Supporting Information

Nitroalkanes as Thioacyl Equivalents to Access Thioamides and Thiopeptides

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1. General Information

Unless otherwise stated, all reagents were used as received from commercial suppliers. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with silica gel F_{254} with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. 1-Nitropropane was purchased from energy-chemical Co. Flash column chromatography was performed using silica gel (200-300 mesh, Merck and Co.). Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers (ν_{max}) are reported in cm^{-1}. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). All ^{1}H NMR and ^{13}C NMR spectra were recorded using a JEOL JNM AL 400 (400 MHz) at 300K. Chemical shifts are given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at $\delta = 7.26$ ppm (^{1}H NMR) and $\delta = 77.16$ (^{13}C NMR). Coupling constants are quoted in Hz (J). ^{1}H NMR splitting patterns were designated as singlet (*s*), doublet (*d*), triplet (*t*), quartet (*q*), pentet (*p*). Splitting patterns that could not be interpreted or adequately resolved are designated as multiplet (*m*) or broad (*br*). All the absorption spectra were measured using a Perkin Elmer Lambda 25 UV/Vis Spectrophotometer.

2. Synthesis of Starting Materials.

2.1 Synthesis of Electrophilic *S*-sources:

The **S** source **3a**, **3b**, **3c** were prepared according to a reported procedure.[1]

The **S** source **3d** was prepared in 87% yield (5 mmol) from isopropol and sulfur chloride according to a reported procedure.[2]

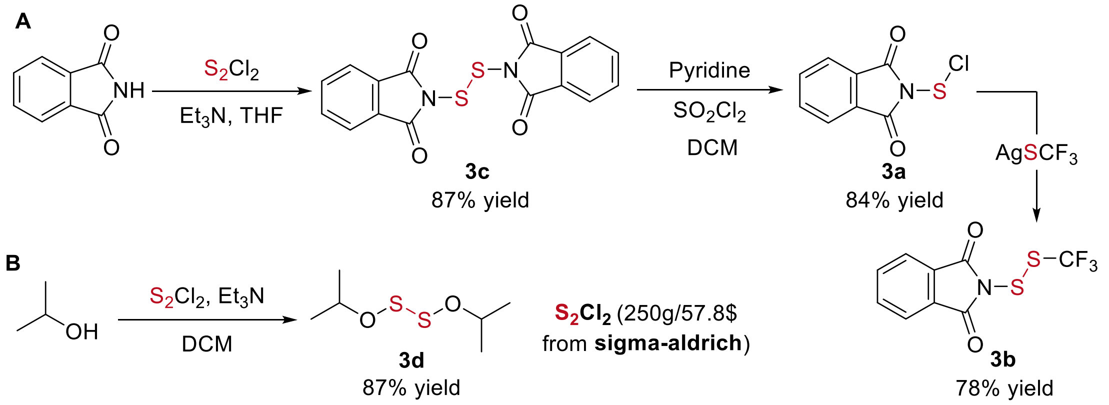
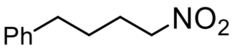


Figure S1 Preparation of electrophilic ***S***-sources **3a–3d**

2.2 Synthesis of nitro compounds:

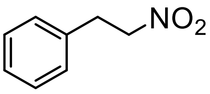
(4-Nitrobutyl)benzene (**1a**)



1a

The nitro compound **1a** was prepared in 51% yield (5 mmol) from 3-phenylpropanal in two steps according to a reported procedure. Spectral data was consistent with literature reported[3].

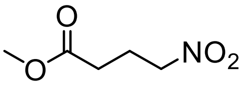
(2-Nitroethyl)benzene (**1b**)



1b

The nitro compound was prepared in 92% yield (2.5 mmol) according to a reported procedure.[4]

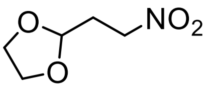
Methyl 4-nitrobutanoate (**1c**)



1c

The nitro compound (**1c**) was prepared in 64% yield (4.2 mmol) according to a reported procedure.[5]

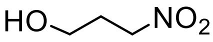
2-(2-Nitroethyl)-1,3-dioxolane (**1d**)



1d

The nitro compound was prepared in 76% yield (5 mmol) from 3-nitropropanal in one step according to a reported procedure.[6]

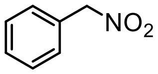
3-Nitropropan-1-ol (**1e**)



1e

The nitro compound was prepared in 70% yield (3 mmol) from acrylaldehyde in two steps according to a reported procedure.[3]

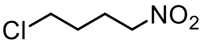
(Nitromethyl)benzene (1f)



1f

The nitro compound was prepared in 89% yield (3.6 mmol) according to a reported procedure.[7]

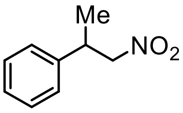
1-Chloro-5-nitropentane (1g)



1g

The nitro compound was prepared in 70% yield (5 mmol) according to a reported procedure.[8]

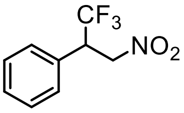
(1-Nitropropan-2-yl)benzene (1h)



1h

The nitro compound was prepared in 92% yield (5 mmol) according to a reported procedure.[9]

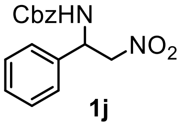
(1,1,1-Trifluoro-3-nitropropan-2-yl)benzene (1i)



1i

The nitro compound was prepared in 71% yield (2.3 mmol) from (*E*)-(3,3,3-trifluoro-1-nitroprop-1-en-2-yl)benzene in one step according to a reported procedure.[10]

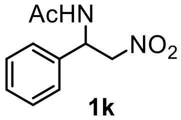
Benzyl (2-nitro-1-phenylethyl)carbamate (1j)



1j

The nitro compound was prepared in 70% yield (5 mmol) according to a reported procedure.[11]

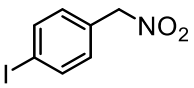
N-(2-nitro-1-phenylethyl)acetamide (1k)



1k

The nitro compound was prepared in 51% yield (5 mmol) according to a reported procedure.[12]

1-Iodo-4-(nitromethyl)benzene (1l)



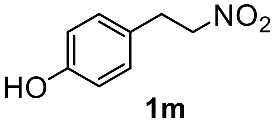
1l

The nitro compound was prepared in 53% yield (5 mmol) from 1-Iodo-4-(iodomethyl)benzene in one step according to a reported procedure.[14]

^{1}H NMR (101 MHz, CDCl$_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 5.37 (s, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 138.4, 131.8, 129.2, 96.5, 79.5.

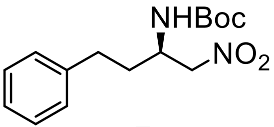
4-(2-Nitroethyl)phenol (1m)



1m

The nitro compound was prepared in 79% yield (5 mmol) from 3-phenylpropanal in two steps according to a reported procedure.[15]

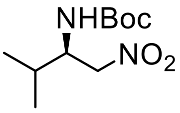
***tert*-Butyl (*R*)-(1-nitro-4-phenylbutan-2-yl)carbamate (7a)**



7a

The nitro compound was prepared in 95% yield (5 mmol) from 3-phenylpropanal through two steps according to a reported procedure,[11] and used after recrystallization (PE/EA=20:1). The ee value of the chiral nitro compound was determined by HPLC using a chiral stationary phase, ee = 99% (Chiralpak AD-H, hexane/*i*-PrOH = 95:5, 254 nm, 0.75 mL/min, t_{major} = 19.6 min, t_{minor} = 21.8 min).

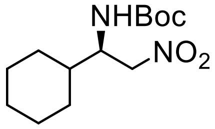
***tert*-Butyl (*R*)-(3-methyl-1-nitrobutan-2-yl)carbamate (7b)**



7b

The nitro compound was prepared in 92% yield (5 mmol) from isobutyraldehyde through two steps according to a reported procedure.[11] and used after recrystallization (PE/EA=20:1). The ee value of the chiral nitro compound was determined by HPLC using a chiral stationary phase, ee > 99% (Chiralpak AD-H, hexane/i-PrOH = 90:10, 254 nm, 0.75 mL/min, t_{major} = 9.1 min, t_{minor} = 13.0 min).

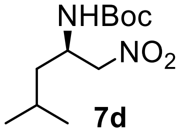
***tert*-Butyl (*R*)-(1-cyclohexyl-2-nitroethyl)carbamate (7c)**



7c

The nitro compound was prepared in 81% yield (5 mmol) from cyclohexanecarbaldehyde through two steps according to a reported procedure.[11] and used after recrystallization (PE/EA=20:1). The ee value of the chiral nitro compound was determined by HPLC using a chiral stationary phase, ee > 99% (Chiralpak AD-H, hexane/*i*-PrOH = 90:10, 254 nm, 1 mL/min, t_{major} = 7.5 min, t_{minor} = 9.5 min).

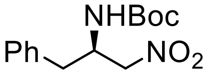
***tert*-Butyl (*R*)-(4-methyl-1-nitropentan-2-yl)carbamate (7d)**



7d

The nitro compound was prepared in 85% yield (5 mmol) from 3-methylbutanal through two steps according to a reported procedure.[16] and used after recrystallization (PE/EA=20:1). The ee value of the chiral nitro compound was determined by HPLC using a chiral stationary phase, ee > 99% (Chiralpak AD-H, hexane/*i*-PrOH = 90:10, 254 nm, 0.8 mL/min, t_{major} = 8.1 min, t_{minor} = 9.5 min).

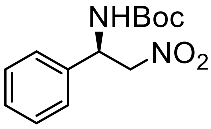
***tert*-Butyl (*R*)-(1-nitro-3-phenylpropan-2-yl)carbamate (7e)**



7e

The nitro compound was prepared in 70% yield (5 mmol) from 2-phenylacetaldehyde through two steps according to a reported procedure.[16] and used after recrystallization (PE/EA=20:1). The ee value of the chiral nitro compound was determined by HPLC using a chiral stationary phase, ee > 99% (Chiralpak AD-H, hexane/*i*-PrOH = 90:10, 254 nm, 1 mL/min, t_{major} = 8.5 min, t_{minor} = 10.7 min).

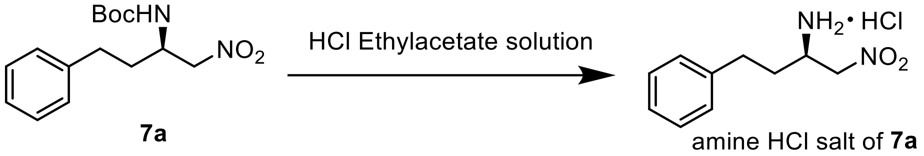
***tert*-Butyl (*R*)-(2-nitro-1-phenylethyl)carbamate (7f)**



7f

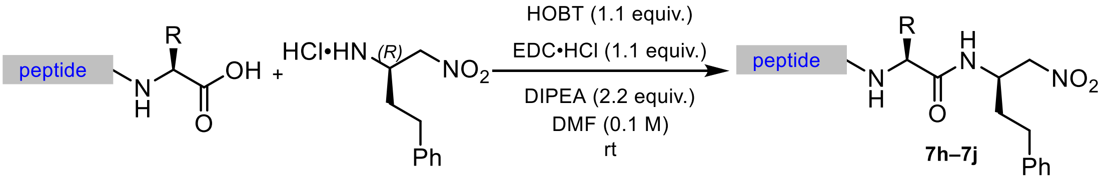
The nitro compound was prepared in 91% yield (5 mmol) from benzaldehyde through two steps according to a reported procedure.[11] and used after recrystallization (PE/EA=20:1). The ee value of the chiral nitro compound was determined by HPLC using a chiral stationary phase, ee > 99% (Chiralpak AD-H, hexane/*i*-PrOH = 95:5, 254 nm, 0.75 mL/min, t_{major} = 51.6 min, t_{minor} = 44.9 min).

(*R*)-1-nitro-4-phenylbutan-2-amine hydrochloride (7g)[17]



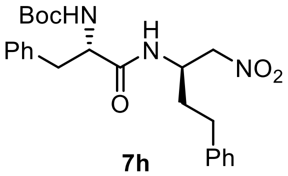
The deprotected amine salt of **7a** was prepared by addition of HCl in ethylacetate, and was used directly for the next step of the reaction.

General procedure to prepare peptide nitroalkanes.



General procedure: *N*-BOC protected amino acid (1 equiv.) and **7g** (1 equiv.) were added to a 50 mL round bottom flask, followed by adding DMF (10 mL). After stirring for 10 minutes in an ice bath, HOBT (1.1 equiv.) and EDC (1.1 equiv.) were added. The reaction was further stirred in an ice bath for 10 minutes, then the DIPEA (2.2 equiv.) was added. The reaction continues to stir in an ice bath for 30 min before rising to room temperature and stirring overnight, quenched with H_2O, extracted with ethyl acetate and the organic phase was collected. The organic phase was extracted with 1M HCl, *sat.* $NaHCO_3$ solution, *sat.* NaCl solution, dried over anhydrous $MgSO_4$. After filtration, the solution was concentrated under reduced pressure and the crude residue was purified by flash-column chromatography (PE/EA = Petroleum ether/Ethyl acetate).

***tert*-Butyl ((*S*)-1-(((*R*)-1-nitro-4-phenylbutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate** (7h)



7h

Following general procedure: **7h** was isolated as a White solid in 74 yield (980 mg; 3 mmol) which was purified by silica gel chromatography (DCM: MeOH = 20:1~10:1, R_f = 0.45 (DCM: MeOH = 10:1).

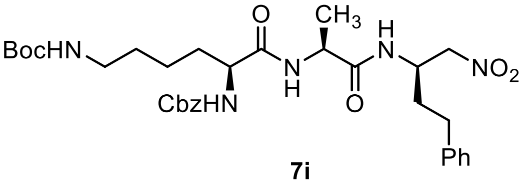
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (q, *J* = 7.0 Hz, 4H), 7.21 (q, *J* = 8.1 Hz, 4H), 7.09 (d, *J* = 7.4 Hz, 2H), 6.51 (d, *J* = 8.5 Hz, 1H), 5.05 (d, *J* = 7.7 Hz, 1H), 4.47 (d, *J* = 4.7 Hz, 1H), 4.34 (q, *J* = 7.4 Hz, 2H), 3.12 – 3.00 (m, 2H), 2.52 (t, *J* = 9.6 Hz, 2H), 1.80 (q, *J* = 7.4 Hz, 2H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 150.9, 135.5, 131.8, 124.7, 124.5, 124.1, 123.9, 123.7, 122.5, 121.7, 75.9, 51.4, 42.6, 33.2, 31.8, 28.3, 27.2, 23.6.

HRMS (ESI): calculated for $C_{24}H_{31}N_3O_5Na$ $[M+Na]^+$ 464.2156; found: 464.2160.

FT-IR (neat): 3304, 2926, 2859, 1687, 1658, 1548, 1495, 1452, 1379, 1082, 1032, 912, 699 cm^{-1}.

Benzyl *tert*-butyl ((*S*)-6-(((*S*)-1-(((*R*)-1-nitro-4-phenylbutan-2-yl)amino)-1-oxopropan-2-yl)amino)-6-oxohexane-1,5-diyl)dicarbamate (**7i**)



7i

Following general procedure: **7i** was isolated as a yellow solid in 69% yield (866 mg; 2 mmol) which was purified by silica gel chromatography (DCM: MeOH = 20:1~10:1, R_f = 0.40 (DCM: MeOH = 10:1).

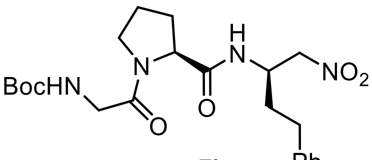
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.07 (m, 11H), 6.65 (s, 1H), 6.33 (s, 1H), 5.19 – 4.97 (m, 2H), 4.78 (s, 1H), 4.62 – 4.26 (m, 4H), 4.04 (s, 1H), 3.10 (d, *J* = 28.6 Hz, 2H), 2.91 – 2.51 (m, 2H), 2.11 – 1.63 (m, 4H), 1.40 (dd, *J* = 16.8, 10.2 Hz, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ172.6, 172.2, 157.6, 157.1, 140.8, 140.4, 136.3, 135.9, 128.7, 128.6, 128.5, 126.2, 79.7, 78.2, 67.7, 56.5, 49.3, 47.7, 38.8, 33.2, 32.1, 30.6, 30.0, 28.5, 22.2, 17.7.

HRMS (ESI): calculated for $C_{32}H_{45}N_5O_8Na$ $[M+Na]^+$ 650.3160; found: 650.3182.

FT-IR (neat): 3355, 3292, 3055, 3029, 2982, 2934, 2863, 1681, 1649, 1530, 1454, 1394, 1366, 1168, 1093, 1040, 912, 696 cm^{-1}.

***tert*-Butyl (2-((*R*)-2-(((*R*)-1-nitro-4-phenylbutan-2-yl)carbamoyl)pyrrolidin-1-yl)-2-oxoethyl)carbamate** (**7j**)



7j

Following general procedure: **7j** was isolated as a yellow solid in 76% yield (682 mg; 2.0 mmol) which was purified by silica gel chromatography (DCM: MeOH = 20:1~10:1, R_f = 0.40 (DCM: MeOH = 10:1).

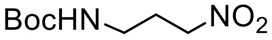
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 3H), 7.23 – 7.16 (m, 3H), 5.36 (s, 1H), 4.64 – 4.51 (m, 2H), 4.48 – 4.35 (m, 2H), 4.07 – 3.83 (m, 2H), 3.55 (td, *J* = 9.1, 3.2 Hz, 1H), 3.40 (td, *J* = 9.6, 7.4 Hz, 1H), 2.80 – 2.63 (m, 2H), 2.47 – 2.39 (m, 1H), 2.16 – 2.05 (m, 1H), 2.01 (ddd, *J* = 11.5, 6.5, 2.3 Hz, 1H), 1.97 – 1.79 (m, 3H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 169.5, 140.4, 128.7, 128.5, 126.4, 80.0, 78.1, 60.1, 47.7, 46.3, 43.3, 33.4, 32.1, 28.4, 26.9, 24.9.

HRMS (ESI): calculated for $C_{22}H_{32}N_4O_6Na$ $[M+Na]^+$ 471.2214; found: 471.2228.

FT-IR (neat): 3323, 1712, 1652, 1552, 1453, 1437, 1366, 1164, 1049, 1032, 915, 702 cm^{-1}.

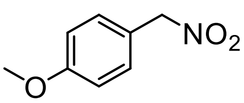
***tert*-Butyl (3-nitropropyl)carbamate** (**12**)



12

The nitro compound was prepared in 48% yield (20 mmol) in one step according to a reported procedure.[18]

1-Methoxy-4-(nitromethyl)benzene (**15**)



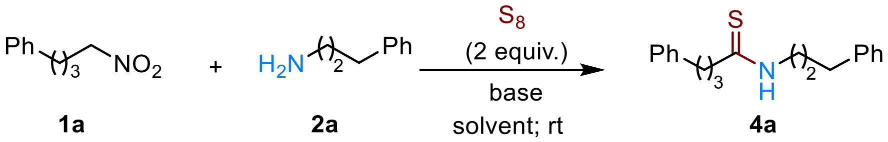
15

The nitro compound was prepared in 58% yield (5 mmol) according to a reported procedure.[19]

3. General procedure and characterization of thioamide products

3.1 Optimization of reaction conditions

Table S1. Details on the Optimization of Thioamidation Reaction Conditions[a]



entry	solvent	base	yield (%)[b]
1	THF	-	12
2	CH_3CN	K_2CO_3	21
3	DMSO	K_2CO_3	25
4	DCE	K_2CO_3	16
5	1,4-dioxane	K_2CO_3	23
6	acetone	K_2CO_3	trace
7	DMF	K_2CO_3	31
8	THF	K_2CO_3	37
9	THF	$KHCO_3$	30
10	THF	Na_2CO_3	24
11	THF	$LiOH\cdot H_2O$	32
12	THF	Cs_2CO_3	28
13	THF	Na_2S	98
14	THF	Et_3N	16
15	THF	DBU	trace
16	THF	pyridine	trace
17	THF	DIPEA	15
18[c]	THF	Na_2S	78

[a] Unless noted otherwise, reactions were carried out with 0.2 mmol of **1a**, 0.4 mmol of **2a**, 0.4 mmol of S_8 and 0.4 mmol of base in 2 ml of solvent until **1a** was consumed monitored with TLC (typically complete for 24h). [b] Yield of isolated product. [c] S_8 (1.25 equiv.) was used.

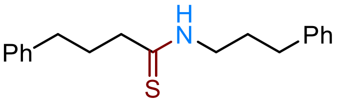
3.2 General thioamidation procedure between nitro compounds and amines.

General procedure A: The reaction was no special precautions from air or water. Nitro compound **1** (0.2 mmol) was added to a 10 mL reaction tube, followed by adding THF (2 mL). then S_8 (2.0 equiv.), Na_2S (2 equiv.) and the amine **2** (2.0 equiv.) were added.

The reaction was monitored by TLC until the nitroalkane was consumed, typically complete for 24h, quenched with *sat.* NH_4Cl, extracted with ethyl acetate, and the organic phase was collected and dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated under reduced pressure and the crude residue was purified by flash-column chromatography (PE/EA = Petroleum ether/Ethyl acetate).

3.2.1 Structural Characterization of thioamide products

4-Phenyl-*N*-(3-phenylpropyl)butanethioamide (4a)



4a

Following procedure A: **4a** was isolated as a yellow oil in 98% yield (58.2 mg; 0.196 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.45 (PE:EA = 5:1)).

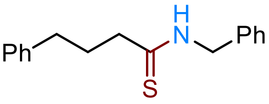
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 4H), 7.19 – 7.13 (m, 6H), 3.69 – 3.62 (m, 2H), 2.64 (dt, *J* = 23.3, 7.5 Hz, 4H), 2.55 – 2.49 (m, 2H), 2.08 – 1.91 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 141.5, 141.2, 128.7, 128.6, 128.6, 128.5, 126.4, 126.2, 46.3, 45.9, 35.0, 33.6, 30.8, 29.5.

HRMS (ESI): calculated for $C_{19}H_{24}NS$ $[M+H]^+$ 298.1624; found: 298.1619.

FT-IR (neat): 3237, 2929, 2857, 1530, 1495, 1453, 1406, 1337, 1123, 1084, 1031, 909, 699 cm^{-1}.

***N*-Benzyl-4-phenylbutanethioamide (4b)**



4b

Following procedure A: **4b** was isolated as yellow oil in 98% yield (52.7 mg; 0.196 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.45 (PE:EA = 5:1)).

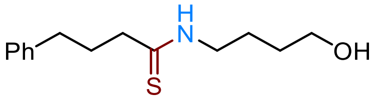
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 8H), 7.17 – 7.10 (m, 3H), 4.77 (d, *J* = 5.2 Hz, 2H), 2.62 (q, *J* = 7.9 Hz, 4H), 2.16 – 2.05 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2, 141.4, 136.3, 129.1, 128.6, 128.6, 128.5, 128.3, 126.2, 50.3, 46.2, 34.9, 30.9

HRMS (ESI): calculated for $C_{17}H_{20}NS$ $[M+H]^+$ 270.1311; found: 270.1301.

FT-IR (neat): 3221, 3025, 1528, 1495, 1453, 1405, 1340, 1125, 947, 698 cm^{-1}.

N-(4-Hydroxybutyl)-4-phenylbutanethioamide (4c)



4c

Following procedure A: **4c** was isolated as yellow oil in 88% yield (44.2 mg; 0.176 mmol) which was purified by silica gel chromatography (PE:EA = 5:1~1:1, R_f = 0.2 (PE:EA = 1:1)).

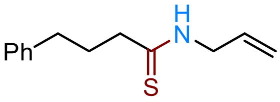
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.30 – 7.24 (m, 2H), 7.21 – 7.13 (m, 3H), 3.63 (dt, *J* = 8.3, 6.6 Hz, 4H), 2.63 (dt, *J* = 9.4, 7.8 Hz, 4H), 2.10 (ddd, *J* = 7.8, 6.6, 1.5 Hz, 2H), 1.73 (p, *J* = 7.0 Hz, 2H), 1.60 (p, *J* = 6.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8, 141.5, 128.6, 128.5, 126.1, 62.1, 46.1, 45.9, 34.9, 30.8, 29.7, 24.6.

HRMS (ESI): calculated for $C_{14}H_{22}NOS$ $[M+H]^+$ 252.1417; found: 252.1411.

FT-IR (neat): 3241, 3024, 2934, 2860, 1541, 1495, 1453, 1410, 1346, 1126, 1069, 1028, 909, 700 cm^{-1}.

N-Allyl-4-phenylbutanethioamide (4d)



4d

Following procedure A: **4d** was isolated as a yellow oil in 88% yield (38.5 mg; 0.176 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.45 (PE:EA = 5:1)).

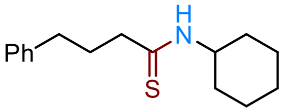
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (dd, *J* = 8.3, 6.3 Hz, 2H), 7.21 – 7.13 (m, 3H), 5.94 – 5.81 (m, 1H), 5.28 – 5.19 (m, 2H), 4.29 – 4.24 (m, 2H), 2.69 – 2.61 (m, 4H), 2.12 (tt, *J* = 8.9, 6.8 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 205.4, 141.4, 131.9, 128.6, 126.2, 118.7 (2C), 48.5, 46.2, 34.9, 30.9.

HRMS (ESI): calculated for $C_{13}H_{18}NS$ $[M+H]^+$ 220.1155; found: 220.1143.

FT-IR (neat): 3237, 3024, 3006, 2987, 2924, 2861, 1646, 1527, 1496, 1453, 1398, 1317, 1180, 1124, 924, 700 cm^{-1}.

<u>*N*-Cyclohexyl-4-phenylbutanethioamide</u> (**4e**)



4e

Following procedure A: **4e** was isolated as a yellow oil in 97% yield (50.6 mg; 0.194 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R$_f$ = 0.5 (PE:EA =5:1)).

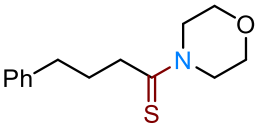
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.24 (m, 2H), 7.20 – 7.15 (m, 3H), 4.43 – 4.31 (m, 1H), 2.62 (dt, *J* = 22.4, 7.6 Hz, 4H), 2.16 – 2.01 (m, 4H), 1.69 (ddt, *J* = 32.5, 12.9, 3.7 Hz, 3H), 1.45 – 1.33 (m, 2H), 1.26 – 1.13 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 203.3, 141.5, 128.6, 128.5, 126.1, 54.3, 46.6, 34.8, 31.7, 30.8, 25.5, 24.8.

HRMS (ESI): calculated for $C_{16}H_{24}NS$ $[M+H]^+$ 262.1624; found: 262.1613.

FT-IR (neat): 3237, 3025, 2929, 2853, 1529, 1495, 1451, 1410, 1347, 1117, 1089, 1028, 892, 699 cm^{-1}.

<u>1-Morpholino-4-phenylbutane-1-thione</u> (**4f**)



4f

Following procedure A: **4f** was isolated as a yellow oil in 93% yield (46.3 mg; 0.186 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.3 (PE:EA = 5:1)).

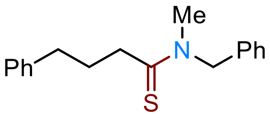
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.20 (td, *J* = 7.3, 1.3 Hz, 3H), 4.34 – 4.30 (m, 2H), 3.78 – 3.73 (m, 2H), 3.65 (dd, *J* = 5.7, 3.6 Hz, 2H), 3.57 (dd, *J* = 5.7, 3.7 Hz, 2H), 2.90 – 2.81 (m, 2H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.09 – 1.99 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4, 141.2, 128.5, 128.5, 126.2, 66.5, 66.5, 50.0, 49.9, 42.6, 35.3, 30.7.

HRMS (ESI): calculated for $C_{14}H_{20}NOS$ $[M+H]^+$ 250.1260; found: 250.1242.

FT-IR (neat): 2963, 2917, 2852, 1485, 1432, 1112, 1004, 921, 699 cm^{-1}.

***N*-Benzyl-*N*-methyl-4-phenylbutanethioamide** (**4g**)



4g

Following procedure A: **4g** was isolated as a yellow oil in 88% yield (49.8 mg; 0.176 mmol) which was purified by silica gel chromatography as a NMR observable rotamers of two thioamide forms A and B on the NMR time scale. (PE:EA = 20:1~5:1, R_f = 0.4 (PE:EA = 5:1)).

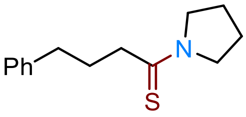
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.09 (m, 11H, A+B), 7.05 – 7.00 (m, 1H), 5.32 (s, 1H, B), 4.69 (s, 1H, A), 3.43 (s, 1H, B), 3.04 (s, 2H, A), 2.88 – 2.81 (m, 2H), 2.75 (t, *J* = 7.5 Hz, 1H), 2.67 (t, *J* = 7.5 Hz, 1H), 2.14 (dddd, *J* = 10.1, 7.5, 5.9, 3.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3(A), 205.1(B), 141.5(A), 141.5(B), 135.7(A), 135.1(B), 129.2(A), 128.9(B), 128.6(A), 128.5, 128.5(B), 128.1, 128.0(A), 126.4(B), 126.2(A), 126.1(B), 58.5(A), 57.4(B), 43.3(A), 43.1(B), 42.6(A), 38.6(B), 35.4(A), 35.3(B), 31.3(A), 30.7(B).

HRMS (ESI): calculated for $C_{18}H_{22}NS$ $[M+H]^+$ 284.1468; found: 284.1454.

FT-IR (neat): 2925, 1495, 1452, 1398, 1127, 1110, 1075, 1027, 963, 699 cm^{-1}.

4-Phenyl-1-(pyrrolidin-1-yl)butane-1-thione (**4h**)



4h

Following procedure A: **4h** was isolated as a yellow oil in 93% yield (43.3 mg; 0.186 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA =5:1)).

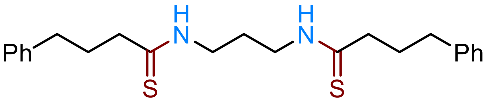
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 3.84 (t, *J* = 6.9 Hz, 2H), 3.48 (t, *J* = 6.8 Hz, 2H), 2.70 (dt, *J* = 18.7, 7.8 Hz, 4H), 2.13 (dq, *J* = 10.0, 7.7 Hz, 2H), 1.98 (ddt, *J* = 30.8, 13.3, 6.7 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 141.7, 128.6, 128.5, 126.0, 53.9, 50.5, 43.1, 35.3, 30.3, 26.4, 24.4.

HRMS (ESI): calculated for $C_{14}H_{20}NS$ $[M+H]^+$ 234.1311; found: 234.1308.

FT-IR (neat): 2967, 2870, 1485, 1472, 1450, 1329, 1100, 910, 701 cm^{-1}.

***N, N'*-(Propane-1,3-diyl)bis(4-phenylbutanethioamide)** (**4i**)



4i

Following procedure A: doubly thioacylated compound **4i** was isolated as a yellow oil in 88% yield (70.1 mg; 0.176 mmol) which was purified by silica gel chromatography (PE:EA= 10:1~1:1, R_f = 0.45 (PE:EA = 1:1)).

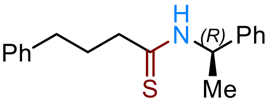
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 2H), 7.31 – 7.15 (m, 10H), 3.70 (q, *J* = 6.1 Hz, 4H), 2.67 (td, *J* = 7.8, 2.9 Hz, 8H), 2.12 (p, *J* = 7.6 Hz, 4H), 1.90 (p, *J* = 6.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 141.2, 128.5, 128.5, 126.1, 46.5, 42.1, 34.9, 30.8, 26.8.

HRMS (ESI): calculated for $C_{23}H_{31}N_2S_2$ $[M+H]^+$ 399.1923; found: 399.1915.

FT-IR (neat): 3219, 2928, 2855, 1536, 1495, 1453, 1406, 1125, 700 cm^{-1}.

(R)-4-Phenyl-N-(1-phenylethyl)butanethioamide (4j)



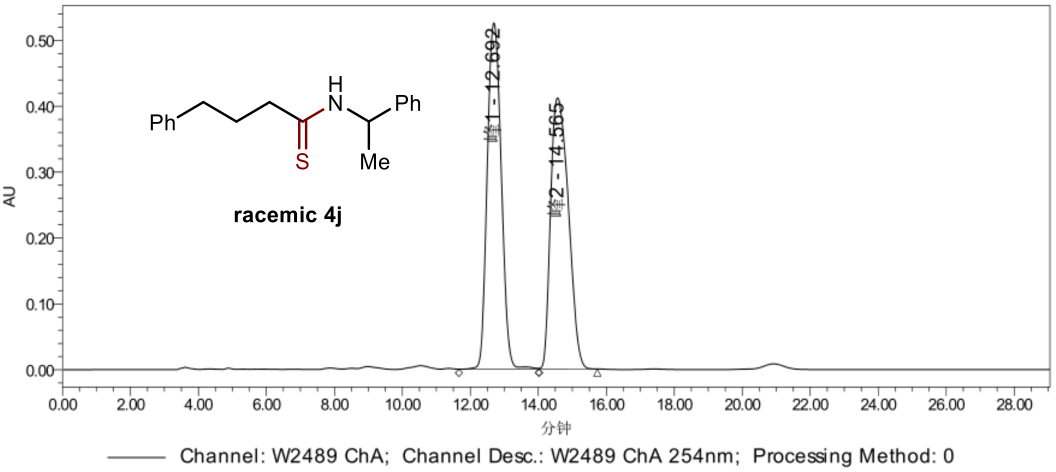
4j

Following procedure A using chiral amine of 98 % ee: **4j** was isolated as a yellow oil in 97% yield (54.9 mg; 0.194 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.6 (PE:EA =5:1)). The ee value was calculated as 98% (Chiralpak AD-H, hexane/*i*-PrOH = 95:5, 254 nm, 1 mL/min, t_{major}= 14.52 min, t_{minor}= 12.84 min).

