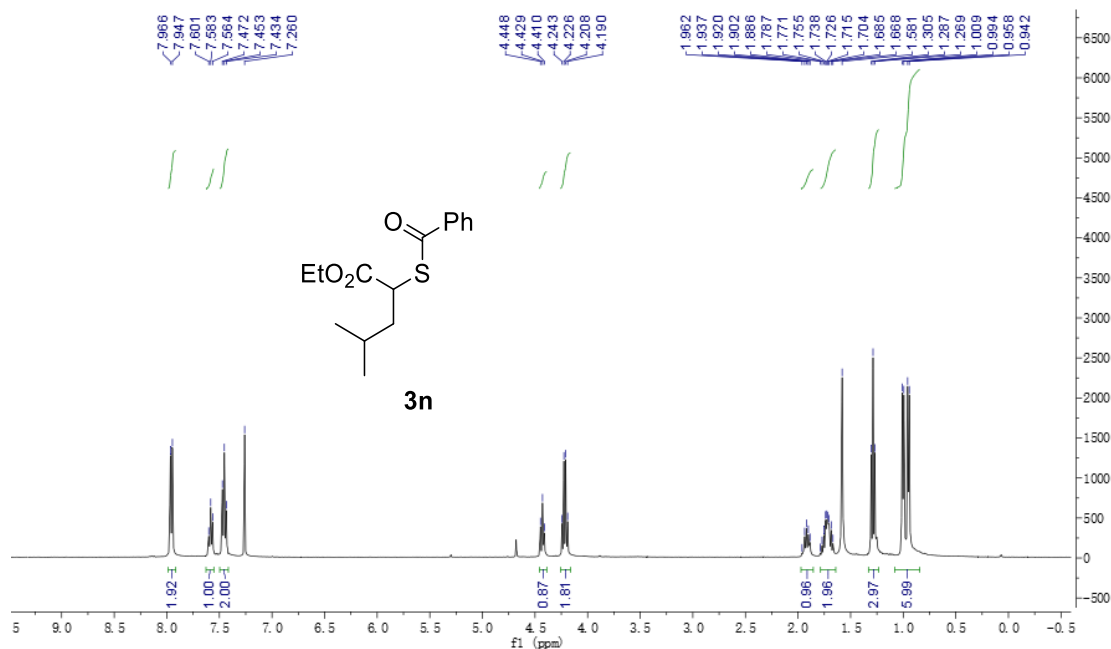
^1H NMR (400 MHz, CDCl_3) spectrum of product 3m



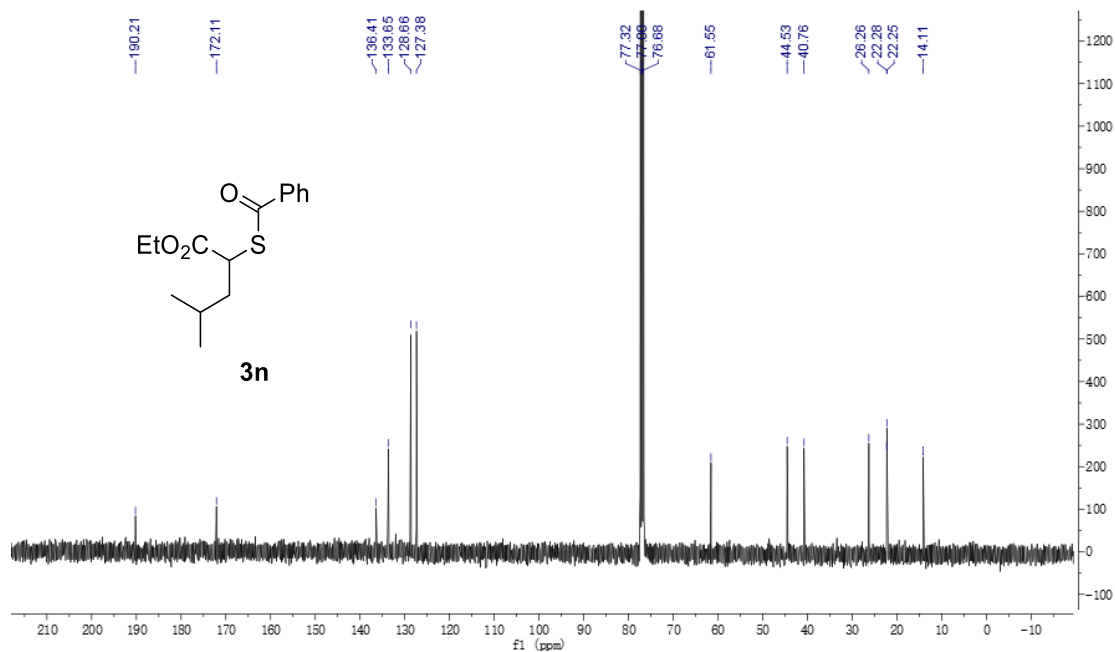
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3m



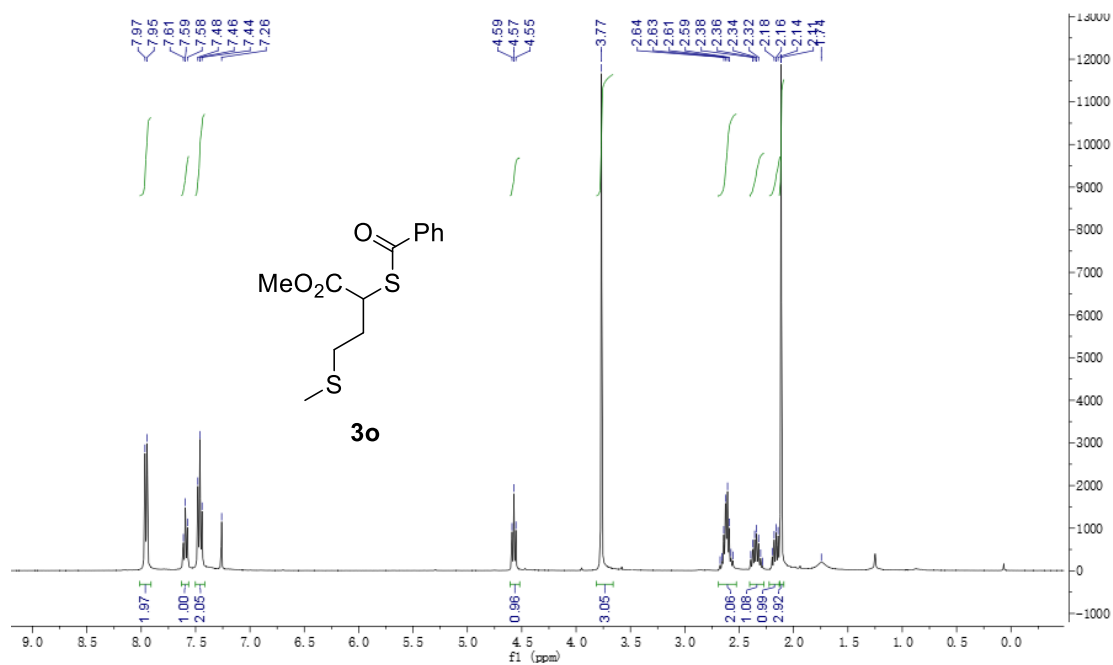
¹H NMR (400 MHz, CDCl₃) spectrum of product 3n



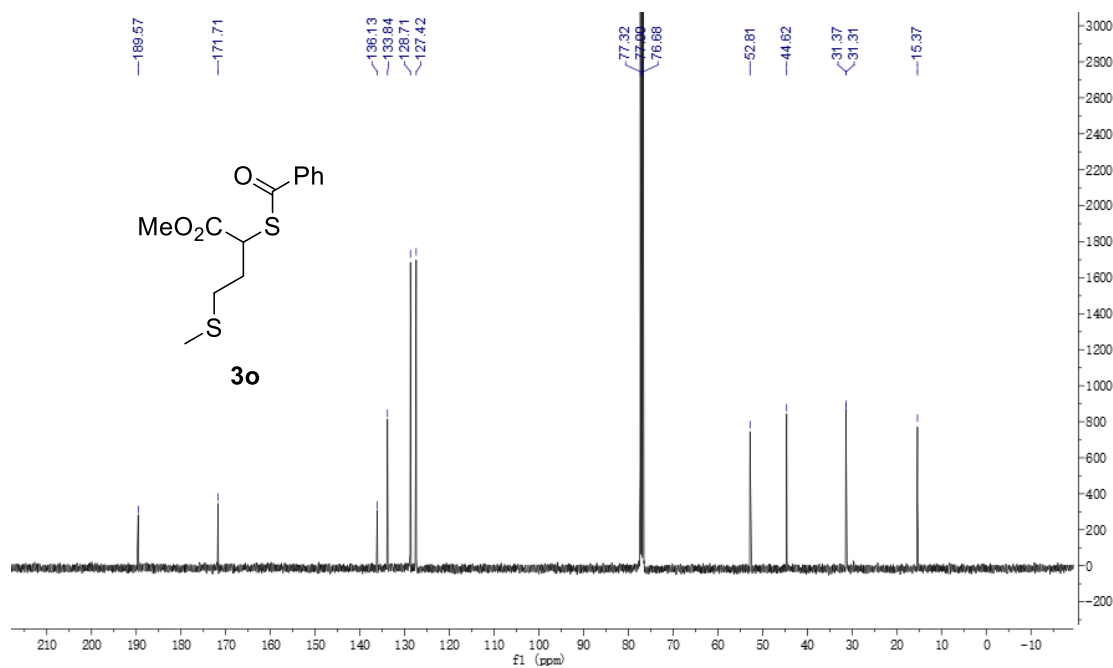
¹³C NMR (100 MHz, CDCl₃) spectrum of product 3n



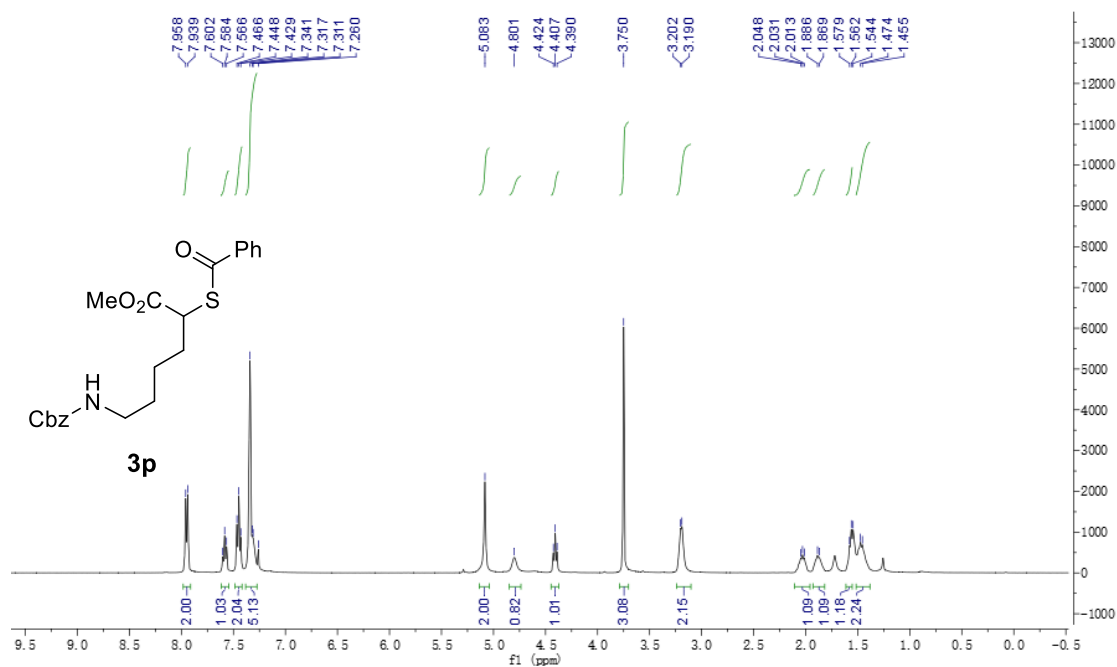
^1H NMR (400 MHz, CDCl_3) spectrum of product 3o



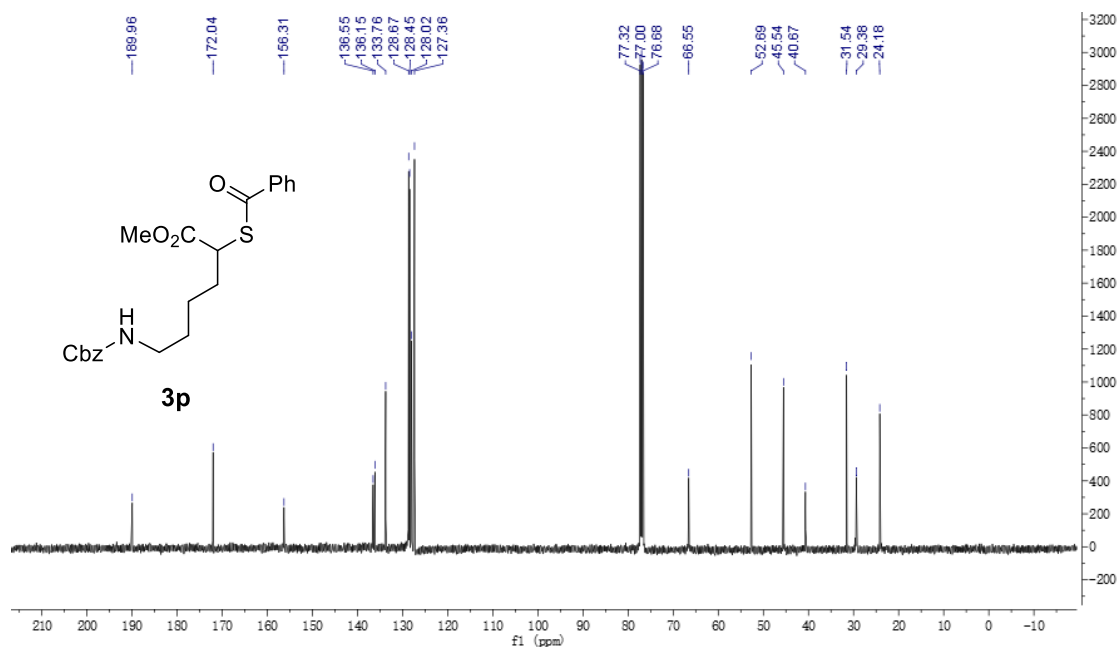
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3o



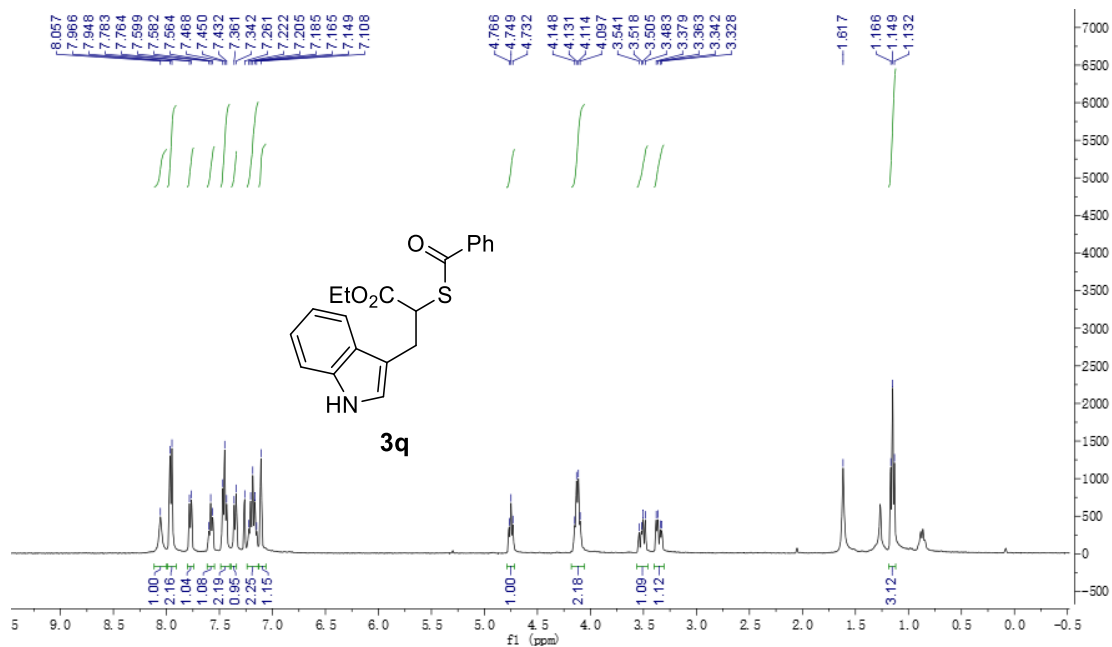
¹H NMR (400 MHz, CDCl₃) spectrum of product 3p



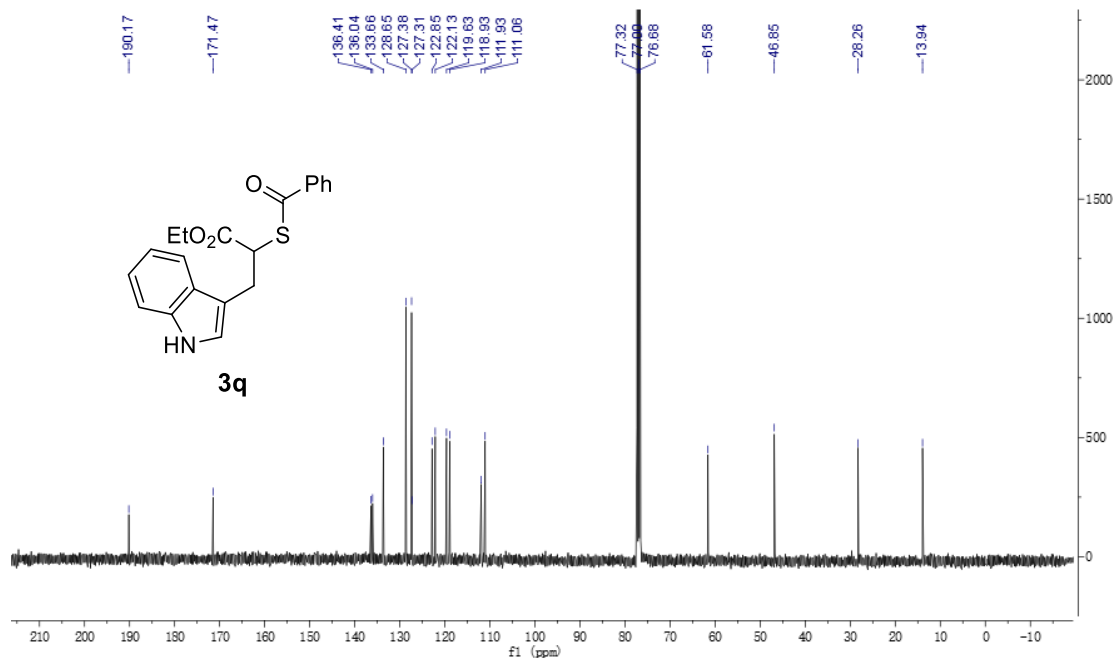
¹³C NMR (100 MHz, CDCl₃) spectrum of product 3p



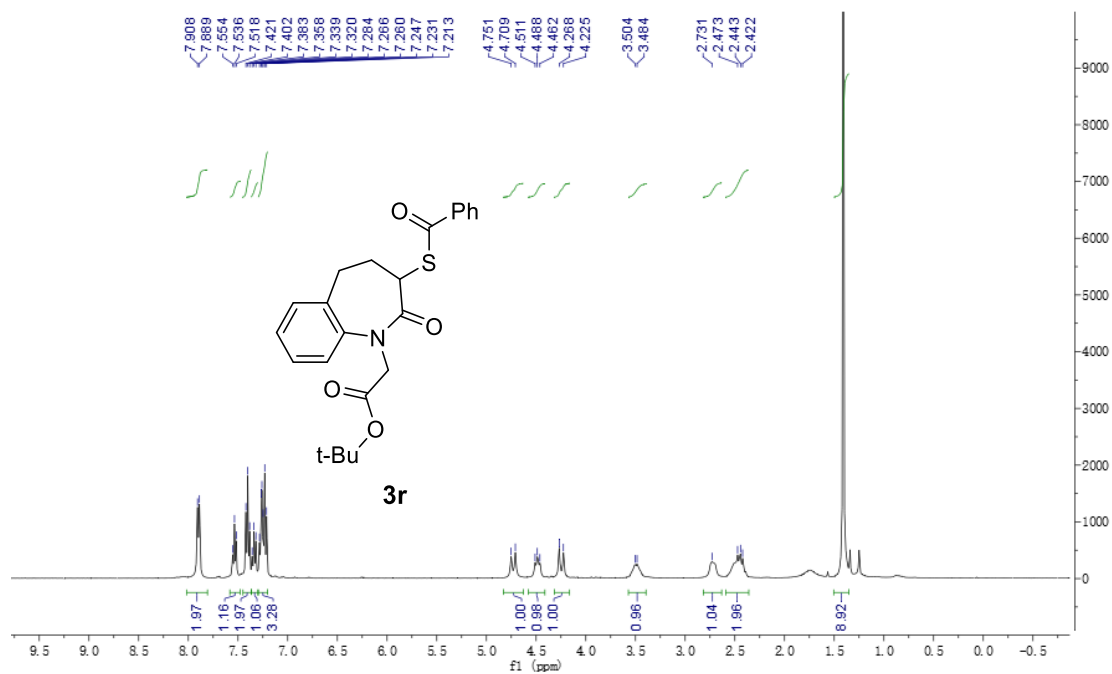
¹H NMR (400 MHz, CDCl₃) spectrum of product 3q



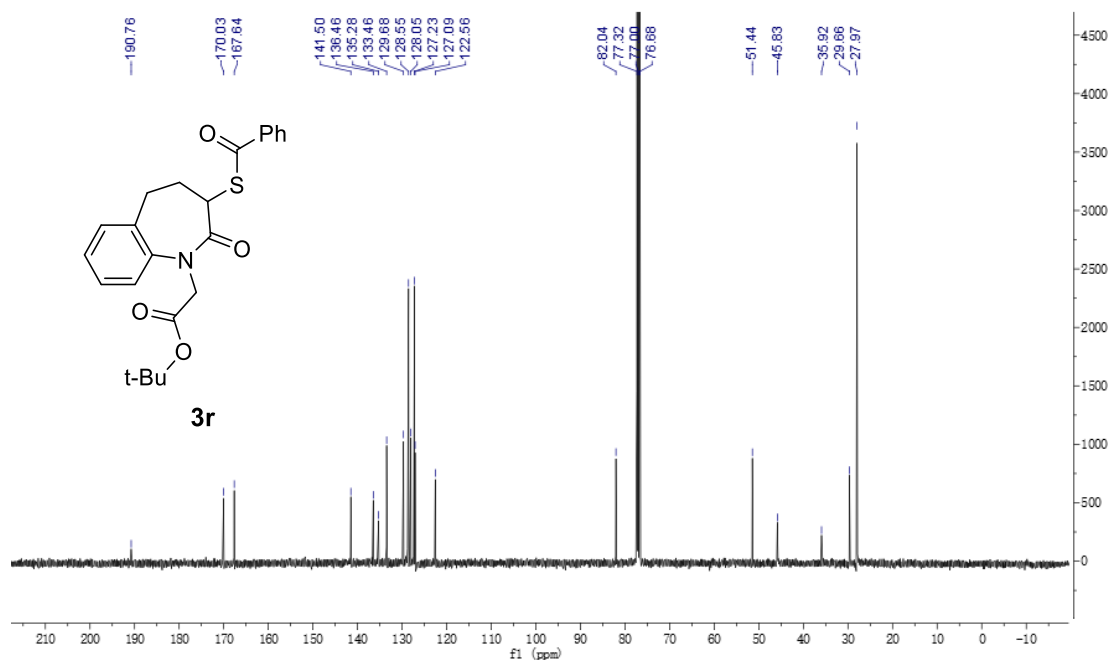
¹³C NMR (100 MHz, CDCl₃) spectrum of product 3q