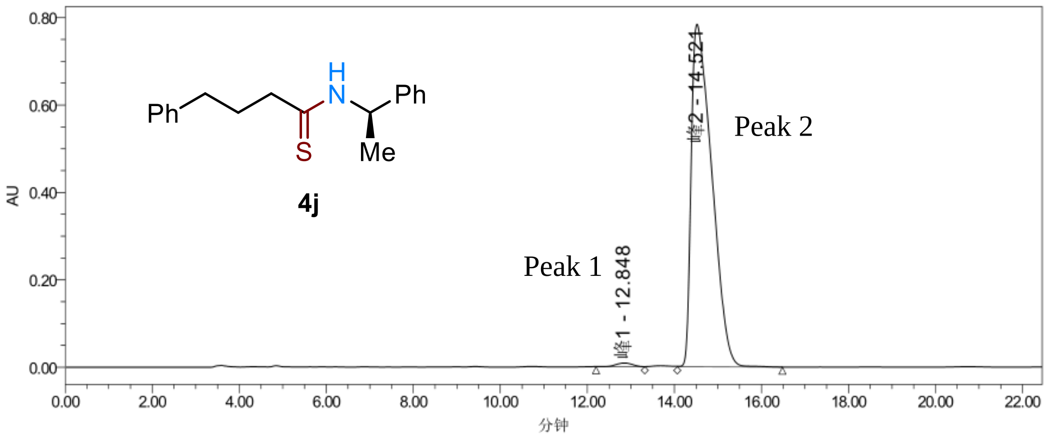
$[\alpha]^{25}_{D}$= -20.6 (*c* = 1.00, CHCl$_3$);

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.27 (m, 6H), 7.26 – 7.23 (m, 1H), 7.20 – 7.11 (m, 3H), 5.78 (p, *J* = 7.0 Hz, 1H), 2.62 (ddt, *J* = 9.5, 7.1, 4.0 Hz, 4H), 2.12 (p, *J* = 7.8 Hz, 2H), 1.59 (d, *J* = 6.9 Hz, 3H).

HPLC traces of compound 4j as racemate and as isolated from reaction:



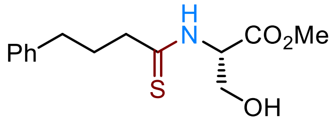
	Channel Description	Peak Name	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	峰1	12.692	15088970	50.21	525854
2	W2489 ChA 254nm	峰2	14.565	14960524	49.79	411786



Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	峰1	12.848	215375	0.83	8212
2	W2489 ChA 254nm	峰2	14.521	25693593	99.17	784715

Methyl (4-phenylbutanethioyl)-*L*-serinate (4k)



4k

Following procedure A: **4k** was isolated as yellow oil in 82% yield (46.1 mg; 0.164 mmol) which was purified by silica gel chromatography (PE:EA = 5:1~1:1, R_f = 0.5).

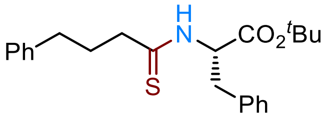
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.22 – 7.16 (m, 3H), 5.34 – 5.28 (m, 1H), 4.07 (d, *J* = 3.3 Hz, 2H), 3.80 (s, 3H), 2.69 (dt, *J* = 12.1, 7.0 Hz, 4H), 2.14 (pd, *J* = 7.4, 2.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 170.4, 141.4, 128.6, 128.6, 126.2, 62.1, 59.6, 53.1, 46.0, 34.8, 30.8.

HRMS (ESI): calculated for $C_{14}H_{20}NO_3S$ $[M+H]^+$ 282.1158; found: 282.1147.

FT-IR (neat): 3310, 2951, 1739, 1517, 1496, 1437, 1406, 1329, 1125, 1067, 909, 701 cm^{-1}.

tert-Butyl (4-phenylbutanethioyl)-*L*-phenylalaninate (4l)



4l

Following procedure A: **4l** was isolated as yellow oil in 80% yield (61.4 mg; 0.160 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

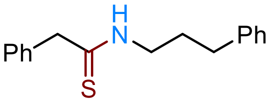
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 6.9 Hz, 1H), 7.26 – 7.19 (m, 4H), 7.19 – 7.11 (m, 5H), 5.26 (td, *J* = 7.1, 4.7 Hz, 1H), 3.34 (dd, *J* = 13.9, 6.7 Hz, 1H), 3.22 (dd, *J* = 13.9, 4.8 Hz, 1H), 2.63 (td, *J* = 7.6, 2.9 Hz, 4H), 2.13 – 2.03 (m, 2H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9, 170.3, 141.4, 135.9, 129.8, 129.6, 128.6, 128.5, 127.3, 126.1, 83.2, 58.8, 46.3, 36.3, 34.9, 30.8, 28.1.

HRMS (ESI): calculated for $C_{23}H_{29}NO_2SNa$ $[M+Na]^+$ 406.18112; found: 406.18003.

FT-IR (neat): 3303, 2977, 1722, 1512, 1496, 1454, 1401, 1367, 1153, 700 cm^{-1}.

<u>2-Phenyl-*N*-(3-phenylpropyl)ethanethioamide</u> (5a)



5a

Following procedure A: **5a** was isolated as a yellow oil in 93% yield (50.1 mg; 0.186 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

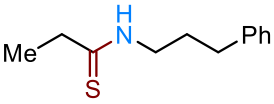
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 3H), 7.25 – 7.15 (m, 5H), 7.07 – 7.03 (m, 2H), 4.05 (s, 2H), 3.67 – 3.56 (m, 2H), 2.57 – 2.48 (m, 2H), 1.85 (p, J = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 141.0, 135.1, 129.6, 129.4, 128.7, 128.5, 128.4, 128.0, 126.3, 53.2, 45.7, 33.2, 29.4.

HRMS (ESI): calculated for $C_{17}H_{20}NS$ $[M+H]^+$ 270.1311; found: 270.1293.

FT-IR (neat): 3359, 2926, 1531, 1494, 1453, 1406, 1343, 1121, 1030, 913, 699 cm^{-1}.

N-(3-Phenylpropyl)propanethioamide (5b)



5b

Following procedure A: **5b** was isolated as a yellow oil in 99% yield (41.0 mg; 0.198 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

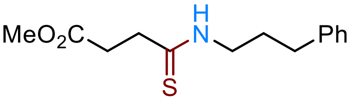
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.19 (td, *J* = 6.6, 1.3 Hz, 3H), 3.70 – 3.62 (m, 2H), 2.72 – 2.64 (m, 2H), 2.58 (q, *J* = 7.5 Hz, 2H), 1.98 (p, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 141.2, 128.7, 128.5, 126.3, 46.0, 40.1, 33.5, 29.5, 13.8.

HRMS (ESI): calculated for $C_{12}H_{18}NS$ $[M+H]^+$ 208.1155; found: 208.1143.

FT-IR (neat): 3231, 2976, 1533, 1496, 1452, 1409, 1364, 1145, 1097, 1029, 955, 699 cm^{-1}.

Methyl 4-((3-phenylpropyl)amino)-4-thioxobutanoate (5c)



5c

Following procedure A: **5c** was isolated as a yellow oil in 58% yield (30.8 mg; 0.116 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.4 (PE:EA = 5:1)).

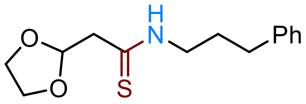
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 3.70 – 3.61 (m, 6H), 2.84 (q, *J* = 1.8 Hz, 4H), 2.70 – 2.65 (m, 2H), 1.98 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 174.0, 141.2, 128.6, 128.5, 126.2, 52.1, 45.9, 40.8, 33.4, 32.9, 29.5.

HRMS (ESI): calculated for $C_{14}H_{20}NO_2S$ $[M+H]^+$ 266.1209; found: 266.1202.

FT-IR (neat): 3321, 2947, 1736, 1535, 1496, 1437, 1343, 1171, 1133, 1088, 919, 700 cm^{-1}.

2-(1,3-Dioxolan-2-yl)-*N*-(3-phenylpropyl)ethanethioamide (5d)



5d

Following procedure A: **5d** was isolated as a yellow oil in 98% yield (52.0 mg; 0.196 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

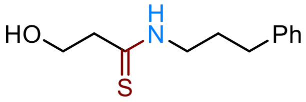
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 5.13 (t, *J* = 4.6 Hz, 1H), 3.98 – 3.84 (m, 4H), 3.70 – 3.63 (m, 2H), 3.04 (d, *J* = 4.6 Hz, 2H), 2.71 – 2.65 (m, 2H), 1.98 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 141.1, 128.6, 128.5, 126.3, 102.3, 65.1, 50.9, 45.9, 33.3, 29.5.

HRMS (ESI): calculated for $C_{14}H_{20}NO_2S$ $[M+H]^+$ 266.1209; found: 266.1199.

FT-IR (neat): 3277, 2925, 2884, 1541, 1496, 1453, 1408, 1361, 1123, 1083, 1033, 943, 909, 701 cm^{-1}.

3-Hydroxy-*N*-(3-phenylpropyl)propanethioamide (5e)



5e

Following procedure A: **5e** was isolated as yellow oil in 90% yield (40.1 mg; 0.18 mmol) which was purified by silica gel chromatography (PE:EA=5:1~1:1, R_f = 0.3 (PE:EA = 5:1)).

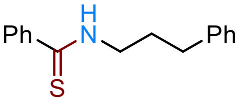
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.33 – 7.27 (m, 2H), 7.21 (td, *J* = 7.7, 6.7, 1.5 Hz, 3H), 3.95 – 3.88 (m, 2H), 3.75 – 3.65 (m, 2H), 2.81 – 2.66 (m, 4H), 2.01 (p, *J* = 7.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 141.1, 128.7, 128.5, 126.4, 60.7, 47.6, 45.8, 33.5, 29.5.

HRMS (ESI): calculated for $C_{12}H_{18}NOS$ $[M+H]^+$ 224.1104; found: 224.1102.

FT-IR (neat): 3239, 2931, 2861, 1542, 1496, 1452, 1404, 1135, 1085, 1045, 914, 700 cm^{-1}.

***N*-(3-Phenylpropyl)benzothioamide** (5f)



5f

Following procedure A: **5f** was isolated as a yellow oil in 92% yield (46.9 mg; 0.184 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.6 (PE:EA = 5:1)).

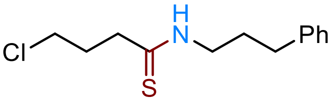
^{1}H NMR (399 MHz, $CDCl_3$) δ 7.61 – 7.48 (m, 3H), 7.46 – 7.38 (m, 1H), 7.35 – 7.27 (m, 4H), 7.26 – 7.18 (m, 3H), 3.84 (td, *J* = 7.0, 5.4 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.09 (p, *J* = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 141.9, 141.2, 131.1, 128.8, 128.5 (2C), 126.7, 126.4, 46.8, 33.8, 29.6.

HRMS (ESI): calculated for $C_{16}H_{18}NS$ $[M+H]^+$ 256.1155; found: 256.1138.

FT-IR (neat): 3361, 2925, 2858, 1522, 1487, 1449, 1388, 1334, 1178, 1100, 1070, 1029, 943, 695 cm^{-1}.

5-Chloro-*N*-(3-phenylpropyl)pentanethioamide (5g)



5g

Following procedure A: **5g** was isolated as a yellow oil in 62% yield (31.7 mg; 0.124 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.45 (PE:EA = 5:1)).

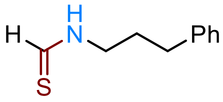
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.25 (m, 2H), 7.19 (dd, *J* = 17.8, 7.2 Hz, 3H), 3.22 (q, *J* = 5.3 Hz, 4H), 2.69 (dt, *J* = 13.7, 7.3 Hz, 4H), 2.06 (dp, *J* = 35.3, 6.8 Hz, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 173.2, 142.2, 128.5, 128.3, 125.7, 57.2, 38.8, 33.8, 33.8, 31.9, 27.0.

HRMS (ESI): calculated for $C_{13}H_{19}ClNS$ $[M+H]^+$ 256.0921; found: 256.0901.

FT-IR (neat): 3268, 2934, 2886, 1538, 1495, 1453, 1409, 1121, 943, 701 cm^{-1}.

N-(3-phenylpropyl)thioformamide (**5h**)



5h

Following procedure A: the thioformamide **5h** was isolated as a yellow oil in 95% yield (34.0 mg; 0.19 mmol) which was purified by silica gel chromatography (PE:EA = 10:1~2:1, R$_f$ = 0.45 (PE:EA = 2:1)).

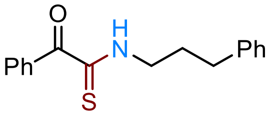
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 5.81 (s, 1H), 3.31 (s, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.88 (p, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 181.4, 141.1, 128.7, 128.5, 126.3, 43.8, 33.3, 30.4.

HRMS (ESI): calculated for $C_{10}H_{14}NS$ $[M+H]^+$ 180.0842; found: 180.0837.

FT-IR (neat): 3257, 2936, 1601, 1552, 1495, 1453, 1354, 1180, 1120, 1030, 907, 700 cm^{-1}.

2-Oxo-2-phenyl-*N*-(3-phenylpropyl)ethanethioamide (**5i**)



5i

Following procedure A: **5i** was isolated as a yellow oil in 62% yield (35.1 mg; 0.124 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R$_f$ = 0.45 (PE:EA = 5:1)).

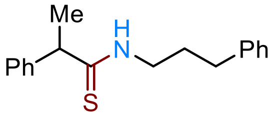
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.41 (s, 1H), 8.03 – 7.98 (m, 2H), 7.60 – 7.53 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.20 (td, *J* = 5.2, 4.8, 2.3 Hz, 3H), 3.86 – 3.75 (m, 2H), 2.79 – 2.72 (m, 2H), 2.10 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.8, 188.0, 140.8, 134.0, 133.8, 130.8, 128.7, 128.5, 128.3, 126.4, 44.9, 33.4, 29.3.

HRMS (ESI): calculated for $C_{17}H_{18}NOS$ [M+H]$^+$ 284.1104; found: 284.1103.

FT-IR (neat): 3281, 2925, 2861, 1663, 1594, 1530, 1448, 1399, 1177, 1119, 1065, 895, 694 cm^{-1}.

(*rac*)-2-Phenyl-*N*-(3-phenylpropyl)propanethioamide (**5j**)



(±) 5j

Following procedure A: racemic **5j** was isolated as a yellow oil in 72% yield (40.8 mg; 0.144 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, Rf = 0.5 (PE:EA =5:1)).

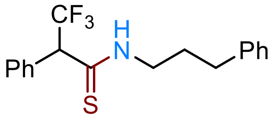
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.16 (m, 8H), 7.08 – 7.02 (m, 2H), 6.91 (s, 1H), 4.03 (q, *J* = 7.2 Hz, 1H), 3.61 (td, *J* = 7.0, 5.8 Hz, 2H), 2.56 – 2.49 (m, 2H), 1.86 (dt, *J* = 14.4, 7.1 Hz, 2H), 1.67 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 207.4, 140.9, 129.1, 128.6, 128.3, 127.8, 126.2, 54.9, 45.5, 33.2, 29.3, 21.2.

HRMS (ESI): calculated for $C_{18}H_{22}NS$ [M+H]$^+$ 284.1468; found: 284.1460.

FT-IR (neat): 3244, 2923, 1537, 1495, 1453, 1412, 1126, 1085, 699 cm^{-1}.

(*rac*)-3,3,3-Trifluoro-2-phenyl-*N*-(3-phenylpropyl)propanethioamide (**5k**)



(±) 5k

Following procedure A: racemic **5k** was isolated as a yellow oil in 60% yield (40.4 mg; 0.120 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.45 (PE:EA = 5:1)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 4H), 7.31 – 7.17 (m, 5H), 7.13 – 7.07 (m, 2H), 4.90 (q, *J* = 9.3 Hz, 1H), 3.65 (tq, *J* = 13.4, 6.7 Hz, 2H), 2.57 (dt, *J* = 13.5, 7.6 Hz, 2H), 1.94 (p, *J* = 7.3 Hz, 2H).

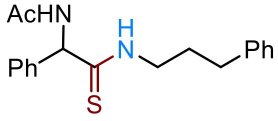
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 140.7, 129.3, 129.3, 129.2, 129.1, 128.7, 128.6, 128.5, 128.4, 126.3, 126.1, 124.3 (d, *J* = 281.6 Hz), 64.7 (q, *J* = 26.9 Hz), 46.0, 33.1, 29.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ 64.71.

HRMS (ESI): calculated for $C_{18}H_{19}F_3NS$ $[M+H]^+$ 338.1185; found: 338.1173.

FT-IR (neat): 3276, 2927, 1558, 1540, 1496, 1456, 1363, 1162, 1116, 913, 700 cm^{-1}.

(*rac*)-*N*-(1-Phenyl-2-((3-phenylpropyl)amino)-2-thioxoethyl)acetamide (5l)



(±) 5l

Following procedure A: racemic **5l** was isolated as a yellow oil in 89% yield (58.1 mg; 0.178 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f= 0.4 (PE:EA = 5:1)).

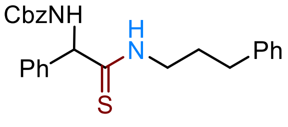
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.26 – 7.18 (m, 5H), 7.17 – 7.11 (m, 1H), 7.04 – 6.98 (m, 2H), 6.20 (d, *J* = 8.0 Hz, 1H), 3.63 – 3.40 (m, 2H), 2.51 (t, *J* = 7.7 Hz, 2H), 2.05 (s, 3H), 1.84 (dtd, *J* = 14.7, 6.3, 3.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 169.4, 141.1, 139.6, 128.7, 128.5, 128.4, 128.2, 126.7, 126.1, 60.6, 45.7, 33.1, 29.1, 23.7.

HRMS (ESI): calculated for $C_{19}H_{22}N_2OSNa$ $[M+Na]^+$ 349.1345; found: 349.1343.

FT-IR (neat): 3248, 2963, 1654, 1496, 1452, 1124, 1080, 969, 699 cm^{-1}.

(*rac*)-Benzyl-(1-phenyl-2-((3-phenylpropyl)amino)-2-thioxoethyl)carbamate (5m)



(±) 5m

Following procedure A: racemic **5m** was isolated as a yellow oil in 75% yield (62.7 mg; 0.15 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f=0.4 (PE:EA = 5:1)).

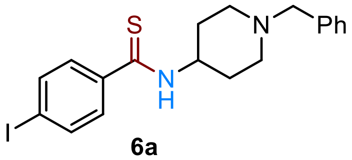
^{1}H NMR (399 MHz, $CDCl_3$) δ 8.39 (d, *J* = 81.5 Hz, 1H), 7.47 – 7.13 (m, 14H), 7.05 – 6.93 (m, 2H), 6.79 (d, *J* = 23.9 Hz, 1H), 5.69 – 5.51 (m, 1H), 5.10 – 4.98 (m, 2H), 3.53 (dqt, *J* = 26.5, 13.2, 6.7 Hz, 2H), 2.48 (h, *J* = 7.4 Hz, 2H), 1.91 – 1.71 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 155.6, 140.9, 139.3, 135.9, 128.9, 128.6, 128.5, 128.5, 128.3, 127.9, 127.8, 126.8, 126.2, 67.2, 63.1, 45.6, 33.1, 29.2.

HRMS (ESI): calculated for $C_{25}H_{27}N_2O_2S$ $[M+H]^+$ 419.1788; found: 419.1785.

FT-IR (neat): 3285, 1701, 1602, 1541, 1497, 1452, 1374, 1217, 1155, 1129, 1084, 1061, 1027, 913, 698 cm^{-1}.

N-(1-Benzylpiperidin-4-yl)-4-iodobenzothioamide (6a)



6a

Following procedure A: **6a** was isolated as a yellow solid in 72% yield (62.7 mg; 0.144 mmol) which was purified by silica gel chromatography (DCM:EA = 100:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

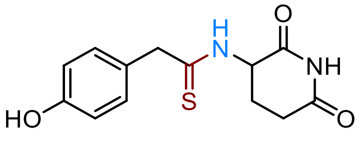
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.9 Hz, 1H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 7.42 (d, *J* = 2.2 Hz, 1H), 7.34 – 7.26 (m, 5H), 4.59 – 4.48 (m, 1H), 3.54 (s, 2H), 2.87 (dt, *J* = 12.4, 3.4 Hz, 2H), 2.30 – 2.13 (m, 4H), 1.71 – 1.56 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 141.5, 138.0, 137.7, 129.3, 128.4, 128.3, 127.4, 97.9, 63.1, 53.3, 52.1, 30.8.

HRMS (ESI): calculated for $C_{19}H_{22}IN_2S$ $[M+H]^+$ 437.0543; found: 437.0532.

FT-IR (neat): 2921, 1580, 1517, 1478, 1398, 1140, 1079, 1005, 943, 825, 697 cm^{-1}.

***N*-(2,6-Dioxopiperidin-3-yl)-2-(4-hydroxyphenyl)ethanethioamide (6b)**



6b

Following procedure A: **6b** was isolated as a yellow solid in 88% yield (48.9 mg; 0.176 mmol) which was purified by silica gel chromatography (PE:EA = 5:1~1:1, R_f = 0.2 (PE:EA = 5:1).

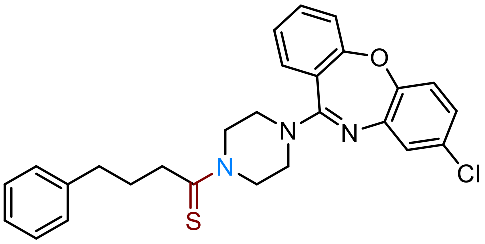
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.99 (s, 1H), 10.37 (d, *J* = 8.2 Hz, 1H), 9.27 (s, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 5.34 (ddd, *J* = 12.9, 8.0, 5.2 Hz, 1H), 3.83 (s, 2H), 2.73 (ddd, *J* = 18.4, 13.3, 5.5 Hz, 1H), 2.53 (t, *J* = 3.8 Hz, 1H), 2.14 – 2.03 (m, 1H), 1.90 (qd, *J* = 12.6, 4.7 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 203.5, 173.2, 171.5, 156.6, 130.3, 128.0, 115.5, 55.2, 51.0, 31.1, 23.4.

HRMS (ESI): calculated for $C_{13}H_{15}N_2O_3S$ $[M+H]^+$ 279.0798; found: 279.0916.

FT-IR (neat): 3234, 2860, 1730, 1682, 1530, 1512, 1453, 1330, 1120, 713 cm^{-1}.

1-(4-(8-Chlorodibenzo[b,f][1,4]oxazepin-11-yl)piperazin-1-yl)-4-phenylbutane-1-thione (6c)



6c

Following procedure A: **6c** was isolated as a yellow solid in 90% yield (85.5 mg; 0.180 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f=0.3 (PE:EA = 5:1)).

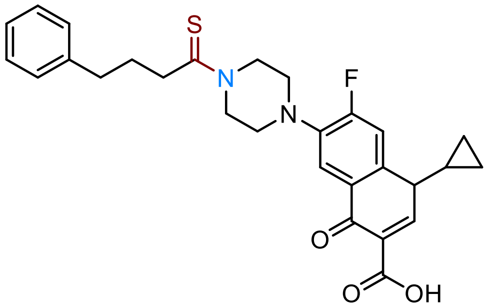
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.32 – 7.24 (m, 3H), 7.22 – 7.13 (m, 5H), 7.13 – 7.07 (m, 2H), 7.05 – 6.99 (m, 1H), 4.38 (s, 2H), 3.64 (d, *J* = 56.9 Hz, 6H), 2.92 – 2.84 (m, 2H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.11 – 2.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 159.5, 158.4, 151.8, 141.3, 139.7, 133.2, 130.6, 128.9, 128.6, 128.6, 127.2, 126.3, 126.1, 125.3, 124.6, 123.1, 120.4, 60.5, 49.4, 48.9, 47.2, 43.1, 35.4, 30.9.

HRMS (ESI): calculated for $C_{27}H_{27}ClN_3OS$ $[M+H]^+$ 476.1558; found: 476.1559.

FT-IR (neat): 2926, 1602, 1588, 1559, 1470, 1433, 1187, 1111, 1002, 700 cm^{-1}.

4-Cyclopropyl-6-fluoro-1-oxo-7-(4-(4-phenylbutanethioyl)piperazin-1-yl)-1,4-dihydronaphthalene-2-carboxylic acid (6d)



6d

Following procedure A: **6d** was isolated as a yellow solid in 56% yield (55.1 mg; 0.112 mmol) which was purified by silica gel chromatography (DCM: MeOH = 100:1~20:1, R_f = 0.5 (DCM: MeOH = 20:1)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 14.88 (s, 1H), 8.68 (s, 1H), 7.95 (d, *J* = 12.9 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.23 – 7.19 (m, 2H), 4.59 – 4.54 (m, 1H), 3.89 – 3.85 (m, 1H), 3.56 (dp, *J* = 7.1, 4.1 Hz, 1H), 3.47 – 3.39 (m, 3H), 2.96 – 2.84 (m, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.15 – 1.97 (m, 2H), 1.43 – 1.13 (m, 6H).

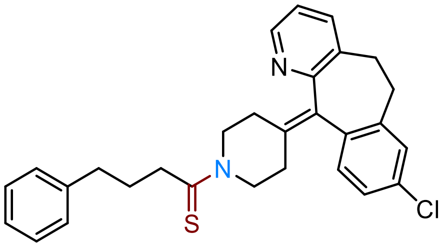
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 177.0, 166.8, 152.2, 147.6, 144.82 (d, *J* = 9.8 Hz), 141.3, 139.1, 128.6, 128.6, 126.3, 120.20 (d, *J* = 7.8 Hz), 112.55 (d, *J* = 23.1 Hz), 108.1, 105.0, 49.9, 49.0, 48.6, 42.9, 35.5, 35.4, 30.9, 8.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -121.22.

HRMS (ESI): calculated for $C_{28}H_{30}FN_2O_3S$ $[M+H]^+$ 493.1956; found: 493.1948.

FT-IR (neat): 3008, 2920, 1723, 1628, 1508, 1491, 1467, 1110, 892, 704 cm^{-1}.

1-(4-(8-Chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidin-1-yl)-4-phenylbutane-1-thione (**6e**)



6e

Following procedure A: **6e** was isolated as a yellow solid in 86% yield (81.2 mg; 0.172 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f=0.3 (PE:EA = 5:1)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 4.9 Hz, 1H), 7.45 (ddd, *J* = 8.0, 3.3, 1.8 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.20 – 7.07 (m, 7H), 4.71 (dt, *J* = 13.2, 5.2 Hz, 1H), 3.89 – 3.71 (m, 2H), 3.50 – 3.24 (m, 3H), 2.93 – 2.65 (m, 7H), 2.62 – 2.31 (m, 3H), 2.11 – 1.94 (m, 2H).

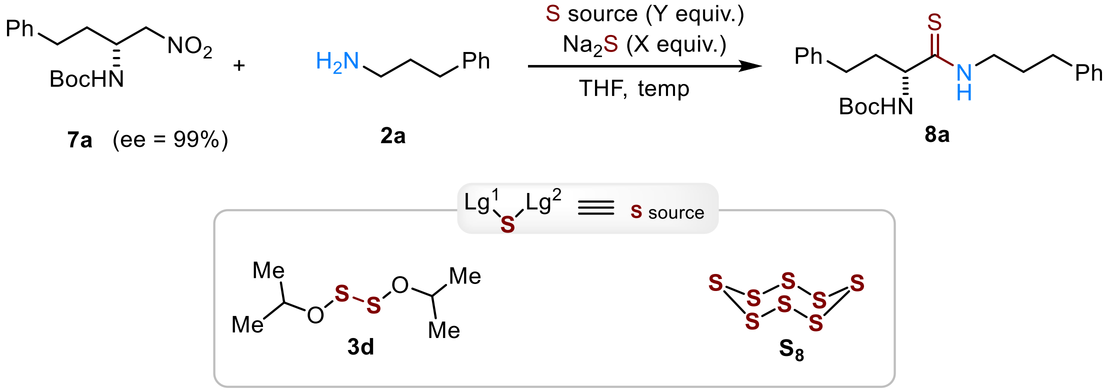
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 156.6, 146.8, 141.4, 139.6, 138.0, 137.3, 135.4, 133.6, 130.5, 130.3, 129.2, 128.5, 126.4, 126.1, 122.6, 50.9, 49.4, 43.3, 35.5, 31.7, 31.2, 30.8, 29.8, 29.5.

HRMS (ESI): calculated for $C_{29}H_{30}ClN_2S$ $[M+H]^+$ 473.1813; found: 473.1804.

FT-IR (neat): 2919, 2861, 1589, 1560, 1494, 1478, 1457, 1437, 1361, 1100, 990, 701 cm^{-1}.

3.2.2 General synthesis of thiopeptides from chiral nitro compounds and chiral amino acid esters.

Table S2. Optimization of reaction conditions with β-amino chiral nitroalkanes[a]

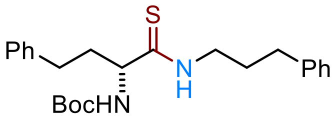


entry	Na_2S (equiv.)	S source (equiv.)	Temperature (°C)	time (h)	yield (%)	ee (%)
1	2	S_8 (1.25)	rt	24	96	76
2	2	S_8 (1.25)	50	24	99	45
3	3	**S_8** (1.25)	rt	24	78	72
4	2	**3d** (2)	rt	24	88	63
5	2	**S_8** (1.25)	0	36	72	98
6	2	**3d** (2)	0	36	85	94
7	2	**3d** (2)	-10	24	73	99
8	2	**3d** (2)	-10	36	81	99

[a] Unless noted otherwise, reactions were carried out with 0.1 mmol of **7a**, 0.2 mmol of **2a**, 0.2 mmol S source and 0.2 mmol of Na_2S in 1 ml of THF. [b] Yield of isolated product.

General procedure B: The chiral β-amino nitro compound **7** (0.1 mmol) was added to a 10 mL reaction tube, followed by the addition of THF (1 mL) and cooled down to -10°C. Then Na_2S (2.0 equiv., 0.2 mmol), **3d** (2 equiv.) and the amine **9** (2 equiv.) were added and stirred at -10°C. The reaction was monitored by TLC until the reaction was complete, typically complete within 36h, quenched with saturated ammonium chloride, and the crude product was extracted with ethyl acetate, and the organic phase collected and dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated under reduced pressure and the crude residue was separated by flash-column chromatography.

***tert*-Butyl (*R*)-(4-phenyl-1-((3-phenylpropyl)amino)-1-thioxobutan-2-yl)carbamate** (**8a**)



8a

Following procedure B: **8a** was isolated as a colorless oil in 81% yield (33.4 mg; 0.081 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.45 (PE:EA = 5:1)). $[\alpha]^{25}_{D}$ = 15.6 (*c* = 1.00, $CHCl_3$). ee = 99% (Chiralpak AD-H, hexane/*i*-PrOH=95:5, 214 nm, 1 mL/min, t_{major}= 21.47 min, t_{minor}= 14.32 min).

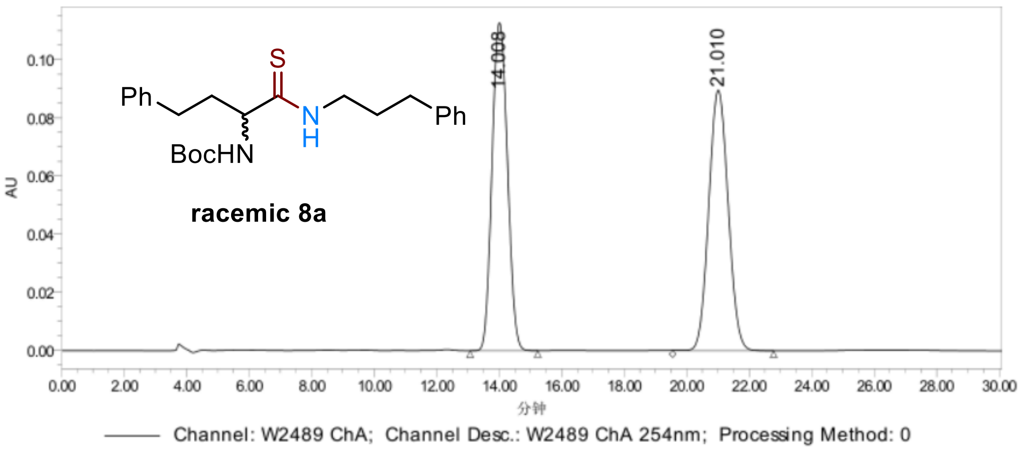
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.30 – 7.11 (m, 11H), 5.45 (d, *J* = 8.7 Hz, 1H), 4.36 (q, *J* = 8.2 Hz, 1H), 3.63 (ddt, *J* = 26.5, 13.1, 6.8 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 4H), 2.20 – 1.85 (m, 4H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 156.0, 141.1, 140.9, 128.7, 128.6, 128.6, 128.5, 126.5, 126.2, 80.4, 60.3, 45.4, 37.3, 33.4, 32.3, 29.4, 28.5.

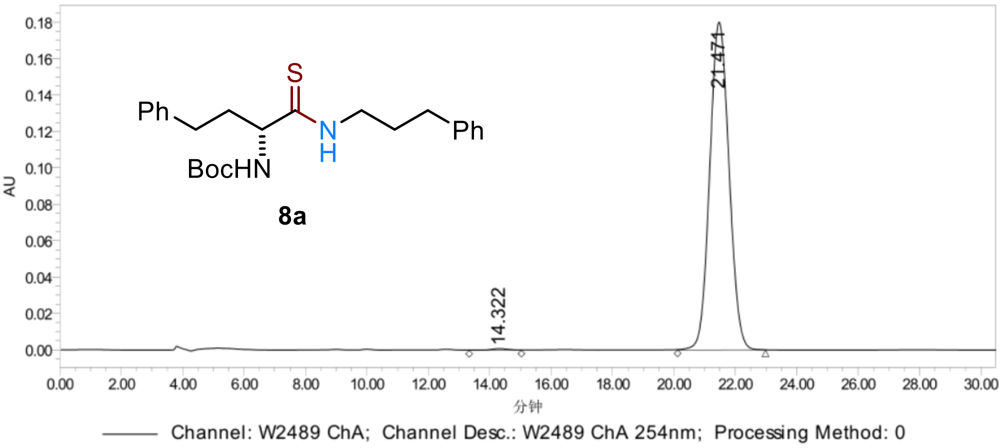
HRMS (ESI): calculated for $C_{24}H_{32}N_2O_2SNa$ $[M+Na]^+$ 435.2077; found: 435.2072.

FT-IR (neat): 3274, 3003, 2986, 1692, 1553, 1496, 1454, 1366, 1166, 1129, 1051, 699 cm^{-1}.