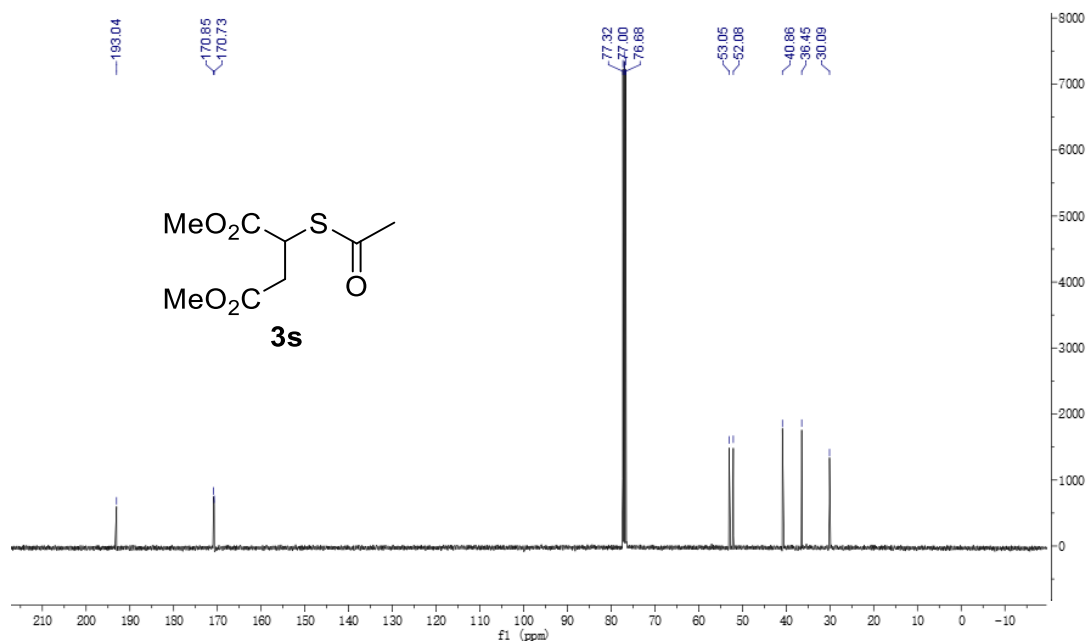
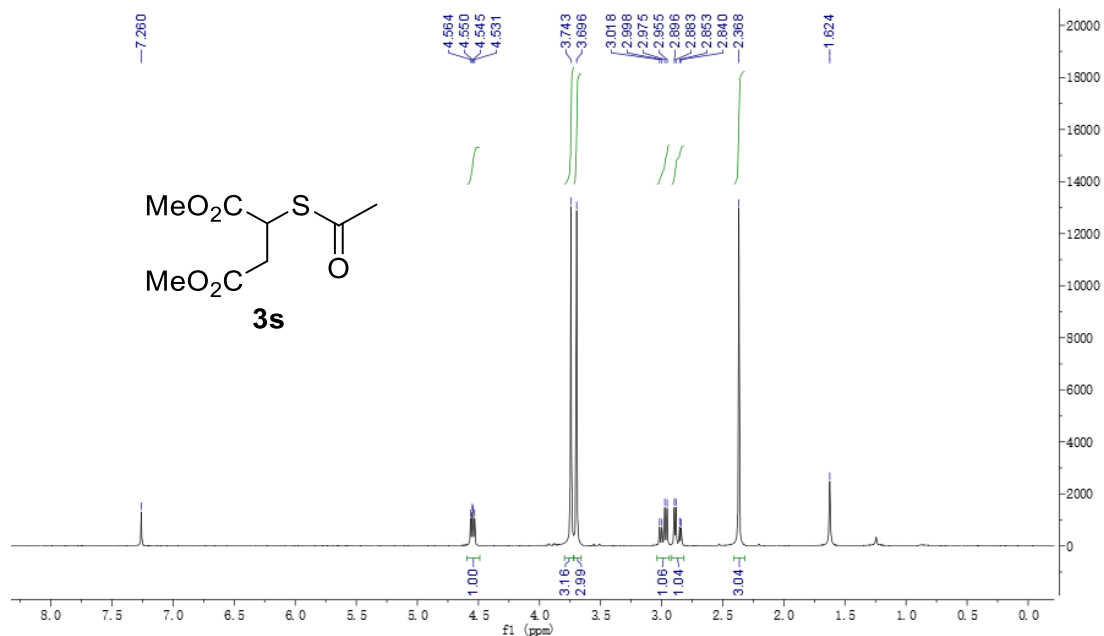
^1H NMR (400 MHz, CDCl_3) spectrum of product 3r



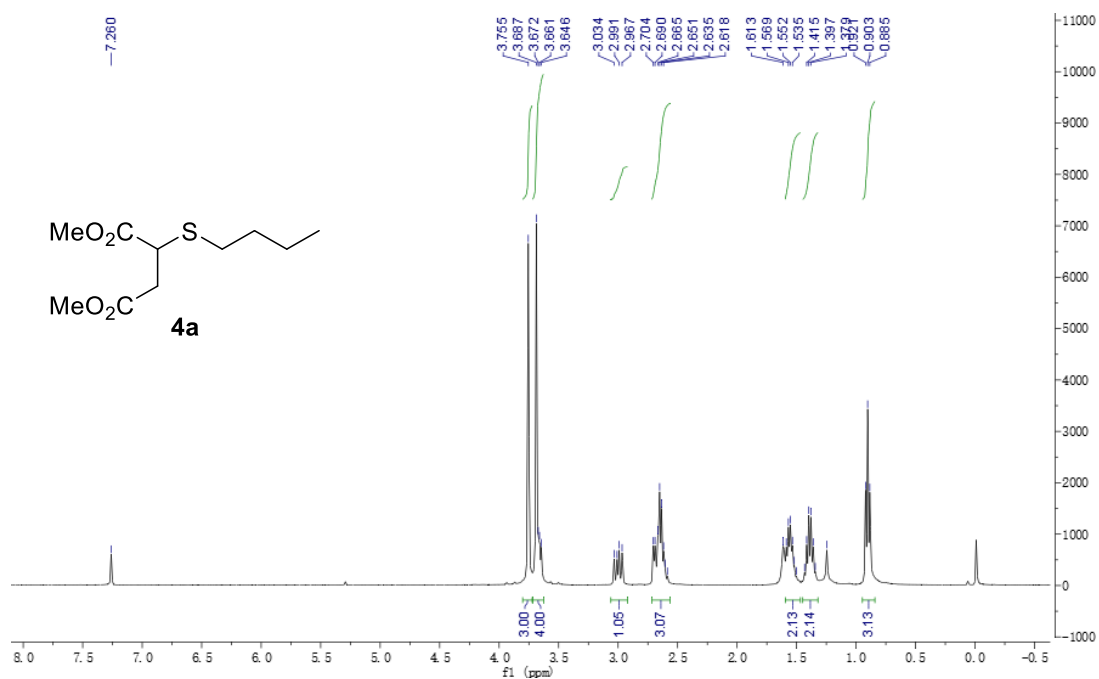
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 3r



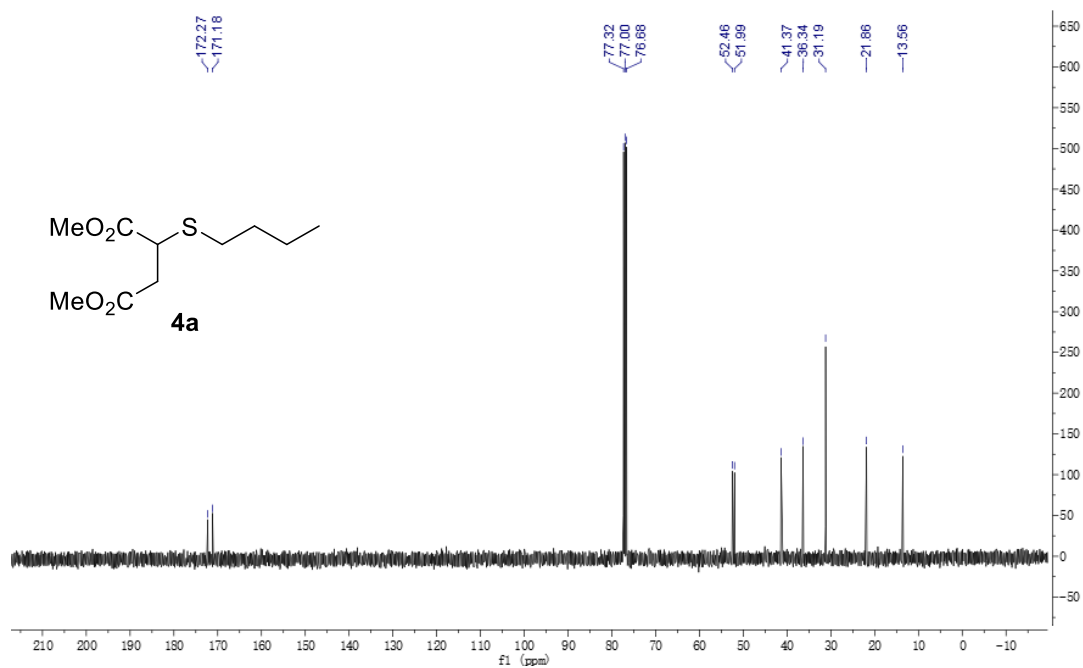
¹H NMR (400 MHz, CDCl₃) spectrum of product 3s



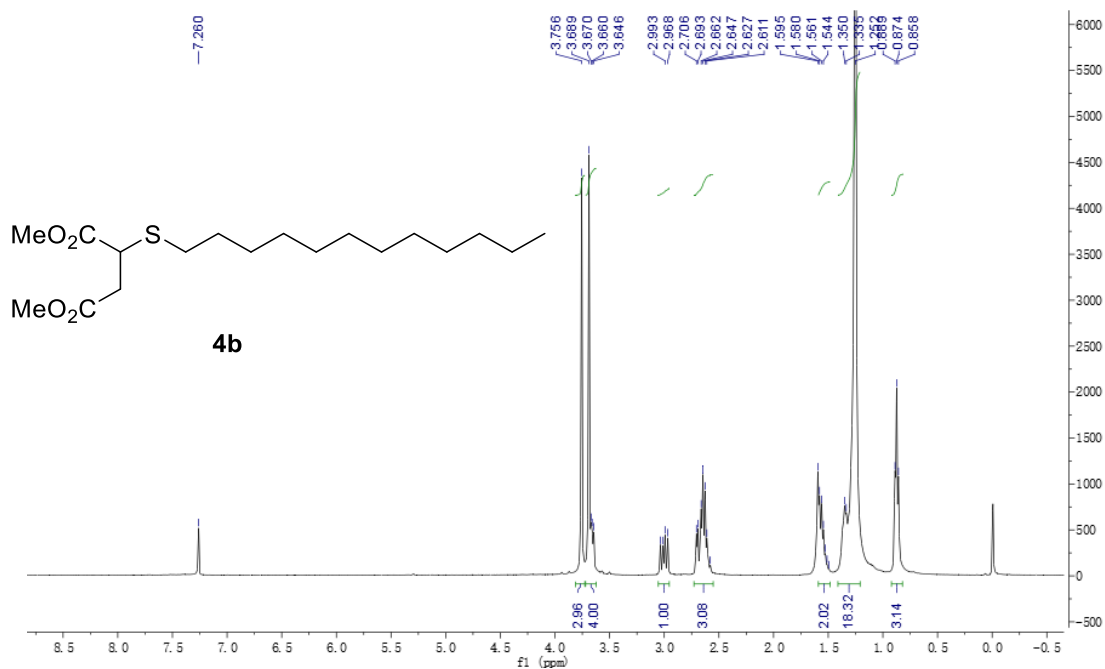
^1H NMR (400 MHz, CDCl_3) spectrum of product 4a



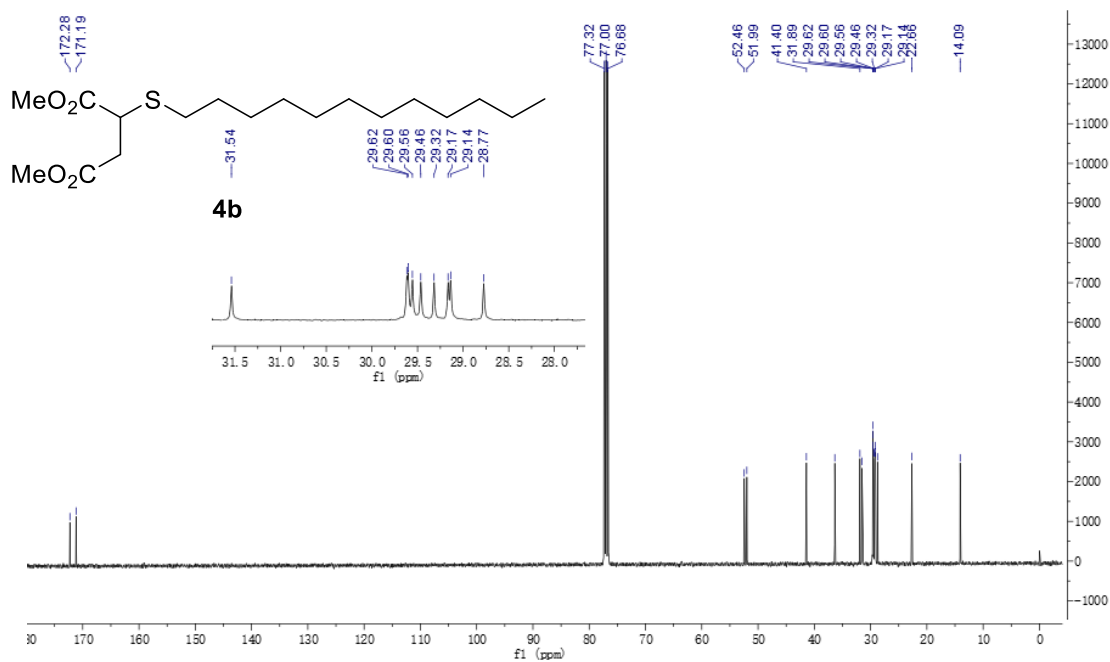
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 4a