HPLC traces of compound **8a**:

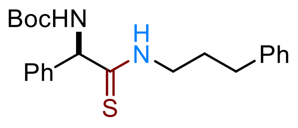


	Channel Description	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	14.008	3858020	49.95	112780
2	W2489 ChA 254nm	21.010	3865105	50.05	89595



	Channel Description	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	14.322	41097	0.52	900
2	W2489 ChA 254nm	21.471	7869211	99.48	180159

***tert*-Butyl (*R*)-(1-phenyl-2-((3-phenylpropyl)amino)-2-thioxoethyl)carbamate** (**8b**)



8b

Followed the general procedure B (at -30°C): **8b** was isolated as a yellow oil in 49% yield. The ee value was 86% (Chiralpak AD-H, hexane/*i*-PrOH=95:5, 254 nm, 1 mL/min, t_{major}= 28.95 min, t_{minor}= 14.37 min).

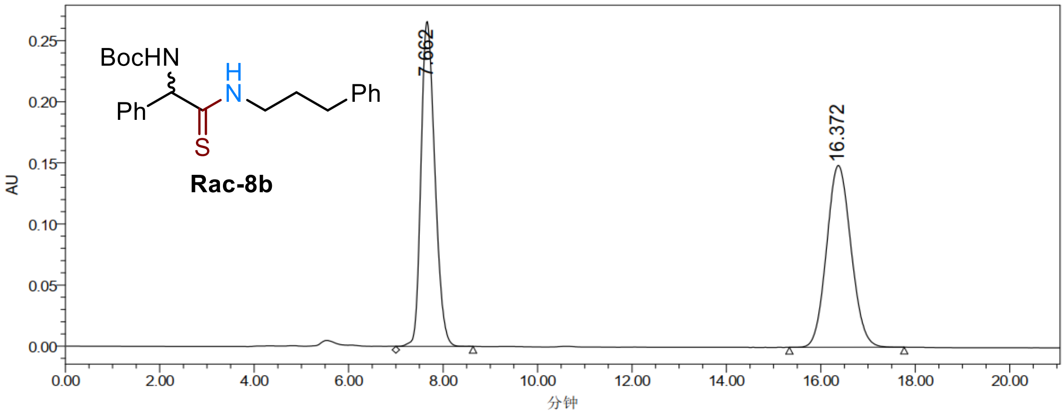
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (s, 1H), 7.41 – 7.15 (m, 10H), 7.12 – 7.05 (m, 2H), 6.15 (s, 1H), 5.40 (d, *J* = 6.4 Hz, 1H), 3.64 (d, *J* = 26.4, 6.8 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.90 (dh, *J* = 13.7, 6.4 Hz, 2H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 201.8, 155.2, 141.0, 139.5, 129.0, 128.6, 128.5, 127.0, 126.3, 80.5, 63.6, 45.6, 33.3, 29.3, 28.4.

HRMS (ESI): calculated for $C_{22}H_{28}N_2O_2S$ $[M+Na]^+$ 407.1764; found: 407.1782.

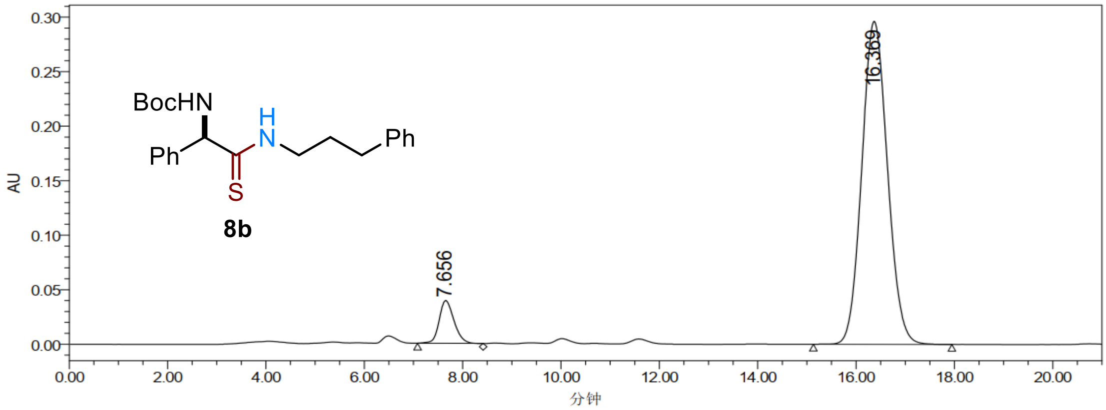
FT-IR (neat): 3279, 2976, 1689, 1553, 1495, 1454, 1366, 1165, 1058, 699 cm^{-1}.

HPLC traces of compound **8b**:



Channel: W2489 ChB; Channel Desc.: W2489 ChB 254nm; Processing Method: 1

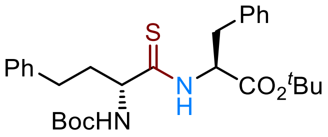
	Channel Description	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChB 254nm	7.662	5414338	50.28	265937
2	W2489 ChB 254nm	16.372	5354513	49.72	148881



Channel: W2489 ChB; Channel Desc.: W2489 ChB 254nm; Processing Method: 1

	Channel Description	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChB 254nm	7.656	824480	7.15	39245
2	W2489 ChB 254nm	16.369	10714201	92.85	296243

***tert*-Butyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-phenylalaninate (10a)**



10a

Following procedure B: **10a** was isolated as a yellow oil in 83% yield (41.0 mg; 0.083 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.55 (PE:EA = 5:1).

[α]$_{25\ D}$ = 25.2 (*c* = 1.20, $CHCl_3$)

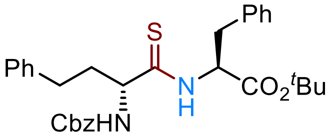
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.34 – 7.04 (m, 11H), 5.25 – 5.12 (m, 2H), 4.46 – 4.26 (m, 1H), 3.25 (q, *J* = 7.8 Hz, 2H), 2.68 – 2.54 (m, 2H), 2.22 (dq, *J* = 14.3, 6.4 Hz, 1H), 1.97 (td, *J* = 14.8, 8.7 Hz, 1H), 1.42 (s, 9H), 1.39 (s, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 169.6, 155.5, 140.9, 135.8, 129.5, 128.6, 128.6, 128.5, 127.2, 126.2, 83.1, 80.3, 60.7, 58.8, 37.5, 36.4, 32.1, 28.4, 28.0.

HRMS (ESI): calculated for $C_{28}H_{38}N_2O_4SNa$ $[M+Na]^+$ 521.2445; found: 521.2446.

FT-IR (neat): 3293, 2978, 1729, 1700, 1603, 1512, 1497, 1454, 1367, 1156, 699 cm^{-1}.

***tert*-Butyl ((*R*)-2-(((benzyloxy)carbonyl)amino)-4-phenylbutanethioyl)-*L*-phenylalaninate (10b)**



10b

Following procedure B: **10b** was isolated as a yellow oil in 75% yield (40.0 mg; 0.075 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

[α]$_{25\ D}$= 23.4 (*c* = 1.10, $CHCl_3$).

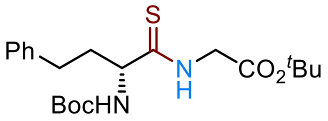
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.38 – 7.29 (m, 5H), 7.26 – 7.08 (m, 10H), 5.60 (d, *J* = 8.5 Hz, 1H), 5.20 (q, *J* = 6.0 Hz, 1H), 5.15 – 5.00 (m, 2H), 4.56 – 4.42 (m, 1H), 3.37 – 3.14 (m, 2H), 2.66 – 2.54 (m, 2H), 2.17 (q, *J* = 8.0 Hz, 1H), 2.06 – 1.92 (m, 1H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 169.6, 156.0, 140.8, 136.3, 135.8, 129.5, 128.7, 128.6, 128.6, 128.5, 128.3, 128.2, 127.3, 126.3, 83.2, 67.2, 61.0, 58.8, 37.7, 36.3, 31.9, 28.0.

HRMS (ESI): calculated for $C_{31}H_{36}N_2O_4SNa$ $[M+Na]^+$ 555.2288; found: 555.2298.

FT-IR (neat): 3331, 3294, 2977, 1728, 1708, 1655, 1603, 1510, 1497, 1454, 1422, 1368, 1153, 1096, 1050, 911, 844, 698 cm^{-1}.

tert-Butyl (*R*)-(2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)glycinate (**10c**)



10c

Following procedure B: **10c** was isolated as a yellow oil in 58% yield (23.7 mg; 0.058 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.55 (PE:EA = 5:1)).

$[\alpha]_{D}^{25}$ = 17.8 (*c* = 1.30, $CHCl_3$).

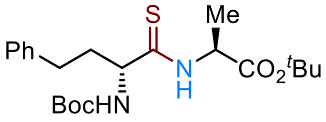
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.30 – 7.23 (m, 2H), 7.21 – 7.14 (m, 3H), 5.37 (s, 1H), 4.46 (d, *J* = 6.6 Hz, 1H), 4.31 (dd, *J* = 19.0, 4.9 Hz, 1H), 4.16 (d, *J* = 4.7 Hz, 1H), 2.74 – 2.63 (m, 2H), 2.24 (d, *J* = 6.6 Hz, 1H), 2.05 (dt, *J* = 13.7, 7.4 Hz, 1H), 1.47 (s, 9H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 167.5, 155.7, 140.9, 128.6, 128.5, 126.2, 83.0, 80.4, 60.4, 47.8, 37.5, 32.2, 28.4, 28.1.

HRMS (ESI): calculated for $C_{21}H_{32}N_2O_4SNa$ $[M+Na]^+$ 431.1975; found: 431.1958.

FT-IR (neat): 3270, 2978, 1743, 1688, 1497, 1455, 1367, 1157, 700 cm^{-1}.

tert-Butyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-alaninate (**10d**)



10d

Following procedure B: **10d** was isolated as a light yellow oil in 84% yield (35.4 mg; 0.084 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

[α]$_{25\ D}$ = 17.1 (*c* = 0.90, $CHCl_3$).

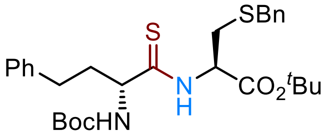
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.31 – 7.24 (m, 3H), 7.20 – 7.16 (m, 3H), 5.41 (s, 1H), 4.93 (p, *J* = 7.0 Hz, 1H), 4.58 – 4.34 (m, 1H), 2.69 (dt, *J* = 16.5, 8.1 Hz, 2H), 2.21 (s, 1H), 2.04 (tt, *J* = 14.0, 7.1 Hz, 1H), 1.49 – 1.45 (m, 12H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 171.2, 155.6, 141.0, 128.6, 128.5, 126.2, 82.7, 80.3, 60.4, 53.8, 37.5, 32.2, 28.4, 28.0, 16.9.

HRMS (ESI): calculated for $C_{22}H_{34}N_2O_4SNa$ $[M+Na]^+$ 445.2132; found: 445.2123.

FT-IR (neat): 3301, 2976, 1740, 1698, 1603, 1555, 1503, 1454, 1366, 1164, 701 cm^{-1}.

tert-Butyl *S*-benzyl-*N*-((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-cysteinate (**10e**)



10e

Following procedure B: **10e** was isolated as a yellow oil in 62% yield (33.7 mg; 0.062 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f= 0.6 (PE:EA = 5:1)).

[α]$_{25\ D}$ = 5.6 (*c* = 0.80, $CHCl_3$).

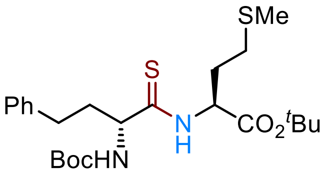
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.46 (s, 1H), 7.71 – 7.63 (m, 1H), 7.47 (ddd, *J* = 8.4, 6.7, 3.0 Hz, 1H), 7.28 (d, *J* = 4.0 Hz, 5H), 7.25 – 7.15 (m, 4H), 5.17 (dd, *J* = 13.3, 8.3 Hz, 2H), 4.43 (s, 1H), 3.70 (d, *J* = 1.9 Hz, 2H), 3.18 (dd, *J* = 13.7, 4.9 Hz, 1H), 2.91 (dd, *J* = 13.7, 5.2 Hz, 1H), 2.70 (t, *J* = 7.9 Hz, 2H), 2.36 – 2.21 (m, 1H), 2.04 (dq, *J* = 15.3, 7.9 Hz, 1H), 1.45 (d, *J* = 7.1 Hz, 18H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 204.4, 168.7, 137.7, 132.3, 132.2, 132.1, 129.1, 128.7, 128.5, 127.3, 126.3, 83.5, 80.4, 61.0, 57.4, 37.3, 36.9, 32.1, 31.9, 29.8, 28.4, 28.0.

HRMS (ESI): calculated for $C_{29}H_{40}N_2O_4S_2Na$ $[M+Na]^+$ 567.2322; found: 567.2326.

FT-IR (neat): 3392, 3327, 2976, 1739, 1699, 1602, 1553, 1496, 1454, 1391, 1367, 1165, 1120, 1048, 1028, 913, 699 cm^{-1}.

***tert*-Butyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-methioninate (10f)**



10f

Following procedure B: **10f** was isolated as a light yellow oil in 74% yield (35.6 mg; 0.074 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R$_f$ = 0.5 (PE:EA = 5:1)).

[α]$^{25}_{D}$= 30.6 (*c* = 1.60, CHCl$_3$).

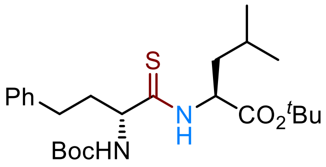
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.61 (s, 1H), 7.32 – 7.27 (m, 2H), 7.21 – 7.16 (m, 3H), 5.23 (d, *J* = 7.7 Hz, 1H), 5.12 – 5.03 (m, 1H), 4.42 (s, 1H), 2.74 – 2.62 (m, 2H), 2.50 (ddd, *J* = 8.2, 6.6, 3.0 Hz, 2H), 2.38 – 2.23 (m, 2H), 2.20 – 2.10 (m, 1H), 2.08 (s, 3H), 2.07 – 1.99 (m, 1H), 1.48 (s, 9H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 204.1, 169.9, 155.5, 140.8, 128.7, 128.5, 126.3, 83.2, 80.5, 61.0, 57.4, 37.1, 32.2, 30.4, 29.7, 28.4, 28.1, 15.6.

HRMS (ESI): calculated for $C_{24}H_{38}N_2O_4S_2Na$ $[M+Na]^+$ 505.2165; found: 505.2160.

FT-IR (neat): 3295, 2977, 1724, 1698, 1553, 1497, 1453, 1367, 1158, 699 cm^{-1}.

tert-Butyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-leucinate (**10g**)



10g

Following procedure B: **10g** was isolated as a yellow oil in 78% yield (36.2 mg; 0.078 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.45 (PE:EA = 5:1)).

$[\alpha]_{25}$ $_{D}$= 13.6 (*c* = 1.00, CHCl$_3$).

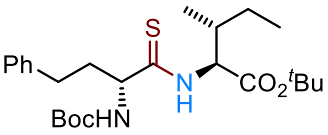
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.49 (s, 1H), 7.31 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 5.31 (s, 1H), 5.02 – 4.94 (m, 1H), 4.43 (d, *J* = 7.7 Hz, 1H), 2.76 – 2.58 (m, 2H), 2.25 (d, *J* = 14.0 Hz, 1H), 2.11 – 1.98 (m, 1H), 1.77 – 1.68 (m, 2H), 1.44 (d, *J* = 8.5 Hz, 18H), 0.95 (dd, *J* = 12.1, 6.3 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ204.1, 170.8, 155.6, 141.0, 128.6, 128.5, 126.2, 82.5, 80.4, 60.9, 57.0, 40.4, 37.0, 32.2, 28.4, 28.1, 25.1, 22.7, 22.5.

HRMS (ESI): calculated for $C_{25}H_{40}N_2O_4SNa$ $[M+Na]^+$ 487.2601; found: 487.2603.

FT-IR (neat): 3304, 2976, 1727, 1697, 1553, 1497, 1454, 1367, 1159, 699 cm^{-1}.

tert-Butyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-alloisoleucinate (**10h**)



10h

Following procedure B: **10h** was isolated as a yellow oil in 72% yield (33.4 mg; 0.072 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.55 (PE:EA = 5:1)).

[α]$_{25}$ $_{D}$= 7.6 (*c* = 0.80, $CHCl_3$).

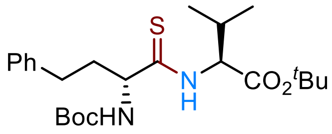
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.31 – 7.25 (m, 2H), 7.19 (td, *J* = 7.2, 1.4 Hz, 3H), 5.21 (s, 1H), 5.06 – 4.98 (m, 1H), 4.40 (s, 1H), 2.77 – 2.61 (m, 2H), 2.33 (dd, *J* = 14.2, 6.1 Hz, 1H), 2.18 – 1.98 (m, 2H), 1.64 – 1.52 (m, 1H), 1.48 (s, 9H), 1.44 (s, 9H), 1.36 – 1.20 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 169.7, 155.5, 140.9, 128.6, 128.5, 126.3, 82.8, 80.5, 61.7, 61.1, 37.2, 37.0, 32.2, 28.4, 28.2, 26.3, 15.2, 11.9.

HRMS (ESI): calculated for $C_{25}H_{41}N_2O_4S$ $[M+H]^+$ 465.2782; found: 465.2773.

FT-IR (neat): 3310, 2974, 1724, 1701, 1497, 1454, 1366, 1159, 699 cm^{-1}.

tert-Butyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-valinate (10i)



10i

Following procedure B: **10i** was isolated as a yellow oil in 68% yield (30.6 mg; 0.068 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.55 (PE:EA = 5:1)).

[α]$_{25}$ $_{D}$= 29.6 (*c* = 1.30, $CHCl_3$).

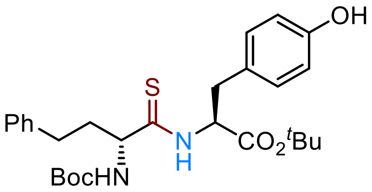
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.28 (td, *J* = 5.4, 2.5 Hz, 2H), 7.19 (td, *J* = 6.3, 1.8 Hz, 3H), 5.25 (d, *J* = 8.5 Hz, 1H), 4.96 (dd, *J* = 8.0, 4.1 Hz, 1H), 4.43 (s, 1H), 2.36 (ddt, *J* = 14.8, 12.4, 7.4 Hz, 2H), 2.14 – 1.98 (m, 1H), 1.48 (s, 9H), 1.44 (s, 9H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 169.7, 155.6, 140.9, 128.6, 128.5, 126.3, 82.7, 80.4, 62.8, 61.2, 37.0, 32.2, 30.9, 28.4, 28.2, 18.7, 18.4.

HRMS (ESI): calculated for $C_{24}H_{38}N_2O_4SNa$ $[M+Na]^+$ 473.2445; found: 473.2452.

FT-IR (neat): 3311, 2976, 1735, 1701, 1497, 1454, 1366, 1158, 702 cm^{-1}.

***tert*-Butyl ((*R*)-2-((tert-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-tyrosinate (10j)**



10j

Following procedure B: **10j** was isolated as a yellow oil in 63% yield (32.4 mg; 0.063 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.3 (PE:EA = 5:1)).

[α]$_{25}$ $_D$= 15.8 (*c* = 1.00, $CHCl_3$).

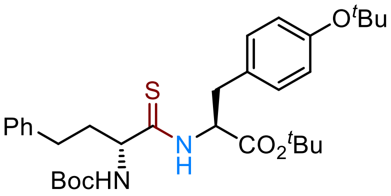
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.25 (d, *J* = 14.6 Hz, 2H), 7.20 – 7.09 (m, 3H), 6.99 – 6.94 (m, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 5.39 (d, *J* = 8.5 Hz, 1H), 5.17 (q, *J* = 6.7 Hz, 1H), 4.41 (s, 1H), 3.25 – 3.08 (m, 2H), 2.59 (s, 2H), 2.22 (dq, *J* = 15.1, 7.7 Hz, 1H), 1.96 (p, *J* = 8.8 Hz, 1H), 1.44 (s, 9H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 170.0, 155.7, 155.4, 140.9, 130.6, 128.6, 128.5, 127.1, 126.2, 115.7, 83.2, 80.6, 60.6, 59.1, 37.5, 35.6, 32.1, 28.4, 28.1.

HRMS (ESI): calculated for $C_{28}H_{38}N_2O_5SNa$ $[M+Na]^+$ 537.2394; found: 537.2392.

FT-IR (neat): 3334, 2978, 1724, 1698, 1614, 1515, 1454, 1367, 1156, 700 cm^{-1}.

***tert*-Butyl (*S*)-3-(4-(*tert*-butoxy)phenyl)-2-((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioamido)propanoate (10k)**



10k

Following procedure B: **10k** was isolated as a yellow oil in 75% yield (42.3 mg; 0.075 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

[α]$_{25}$ $_D$= 12.4 (c = 1.50, $CHCl_3$).

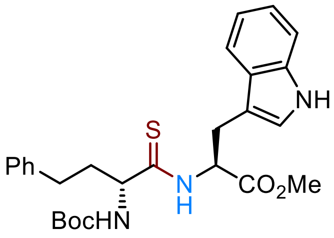
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.30 – 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 7.08 – 7.03 (m, 2H), 6.89 – 6.85 (m, 2H), 5.25 (d, J = 7.4 Hz, 1H), 5.21 – 5.13 (m, 1H), 4.40 (s, 1H), 3.20 (t, J = 4.8 Hz, 2H), 2.68 (dt, J = 22.3, 8.0 Hz, 2H), 2.35 – 2.17 (m, 1H), 2.06 – 1.76 (m, 2H), 1.44 (s, 9H), 1.37 (s, 9H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 169.7, 154.5, 140.9, 130.7, 130.0, 128.7, 128.6, 128.5, 126.5, 126.2, 124.3, 83.1, 80.4, 78.5, 60.6, 59.0, 37.5, 35.9, 32.1, 28.9, 28.4, 28.0.

HRMS (ESI): calculated for $C_{32}H_{46}N_2O_5SNa$ $[M+Na]^+$ 593.3020; found: 593.3026.

FT-IR (neat): 3326, 2977, 1718, 1701, 1607, 1554, 1506, 1454, 1366, 1160, 700 cm^{-1}.

Methyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-tryptophanate (10l)



10l

Following procedure B: **10l** was isolated as a yellow oil in 58% yield (28.7 mg; 0.058 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.35 (PE:EA = 5:1)).

[α]$_{25}$ $_D$= 39.2 (*c* = 1.60, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.08 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.21 (m, 3H), 7.21 – 7.14 (m, 2H), 7.10 – 7.03 (m, 3H), 6.97 (d, *J* = 2.5 Hz, 1H), 5.44 – 5.36 (m, 1H), 5.21 (d, *J* = 8.2 Hz, 1H), 4.36 (s, 1H), 3.67 (s, 3H), 3.53 (d, *J* = 13.2

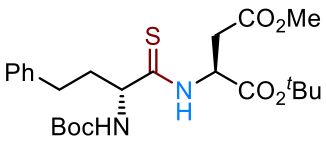
Hz, 1H), 3.41 (dd, *J* = 14.8, 5.8 Hz, 1H), 2.66 – 2.45 (m, 2H), 2.13-2.19 (m, 1H), 1.96 (s, 1H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 171.4, 155.6, 140.9, 136.2, 128.6, 128.5, 127.4, 126.2, 123.1, 122.5, 119.9, 118.5, 111.4, 109.4, 80.4, 60.5, 58.1, 52.7, 37.2, 31.9, 28.4, 26.4.

HRMS (ESI): calculated for $C_{27}H_{33}N_3O_4SNa$ $[M+Na]^+$ 518.2084; found: 518.2078.

FT-IR (neat): 3325, 2976, 1731, 1692, 1502, 1454, 1366, 1164, 700 cm^{-1}.

1-(*tert*-Butyl) 4-methyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-aspartate (10m)



10m

Following procedure B: **10m** was isolated as a yellow oil in 73% yield (35.1 mg; 0.073 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

[α]$_{25}$ $_{D}$= 8.2 (*c* = 1.00, $CHCl_3$).

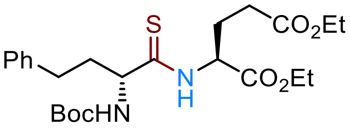
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 5.8 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.21 – 7.15 (m, 3H), 5.30 – 5.15 (m, 2H), 4.43 (s, 1H), 3.64 (s, 3H), 3.08 (qd, *J* = 17.0, 4.3 Hz, 2H), 2.76 – 2.55 (m, 2H), 2.25 (ddt, *J* = 13.7, 9.9, 5.9 Hz, 1H), 2.12 – 1.95 (m, 1H), 1.47 (s, 9H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 171.2, 168.6, 155.2, 140.8, 128.6, 128.5, 126.3, 83.4, 80.4, 61.1, 54.1, 52.1, 37.4, 34.6, 32.0, 28.4, 28.0.

HRMS (ESI): calculated for $C_{24}H_{36}N_2O_6SNa$ $[M+Na]^+$ 503.2186; found: 503.2185.

FT-IR (neat): 3305, 2978, 1739, 1700, 1557, 1497, 1436, 1367, 1160, 701 cm^{-1}.

Diethyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-glutamate (10n)



10n

Following procedure B: **10n** was isolated as a light yellow oil in 64% yield (30.7 mg; 0.064 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.4 (PE:EA = 5:1)).

[α]$_{25}$ $_D$ = 25.6 (*c* = 2.40, $CHCl_3$).

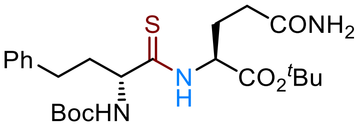
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.31 – 7.25 (m, 2H), 7.19 (td, *J* = 5.9, 1.8 Hz, 3H), 5.28 (d, *J* = 8.0 Hz, 1H), 5.10 (td, *J* = 7.1, 5.1 Hz, 1H), 4.44 (d, *J* = 6.0 Hz, 1H), 4.21 (qd, *J* = 7.1, 2.2 Hz, 2H), 4.11 (qd, *J* = 7.1, 1.4 Hz, 2H), 2.78 – 2.61 (m, 2H), 2.51 – 2.12 (m, 5H), 2.06 (h, *J* = 8.5 Hz, 1H), 1.44 (s, 9H), 1.26 (dt, *J* = 20.9, 7.1 Hz, 6H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 204.9, 172.9, 170.6, 155.6, 140.9, 128.6, 128.5, 126.3, 80.4, 70.1, 62.0, 61.0, 57.0, 39.8, 37.0, 32.1, 30.2, 28.4, 26.1, 14.2.

HRMS (ESI): calculated for $C_{24}H_{36}N_2O_6SNa$ $[M+Na]^+$ 503.2186; found: 503.2193.

FT-IR (neat): 3303, 2983, 1736, 1700, 1497, 1453, 1367, 1166, 701 cm^{-1}.

tert-Butyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-glutaminate (10o)



10o

Following procedure B: **10o** was isolated as a light yellow oil in 88% yield (42.2 mg; 0.088 mmol) which was purified by silica gel chromatography (PE:EA = 10:1~1:1, R_f = 0.3 (PE:EA = 1:1)).

[α]$_{25}$ $_D$= 7.6 (*c* = 1.20, $CHCl_3$).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.16 (m, 3H), 5.87 (s, 1H), 5.50 (s, 1H), 5.18 (d, *J* = 7.1 Hz, 1H), 4.95 (q, *J* = 6.3 Hz, 1H), 4.44

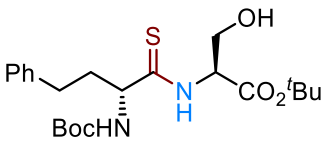
(q, *J* = 7.6 Hz, 1H), 2.68 (dpd, *J* = 20.6, 13.9, 5.7 Hz, 2H), 2.39 – 2.14 (m, 5H), 2.04 (dq, *J* = 18.4, 7.2 Hz, 1H), 1.47 (s, 9H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 174.5, 169.7, 155.6, 140.8, 128.7, 128.5, 126.3, 83.1, 80.7, 57.6, 37.0, 32.2, 31.4, 29.8, 28.4, 28.1, 26.6.

HRMS (ESI): calculated for $C_{24}H_{38}N_3O_5S$ $[M+H]^+$ 480.2527; found: 480.2525.

FT-IR (neat): 3331, 2977, 1724, 1704, 1682, 1669, 1655, 1558, 1520, 1506, 1456, 1393, 1367, 1161, 1046, 913, 697 cm^{-1}.

tert-Butyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-serinate (10p)



10p

Following procedure B: **10p** was isolated as a yellow oil in 67% yield (29.3 mg; 0.067 mmol) which was purified by silica gel chromatography (PE:EA= 10:1~1:1, R_f= 0.4 (PE:EA = 1:1)).

$[\alpha]_{25\ D}$= 5.6 (*c* = 1.20, $CHCl_3$).

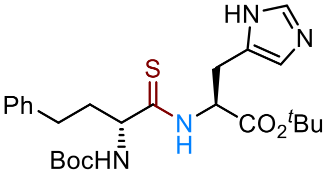
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.30 – 7.25 (m, 2H), 7.19 (td, *J* = 6.0, 1.6 Hz, 3H), 5.28 (s, 1H), 5.06 – 4.98 (m, 1H), 4.51 – 4.39 (m, 1H), 4.24 (s, 1H), 3.97 (d, *J* = 10.2 Hz, 1H), 2.70 (tt, *J* = 13.7, 6.9 Hz, 3H), 2.31 (dddd, *J* = 14.3, 9.6, 6.6, 4.9 Hz, 1H), 2.06 (td, *J* = 14.6, 9.1 Hz, 1H), 1.49 (s, 9H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 168.8, 156.0, 140.7, 128.7, 128.5, 126.3, 83.4 (2C), 80.9, 61.5, 60.0, 36.9, 32.2, 28.3, 28.1.

HRMS (ESI): calculated for $C_{22}H_{34}N_2O_5SNa$ $[M+Na]^+$ 461.2081; found: 461.2085.

FT-IR (neat): 3304, 2978, 1727, 1697, 1498, 1454, 1368, 1159, 699 cm^{-1}.

tert-Butyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-histidinate (10q)



10q

Following procedure B: **10q** was isolated as a yellow oil in 43% yield (21.0 mg; 0.043 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.2 (PE:EA = 5:1)).

[α]$_{25}$ $_D$= 28.4 (*c* = 1.00, $CHCl_3$).

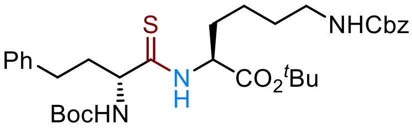
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.45 (s, 1H), 7.30 – 7.27 (m, 1H), 7.26 (d, *J* = 1.8 Hz, 1H), 7.21 – 7.16 (m, 3H), 6.79 (s, 1H), 5.37 (d, *J* = 7.7 Hz, 1H), 5.17 – 5.05 (m, 1H), 4.46 (td, *J* = 8.2, 4.9 Hz, 1H), 3.36 (d, *J* = 11.3 Hz, 1H), 3.17 (dd, *J* = 15.2, 5.4 Hz, 1H), 2.68 (dddd, *J* = 23.6, 13.7, 9.8, 5.8 Hz, 2H), 2.42 – 2.28 (m, 1H), 2.08 (s, 1H), 1.43 (s, 9H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 175.2, 169.1, 155.9, 140.9, 135.3, 128.6, 128.5, 126.2, 118.4, 82.8, 80.6, 61.7, 58.3, 37.3, 32.1, 28.4, 28.0, 21.8.

HRMS (ESI): calculated for $C_{25}H_{36}N_4O_4SNa$ $[M+Na]^+$ 511.2350; found: 511.2348.

FT-IR (neat): 3218, 2977, 1720, 1705, 1496, 1454, 1467, 1367, 1157, 699 cm^{-1}.

***tert*-Butyl N^6-((benzyloxy)carbonyl)-N^2-((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-lysinate (10r)**



10r

Following procedure B: **10r** was isolated as a yellow oil in 68% yield (41.7 mg; 0.068 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f= 0.45 (PE:EA = 5:1)).

[α]$_{25}$ $_D$= 9.0 (*c* = 1.50, $CHCl_3$).

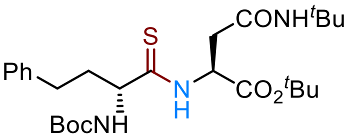
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.56 (s, 1H), 7.37 – 7.23 (m, 7H), 7.21 – 7.13 (m, 3H), 5.25 (t, *J* = 6.9 Hz, 1H), 5.08 (s, 2H), 4.94 (q, *J* = 5.9 Hz, 2H), 4.42 (s, 1H), 3.15 (p, *J* = 6.9 Hz, 2H), 2.67 (dt, *J* = 9.3, 6.0 Hz, 2H), 2.38 – 2.21 (m, 1H), 2.11 – 1.93 (m, 2H), 1.90 – 1.76 (m, 1H), 1.57 – 1.49 (m, 2H), 1.46 (s, 9H), 1.42 (s, 9H), 1.40 – 1.21 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 203.8, 170.4, 156.6, 155.5, 140.9, 136.7, 128.6, 128.6, 128.5, 128.2, 128.2, 126.3, 82.9, 80.5, 66.7, 61.0, 57.7, 40.5, 37.0, 32.2, 30.5, 29.6, 28.4, 28.1, 22.0.

HRMS (ESI): calculated for $C_{33}H_{47}N_3O_6SNa$ $[M+Na]^+$ 636.3078; found: 636.3079.

FT-IR (neat): 3314, 2977, 1730, 1701, 1769, 1653, 1521, 1496, 1453, 1366, 1157, 699 cm^{-1}.

***tert*-Butyl *N*^{2}-((*R*)-2-((tert-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*N*^{4}-(tert-butyl)-*L*-asparaginate (10s)**



10s

Following procedure B: **10s** was isolated as a yellow oil in 67% yield (34.9 mg; 0.067 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R$_f$ = 0.4 (PE:EA = 5:1)).

[α]$_{25}$ $_D$= 11.4 (*c* = 0.90, CHCl$_3$).

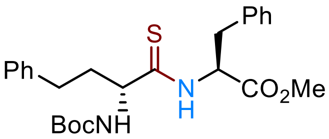
^{1}H NMR (400 MHz, CDCl$_3$) δ 9.05 (s, 1H), 7.29 – 7.23 (m, 2H), 7.20 – 7.14 (m, 3H), 5.42 (s, 1H), 5.33 (d, *J* = 6.3 Hz, 1H), 5.23 (dt, *J* = 8.0, 4.1 Hz, 1H), 4.49 (s, 1H), 2.86 – 2.75 (m, 2H), 2.74 – 2.56 (m, 2H), 2.29 – 2.16 (m, 1H), 2.06 – 1.96 (m, 1H), 1.46 (s, 9H), 1.43 (s, 9H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 203.6, 169.1, 168.9, 155.1, 141.0, 128.5, 128.5, 126.2, 82.9, 80.1, 61.2, 55.0, 51.7, 38.0, 36.9, 32.1, 28.7, 28.4, 28.0.

HRMS (ESI): calculated for $C_{27}H_{43}N_3O_5SNa$ $[M+Na]^+$ 544.2816; found: 544.2826.

FT-IR (neat): 3339, 2976, 1730, 1703, 1662, 1511, 1454, 1366, 1161, 699 cm^{-1}.

Methyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-phenylalaninate (10t)


10t

Following procedure B: **10t** was isolated as a yellow oil in 73% yield (33.3 mg; 0.073 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.55 (PE:EA = 5:1)).

[α]$_{25}$ $_{D}$= 18.6 (*c* = 0.90, $CHCl_3$).

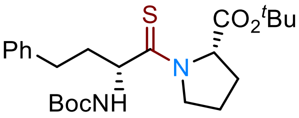
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.32 – 7.16 (m, 7H), 7.15 – 7.06 (m, 4H), 5.37 (q, *J* = 5.9 Hz, 1H), 5.17 (d, *J* = 6.5 Hz, 1H), 4.43 – 4.31 (m, 1H), 3.73 (s, 3H), 3.36 (dd, *J* = 13.8, 5.1 Hz, 1H), 3.20 (dd, *J* = 14.0, 5.7 Hz, 1H), 2.68 – 2.52 (m, 2H), 2.27 – 2.15 (m, 1H), 1.98 (dt, *J* = 14.0, 7.1 Hz, 1H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6, 171.0, 155.6, 140.8, 135.4, 129.3, 128.8, 128.6, 128.5, 127.4, 126.2, 60.6, 58.4, 52.6, 37.3, 36.5, 32.0, 29.8, 28.4.

HRMS (ESI): calculated for $C_{25}H_{33}N_2O_4S$ [M+H]$^+$ 457.2156; found: 457.2186.

FT-IR (neat): 3295, 2976, 1740, 1701, 1603, 1496, 1454, 1437, 1366, 1169, 1047, 700 cm^{-1}.

tert-Butyl ((*R*)-2-((*tert*-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-prolinate (10u)


10u

Following procedure B: **10u** was isolated as a yellow oil in 82% yield (36.8 mg; 0.082 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f= 0.45 (PE:EA = 5:1)).

[α]$_{25}$ $_D$= 14.1 (*c* = 2.00, $CHCl_3$).

A mixture of two stereoisomers A and B in approximately 5.6:1 ratio.

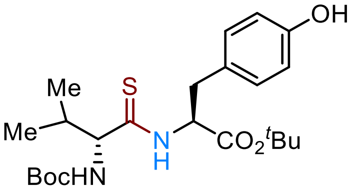
^{1}H NMR (400 MHz, $CDCl_3$) δ **major rotamer:** 7.32 – 7.13 (m, 5H), 5.63 (dd, *J* = 22.2, 9.4 Hz, 1H), 4.83 – 4.61 (m, 1H), 3.96 – 3.65 (m, 1H), 3.48 – 3.16 (m, 1H), 2.84 – 2.53 (m, 2H), 2.36 – 1.86 (m, 6H), 1.46 (d, *J* = 3.8 Hz, 9H), 1.43 (d, *J* = 1.9 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) **major rotamer:** δ 202.6, 169.1, 155.4, 141.3, 128.7, 128.6, 126.2, 81.9, 79.7, 66.4, 55.8, 50.6, 38.5, 32.0, 29.0, 28.5, 28.0, 24.4.

HRMS (ESI): calculated for $C_{24}H_{36}N_2O_4SNa$ $[M+Na]^+$ 471.2288; found: 471.2283.

FT-IR (neat): 3000, 2979, 1737, 1711, 1498, 1469, 1452, 1366, 1153, 704 cm^{-1}.

*tert*-Butyl ((*R*)-2-((tert-butoxycarbonyl)amino)-3-methylbutanethioyl)-*L*-tyrosinate (10v)



10v

Following procedure B: **10v** was isolated as a yellow oil in 59% yield (26.7 mg; 0.059 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

[α]$_{25}$ $_D$= 8.1 (*c* = 1.60, $CHCl_3$).

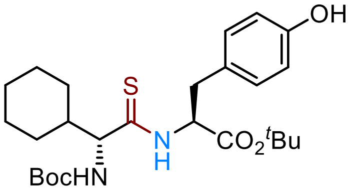
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.03 – 6.98 (m, 2H), 6.75 – 6.69 (m, 2H), 5.21 (dt, J = 13.2, 7.7 Hz, 2H), 4.20 – 4.13 (m, 1H), 3.20 – 3.12 (m, 2H), 2.39 – 2.28 (m, 1H), 1.43 (s, 9H), 1.41 (s, 9H), 0.86 (t, J = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 169.9, 155.9, 155.2, 130.6, 127.4, 115.6, 83.1, 80.4, 66.5, 59.1, 35.8, 33.2, 28.4, 28.0, 19.8, 17.2.

HRMS (ESI): calculated for $C_{23}H_{36}N_2O_5SNa$ $[M+Na]^+$ 475.2237; found: 475.2240.

FT-IR (neat): 3340, 2980, 1729, 1692, 1515, 1450, 1367, 1156, 843 cm^{-1}.

***tert*-Butyl ((*R*)-2-((tert-butoxycarbonyl)amino)-2-cyclohexylethanethioyl)-*L*-tyrosinate (10w)**



10w

Following procedure B: **10w** was isolated as a yellow oil in 78% yield (38.4 mg; 0.078 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

[α]$_{25}$ $_D$= 17.4 (*c* = 1.00, $CHCl_3$).

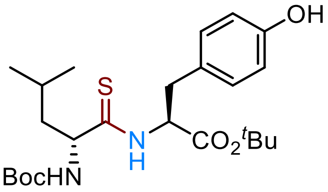
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.04 – 6.99 (m, 2H), 6.74 (d, J = 2.0 Hz, 1H), 6.73 (d, J = 2.0 Hz, 1H), 5.33 – 5.14 (m, 2H), 4.21 – 4.08 (m, 1H), 3.17 (d, J = 5.8 Hz, 2H), 1.76 – 1.51 (m, 5H), 1.43 (s, 9H), 1.41 (s, 9H), 1.27 – 1.05 (m, 4H), 0.88 (ddt, J = 15.0, 11.6, 4.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 169.8, 155.8, 155.1, 130.6, 127.5, 115.6, 83.1, 80.3, 65.9, 59.1, 42.7, 35.8, 30.1, 28.4, 28.0, 27.8, 26.2, 26.0, 26.0.

HRMS (ESI): calculated for $C_{26}H_{40}N_2O_5SNa$ $[M+Na]^+$ 515.2550; found: 515.2552.

FT-IR (neat): 3342, 2979, 1724, 1701, 1686, 1513, 1458, 1367, 1156, 844 cm^{-1}.

***tert*-Butyl ((*R*)-2-((tert-butoxycarbonyl)amino)-4-methylpentanethioyl)-*L*-tyrosinate (10y)**



10x

Following procedure B: **10y** was isolated as a yellow oil in 84% yield (39.2 mg; 0.084 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

[α]$_{25\ D}$= 11.4 (*c* = 1.00, $CHCl_3$).

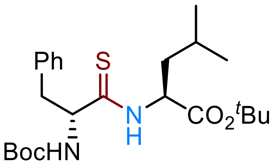
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.00 – 6.95 (m, 2H), 6.73 – 6.68 (m, 2H), 6.13 (s, 1H), 5.21 – 5.04 (m, 2H), 4.40 (td, *J* = 8.8, 5.1 Hz, 1H), 3.76 (ddt, *J* = 5.8, 4.1, 2.2 Hz, 1H), 3.16 (td, *J* = 14.6, 4.7 Hz, 2H), 1.89 – 1.83 (m, 1H), 1.42 (d, *J* = 2.5 Hz, 18H), 0.90 (dd, *J* = 8.5, 6.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9, 170.0 (2C), 155.2, 130.6, 127.3, 115.6, 83.2, 68.1, 58.9, 45.0, 35.5, 28.4, 28.1, 25.7, 25.0, 23.0.

HRMS (ESI): calculated for $C_{24}H_{37}N_2O_5S$ [M-H]$^-$ 465.2429; found: 465.2480.

FT-IR (neat): 3373, 3322, 2976, 1727, 1690, 1603, 1551, 1495, 1478, 1454, 1392, 1367, 1153, 1078, 1030, 993, 913, 847, 700 cm^{-1}.

tert-Butyl ((_R_)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanethioyl)-_L_-leucinate (**10x**)



10y

Following procedure B: **10x** was isolated as a yellow oil in 72% yield (32.4 mg; 0.072 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

[α]$_{25\ D}$= 6.8 (*c* = 1.20, $CHCl_3$).

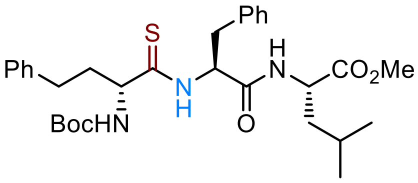
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.31 – 7.18 (m, 6H), 5.32 (s, 1H), 4.91 (dd, *J* = 7.8, 4.0 Hz, 1H), 4.60 (q, *J* = 6.9 Hz, 1H), 3.18 (d, *J* = 7.1 Hz, 2H), 1.91 – 1.78 (m, 1H), 1.73 (d, *J* = 3.3 Hz, 1H), 1.45 (s, 9H), 1.41 (s, 9H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.58 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 169.5, 155.0, 136.6, 129.3, 128.8, 127.1, 82.8, 80.4, 61.7, 41.8, 37.3, 28.3, 28.2, 26.3, 14.9, 11.8.

HRMS (ESI): calculated for $C_{24}H_{38}N_2O_4SNa$ $[M+Na]^+$ 473.2445; found: 473.2449.

FT-IR (neat): 3408, 3292, 2974, 1705, 1604, 1496, 1455, 1435, 1392, 1367, 1160, 1078, 1047, 1024, 844, 700 cm^{-1}.

Methyl ((*R*)-2-((tert-butoxycarbonyl)amino)-4-phenylbutanethioyl)-*L*-phenylalanyl- *L*-leucinate (11a)



11a

Following procedure B: **11a** was isolated as a yellow oil in 54% yield (30.7 mg; 0.054 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f= 0.4 (PE:EA = 5:1)).

[α]$_{D}^{25}$= 35.6 (*c* = 1.40, $CHCl_3$).

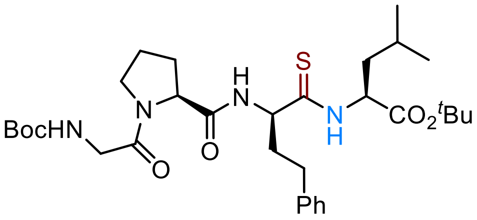
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.28 (t, *J* = 6.3 Hz, 6H), 7.20 (d, *J* = 7.1 Hz, 3H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.29 (s, 1H), 5.27 (dd, *J* = 20.9, 6.3 Hz, 2H), 4.59 – 4.45 (m, 1H), 4.26 (q, *J* = 7.8 Hz, 1H), 3.69 (s, 2H), 3.42 – 3.28 (m, 1H), 3.15 (s, 1H), 2.54 (d, *J* = 16.5 Hz, 2H), 2.09 (s, 1H), 2.02 – 1.87 (m, 1H), 1.42 (s, 9H), 1.25 (s, 3H), 0.86 (d, *J* = 4.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 172.5, 169.3, 140.7, 136.0, 129.4, 128.9, 128.6, 128.4, 127.4, 126.3, 121.3, 80.4, 61.2, 59.3, 52.4, 51.2, 41.1, 37.2, 36.8, 31.9, 29.8, 28.4, 24.8, 22.8, 21.9.

HRMS (ESI): calculated for $C_{31}H_{43}N_3O_5SNa$ $[M+Na]^+$ 592.2816; found: 592.2820.

FT-IR (neat): 3304, 2956, 1743, 1727, 1685, 1510, 1497, 1454, 1437, 1337, 1165, 699 cm^{-1}.

tert-Butyl ((*S*)-2-((*R*)-1-((tert-butoxycarbonyl)glycyl)pyrrolidine-2-carboxamido)-4-phenylbutanethioyl)-*L*-leucinate (**11b**)



11b

Following procedure B: **11b** was isolated as a yellow oil in 50% yield (30.9 mg; 0.078 mmol) which was purified by silica gel chromatography (DCM:EA = 20:1~5:1, R_f = 0.5 (DCM:EA = 5:1)).

[α]$_{25\ D}$= 11.4 (*c* = 1.20, $CHCl_3$).

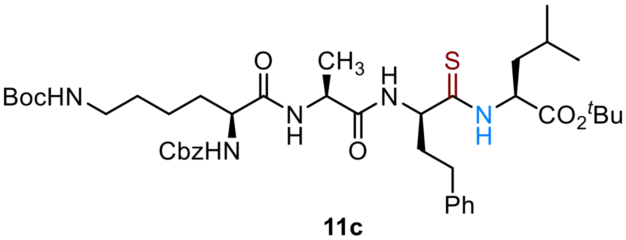
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 3H), 5.45 (s, 1H), 4.99 (q, *J* = 6.9 Hz, 1H), 4.70 (td, *J* = 8.4, 4.5 Hz, 1H), 4.45 (dd, *J* = 8.0, 3.3 Hz, 1H), 4.14 – 4.02 (m, 1H), 3.94 – 3.85 (m, 1H), 3.55 (td, *J* = 8.4, 3.7 Hz, 1H), 3.46 – 3.37 (m, 1H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.47 (td, *J* = 13.6, 8.0 Hz, 1H), 2.32 (tt, *J* = 7.1, 3.4 Hz, 1H), 2.13 (dq, *J* = 14.8, 7.8 Hz, 2H), 2.02 – 1.89 (m, 2H), 1.80 – 1.57 (m, 3H), 1.47 (s, 9H), 1.44 (s, 9H), 0.92 (dd, *J* = 10.2, 6.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 171.1, 169.1, 155.8, 141.0, 128.6, 126.2, 82.5, 79.9, 60.4, 59.5, 57.0, 46.4, 43.2, 40.3, 36.4, 32.2, 28.4, 28.1, 27.7, 25.0, 22.8, 22.5.

HRMS (ESI): calculated for $C_{32}H_{50}N_4O_6SNa$ $[M+Na]^+$ 641.3343; found: 641.3366.

FT-IR (neat): 3347, 3289, 2976, 1739, 1718, 1653, 1512, 1456, 1367, 1157, 1135, 913, 702 cm^{-1}.

tert-Butyl ((*R*)-2-((*S*)-2-((*S*)-2-(((benzyloxy)carbonyl)amino)-6-((tert-butoxy carbonyl)amino)hexanamido)propanamido)-4-phenylbutanethioyl)-*L*-leucinate (**11c**)



11c

Following procedure B: **11c** was isolated as a yellow oil in 58% yield (46.3 mg; 0.058 mmol) which was purified by silica gel chromatography (DCM:EA = 20:1~5:1, R_f = 0.5 (DCM:EA = 5:1)).

[α]$_{25}$ $_{D}$= 7.2 (*c* = 1.00, CHCl$_3$).

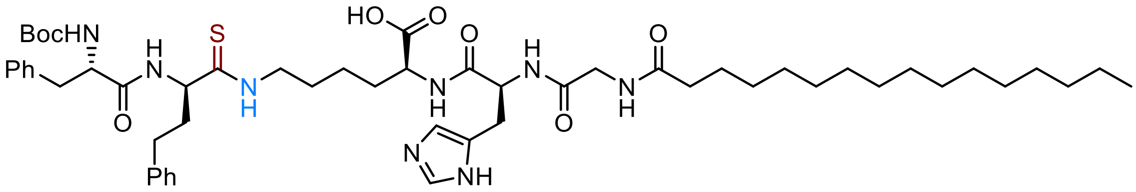
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, *J* = 3.0 Hz, 5H), 7.23 (d, *J* = 6.9 Hz, 2H), 7.16 (t, *J* = 6.9 Hz, 3H), 5.07 (s, 2H), 4.94 (q, *J* = 7.4 Hz, 2H), 4.56 (t, *J* = 7.0 Hz, 1H), 4.35 (s, 1H), 3.05 (dd, *J* = 12.0, 6.2 Hz, 2H), 2.76 – 2.50 (m, 2H), 2.28 – 1.97 (m, 2H), 1.89 – 1.57 (m, 5H), 1.44 (s, 9H), 1.42 – 1.23 (m, 16H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.92 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 203.8, 172.0, 171.6, 170.6, 156.6, 141.1, 136.1, 128.6, 128.6, 128.5, 128.3, 128.2, 126.1, 82.3, 79.2, 77.3, 67.3, 58.0, 57.3, 54.9, 49.2, 40.4, 39.7, 37.7, 32.8, 31.9, 29.9, 28.5, 28.1, 25.2, 22.7, 22.4, 19.3.

HRMS (ESI): calculated for $C_{42}H_{64}N_5O_8S$ $[M+H]^+$ 798.4470; found: 798.4498.

FT-IR (neat): 3282, 2976, 1733, 1699, 1684, 1637, 1519, 1454, 1392, 1366, 1155, 1135, 1050, 912, 844, 698 cm^{-1}.

***N*^{6}-((*S*)-2-((*R*)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-4-phenylbutanethioyl)-*N*^{2}-palmitoylglycyl-*D*-histidyl-*L*-lysine (11d)**



11d

Following procedure B: **11d** was isolated as a yellow oil in 73% yield (36.6 mg; 0.0365 mmol) which was purified by silica gel chromatography (DCM:MeOH = 50:1~5:1, R$_f$ = 0.3 (DCM:MeOH = 5:1)).

[α]$_{25}$ $_{D}$= 29.4 (*c* = 1.00, CHCl$_3$).

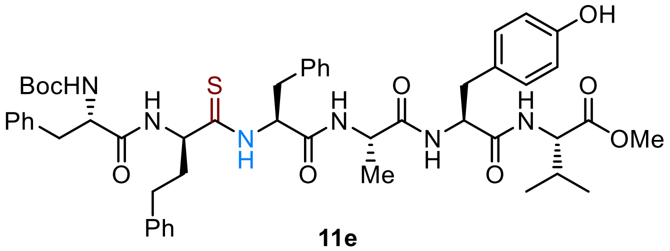
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.22 (s, 1H), 7.45 – 7.32 (m, 2H), 7.25 (q, *J* = 8.1 Hz, 7H), 7.21 – 7.02 (m, 5H), 6.64 (d, *J* = 25.8 Hz, 1H), 6.50 (s, 1H), 6.37 (s, 1H), 4.45 (s, 2H), 4.29 (d, *J* = 8.0 Hz, 1H), 4.25 – 4.01 (m, 2H), 3.87 (s, 1H), 3.69 (dd, *J* = 6.0, 2.5 Hz, 3H), 3.57 (s, 2H), 3.09 (td, *J* = 7.3, 4.3 Hz, 2H), 3.04 – 2.68 (m, 6H), 2.56 (d, *J* = 12.4 Hz, 1H), 2.35 (dd, *J* = 30.5, 9.6 Hz, 2H), 2.12 (t, *J* = 7.6 Hz, 3H), 1.99 (p, *J* = 6.9 Hz, 1H), 1.89 – 1.37 (m, 14H), 1.32 (s, 9H), 1.27 – 1.04 (m, 10H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 202.5, 175.6, 173.1, 172.1, 169.6, 169.1, 163.3, 156.1, 149.7, 141.8, 138.4, 136.9, 130.2, 129.8, 128.8, 128.6, 127.0, 126.3, 78.8, 76.5, 76.5, 66.4, 61.5, 59.7, 57.0, 55.9, 54.8, 51.0, 50.1, 45.6, 42.7, 37.7, 35.5, 32.0, 31.8, 29.6, 29.6, 29.4, 29.3, 29.1, 28.7, 28.5, 27.3, 27.1, 25.7, 25.2, 22.6, 18.2, 14.5.

HRMS (ESI): calculated for $C_{54}H_{86}N_9O_8S$ $[M+NH_4]^+$1020.6315; found: 1020.6313.

FT-IR (neat): 3277, 2977, 1709, 1674, 1668, 1586, 1555, 1496, 1454, 1417, 1369, 1153, 1087, 1045, 699 cm^{-1}.

Methyl ((*R*)-2-((*R*)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-4-phenylbutanethioyl)-*L*-phenylalanyl-*L*-alanyl-*L*-tyrosylvalinate (11e)



11e

Following procedure B: **11e** was isolated as a yellow oil in 51% yield (47.7 mg; 0.051 mmol) which was purified by silica gel chromatography (DCM:MeOH = 50:1~10:1, R$_f$ = 0.5 (DCM:MeOH = 10:1)).

[α]$_{25}$ $_{D}$= 15.6 (*c* = 1.40, CHCl$_3$).

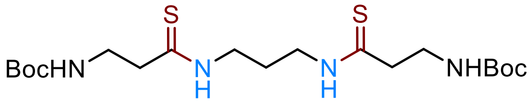
^{1}H NMR (400 MHz, MeOD-*d*$_4$) δ 7.34 – 7.04 (m, 15H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 7.1 Hz, 2H), 6.67 (dd, *J* = 8.6, 4.9 Hz, 2H), 5.38 (dd, *J* = 10.9, 4.2 Hz, 1H), 4.65 – 4.48 (m, 1H), 4.47 – 4.08 (m, 4H), 3.71 – 3.57 (m, 3H), 3.39 (dd, *J* = 14.4, 4.1 Hz, 1H), 3.15 – 2.93 (m, 3H), 2.92 – 2.74 (m, 2H), 2.22 – 1.97 (m, 3H), 1.90 – 1.59 (m, 2H), 1.39 (d, *J* = 6.4 Hz, 2H), 1.36 (s, 9H), 1.31 – 1.19 (m, 1H), 0.92 (dt, *J* = 6.9, 5.4 Hz, 6H).

^{13}C NMR (101 MHz, MeOD-*d*$_4$) δ 206.0, 173.0, 172.5, 171.9, 171.7, 170.8, 155.9, 141.1, 137.3, 136.9, 130.1, 130.0, 129.0, 128.8, 128.2, 128.2, 128.1, 128.0, 127.3, 126.6, 126.4, 125.6, 114.9, 79.5, 60.0, 59.3, 57.9, 56.3, 54.9, 51.2, 49.5, 37.8, 36.7, 36.3, 31.1, 30.7, 27.4, 18.1, 17.4, 16.5.

HRMS (ESI): calculated for $C_{51}H_{65}N_6O_9S$ $[M+H]^+$ 937.4528; found: 937.4526.

FT-IR (neat): 3281, 3064, 3028, 2969, 2931, 1728, 1633, 1516, 1496, 1451, 1436, 1367, 1168, 916, 699 cm^{-1}.

Di-*tert*-butyl ((propane-1,3-diylbis(azanediyl))bis(3-thioxopropane-3,1-diyl)) dicarbamate (13)



13

Following procedure A: the bis-thioamidated product **13** was isolated as a yellow solid in 94% yield (1.265 g; 2.82 mmol) which was purified by silica gel chromatography (DCM: MeOH= 100:1~20:1, R_f = 0.5 (DCM: MeOH = 20:1)).

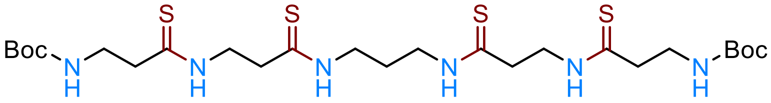
^{1}H NMR (400 MHz, CDCl$_3$) δ 9.02 (s, 1H), 5.36 (s, 1H), 3.75 (d, *J* = 5.7 Hz, 2H), 3.54 (q, *J* = 6.2 Hz, 2H), 2.87 (s, 2H), 1.98 (p, *J* = 6.1 Hz, 1H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 202.6, 156.4, 79.8, 46.2, 42.6, 39.4, 28.5, 26.5.

HRMS (ESI): calculated for $C_{19}H_{37}N_4O_4S_2$ $[M+H]^+$ 449.2251; found: 449.2253.

FT-IR (neat): 3267, 2979, 1688, 1521, 1458, 1410, 1365, 1170, 1094, 1046, 859, 706 cm^{-1}.

Di-*tert*-butyl (3,7,13,17-tetrathioxo-4,8,12,16-tetraazanonadecane-1,19-diyl)dicarbamate (14)



14

Following procedure A after *bis*-*N*-boc deptrotection of **13** with 4M HCl in 1,4-dioxane solution: the tetrakis-thioamide **14** was isolated as a yellow solid in 91% yield (113.2 mg; 0.182 mmol) which was purified by silica gel chromatography (DCM: MeOH= 100:1~20:1, R_f= 0.45 (DCM: MeOH = 20:1)).

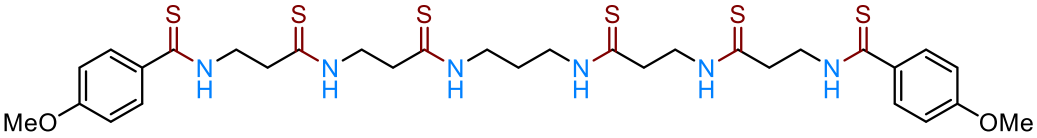
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 9.00 (s, 1H), 5.39 (t, *J* = 6.0 Hz, 1H), 4.16 – 4.02 (m, 2H), 3.75 (s, 2H), 3.51 (s, 2H), 3.02 (s, 2H), 2.85 (s, 2H), 2.03 (s, 1H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 156.5, 79.9, 46.5, 44.7, 43.5, 42.9, 39.8, 28.5, 26.3.

HRMS (ESI): calculated for $C_{25}H_{46}N_6O_4S_4Na$ $[M+Na]^+$ 645.2356; found: 645.2355.

FT-IR (neat): 3265, 2977, 1685, 1520, 1506, 1457, 1364, 1165, 1087, 1043, 867 cm^{-1}.

N,*N'*-(3,7,13,17-tetrathioxo-4,8,12,16-tetraazanonadecane-1,19-diyl)bis(4-methoxybenzothioamide) (16)



16

Following **procedure A** after *bis*-*N*-Boc deprotection of **14** with 4M HCl in 1,4-dioxane solution: the hexakis-thioamide **16** was isolated as a yellow oil in 55% yield (79.4 mg; 0.11 mmol) which was purified by silica gel chromatography (DCM: MeOH= 100:1~20:1, R_f = 0.5(DCM: MeOH = 20:1)).

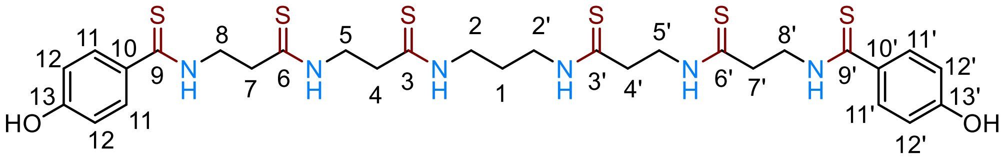
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.74 (s, 1H), 8.43 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.16 – 4.09 (m, 2H), 4.07 – 3.99 (m, 2H), 3.84 (s, 3H), 3.57 (d, *J* = 5.4 Hz, 2H), 3.14 – 3.03 (m, 2H), 2.99 – 2.89 (m, 2H), 1.81 (dd, *J* = 16.1, 9.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 202.0, 196.8, 162.6, 133.2, 129.0, 113.9, 55.7, 45.1, 44.4, 43.3, 42.7, 26.5.

HRMS (ESI): calculated for $C_{31}H_{43}N_6O_2S_6$ $[M+H]^+$ 723.1766; found: 723.1768.

FT-IR (neat): 3205, 2935, 1604, 1527, 1502, 1439, 1403, 1326, 1169, 1087, 917, 713 cm^{-1}.

***N,N'*-(3,7,13,17-tetrathioxo-4,8,12,16-tetraazanonadecane-1,19-diyl)bis(4-hydroxybenzothioamide) (Closthioamide)**



Closthioamide

Following reported BBr_3 demethylation of **16** with in DCM at -78 °C to 0 °C,[20] **Closthioamide** was isolated as a yellow oil in 62% yield (21.7 mg; 0.031 mmol) which was purified by silica gel chromatography (DCM: MeOH = 100:1~20:1, R_f = 0.5 (DCM: MeOH = 20:1)).

^{1}H NMR (400 MHz, CD_3OD) δ 9.73 (d, *J* = 30.2 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 4.11 (t, *J* = 6.8 Hz, 2H), 4.01 (t, *J* = 6.7 Hz, 2H), 3.62 (t, *J* = 6.9 Hz, 2H), 3.03 (t, *J* = 6.8 Hz, 2H), 2.93 (t, *J* = 6.7 Hz, 2H), 1.95 (p, *J* = 6.9 Hz, 1H).

^{13}C NMR (101 MHz, CD_3OD) δ 203.3, 202.9, 199.1, 161.8, 134.0, 130.3, 115.7, 46.5, 45.8, 44.1, 44.1, 43.8, 27.1.

HRMS (ESI): calculated for $C_{29}H_{39}N_6O_2S_6$ $[M+H]^+$ 695.1453; found: 695.1448.

FT-IR (neat): 3208, 2936, 1527, 1502, 1438, 1402, 1325, 1169, 1086, 916, 714 cm^{-1}.

	Isolated Closthioamide[21]		**Synthesized Closthioamide**	
Position	δ_H (*J*[Hz], m)	δ_C	δ_H (*J*[Hz], m)	δ_C

1	1.94 (6.9, p)	27.1	1.95 (6.9, p)	27.1
2,2’	3.62 (6.9, t)	44.1	3.62 (6.9, t)	44.1
3,3’	-	202.9	-	202.9
4,4’	2.93 (6.8, t)	43.8	2.93 (6.7, t)	43.8
5,5’	4.01 (6.8, t)	45.8	4.01 (6.7, t)	45.8
6,6’	-	203.3	-	203.3
7,7’	3.02 (6.8, t)	44.1	3.03 (6.8, t)	44.1
8,8’	4.11 (6.8, t)	46.5	4.11 (6.8, t)	46.5
9,9’	-	199.1	-	199.1
10,10’	-	133.9	-	134.0
11,11’	7.71 (8.9, d)	130.3	7.72 (8.7, d)	130.3
12,12’	6.75 (8.9, d)	115.7	6.76 (8.7, d)	115.7
13,13’	-	161.8	-	161.8

4. Mechanistic experiments

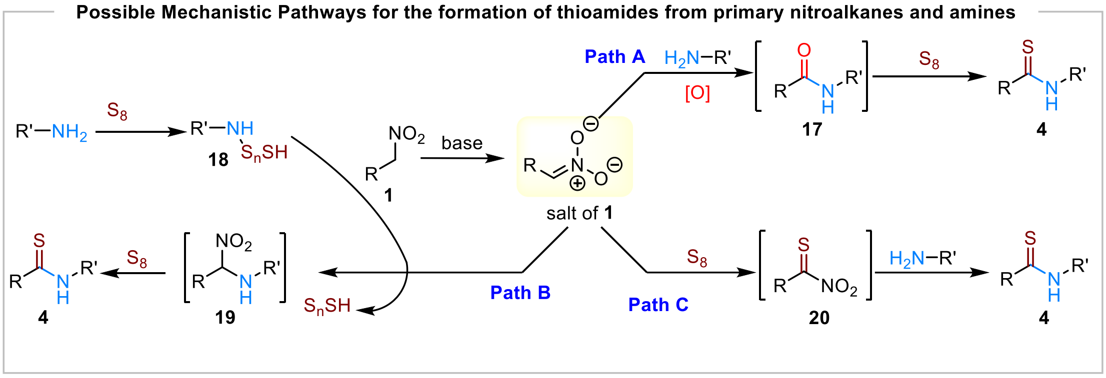
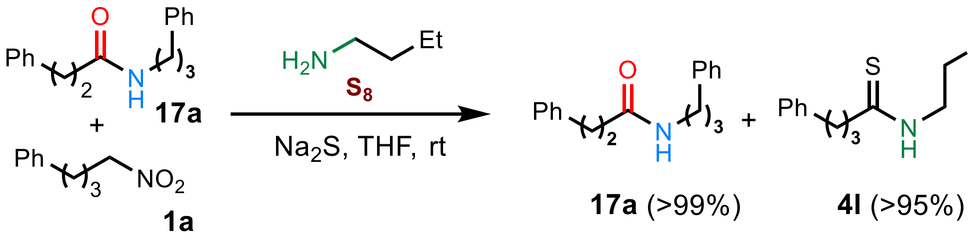


Figure S2 Three possible mechanistic pathways

4.1 Control reactions to interrogate path A.



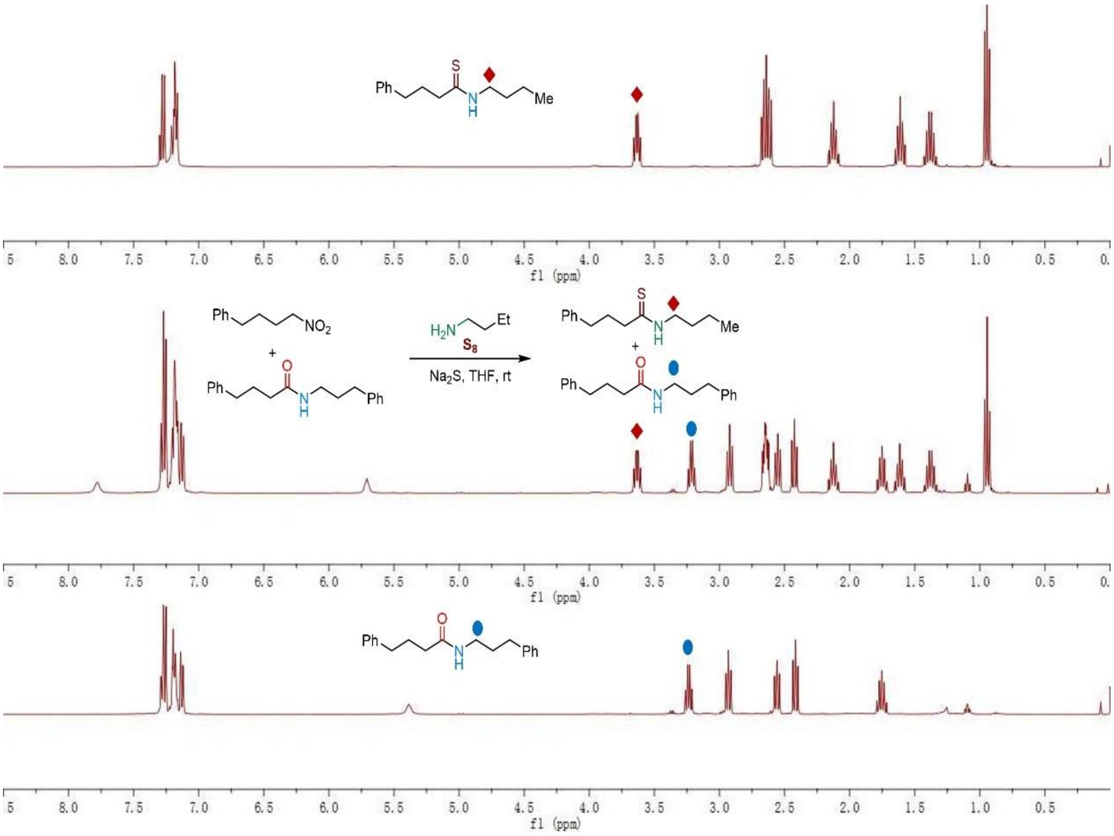
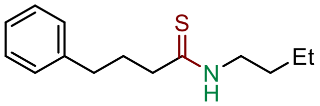


Figure S3 Comparision of the possibility of oxamide to thioamide.