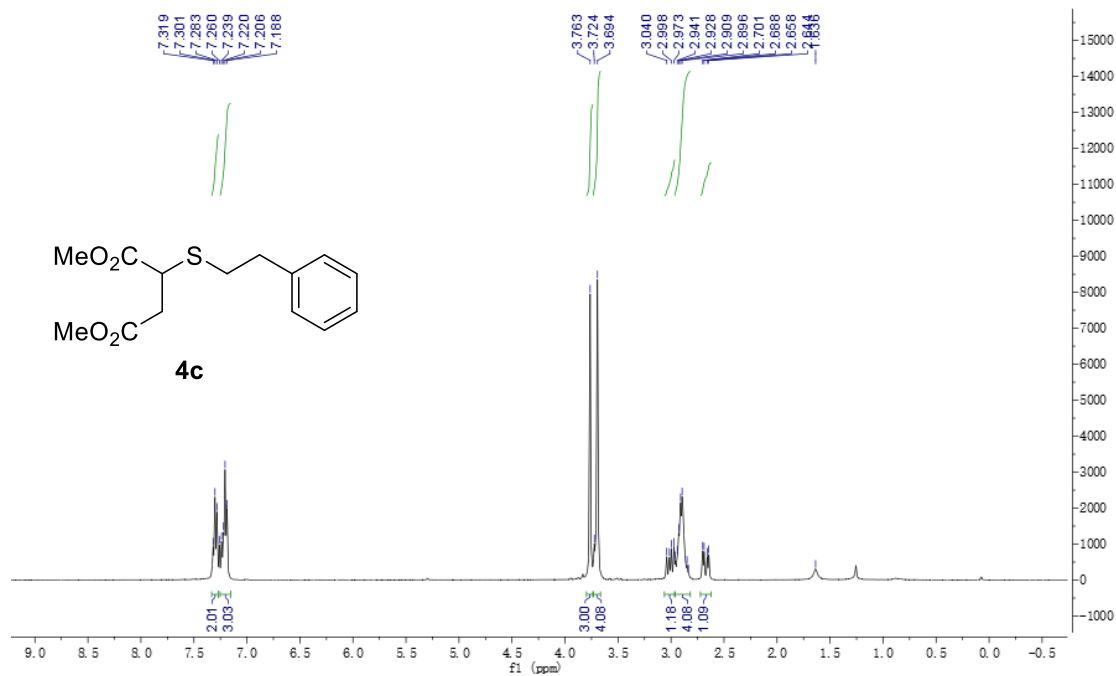
^1H NMR (400 MHz, CDCl_3) spectrum of product 4a



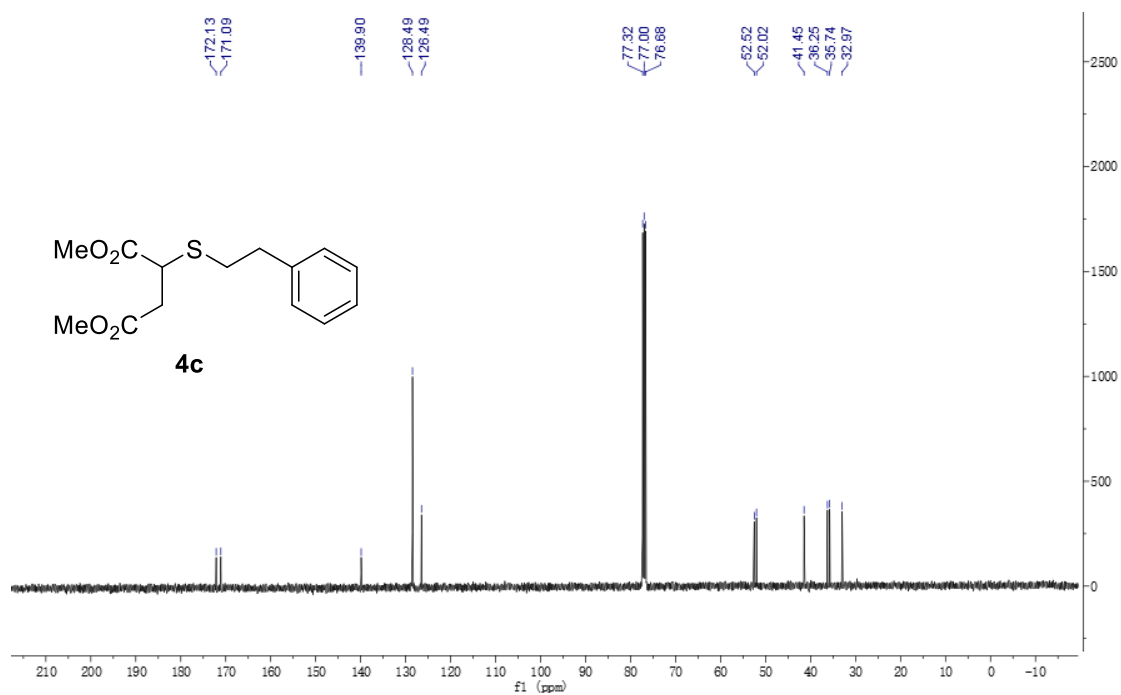
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 4b



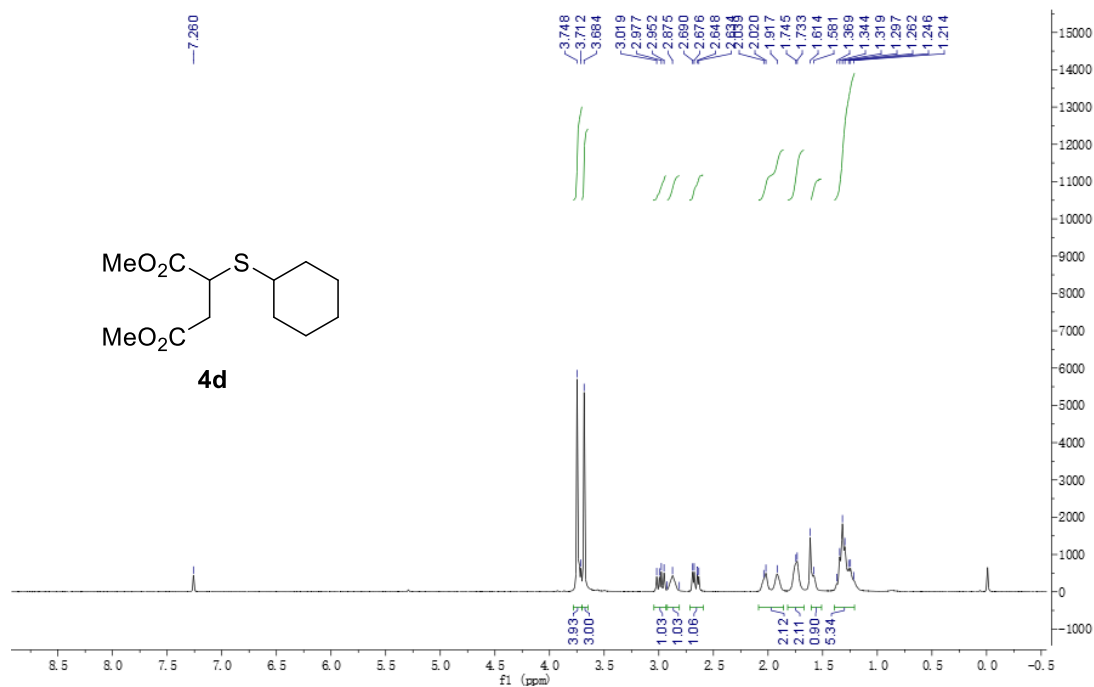
^1H NMR (400 MHz, CDCl_3) spectrum of product 4c



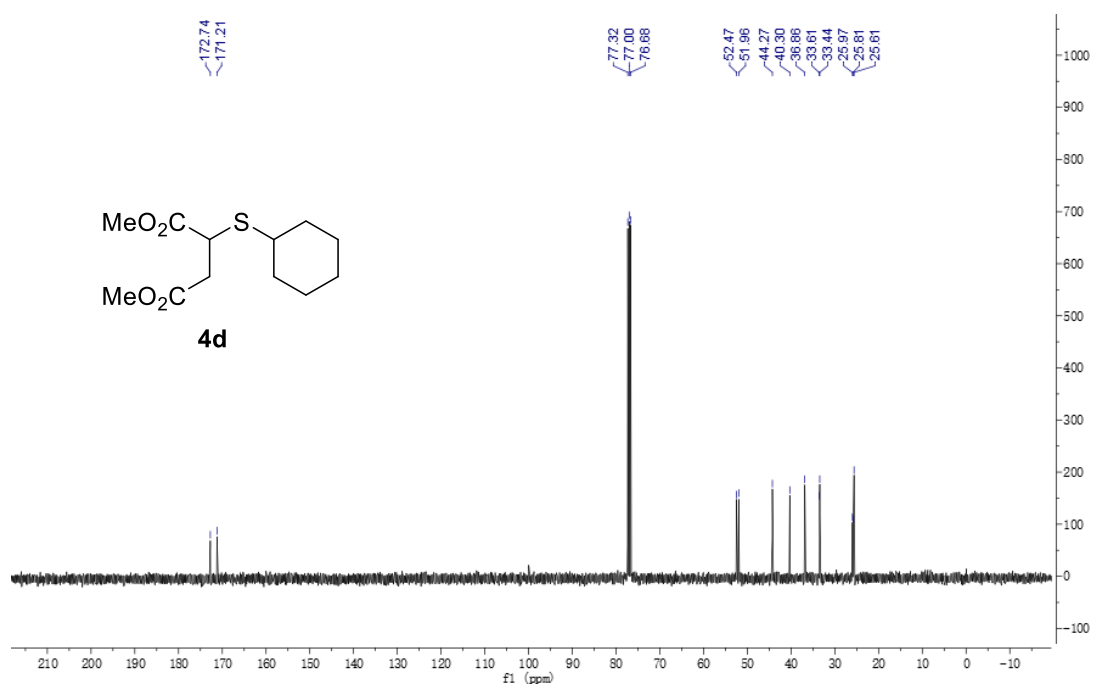
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 4c



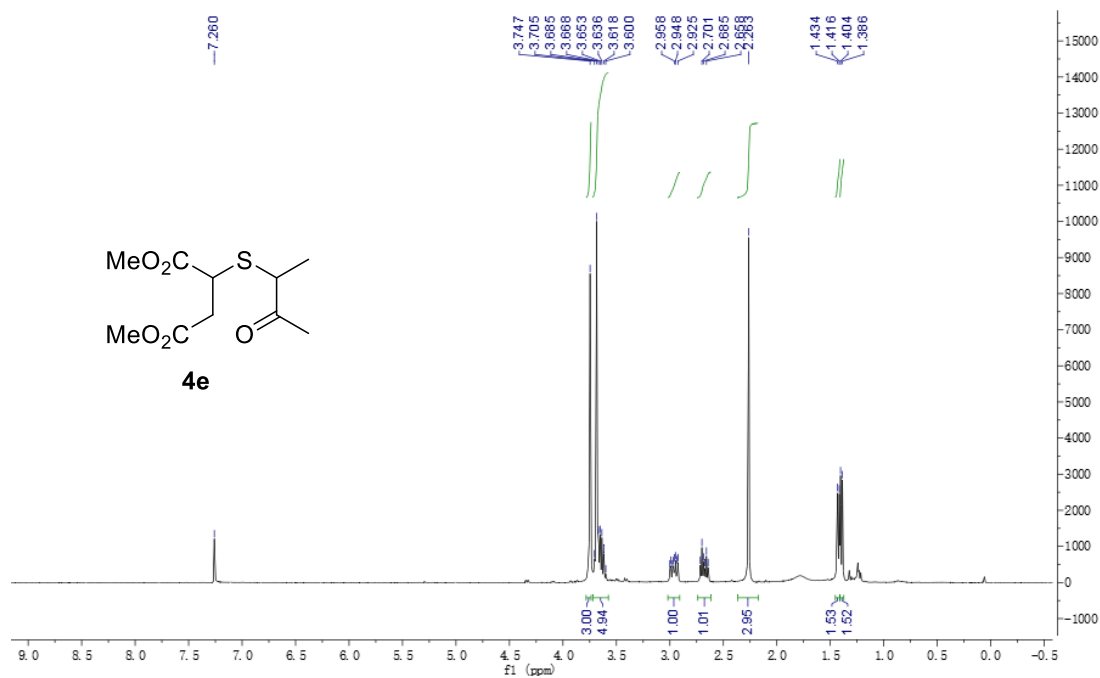
^1H NMR (400 MHz, CDCl_3) spectrum of product 4d