We synthesize oxamide **17a** via reported procedure[22], then treated with our standard condition, however, all the oxamide was completely recovered and no thioamide was observed at all (Eq. 1 in main).

***N*-butyl-4-phenylbutanethioamide** (**4l**)



4l

Following procedure A: **4l** was isolated as a yellow oil in 98% yield (46.1 mg; 0.196 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 5:1)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 6.9 Hz, 2H), 7.22 – 7.15 (m, 3H), 3.71 – 3.57 (m, 2H), 2.64 (dt, *J* = 15.1, 7.7 Hz, 4H), 2.19 – 2.05 (m, 2H), 1.68 – 1.56 (m, 2H), 1.38 (h, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 141.4, 128.6, 128.5, 126.1, 46.4, 46.0, 34.9, 30.8, 30.2, 20.3, 13.9.

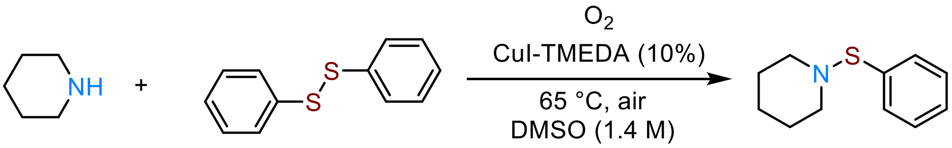
HRMS (ESI): calculated for $C_{14}H_{22}NS$ $[M+H]^+$ 236.1473; found: 236.1476.

FT-IR (neat): 3353, 2931, 2856, 1530, 1495, 1453, 1406, 1340, 1123, 1085, 1030, 909, 699 cm^{-1}.

Conclusion: Based on all control reaction in **Section 4.1**, thioamide formation via oxamide in *Figure S2* (**Path A**) was ruled out.

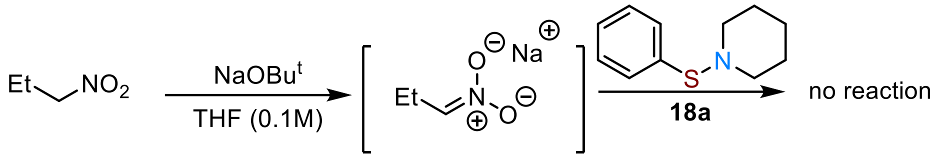
4.2 Control reactions to interrogate path B.

4.2.1 Synthesis 1-(phenylthio)piperidine (18a)



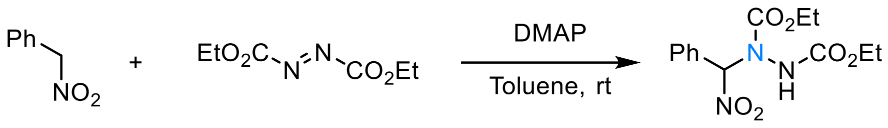
1.05 mmol 0.5 mmol **18a** (88%)

Sulfenamide **18a** was synthesize via reported procedure.[23]



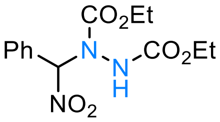
1b sodium salt of **1b**

4.2.2 Synthesis of Diethyl 1-(nitro(phenyl)methyl)hydrazine-1,2-dicarboxylate (19a)



19a (45%)

19a was prepared from (nitromethyl)benzene in one step according to a reported procedure,[24] which was isolated as a colorless oil in 45% yield (140.0 mg; 0.45 mmol) after purification by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.4 (PE:EA = 10:1)).



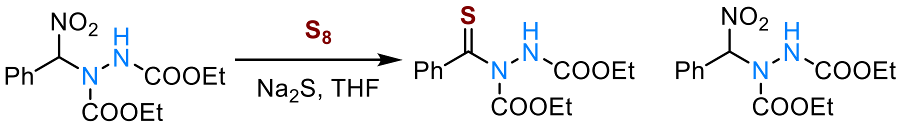
19a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.70 (s, 1H), 7.57 – 7.42 (m, 4H), 4.24 (q, *J* = 7.1 Hz, 4H), 4.01 (d, *J* = 7.1 Hz, 1H), 1.34 – 1.25 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 153.9, 130.7, 129.5, 128.3(2C), 63.2, 62.5, 14.6, 14.5, 13.9.

HRMS (ESI): calculated for $C_{13}H_{21}N_4O_6$ $[M+NH_4]^+$ 318.1272; found: 318.1273.

FT-IR (neat): 3371, 2986, 1732, 1503, 1375, 1323, 1218, 1096, 1056, 1031, 702 cm^{-1}.



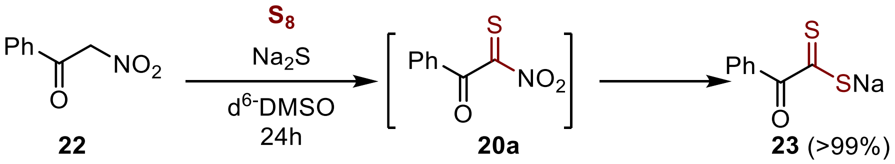
19a **21** (not observed) **19a** (>97%)

19a was treated with S_8 in our standard condition, we try to see it is any possible to generate thioamide, but only starting materials was generated.

Conclusion: Based on all control reaction in **Section 4.2**, thioamide formation via α-amino nitroalkane in *Figure S2* (**Path b**) was ruled out.

4.3 Control reactions to trap proposed **thioacyl intermediate 20** (Pathc).

4.3.1 NMR and HRMS studies of **nitroalkane 22** was mixed with Na_2S and S_8 in **d^6-DMSO**



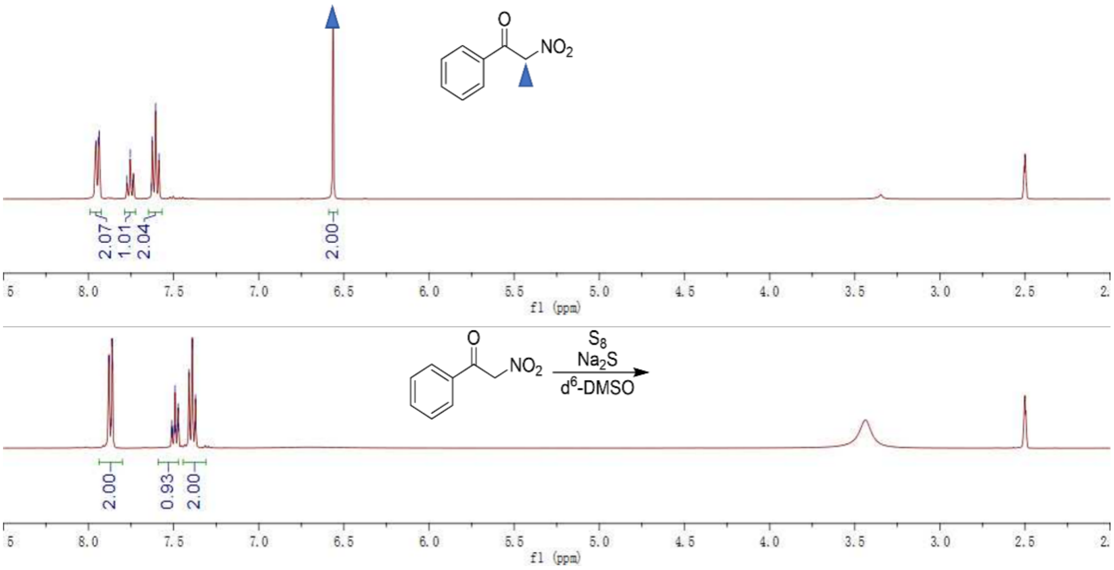


Figure. S4 **In situ NMR studies of nitroalkane reacts with S_8 and Na_2S**

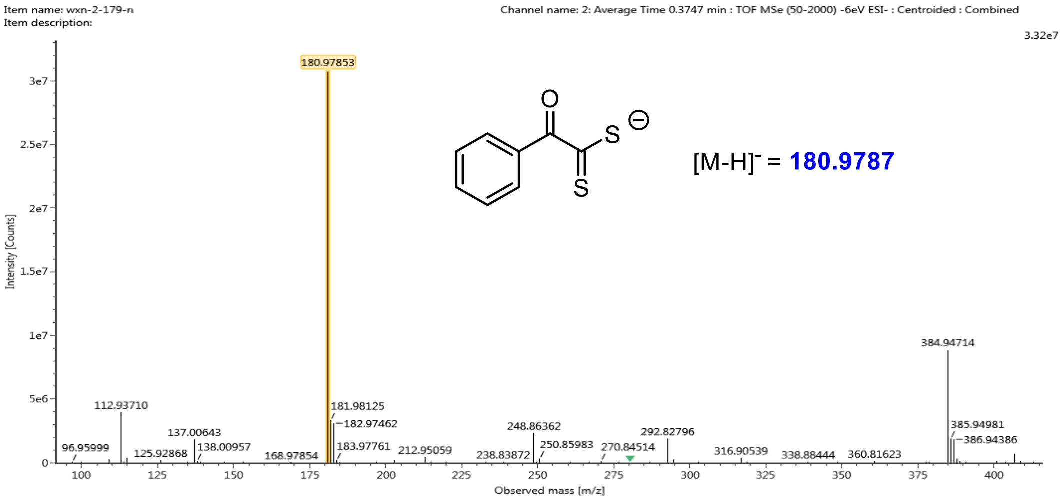
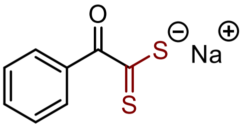


Figure S4 **In-situ HRMS study by negative ion mode**

Character of **Sodium 2-oxo-2-phenylethanedithioate** (23)



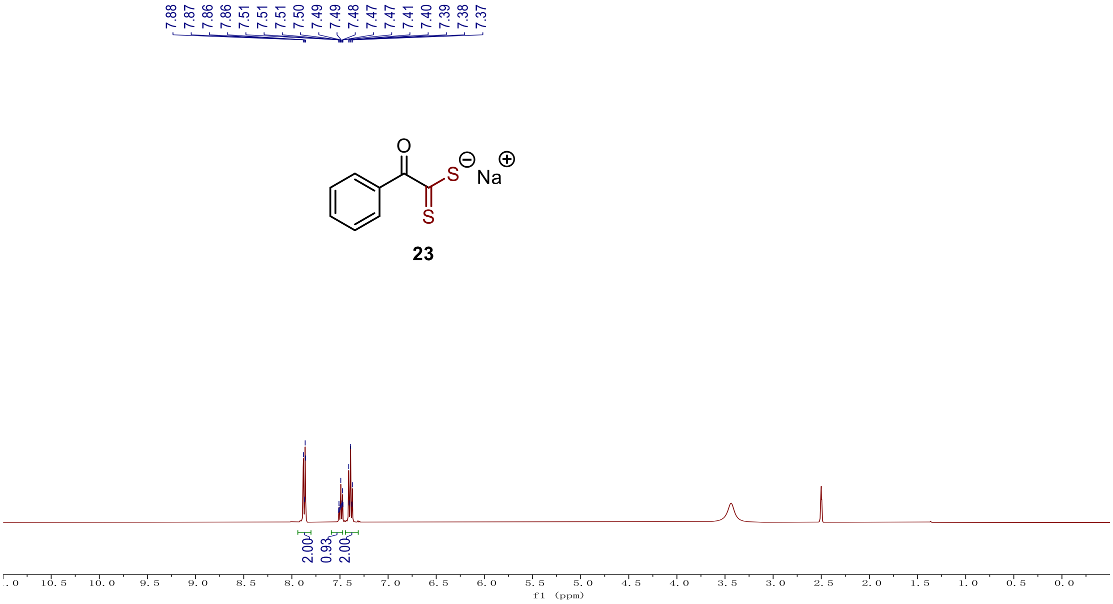
23

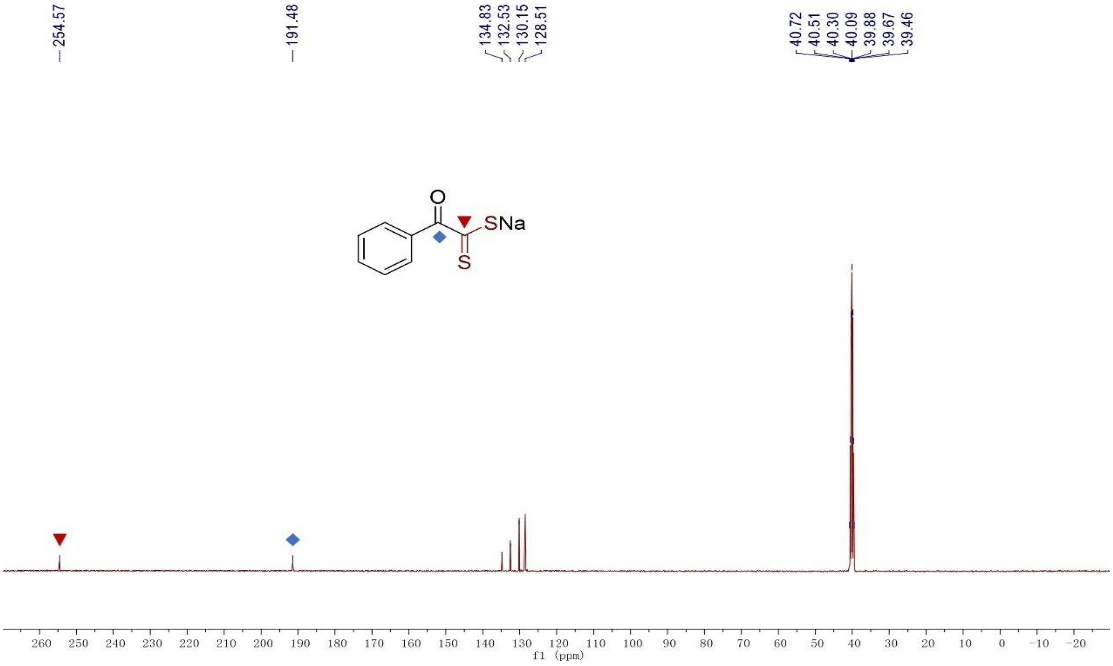
The yield determined by ^{1}H NMR, >99%.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.94 – 7.80 (m, 2H), 7.59 – 7.47 (m, 1H), 7.44 – 7.31 (m, 2H).

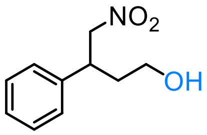
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 254.6, 191.5, 134.8, 132.5, 130.2, 128.5.

HRMS (ESI): calculated for $C_8H_4OS_2Na$ [M-H]$^-$ 180.9785; found: 180.9787.





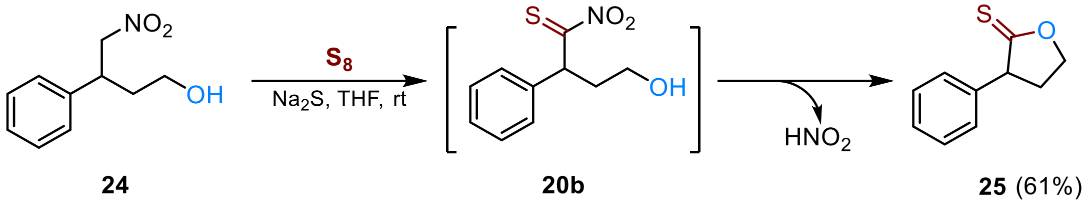
4.3.2 Intramolecular trapping thioacyl nitrate with alcohol nucleophiles



24

The **4-Nitro-3-phenylbutan-1-ol** (**24**) was prepared in 83% yield (5 mmol) from 3-Phenylpropanal in two steps according to a reported procedure.[25]

a. Intramolecular experiment to trap acyl nitrate with alcohol:



b. Intermolecular and intramolecular competing experiment to trap acyl nitrate with alcohol:

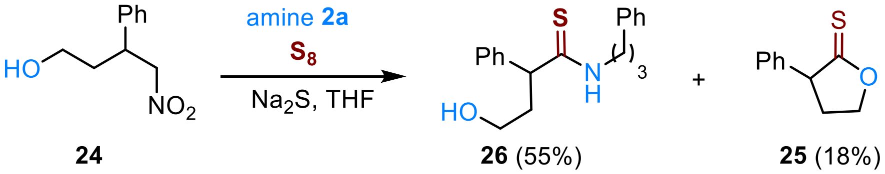
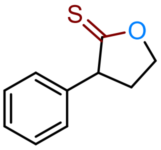


Figure. S5 **Control reaction**

3-Phenyldihydrofuran-2(3H)-thione (25)



25

Following procedure A: **25** was isolated as a yellow oil in 61% yield (21.7 mg; 0.122 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 7:1)).

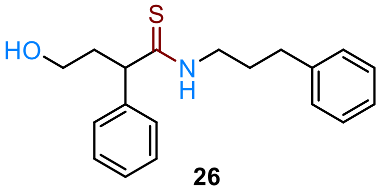
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 4.82 (ddd, *J* = 9.2, 8.2, 4.1 Hz, 1H), 4.68 (td, *J* = 9.1, 6.9 Hz, 1H), 4.14 (t, J = 9.0 Hz, 1H), 2.78 (dddd, *J* = 12.7, 8.5, 6.8, 4.0 Hz, 1H), 2.45 (dq, *J* = 12.8, 8.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 223.8, 139.3, 129.0, 128.4, 127.8, 75.0, 60.2, 33.5.

HRMS (ESI): calculated for $C_{10}H_{10}OSNa$ $[M+Na]^+$ 201.0345; found: 201.0341.

FT-IR (neat): 2963, 1494, 1473, 1454, 1370, 1149, 699 cm^{-1}.

4-Hydroxy-2-phenyl-N-(3-phenylpropyl)butanethioamide (26)



26

Following procedure A: **26** was isolated as a yellow oil in 55% yield (17.2 mg; 0.055 mmol) which was purified by silica gel chromatography (PE:EA = 20:1~2:1, R_f = 0.5 (PE:EA = 1:1)).

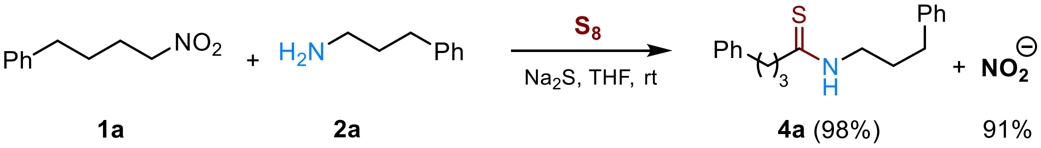
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 6H), 7.25 – 7.16 (m, 3H), 7.07 (d, *J* = 7.1 Hz, 2H), 4.07 (t, *J* = 7.6 Hz, 1H), 3.70 (ddd, *J* = 12.1, 7.1, 5.2 Hz, 1H), 3.66 – 3.57 (m, 3H), 2.58 – 2.51 (m, 3H), 2.15 (dtd, *J* = 14.0, 7.0, 5.1 Hz, 1H), 1.99 – 1.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 141.0, 139.8, 129.2, 128.7, 128.4, 128.1, 127.9, 126.3, 60.5, 57.0, 45.7, 37.8, 33.3, 29.4.

HRMS (ESI): calculated for $C_{19}H_{24}NOS$ $[M+H]^+$ 314.1573; found: 314.1573.

FT-IR (neat): 3343, 3240, 2930, 2880, 1550, 1533, 1495, 1453, 1378, 1132, 1051, 1029, 913, 699 cm^{-1}.

c. Ion chromatography experiment to detect the formation of NO_2^-



The nitro compound **1a** (0.2 mmol) and Na_2S (2 equiv.) were added to a 10 mL reaction tube, followed by THF (2 mL). After stirring for 10 minutes, S_8 (2.0 equiv.) was added. Next, the reaction was stirred at rt for another 10 minutes and the amine **2a** (2.0 equiv.) was added. The reaction was monitored by TLC until the nitroalkane was consumed. The mixture was then concentrated under reduced pressure and distilled water (5 mL) was added to the crude residue. Ultrasonication at 45 °C for one hour and centrifugation for 10 minutes then gave a clear liquid. This set of operations was repeated four times to give four water samples, which were combined, filtered and analyzed by ion chromatography in triplicate. In this way, the amount of $\mathbf{NO_2^-}$ via ion chromatographic analysis was performed 3 times to give an average concentration.

Theoretical concentration:

$\mathbf{NO_2^-}$ = 0.0133 mmol/mL = 13.3 mmol/L

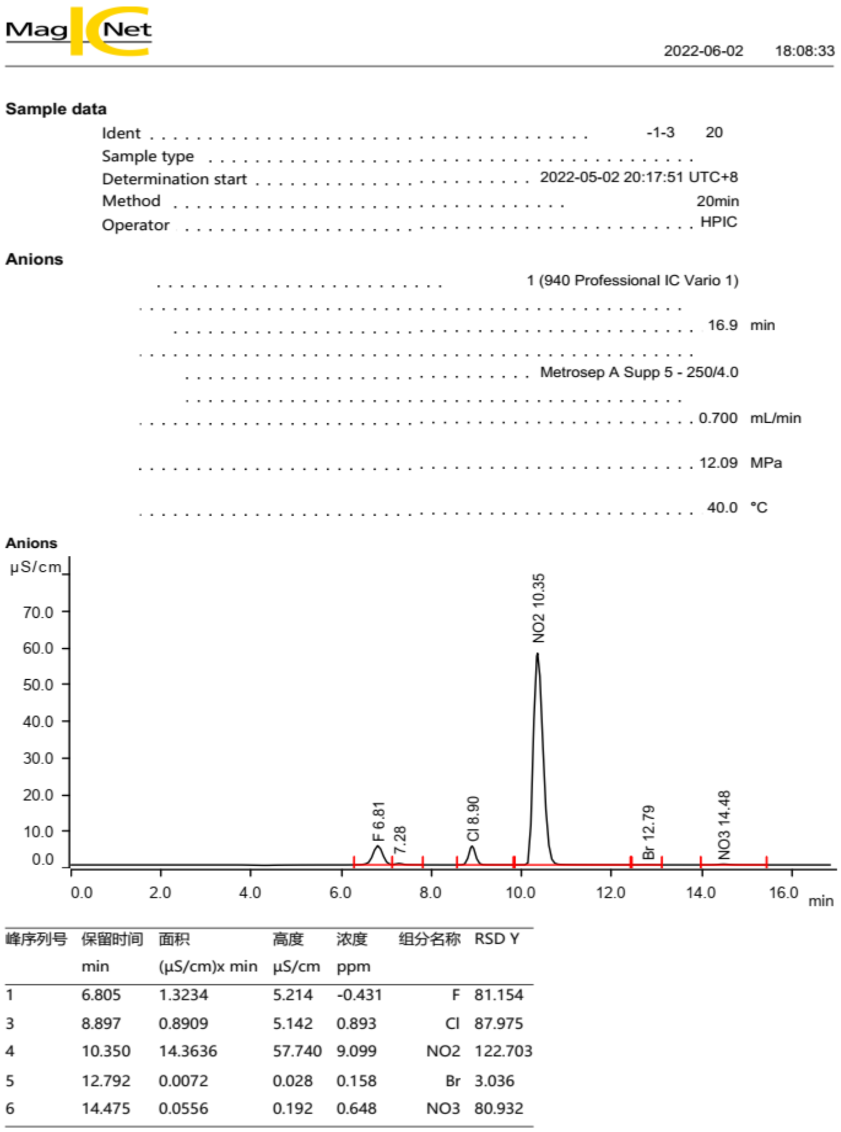
Analysis results:

$\mathbf{NO_2^-}$ = (9.473 × 20 × 2.94÷ 46) mmol/L = 12.1 mmol/L

Average value	9.473
SD	0.216ppm
RSD	2.277%

Test conditions:

Test column	MetrosepA Supp 5 (250 mmH×4.0 mm IC)
Guard column type	Metrosep A Supp 5 Guard/ 4.0
Sample volume	200ul
Eluent	3.2 mmol/L Na_2CO_3 - 1.0 mmol/L $NaHCO_3$
Temperature	40 °C
Flow	0.700 mL/min
Suppressor	MSM-HC (Metrohm, regeneration fluid: 0.5% H_2SO_4)
Suppressor	MCS (Metrohm)
Detector	Conductivity detector (Metrohm)
Software	MagIC Net^{TM}



2022-06-02 18:08:33

Sample data

Ident -1-3 20
Sample type
Determination start 2022-05-02 20:17:51 UTC+8
Method 20min
Operator HPIC

Anions

1 (940 Professional IC Vario 1)

16.9 min

Metrosep A Supp 5 - 250/4.0

0.700 mL/min

12.09 MPa

40.0 °C

Anions

峰序列号	保留时间 min	面积 (µS/cm)x min	高度 µS/cm	浓度 ppm	组分名称	RSD Y
1	6.805	1.3234	5.214	-0.431	F	81.154
3	8.897	0.8909	5.142	0.893	Cl	87.975
4	10.350	14.3636	57.740	9.099	NO2	122.703
5	12.792	0.0072	0.028	0.158	Br	3.036
6	14.475	0.0556	0.192	0.648	NO3	80.932

Figure S6 **Ion chromatographic analysis**

Conclusion: Based on all control reaction in **Section 4.3**, thioamide formation via thioacyl nitrate as a key intermediate in *Figure S2* (**Path B**).

4.4 Control reaction to determine how thioacyl nitrate can form.

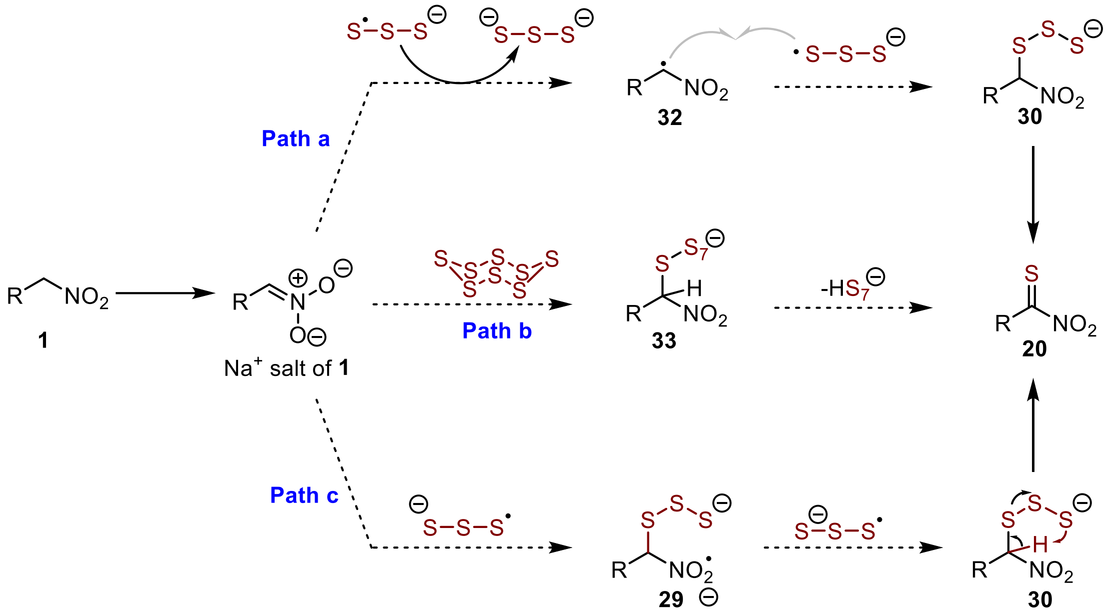


Figure S7 Three possible mechanistic pathways to thioamide bond formation

Based on relevant literature and results herein, there are three possible mechanistic pathways to form thioamides from nitroalkanes. These are proposed in ***Figure S7***. Below, we present evidence to distinguish the reasonable mechanistic pathway.

4.4.1 Control reactions to rule out **Path a** and **Path b**

We designed a nitroalkanes bearing a *cis*-cycopropane; if a radical intermediate like **32** is formed, we would observe the *trans*-thioamide ***trans*-28** via radical ring opening and closing. Indeed, we only observed and isolated thioamide ***cis*-28**.

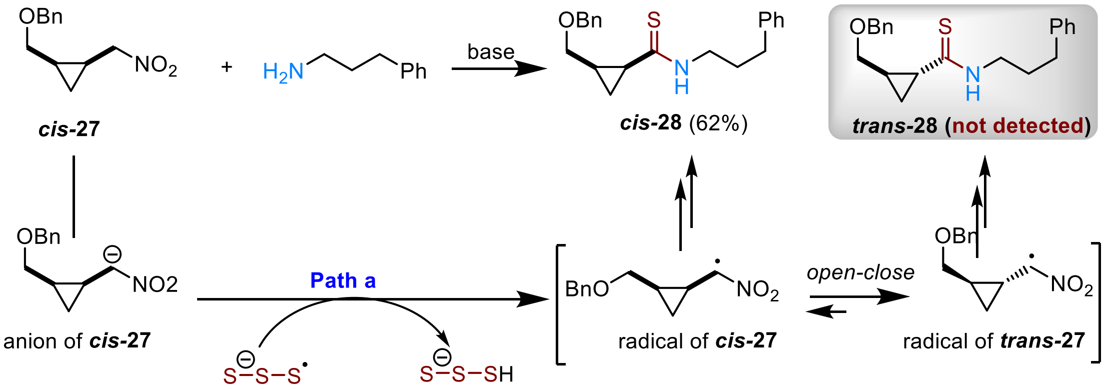


Figure S8 Radical clock reaction

Conclusion: Based on this reaction, **Path a** in Figure. **27** was ruled out.

4.4.2 Control reaction to distinguish Path b and Path c

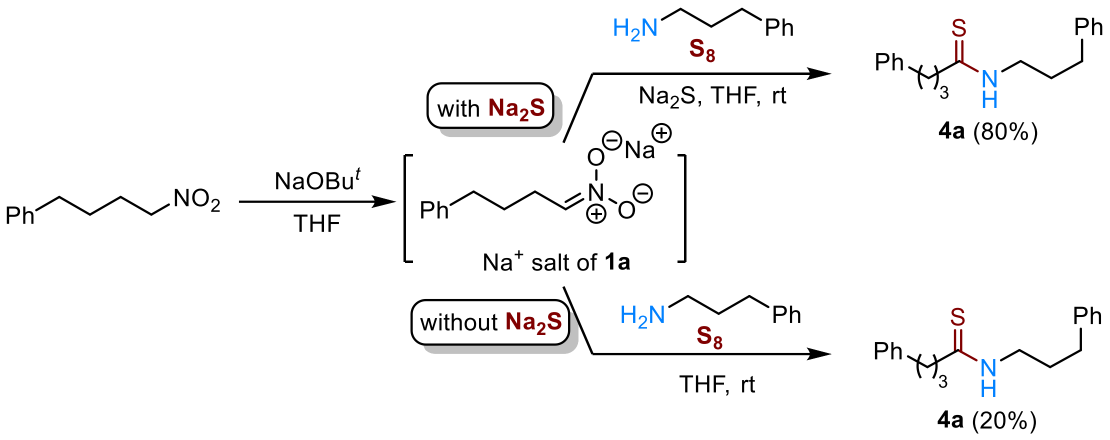


Figure S9 Na^+ salt of **1a** reacts with S_8 and S_3 radical anion

Conclusion: Based on above reaction and ref. 36, 37 of paper, Path b was ruled out.

((((*1R,2S*)-2-(Nitromethyl)cyclopropyl)methoxy)methyl)benzene (*cis*-27)

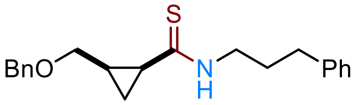
***cis*-27**

The nitro compound was prepared in 43% yield (2 mmol) through two steps according to a reported procedure.[26]

^{1}H NMR (101 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 4.57 – 4.41 (m, 3H), 4.26 (dd, *J* = 13.8, 8.2 Hz, 1H), 3.74 (dd, *J* = 10.5, 5.4 Hz, 1H), 3.29 (dd, *J* = 10.5, 8.3 Hz, 1H), 1.62 (pd, *J* = 8.3, 5.6 Hz, 1H), 1.46 (qt, *J* = 8.5, 5.7 Hz, 1H), 0.99 (td, *J* = 8.4, 5.4 Hz, 1H), 0.50 (q, *J* = 5.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 128.6(2C), 127.9, 76.1, 73.1, 69.2, 16.2, 13.3, 8.9.

(*1S,2R*)-2-((Benzyloxy)methyl)-*N*-(3-phenylpropyl)cyclopropane-1-carbothioamide (28)



***cis*-28**

Following procedure B: In crude ^{1}H NMR, we only observed one isomer, which was isolated as a yellow oil in 62% yield (42.1 mg; 0.124 mmol) by silica gel chromatography (PE:EA = 20:1~5:1, R_f = 0.5 (PE:EA = 7:1)), and further conformed by 2D NMR as *cis*-isomer **28**.

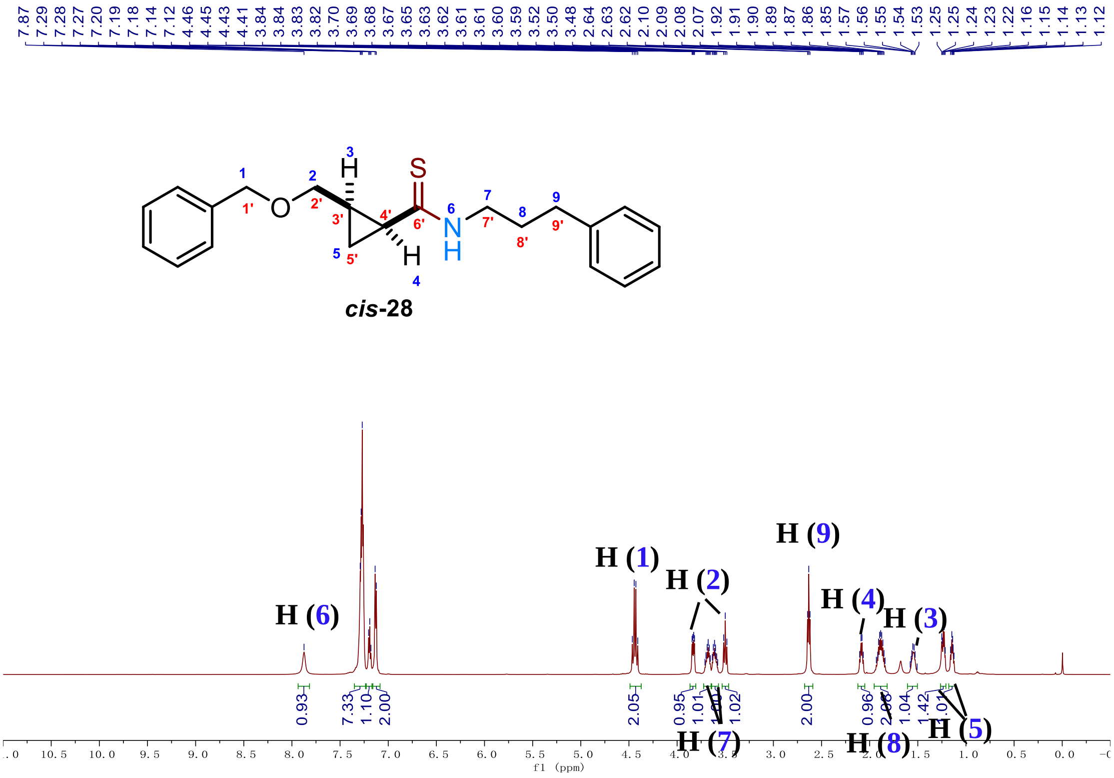
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.37 – 7.26 (m, 7H), 7.24 – 7.17 (m, 1H), 7.16 – 7.11 (m, 2H), 4.49 – 4.40 (m, 2H), 3.84 (dd, *J* = 10.3, 5.0 Hz, 1H), 3.74 – 3.56 (m, 2H), 3.54 – 3.47 (m, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.09 (td, *J* = 8.5, 6.0 Hz, 1H), 1.90 (tt, *J* = 14.7, 7.1 Hz, 2H), 1.55 (qdd, *J* = 8.8, 6.6, 5.0 Hz, 1H), 1.23 (dd, *J* = 11.8, 5.9 Hz, 2H), 1.15 (td, *J* = 8.5, 5.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 141.2, 138.0, 128.6, 128.6, 128.4, 127.9, 126.2, 73.2, 69.2, 46.0, 33.4, 30.0, 29.5, 21.1, 12.1.

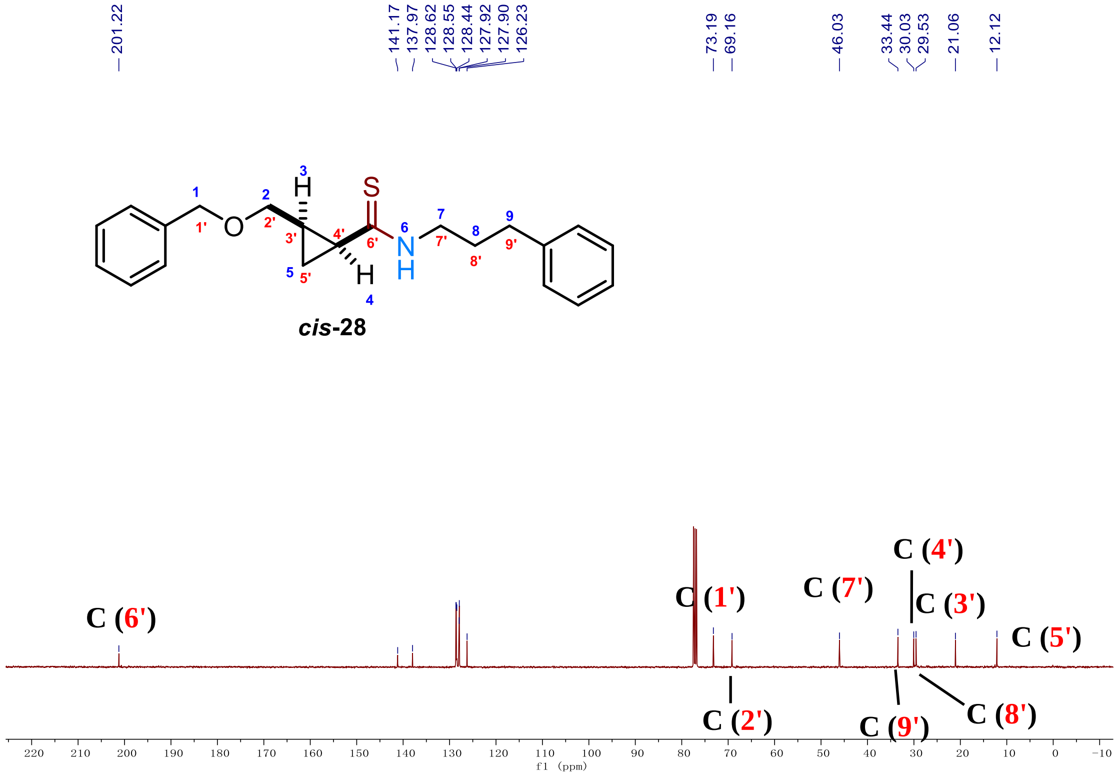
HRMS (ESI): calculated for $C_{21}H_{26}NOS$ $[M+H]^+$ 340.1730; found: 340.1731.

FT-IR (neat): 3265, 2928, 2855, 1602, 1541, 1496, 1452, 1404, 1329, 1163, 1108, 1071, 912, 699 cm^{-1}.

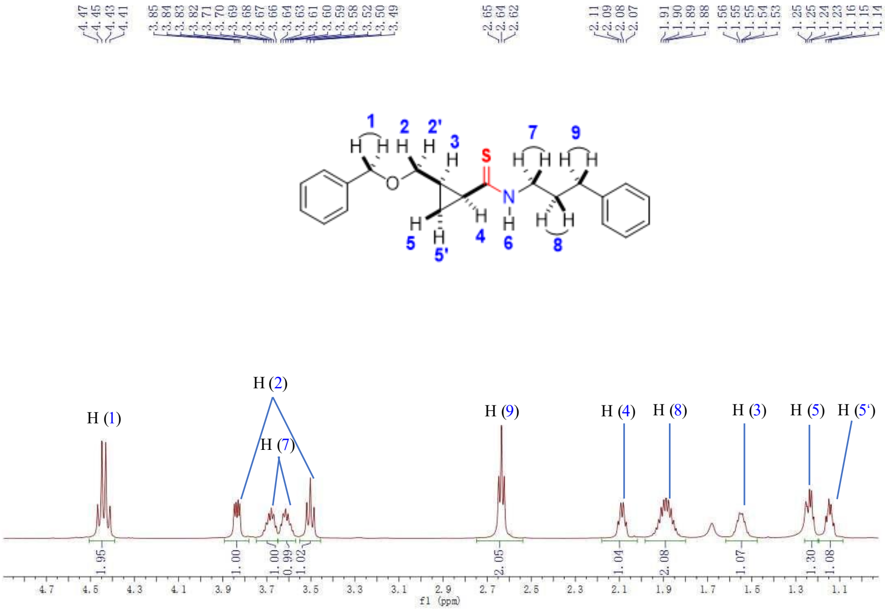
2D NMR spectra was used to confirm the structure of **28** was *cis* isomer.



^{1}H NMR (400 MHz, Chloroform-*d*) (**28**):



^{13}**C NMR** (101 MHz, Chloroform-*d*) (**28**):



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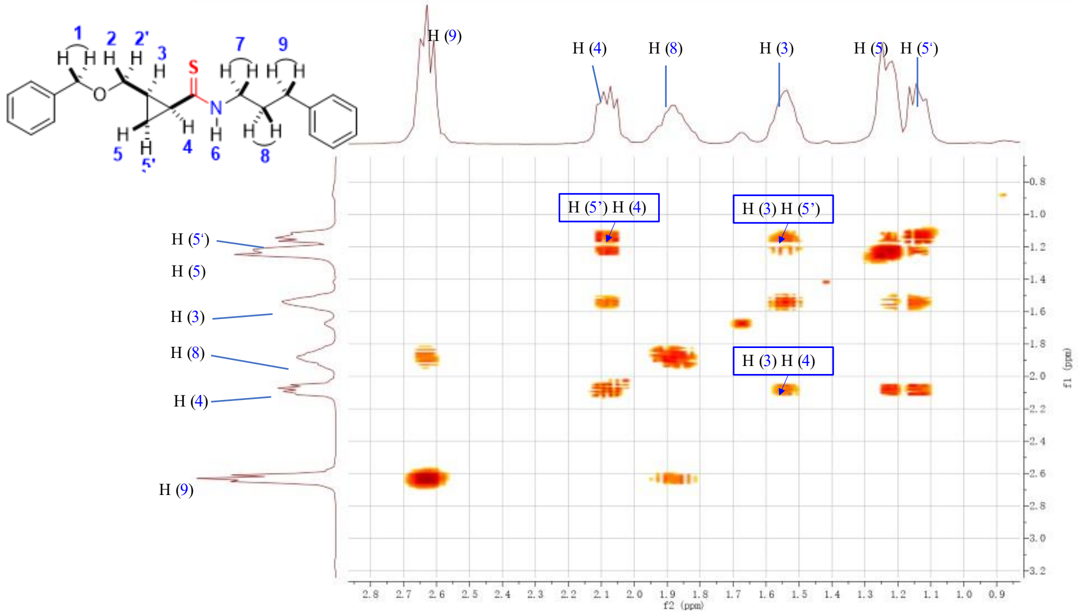
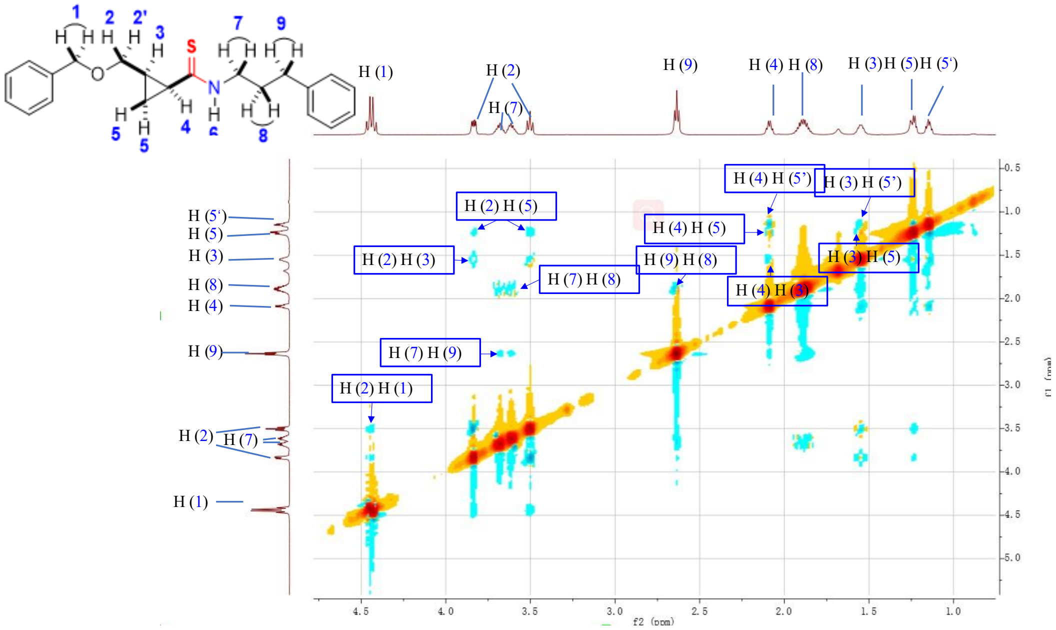
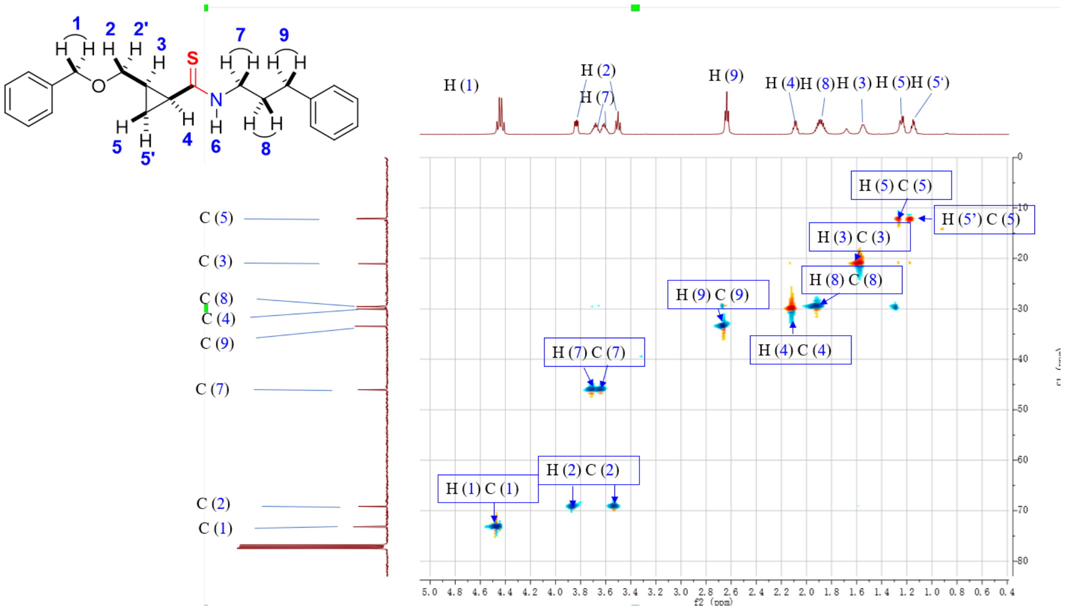


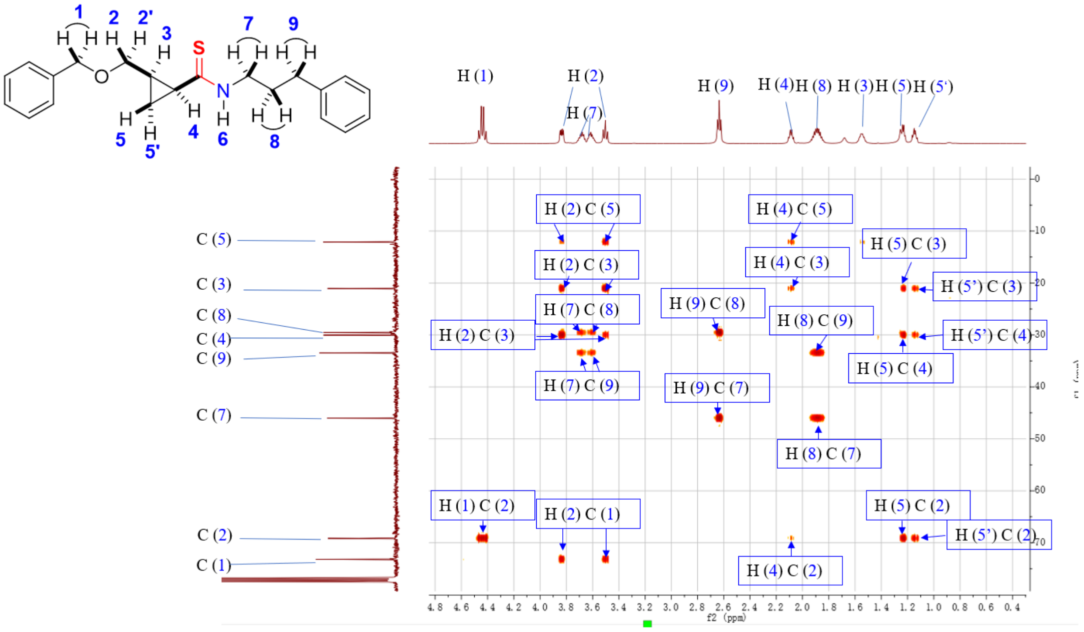
2D COSY spectrum of **28**:



2D HSQC spectrum of **28:**



2D HMBC spectrum of **28:**



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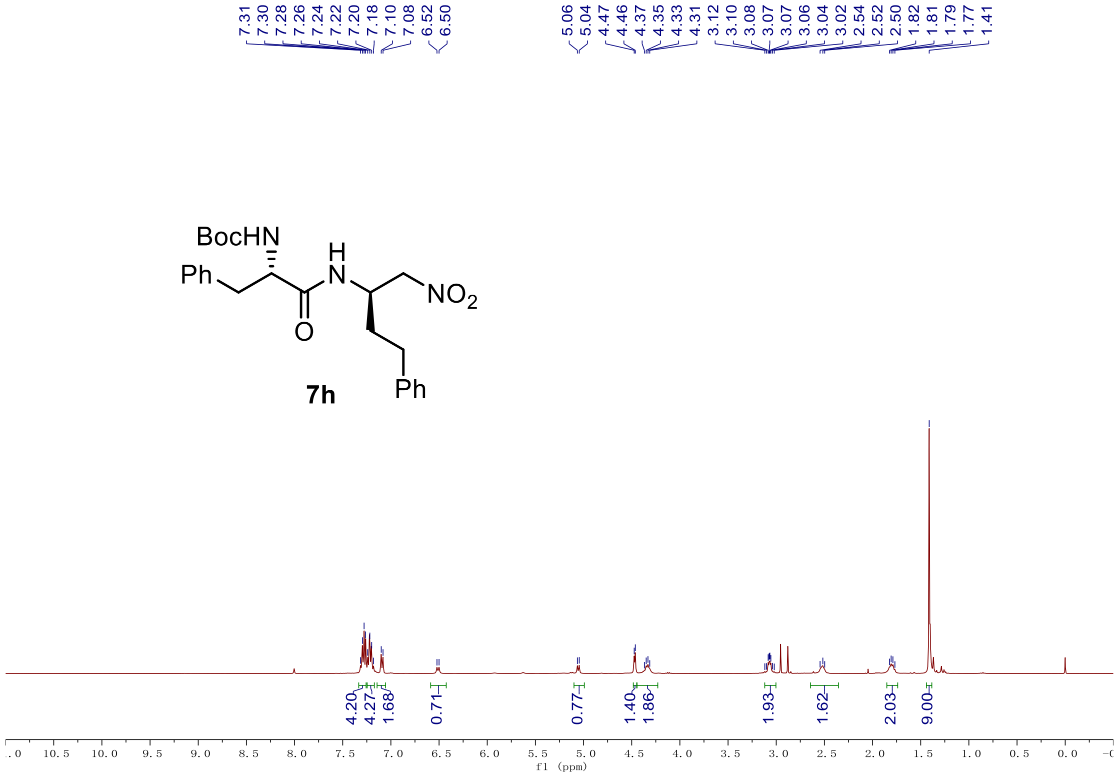
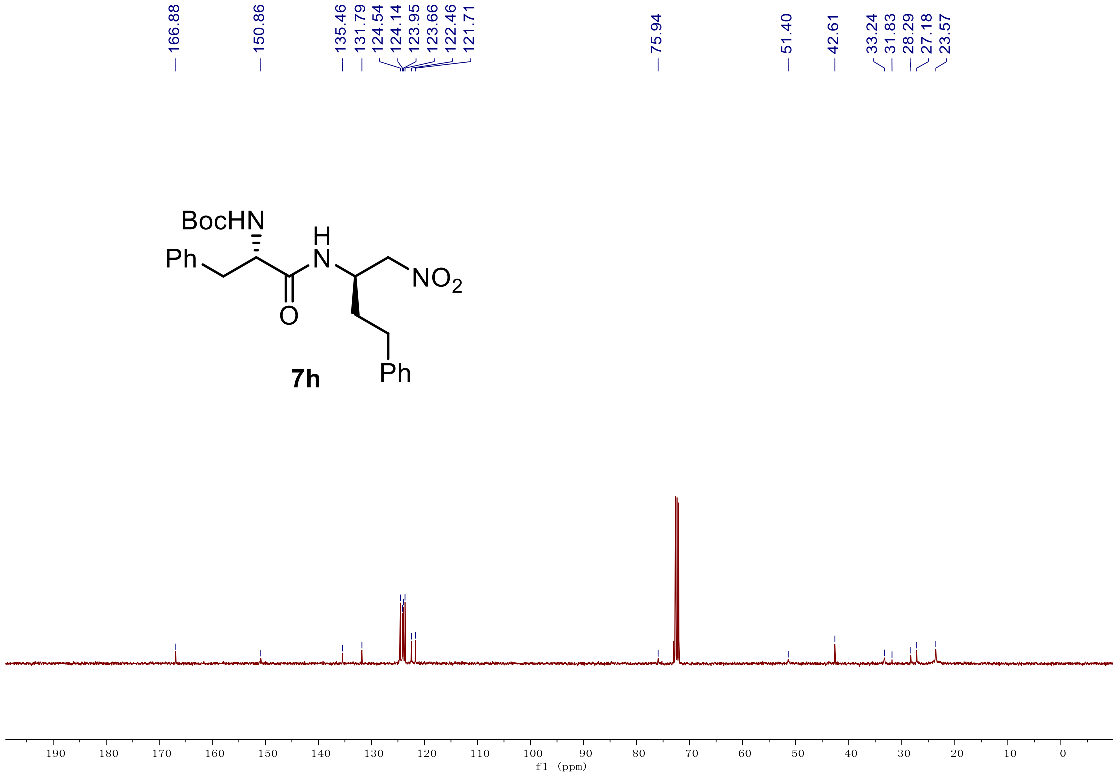
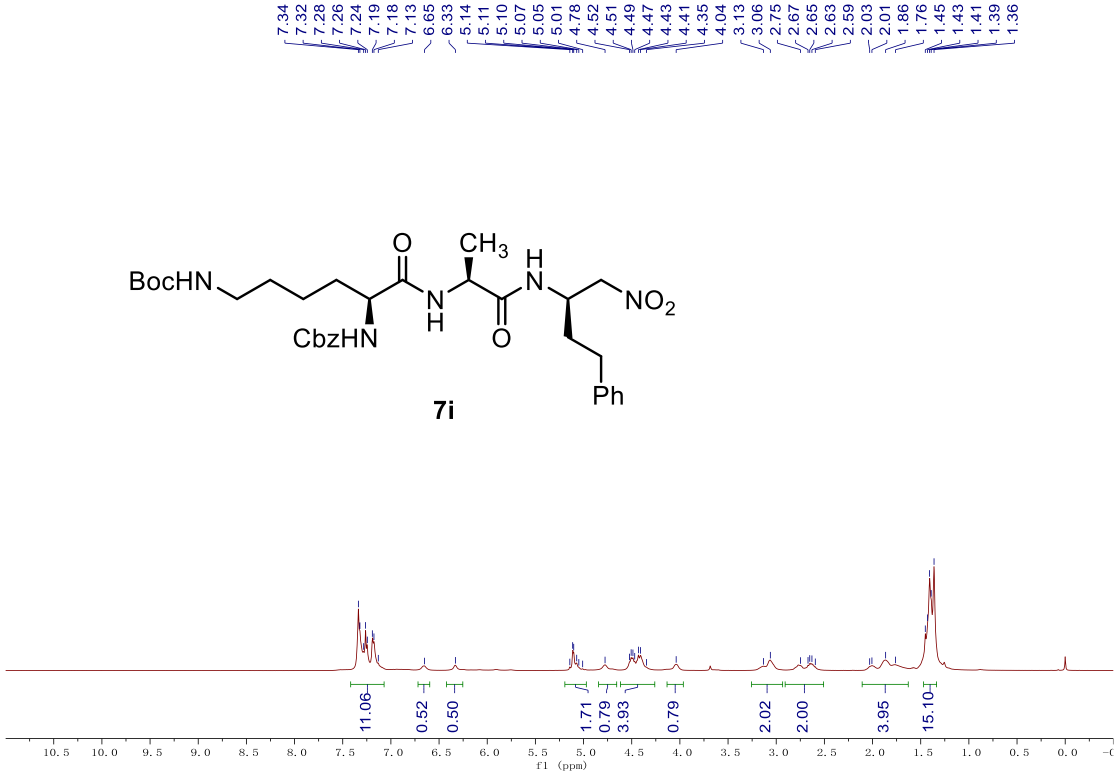
6. NMR spectra