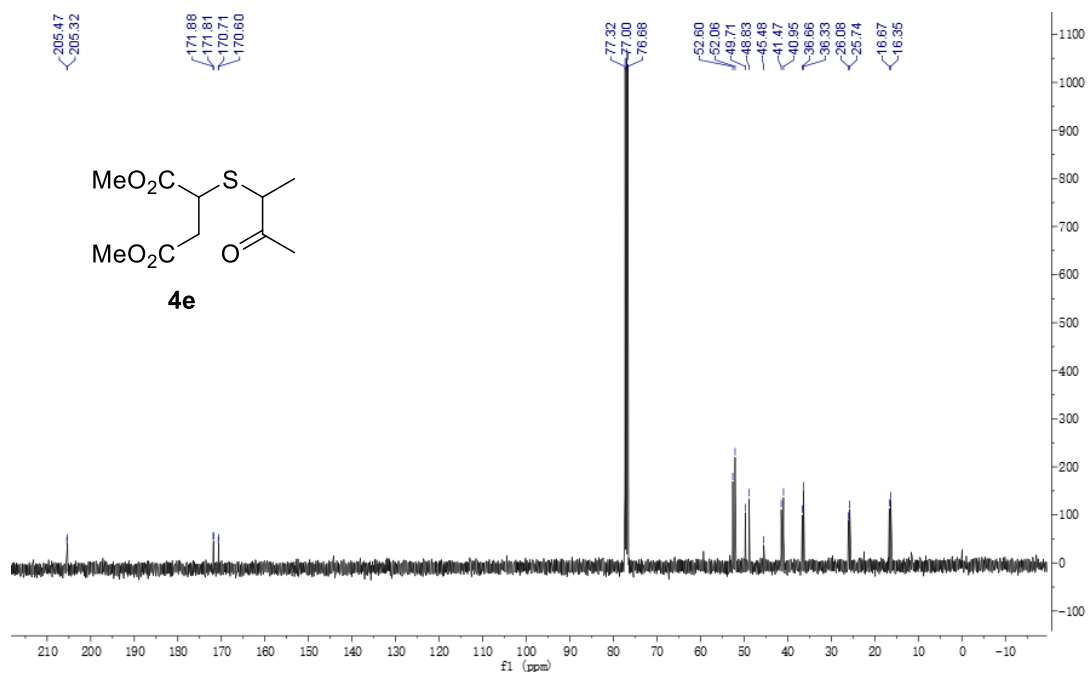
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 4d



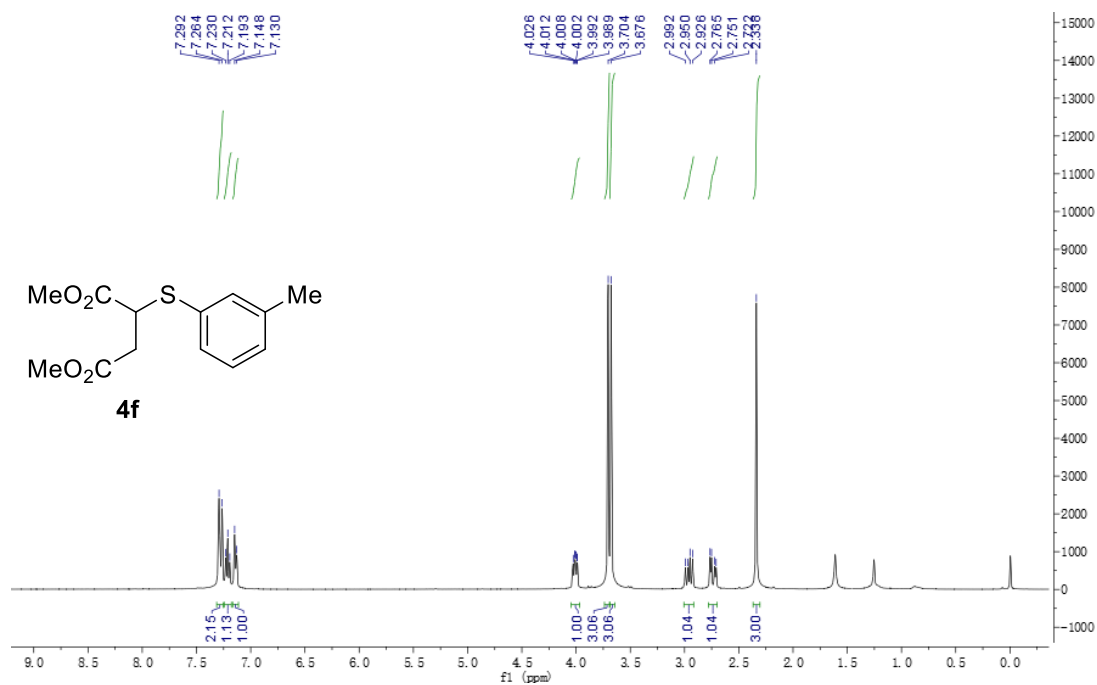
¹H NMR (400 MHz, CDCl₃) spectrum of product 4e



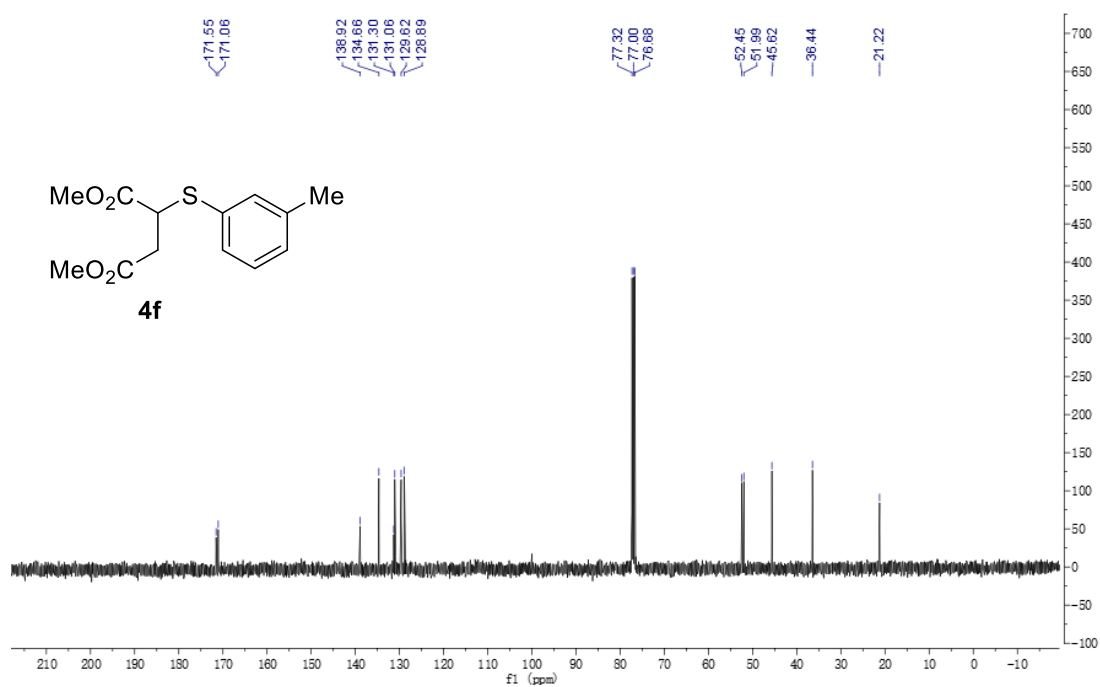
¹³C NMR (100 MHz, CDCl₃) spectrum of product 4e



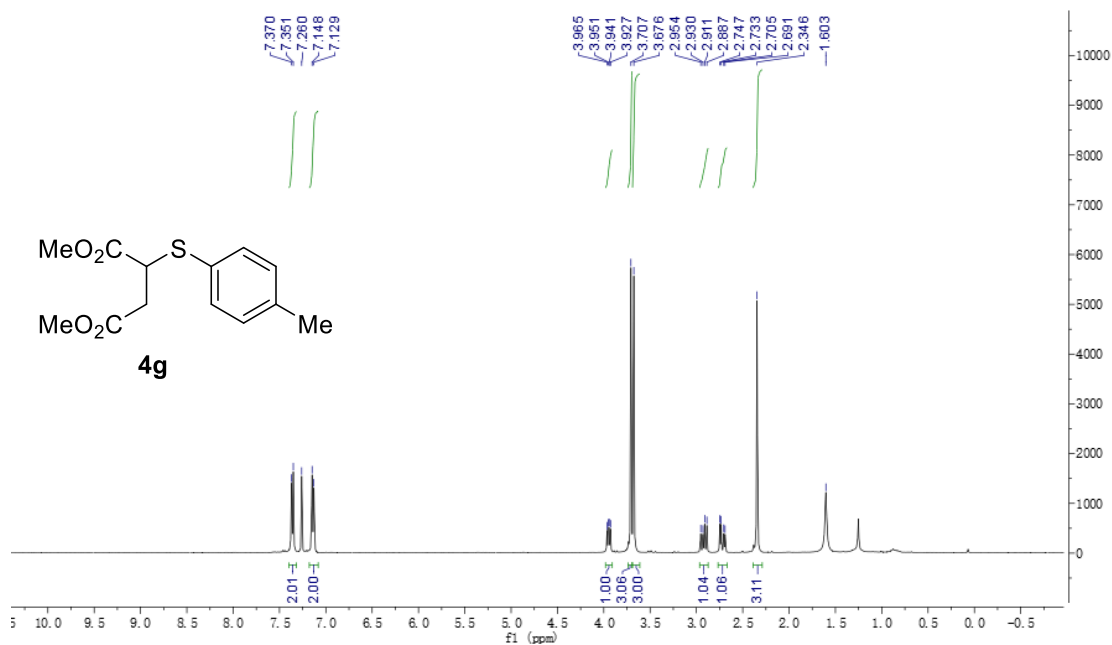
^1H NMR (400 MHz, CDCl_3) spectrum of product 4f



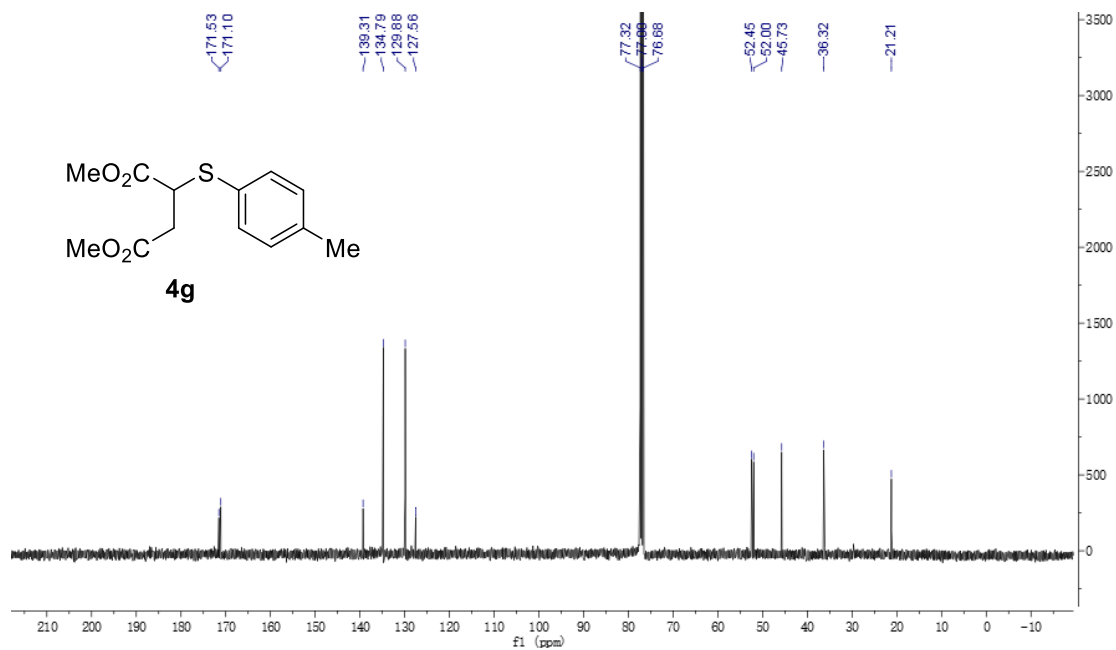
^{13}C NMR (100 MHz, CDCl_3) spectrum of product 4f