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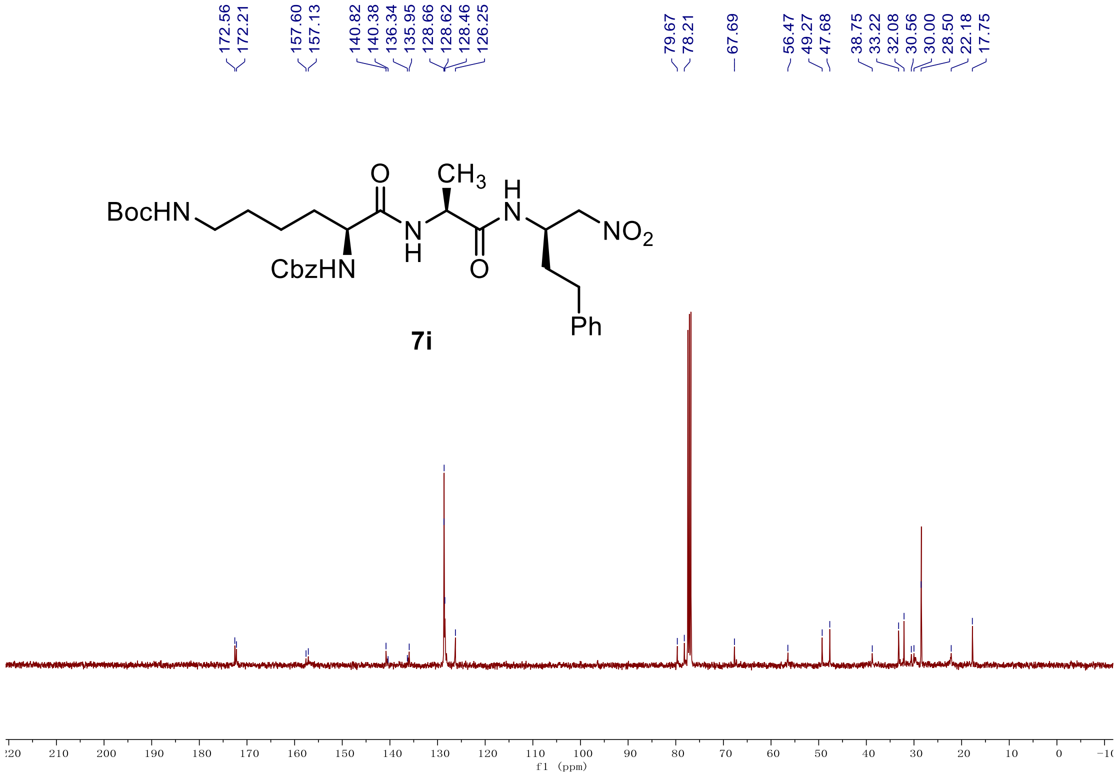
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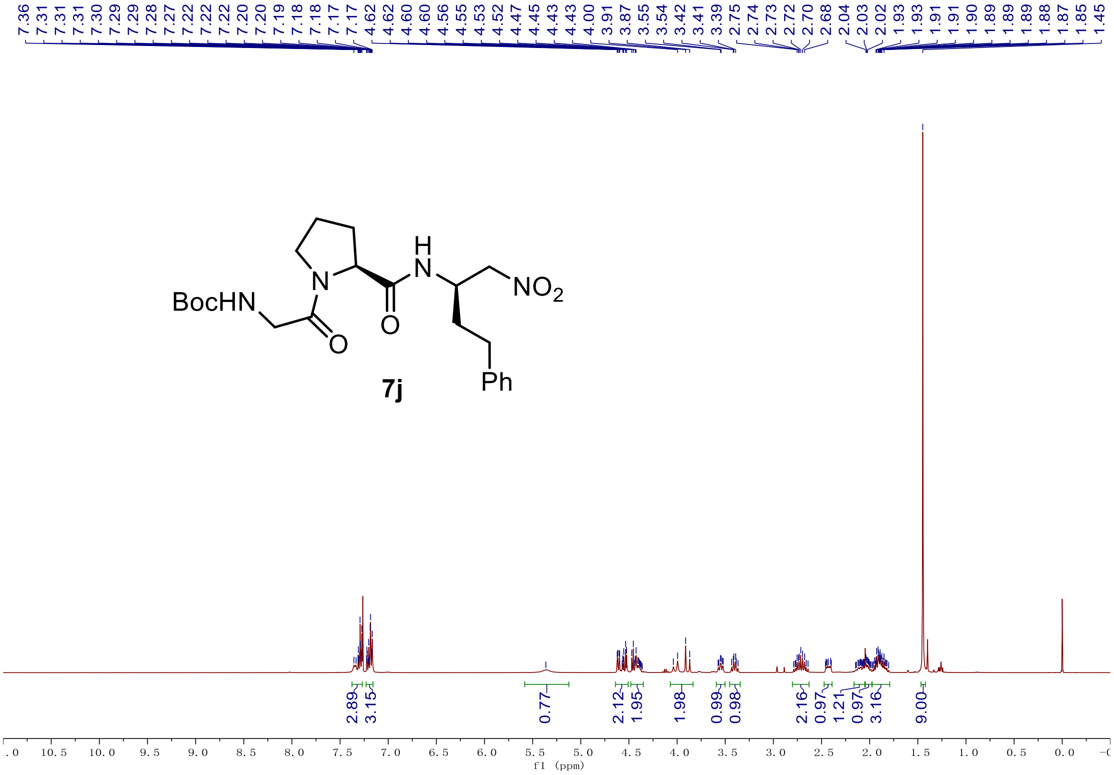
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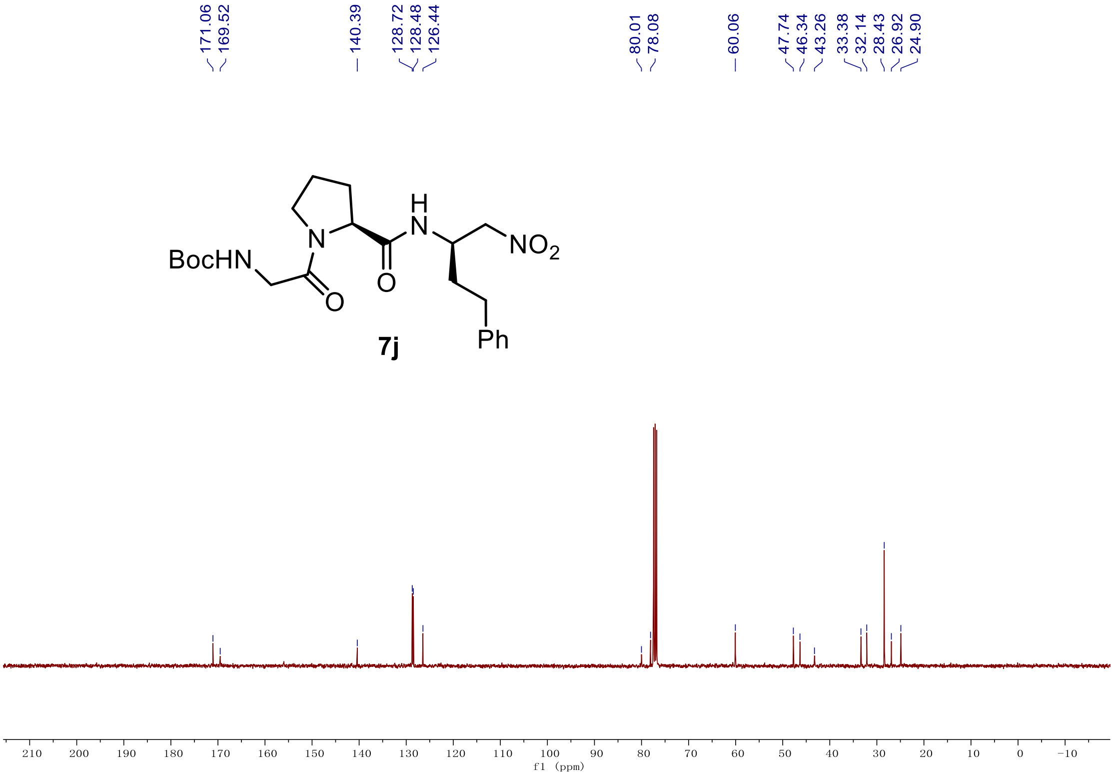
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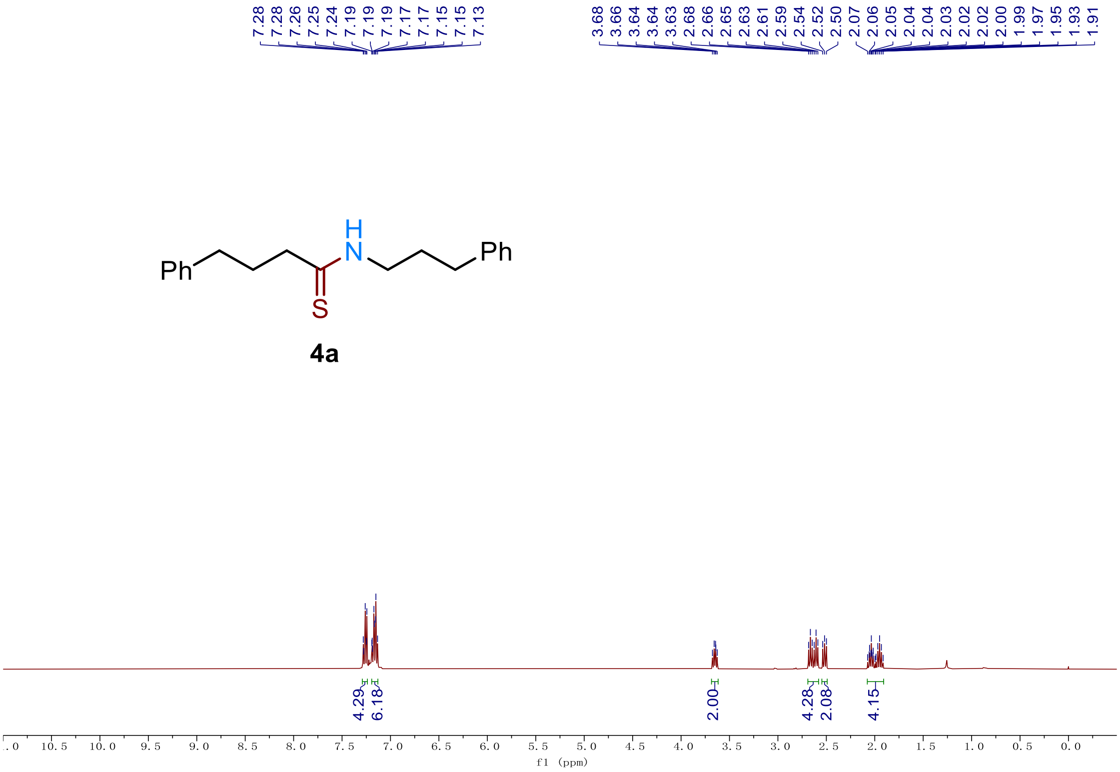
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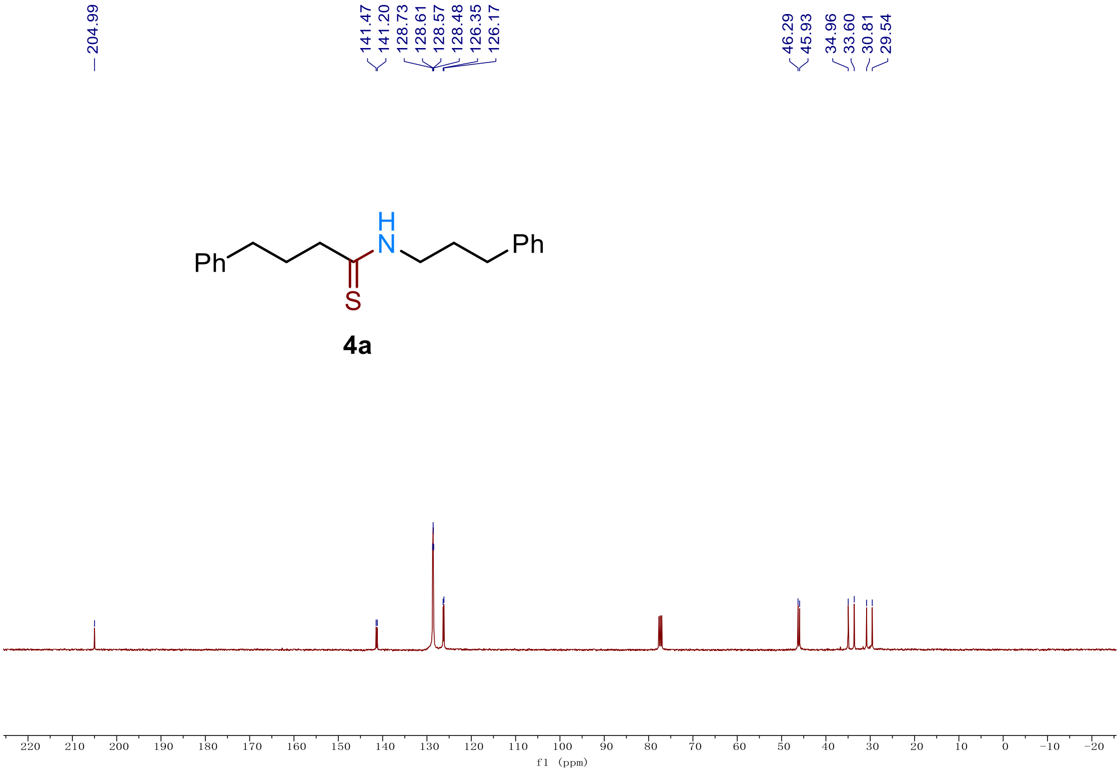
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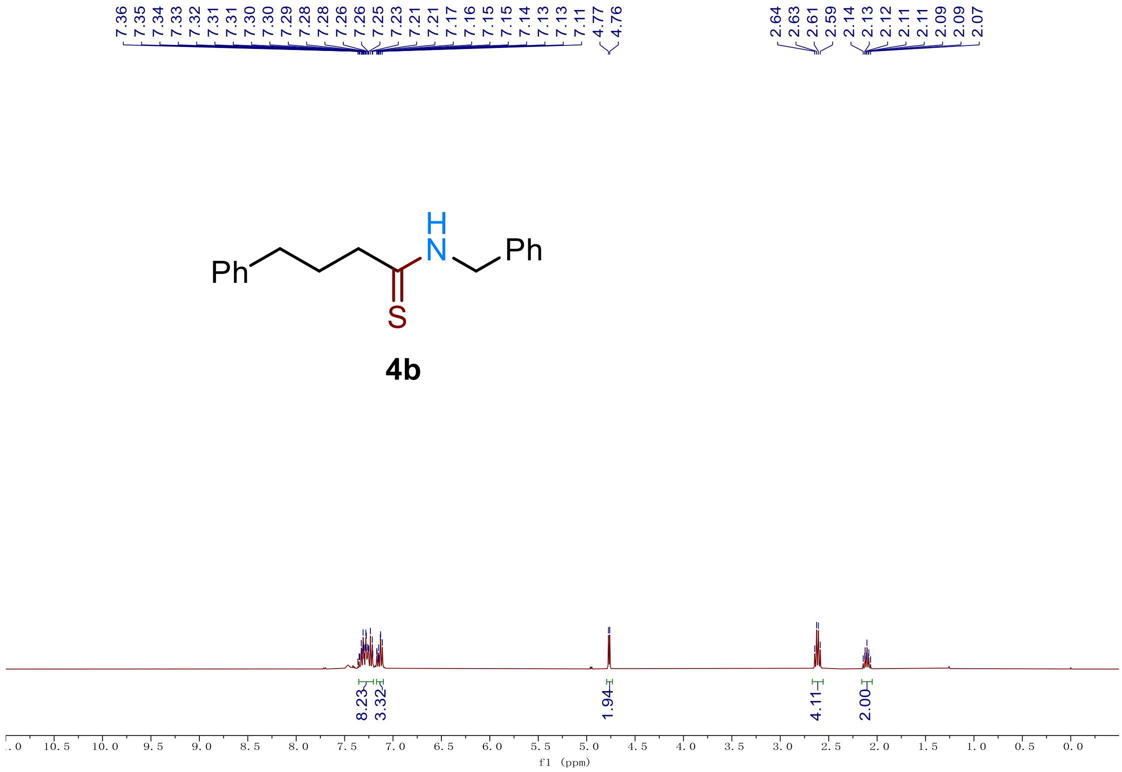
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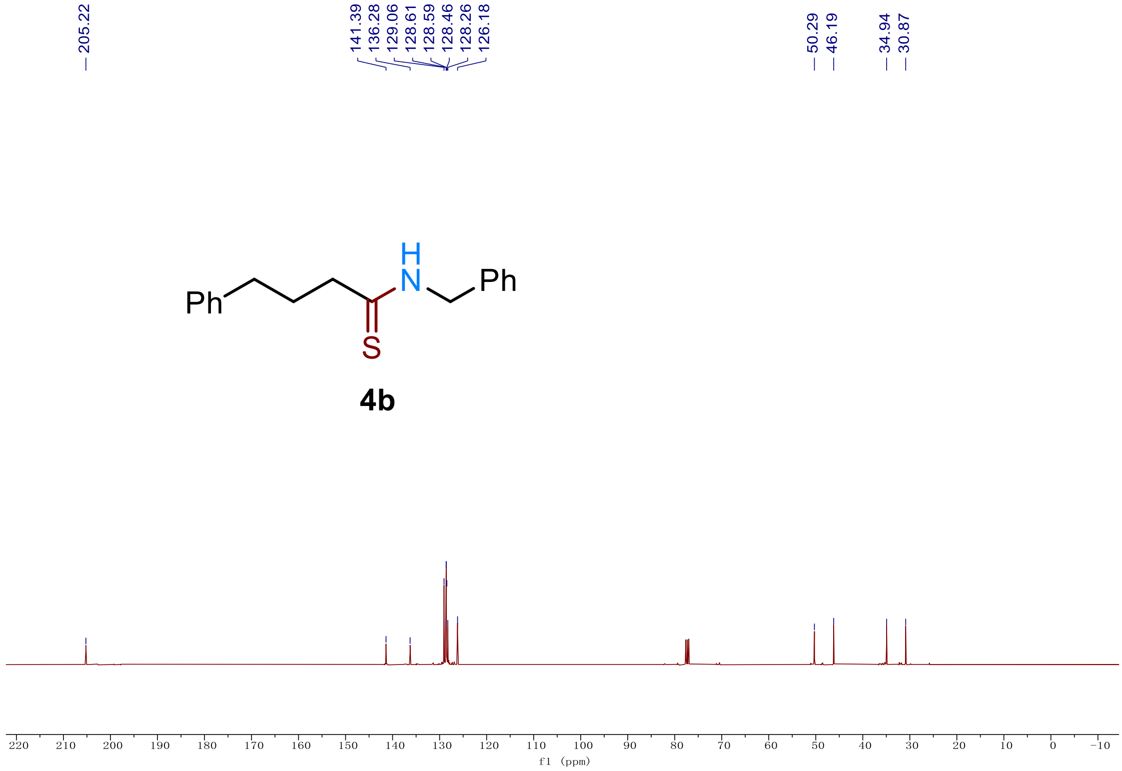
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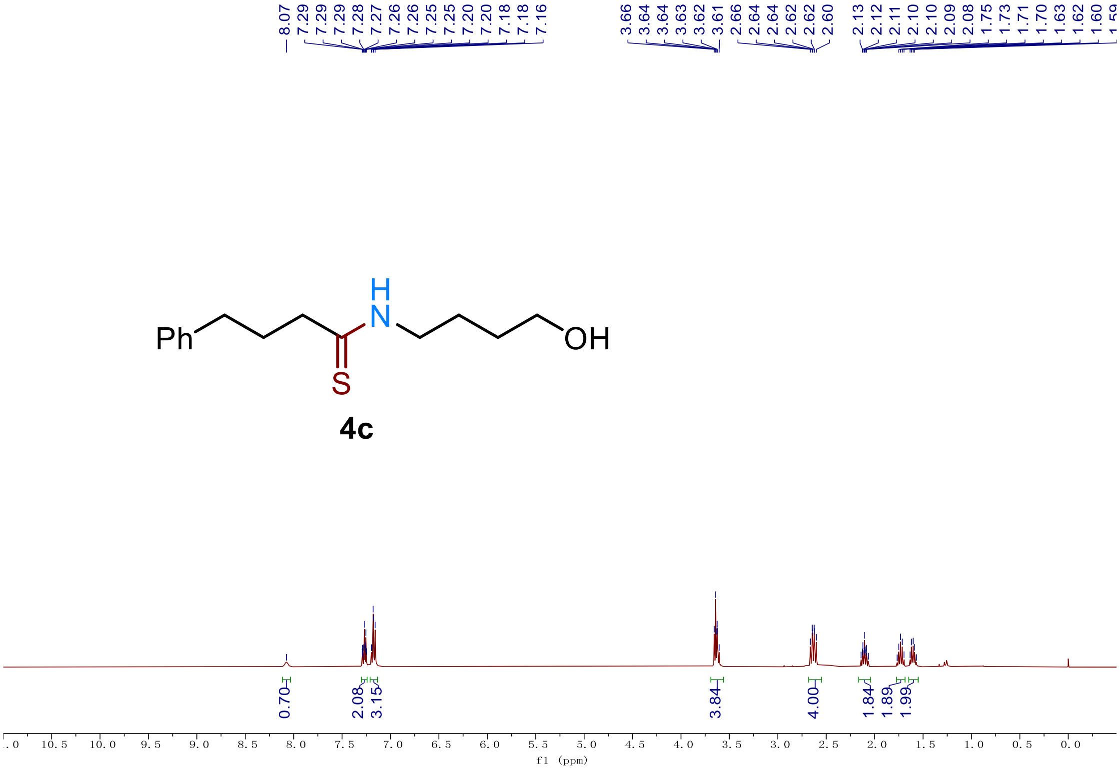
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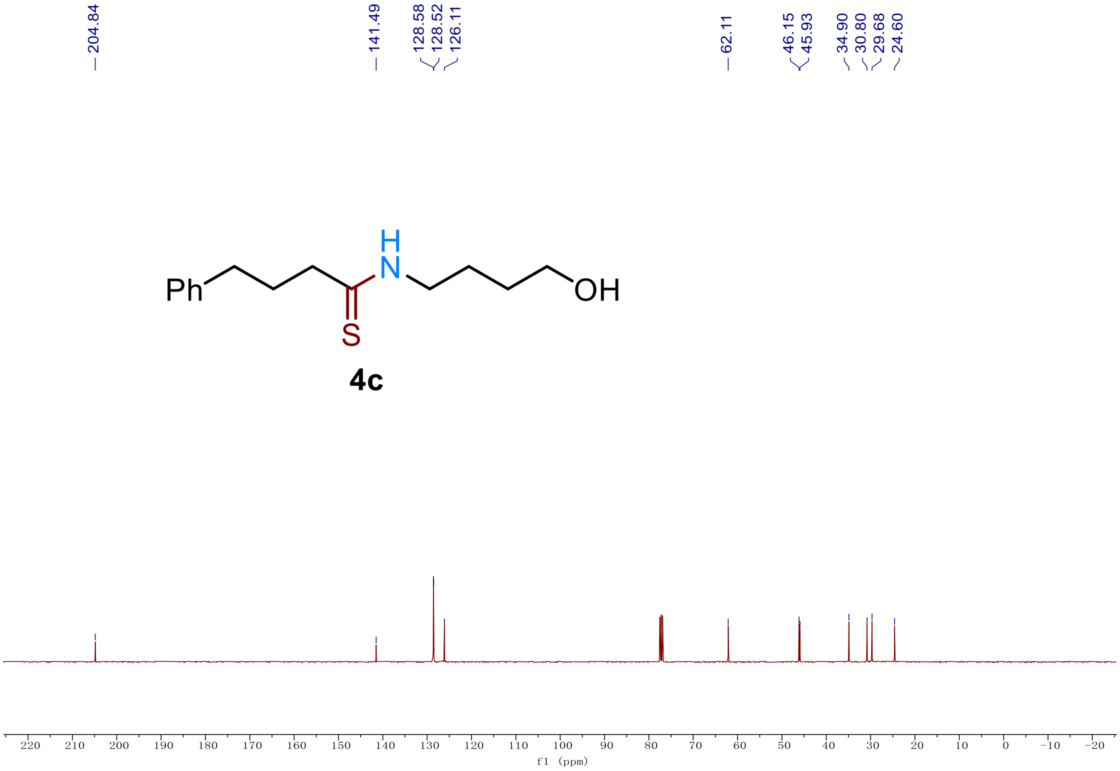
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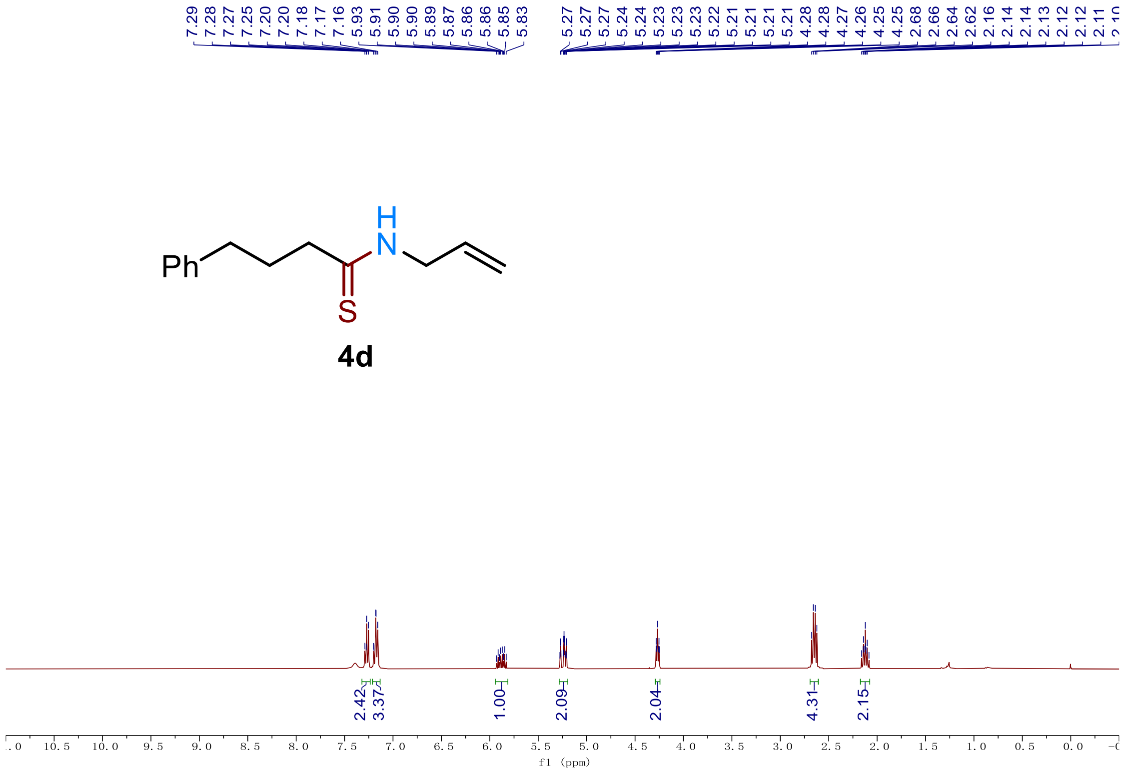
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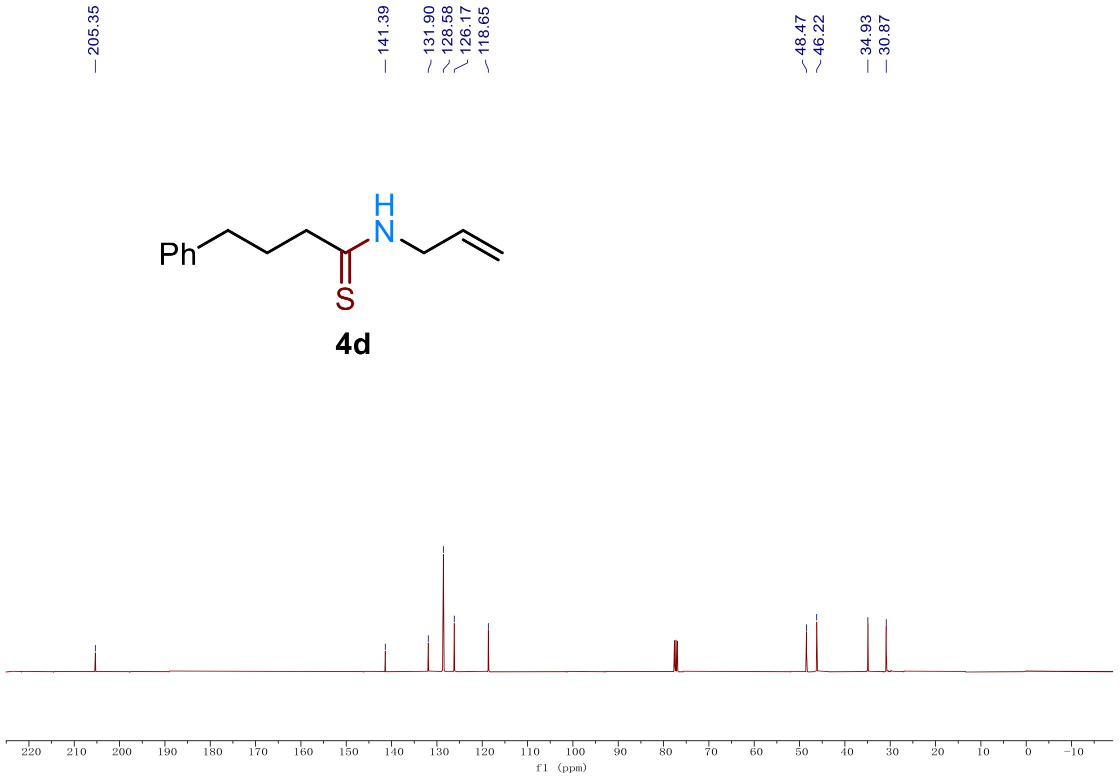
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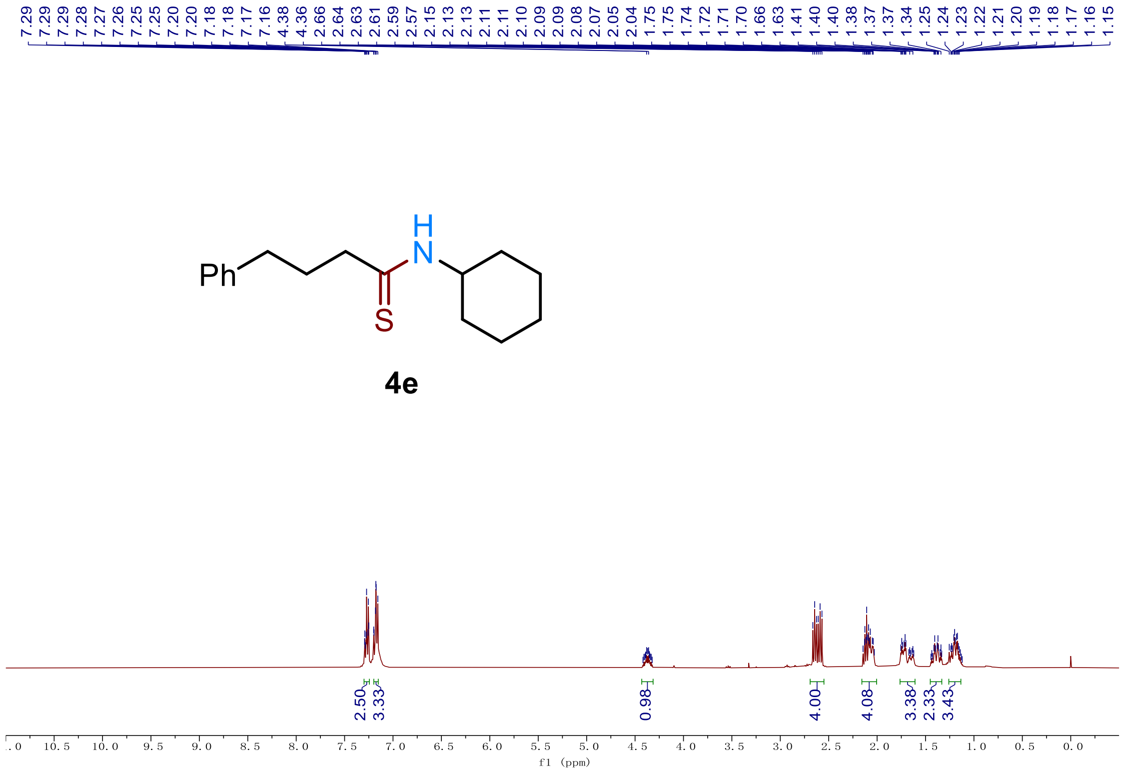
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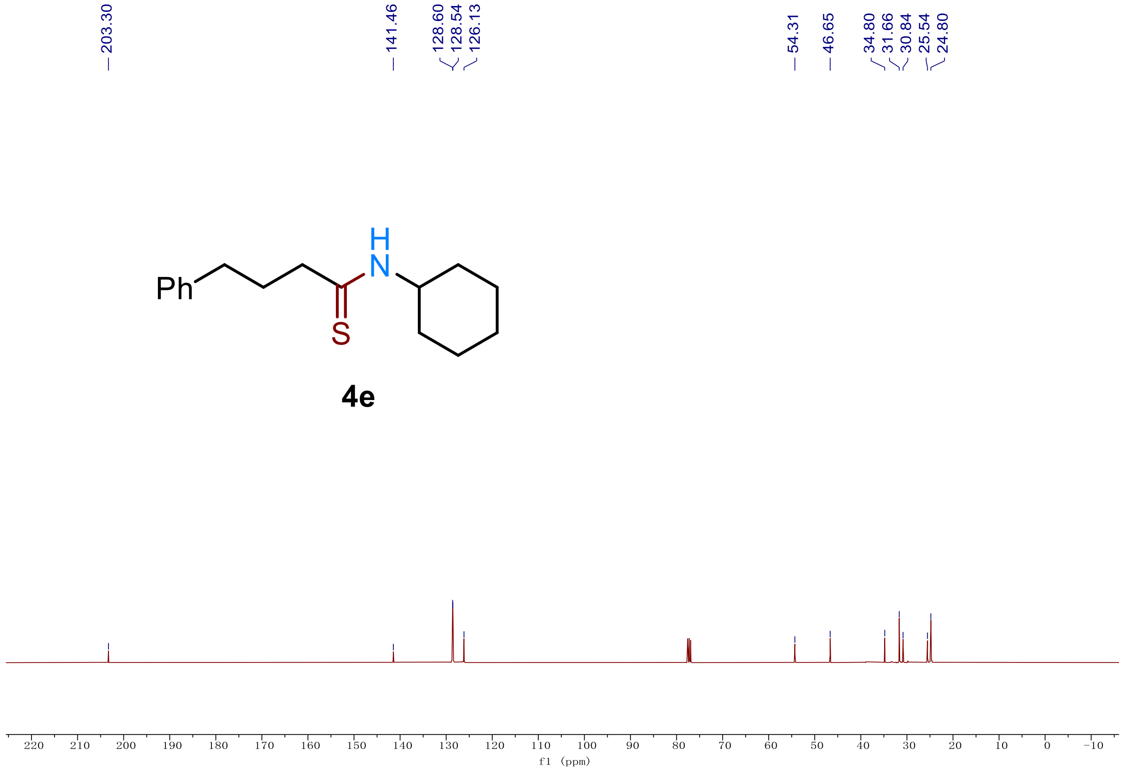
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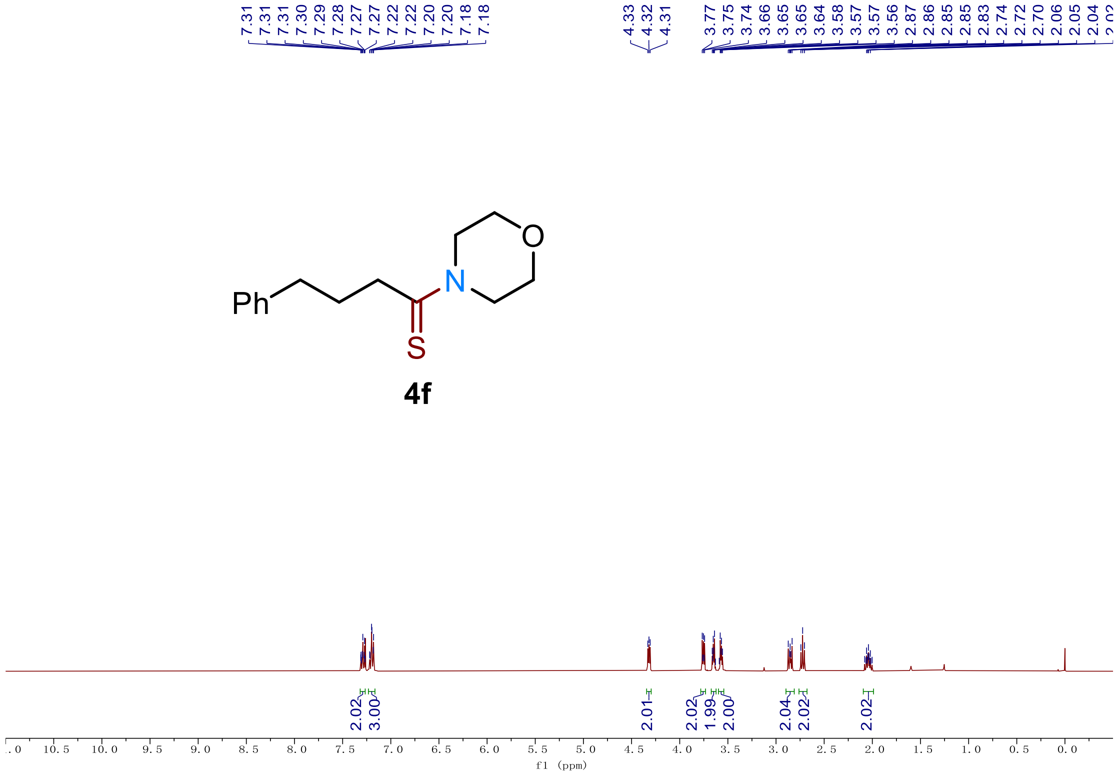
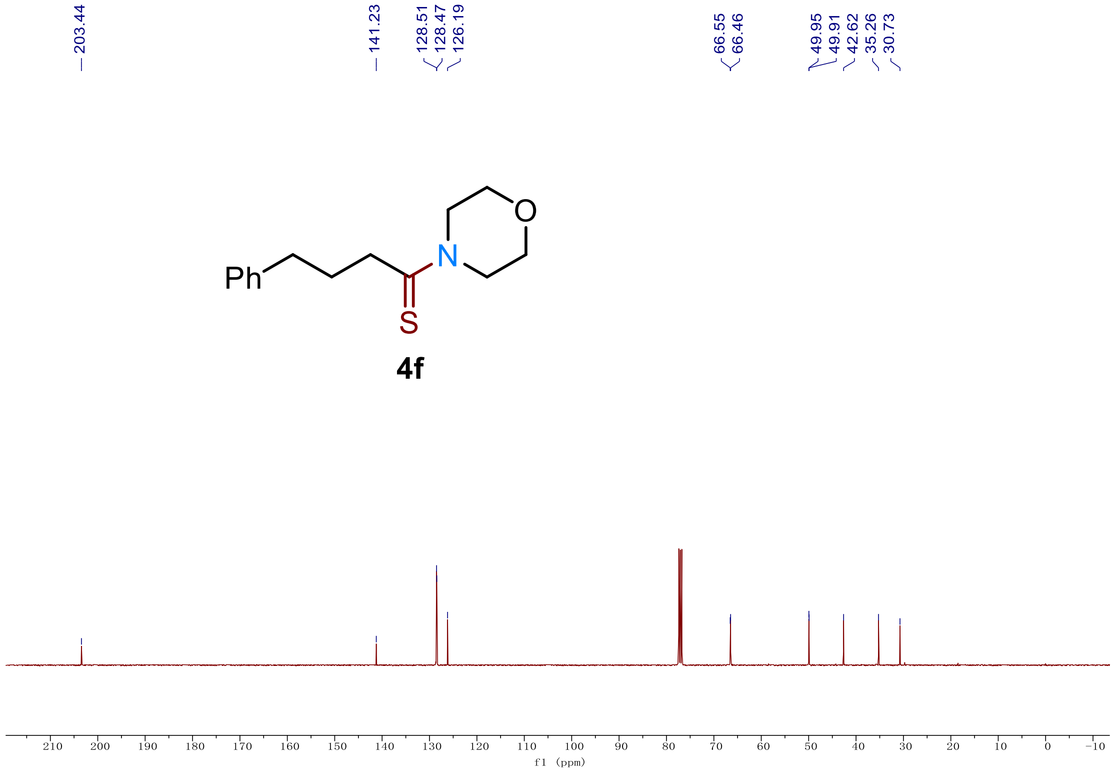
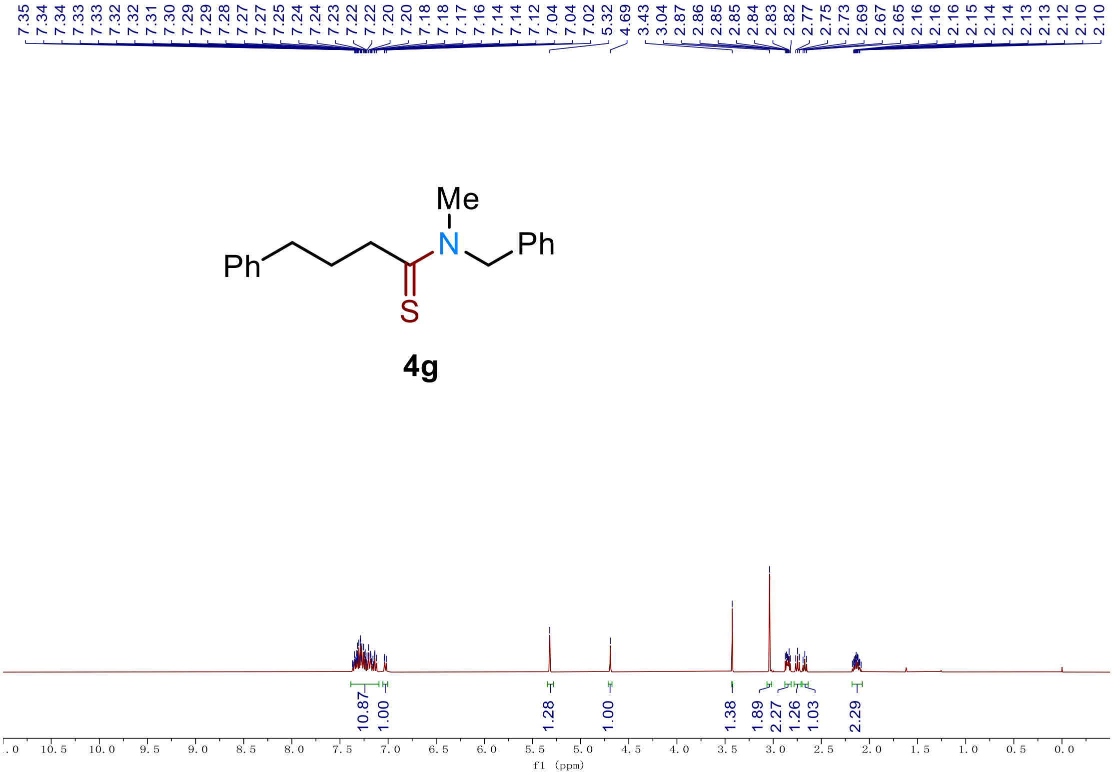
−10
f1 (ppm)