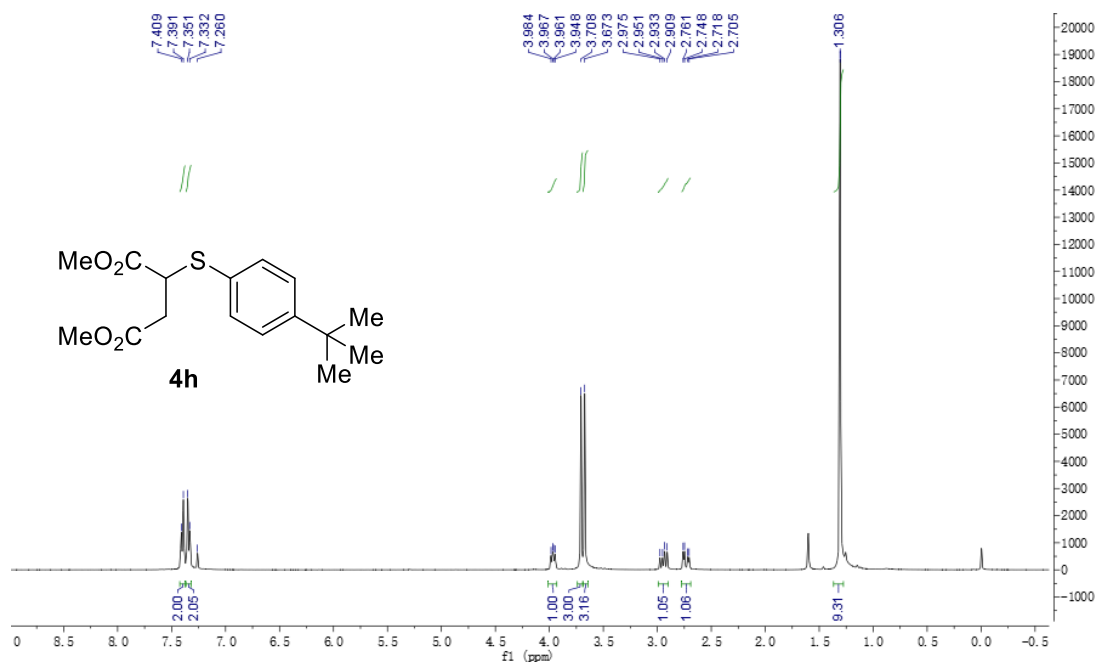
¹H NMR (400 MHz, CDCl₃) spectrum of product 4g



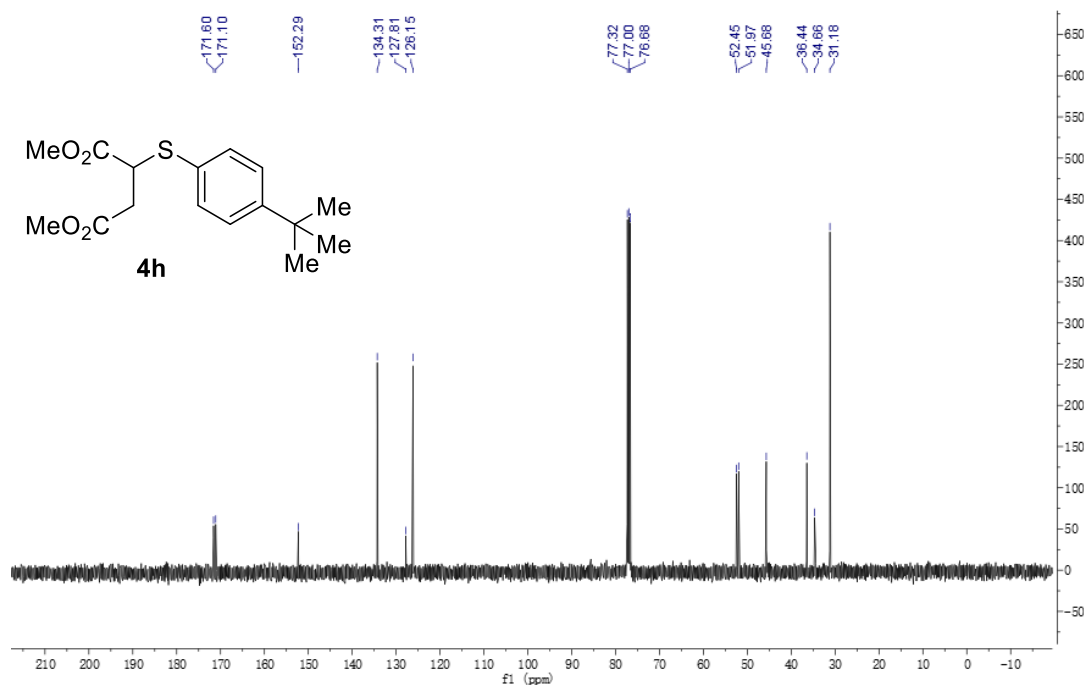
¹³C NMR (100 MHz, CDCl₃) spectrum of product 4g



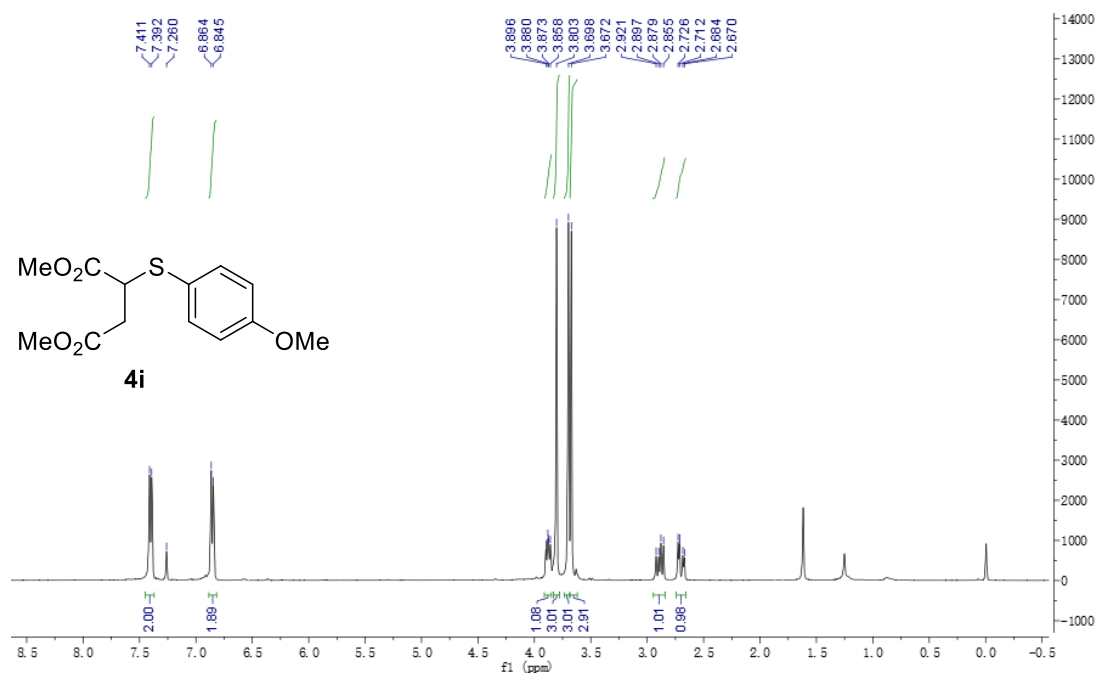
¹H NMR (400 MHz, CDCl₃) spectrum of product 4h



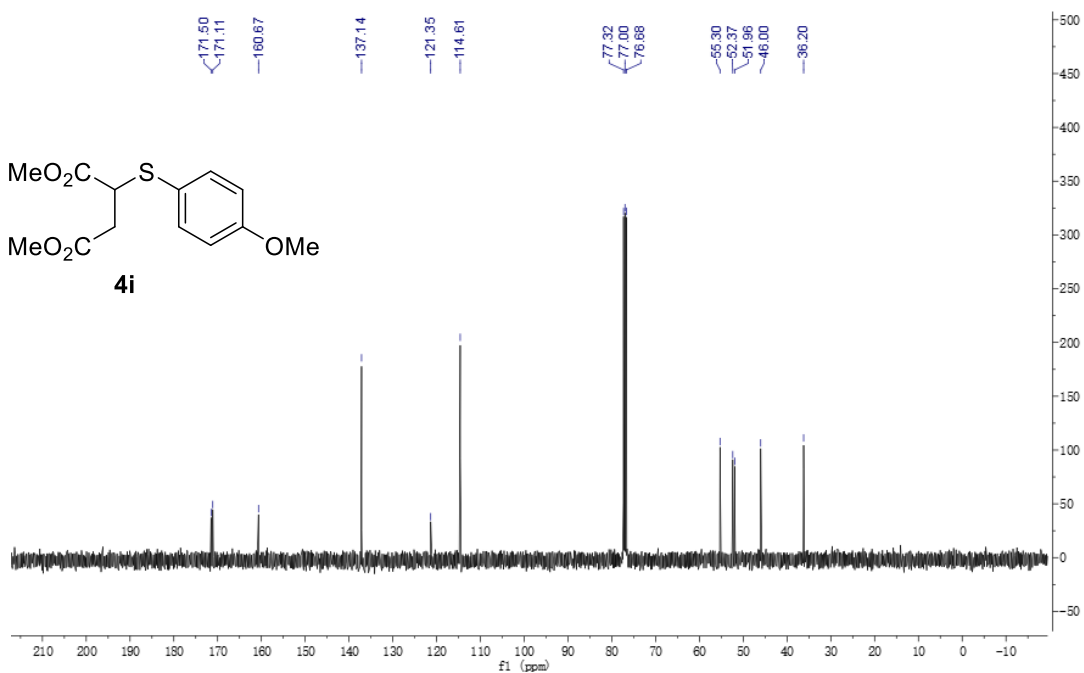
¹³C NMR (100 MHz, CDCl₃) spectrum of product 4h



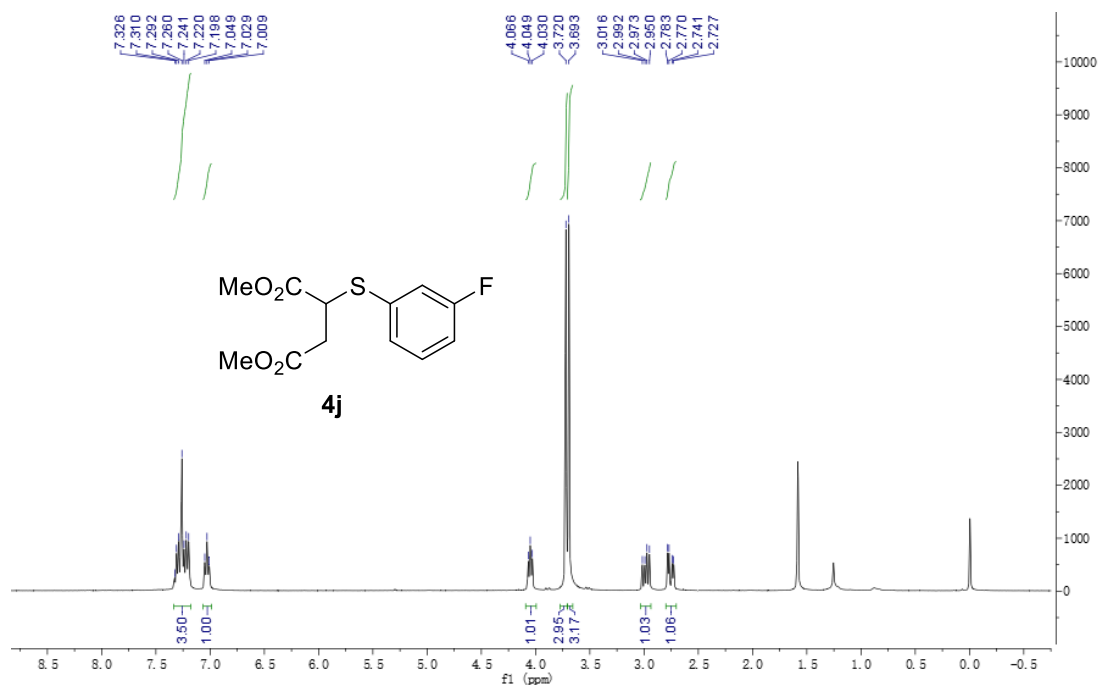
¹H NMR (400 MHz, CDCl₃) spectrum of product 4i



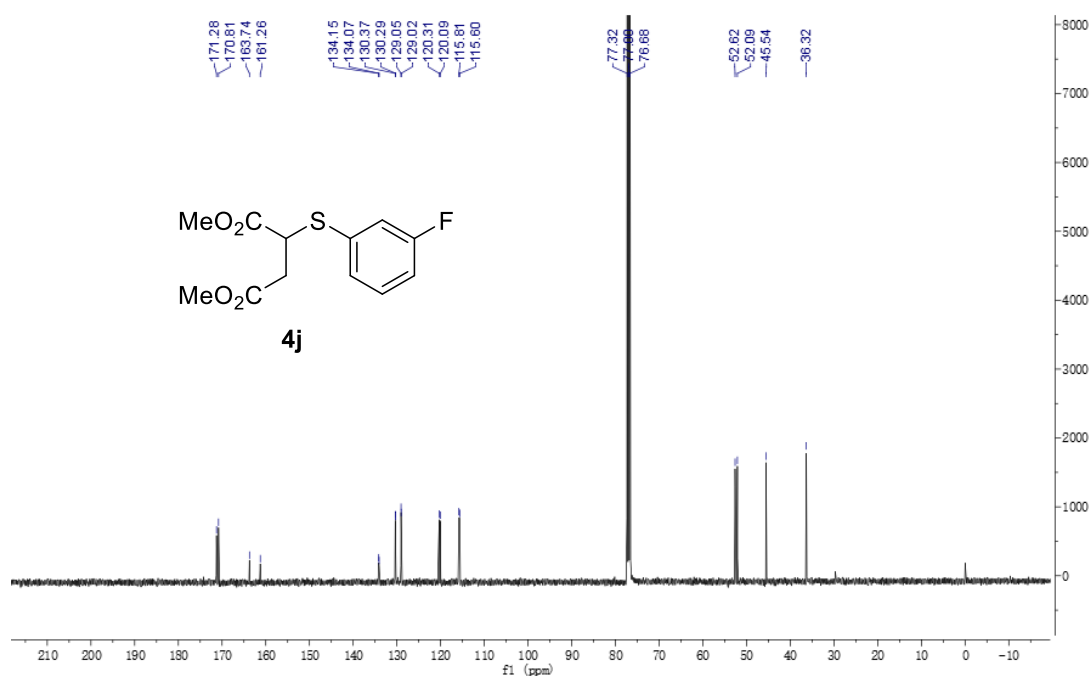
¹³C NMR (100 MHz, CDCl₃) spectrum of product 4i



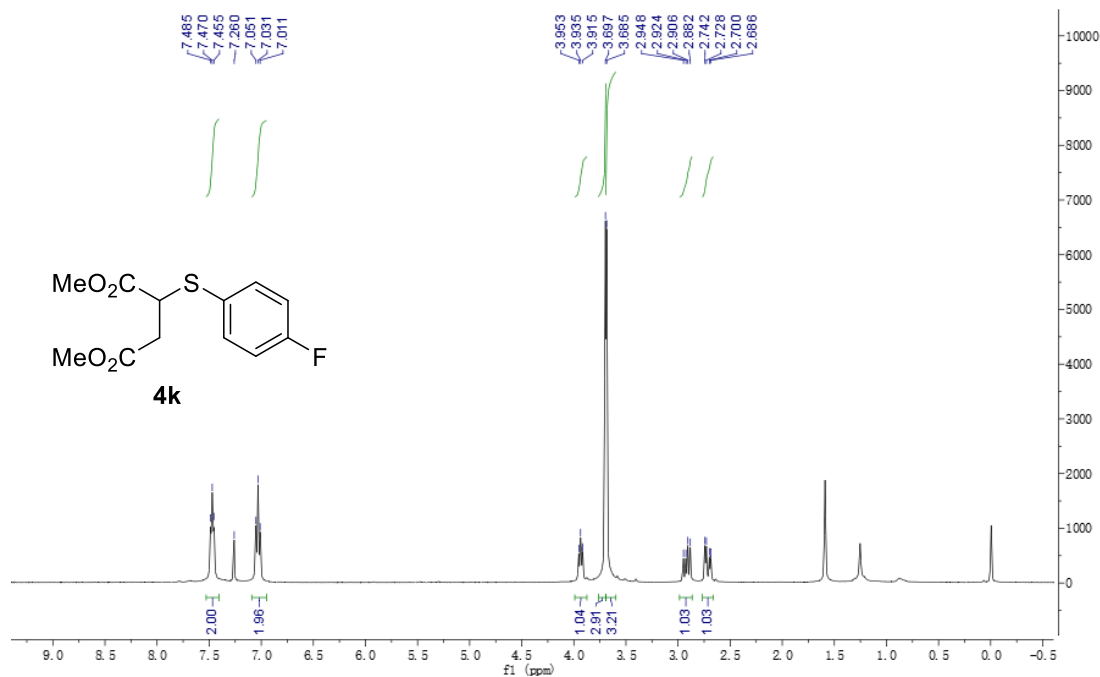
¹H NMR (400 MHz, CDCl₃) spectrum of product 4j



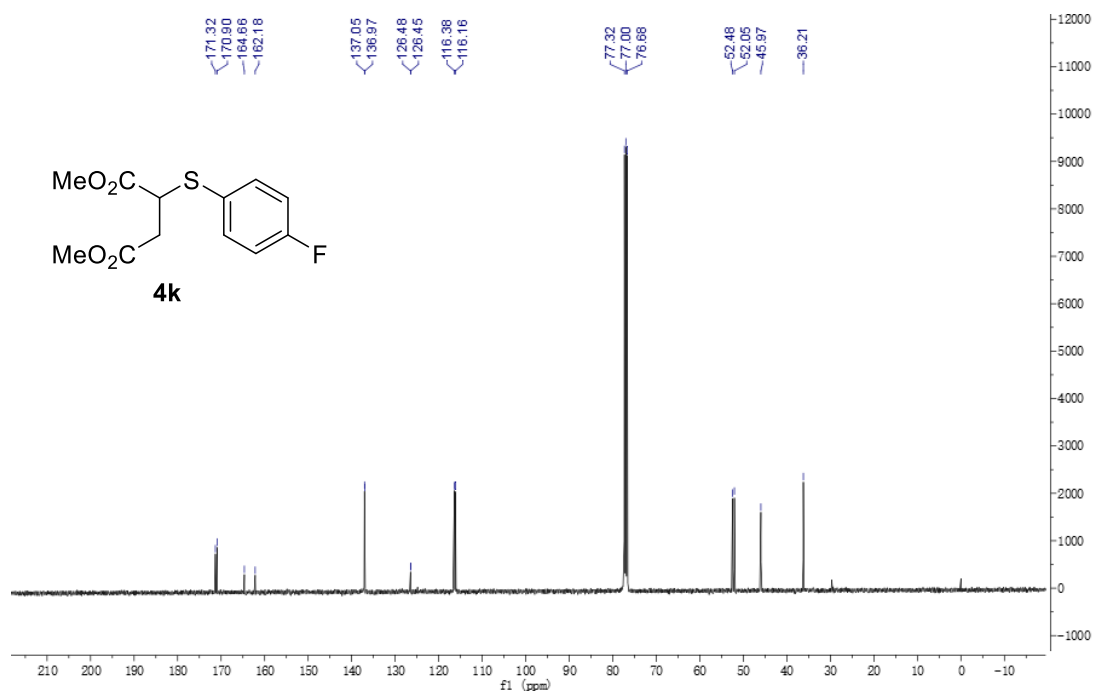
¹³C NMR (100 MHz, CDCl₃) spectrum of product 4j



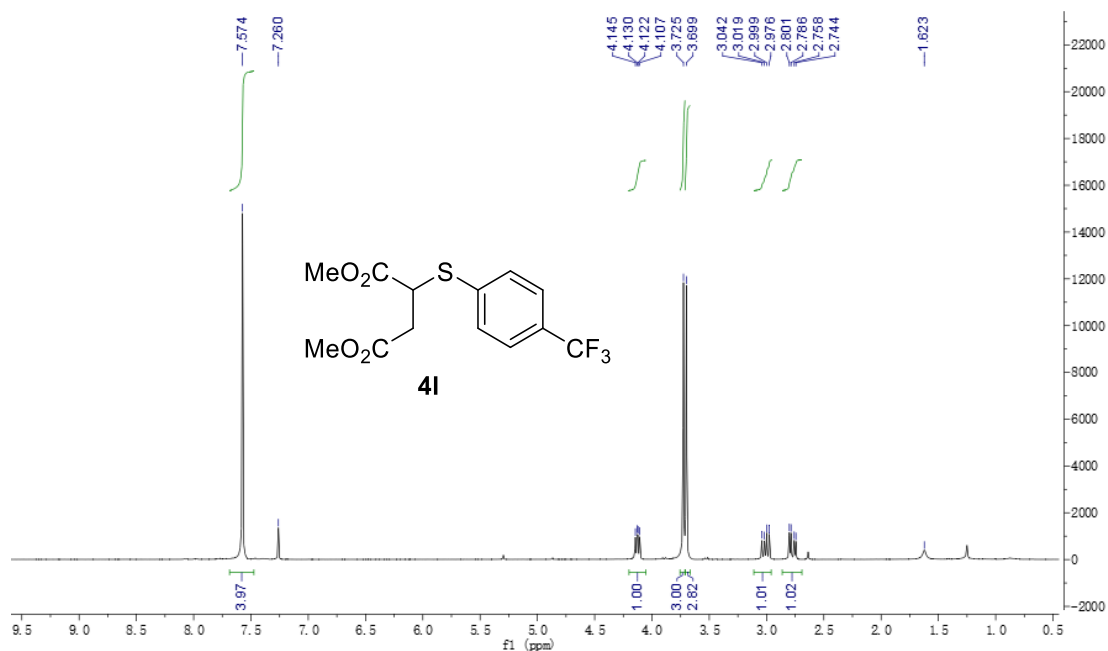
¹H NMR (400 MHz, CDCl₃) spectrum of product 4k



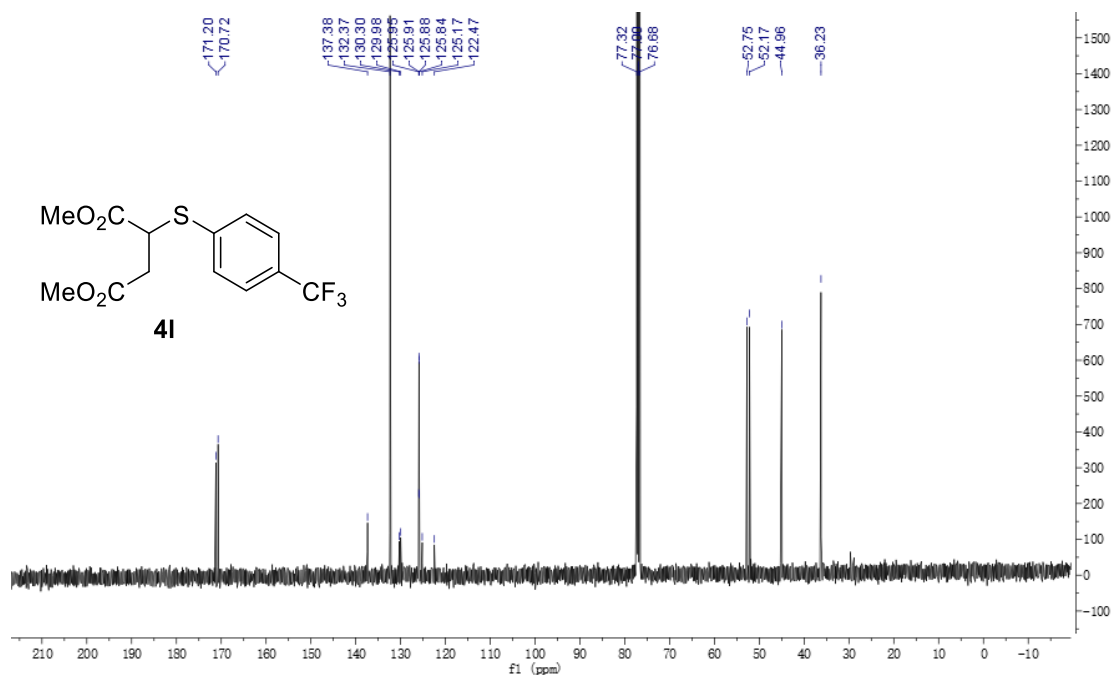
¹³C NMR (100 MHz, CDCl₃) spectrum of product 4k



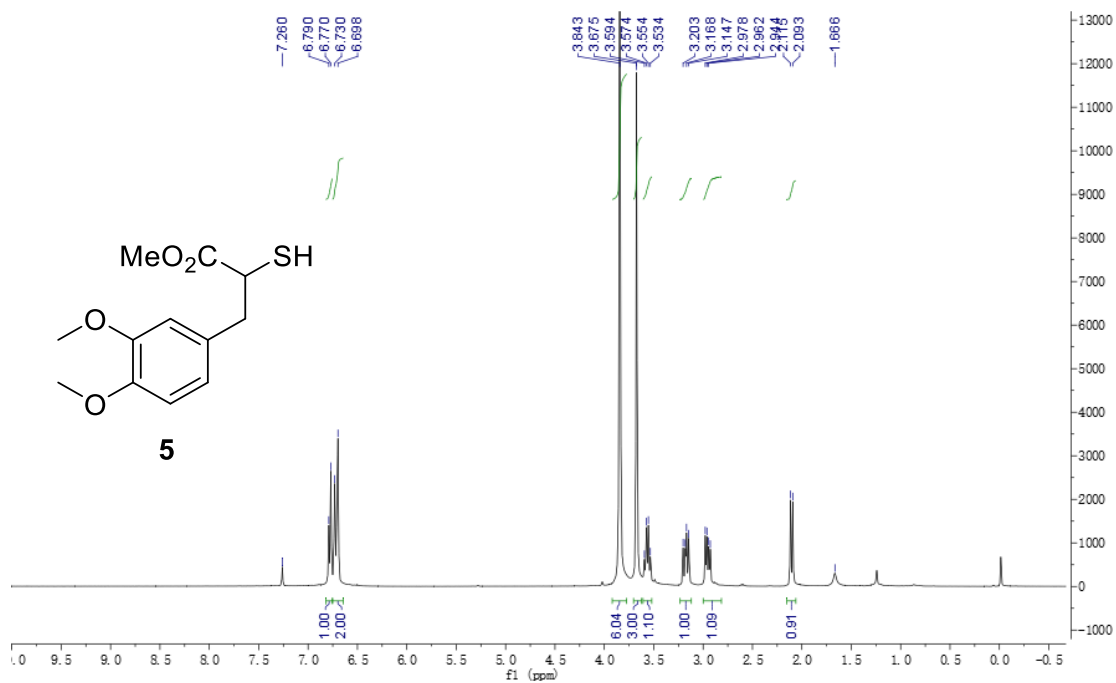
¹H NMR (400 MHz, CDCl₃) spectrum of product 4I



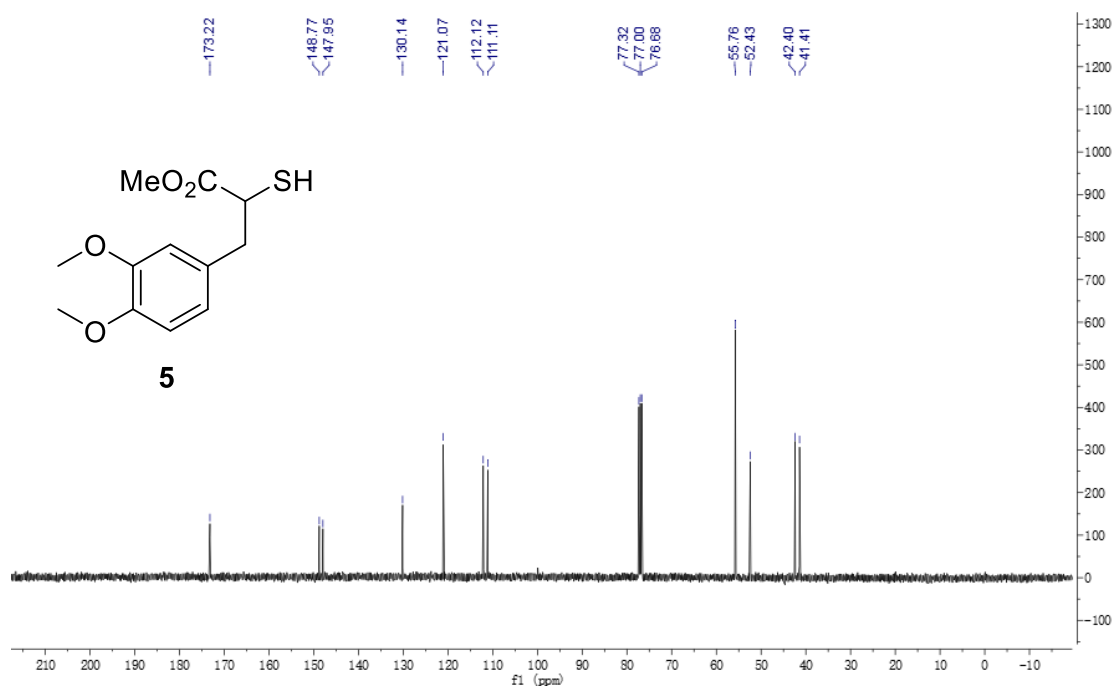
¹³C NMR (100 MHz, CDCl₃) spectrum of product 4I



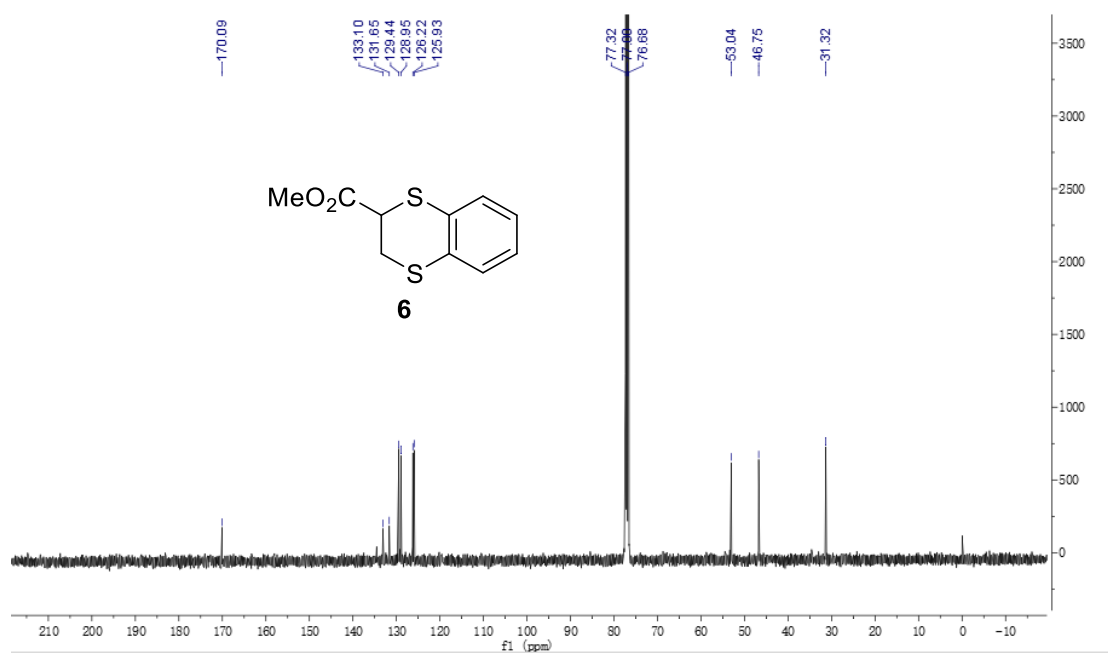
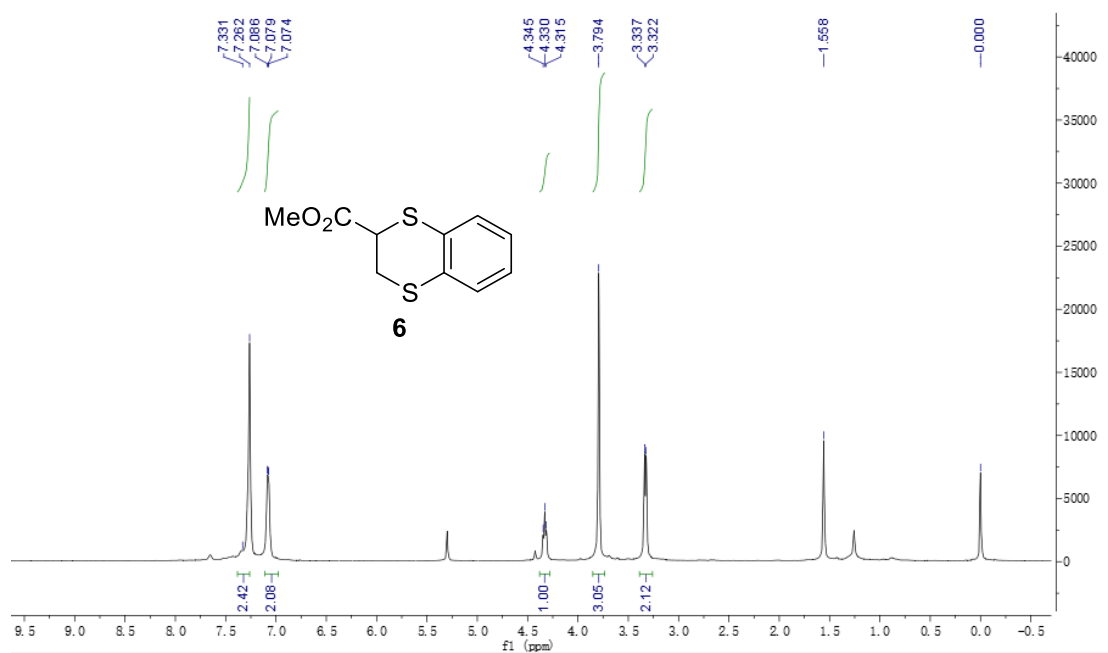
¹H NMR (400 MHz, CDCl₃) spectrum of product 5



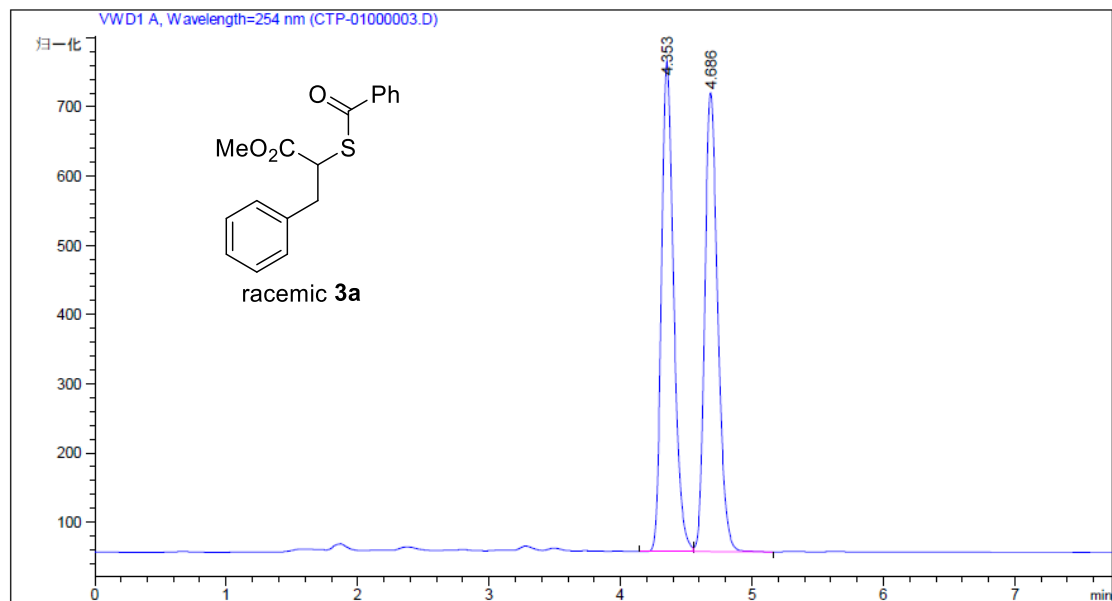
¹³C NMR (100 MHz, CDCl₃) spectrum of product 6



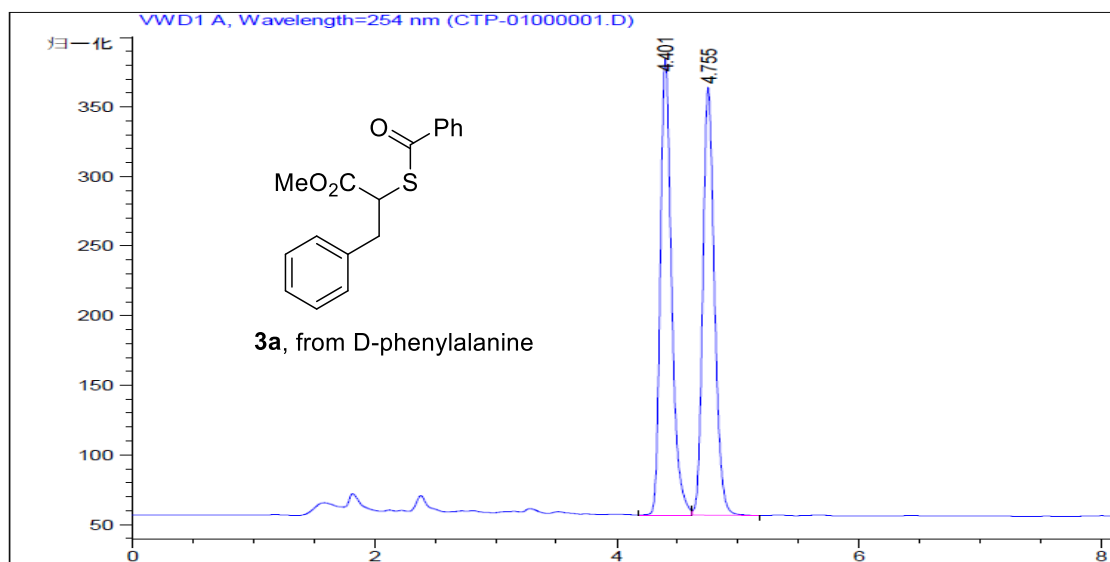
¹H NMR (400 MHz, CDCl₃) spectrum of product 6



9. HPLC Traces



Peak #	Ret. Time (detected)	mold	Area [mAU*s]	Height [mAU]	Area %
1	4.353	BV	4581.93018	708.14648	50.0970
2	4.686	VB	4564.19482	663.33612	49.9030



Peak #	Ret. Time (detected)	mold	Area [mAU*s]	Height [mAU]	Area %
1	4.401	BV	2117.57349	327.36856	50.6413
2	4.755	VB	2063.93726	307.18964	49.3587