7.31
7.31
7.31
7.30
7.29
7.28
7.27
7.27
7.22
7.22
7.20
7.20
7.18
7.18
4.33
4.32
4.31
3.77
3.75
3.74
3.66
3.65
3.65
3.64
3.58
3.57
3.56
2.87
2.86
2.85
2.85
2.83
2.74
2.72
2.70
2.06
2.05
2.04
2.0
Ph
N
O
S
2.02
3.00
2.01
2.02
1.99
2.00
2.04
2.02
2.02
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4f


203.44
141.23
128.51
128.47
126.19
66.55
66.46
49.95
49.91
42.62
35.26
30.73
Ph
N
O
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

4f


7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.29
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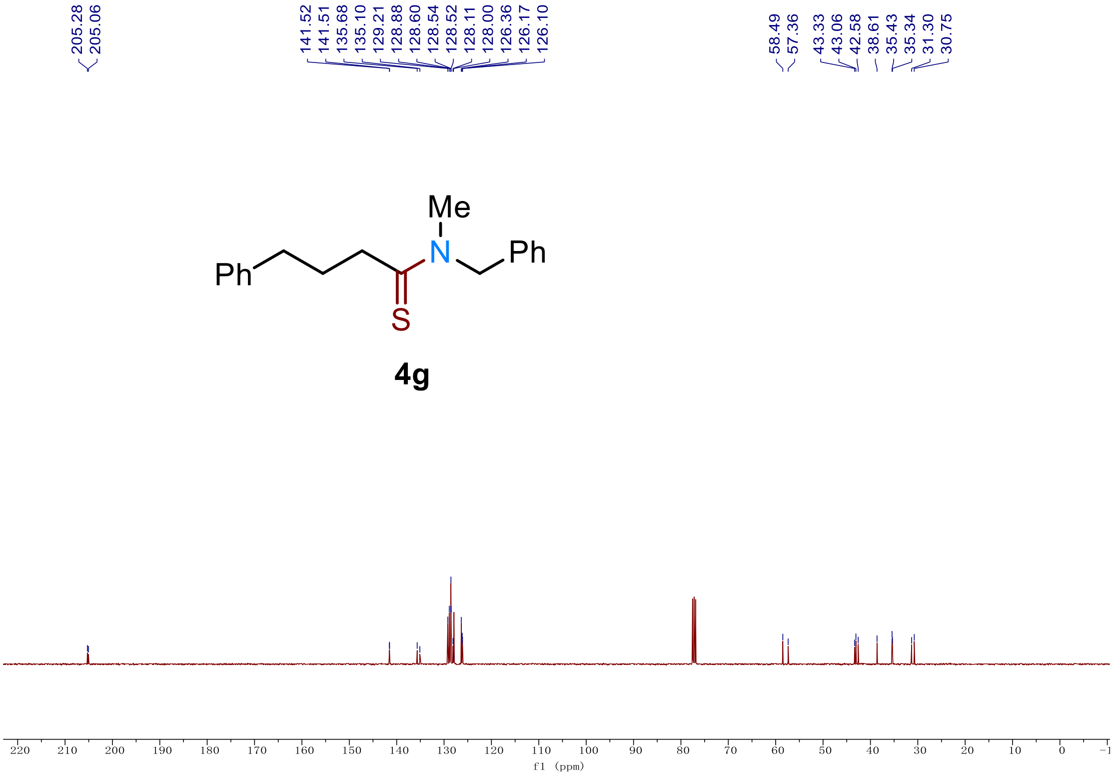
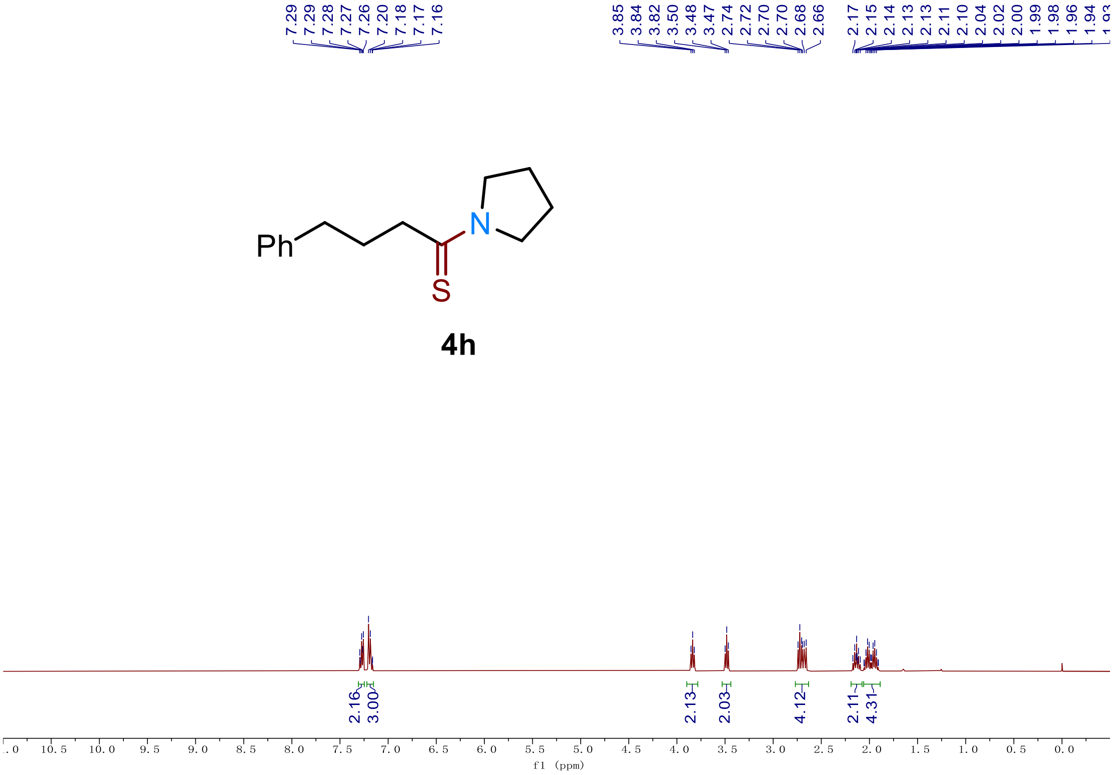
7.27
7.27
7.25
7.24
7.24
7.23
7.22
7.22
7.20
7.20
7.18
7.18
7.17
7.16
7.14
7.14
7.12
7.04
7.04
7.02
5.32
4.69
3.43
3.04
2.87
2.86
2.85
2.85
2.84
2.83
2.83
2.82
2.77
2.75
2.73
2.69
2.67
2.65
2.16
2.16
2.16
2.15
2.14
2.14
2.13
2.13
2.12
2.10
2.10
Me
N
Ph
Ph
S
10.87
1.00
1.28
1.00
1.38
1.89
2.27
1.26
1.03
2.29
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4g


205.28
205.06
141.52
141.51
135.68
135.10
129.21
128.88
128.60
128.54
128.52
128.11
128.00
126.36
126.17
126.10
58.49
57.36
43.33
43.06
42.58
38.61
35.43
35.34
31.30
30.75
Me
N
Ph
Ph
S
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

4g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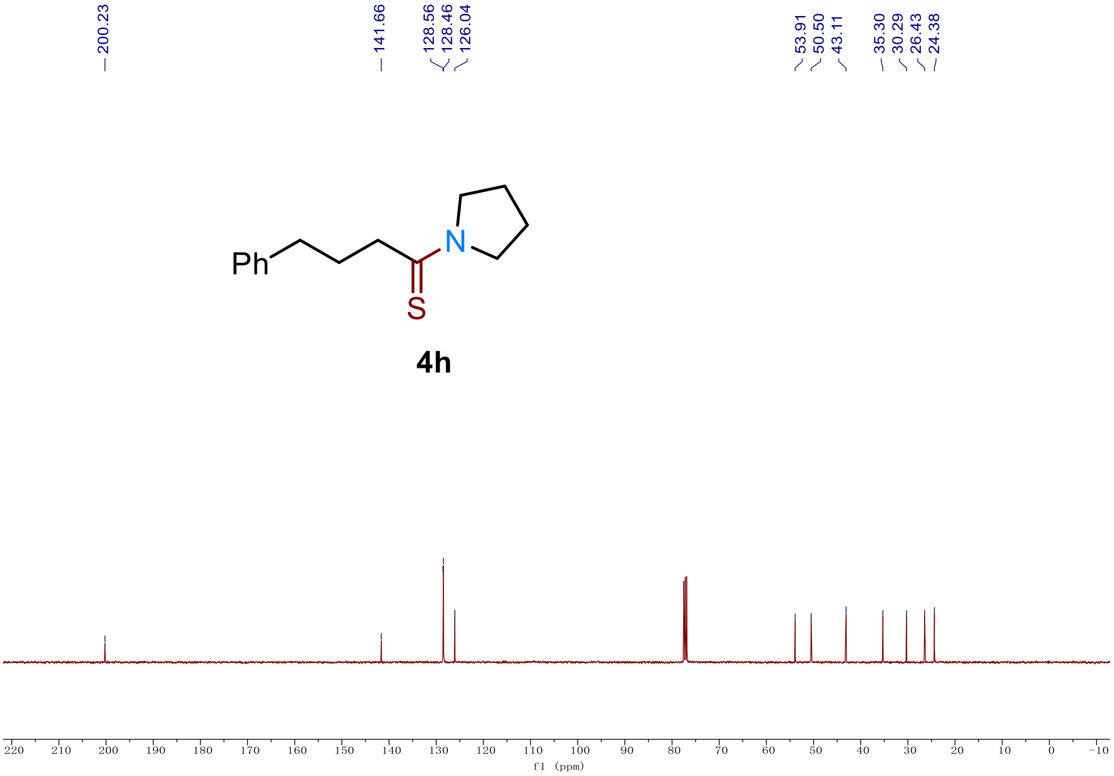
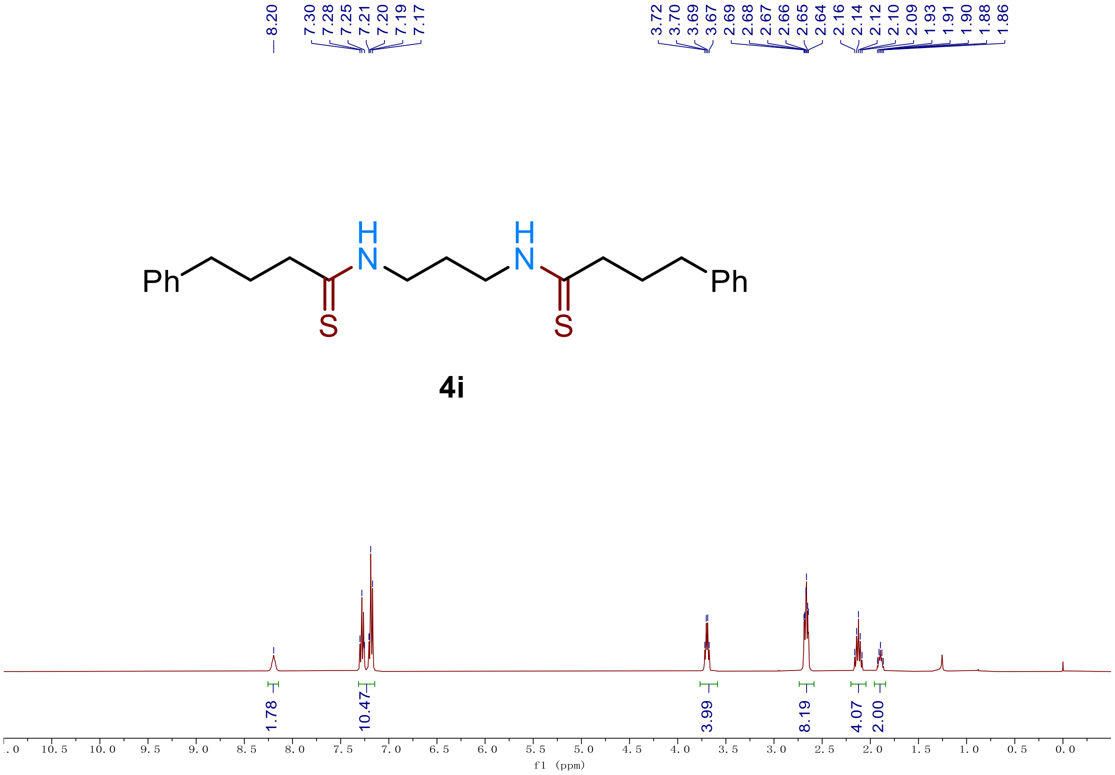
7.29
7.28
7.27
7.26
7.20
7.18
7.17
7.16
3.85
3.84
3.82
3.50
3.48
3.47
2.74
2.72
2.70
2.70
2.68
2.66
2.17
2.15
2.14
2.13
2.13
2.11
2.10
2.04
2.02
2.00
1.99
1.98
1.96
1.94
1.9
Ph
N
S
2.16
3.00
2.13
2.03
4.12
2.11
4.31
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4h


200.23
141.66
128.56
128.46
126.04
53.91
50.50
43.11
35.30
30.29
26.43
24.38
Ph
N
S
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4h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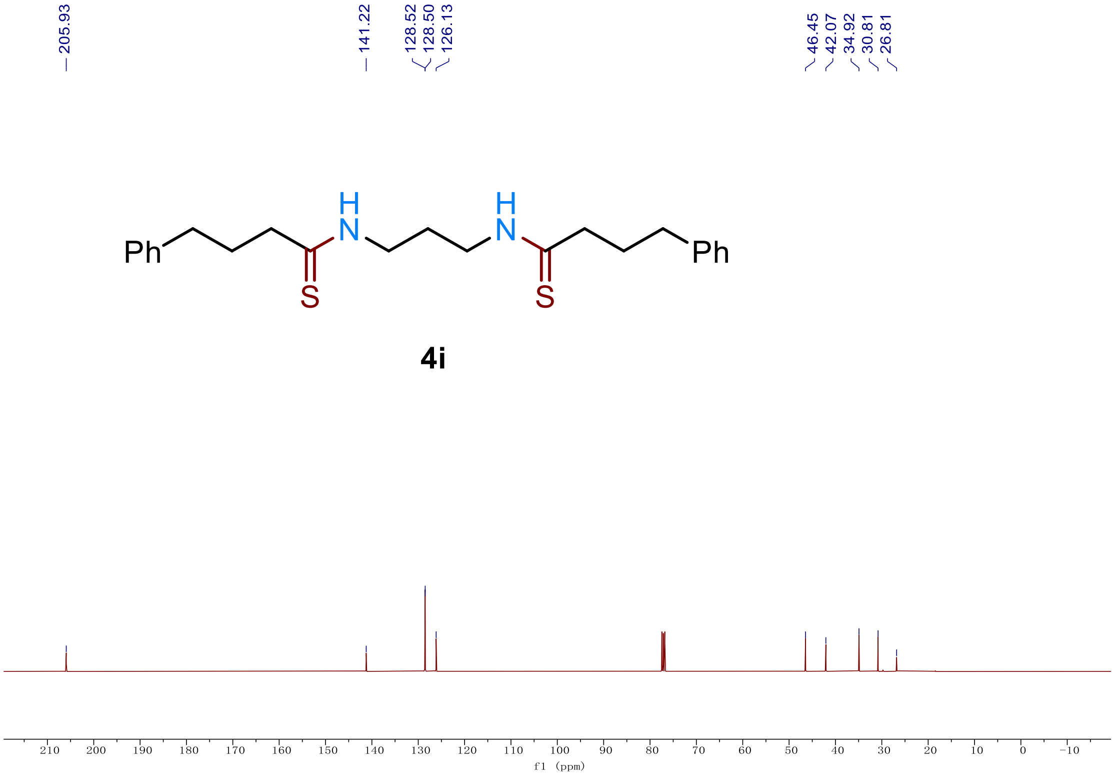
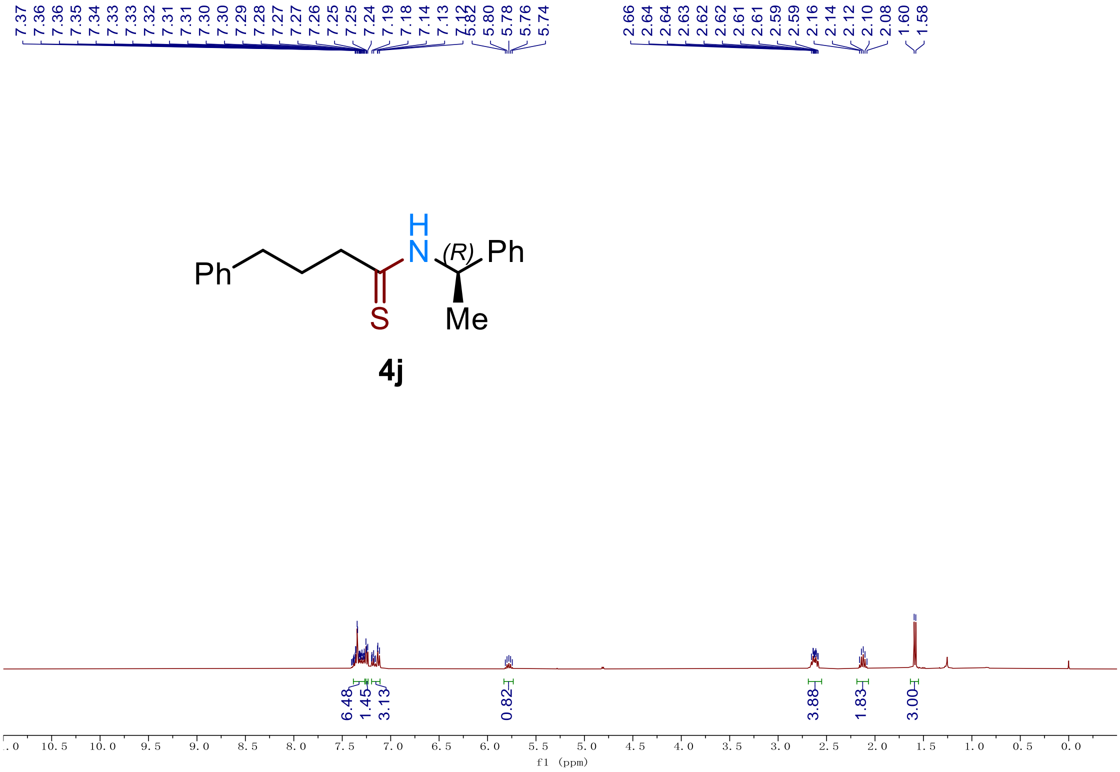
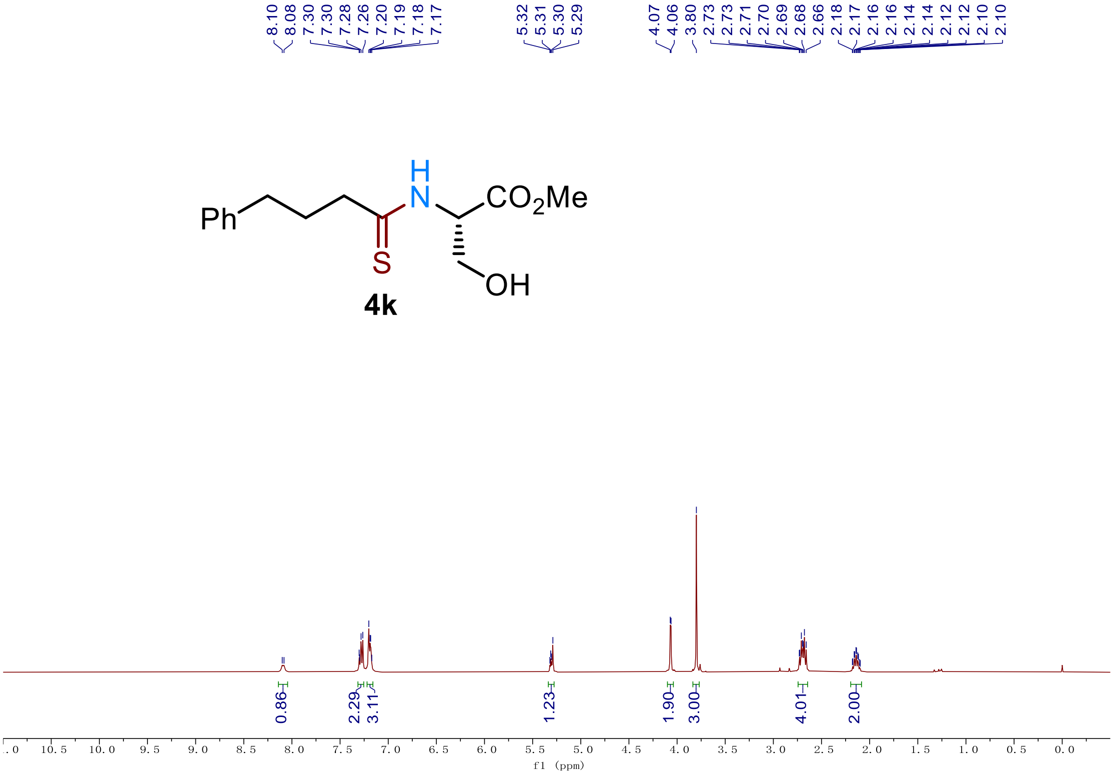
7.30
7.28
7.25
7.21
7.20
7.19
7.17
3.72
3.70
3.69
3.67
2.69
2.68
2.67
2.66
2.65
2.64
2.16
2.14
2.12
2.10
2.09
1.93
1.91
1.90
1.88
1.86
Ph
H
N
S
Ph
4i
1.78
10.47
3.99
8.19
4.07
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


205.93
141.22
128.52
128.50
126.13
46.45
42.07
34.92
30.81
26.81
Ph
H
N
S
Ph
4i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.19
7.18
7.14
7.13
7.12
5.82
5.80
5.78
5.76
5.74
2.66
2.64
2.63
2.62
2.62
2.61
2.61
2.59
2.16
2.14
2.12
2.10
2.08
1.60
1.58
6.48
1.45
3.13
0.82
3.88
1.83
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

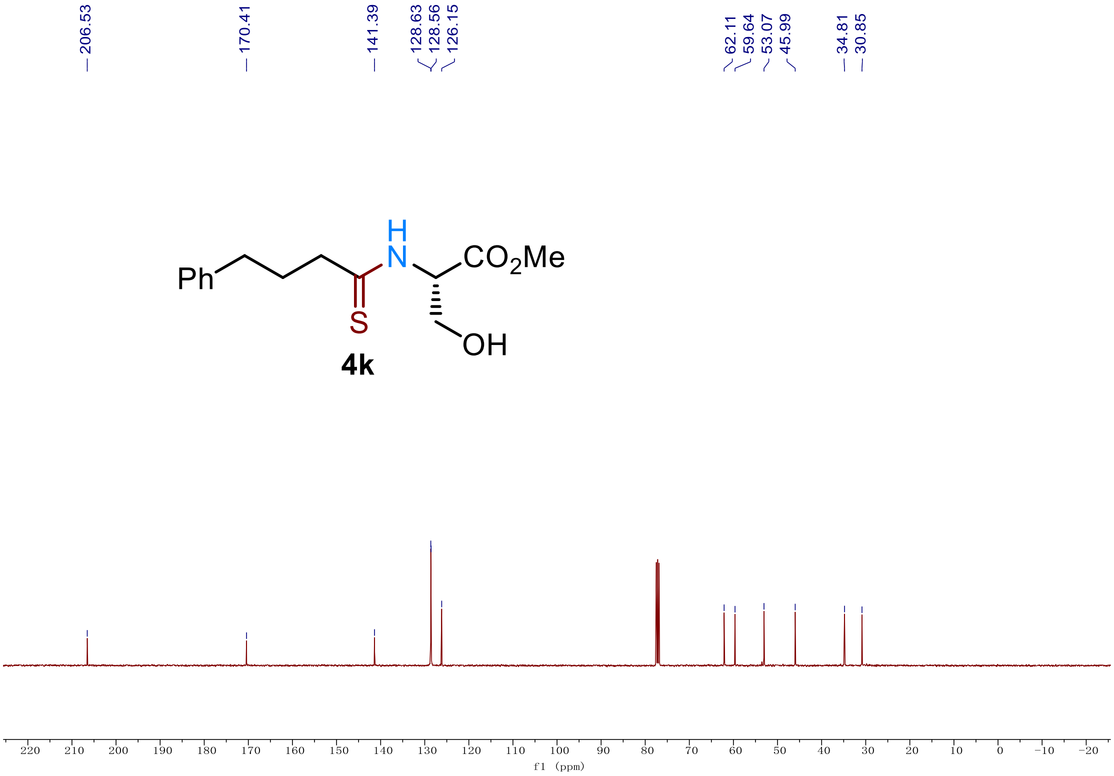
H
N
(R)
Ph
Ph
S
Me

4j

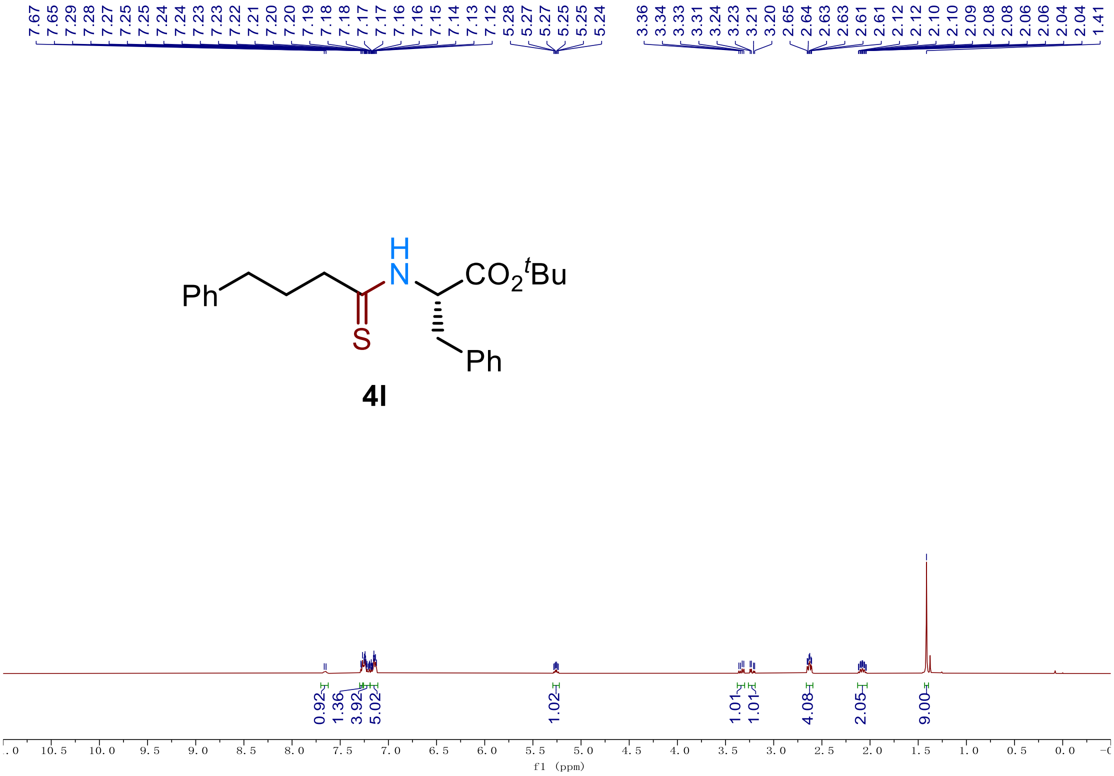

8.10
8.08
7.30
7.28
7.26
7.20
7.19
7.18
7.17
5.32
5.31
5.30
5.29
4.07
4.06
3.80
2.73
2.73
2.71
2.70
2.69
2.68
2.66
2.18
2.17
2.16
2.16
2.14
2.14
2.12
2.12
2.10
2.10
0.86
2.29
3.11
1.23
1.90
3.00
4.01
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

H
N
CO2Me
Ph
S
OH

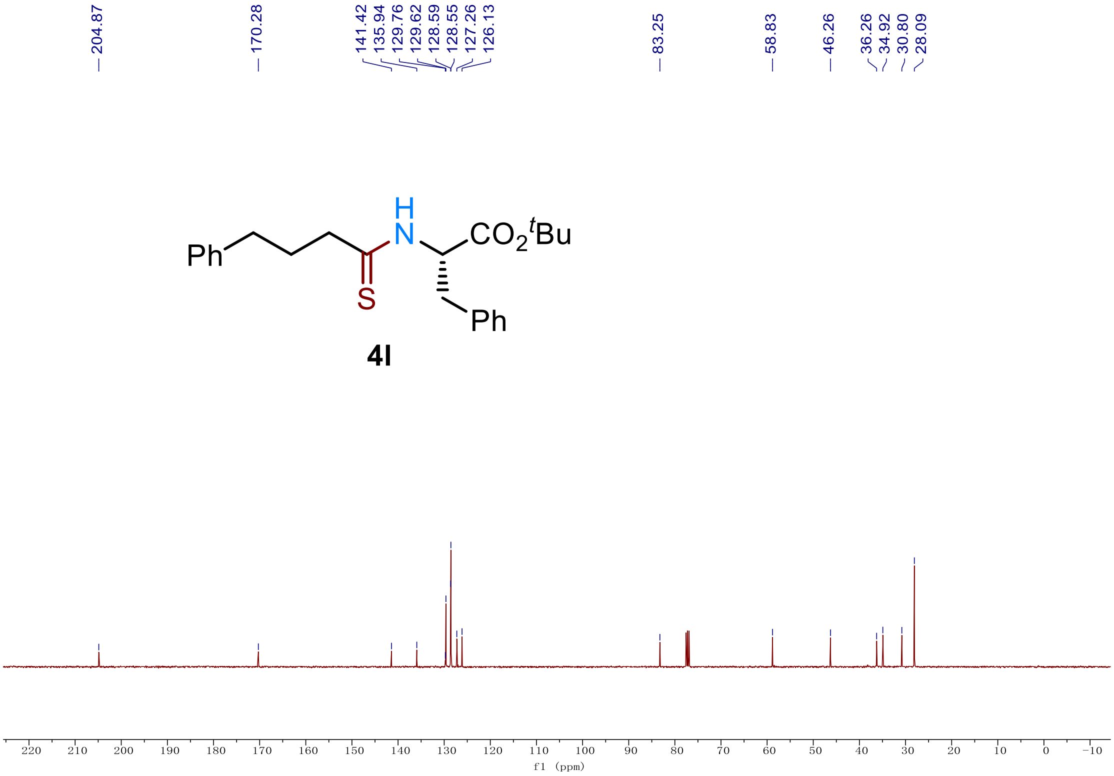
4k


206.53
170.41
141.39
128.63
128.56
126.15
62.11
59.64
53.07
45.99
34.81
30.85
Ph
H
N
CO$_2$Me
S
OH
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

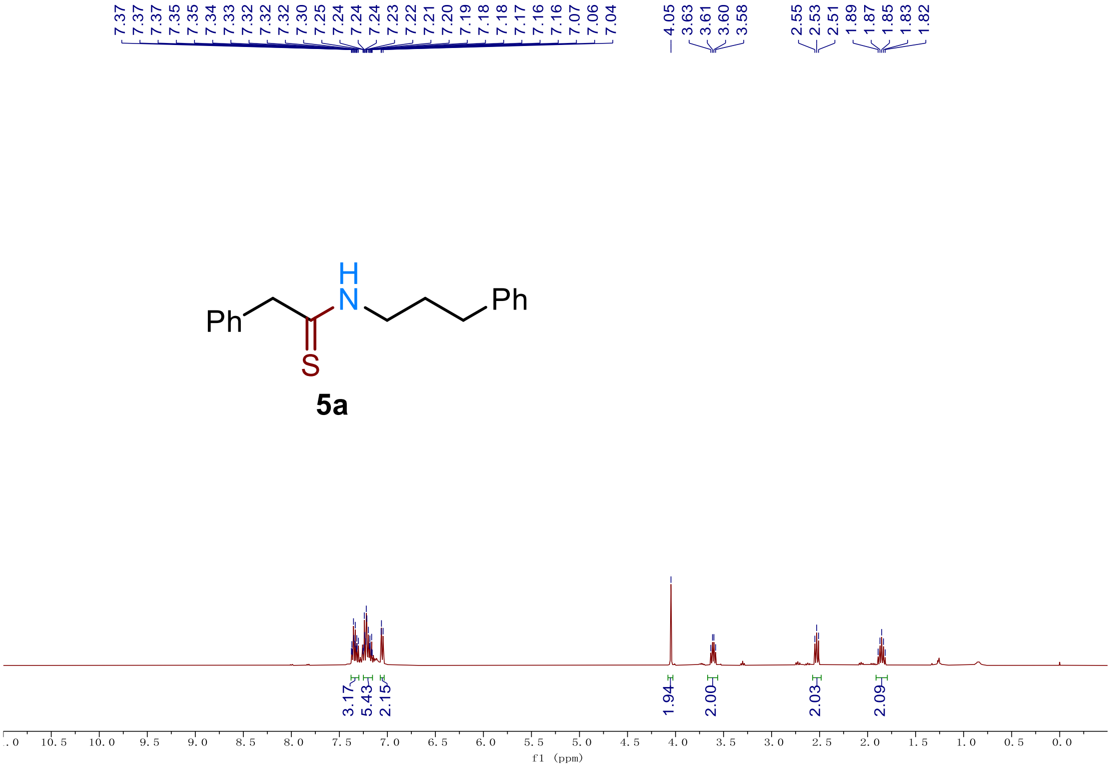
4k


7.67
7.65
7.29
7.28
7.27
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.13
7.12
5.28
5.27
5.27
5.25
5.25
5.24
3.36
3.34
3.33
3.31
3.24
3.23
3.21
3.20
2.65
2.64
2.63
2.63
2.61
2.61
2.12
2.12
2.10
2.10
2.09
2.08
2.08
2.06
2.04
2.04
1.41
Ph
H
N
CO$_2$^{t}Bu
S
Ph
0.92
1.36
3.92
5.02
1.02
1.01
1.01
4.08
2.05
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

4l


204.87
170.28
141.42
135.94
129.76
129.62
128.59
128.55
127.26
126.13
83.25
58.83
46.26
36.26
34.92
30.80
28.09
Ph
H
N
CO$_2$^{t}Bu
S
Ph
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4l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7.37
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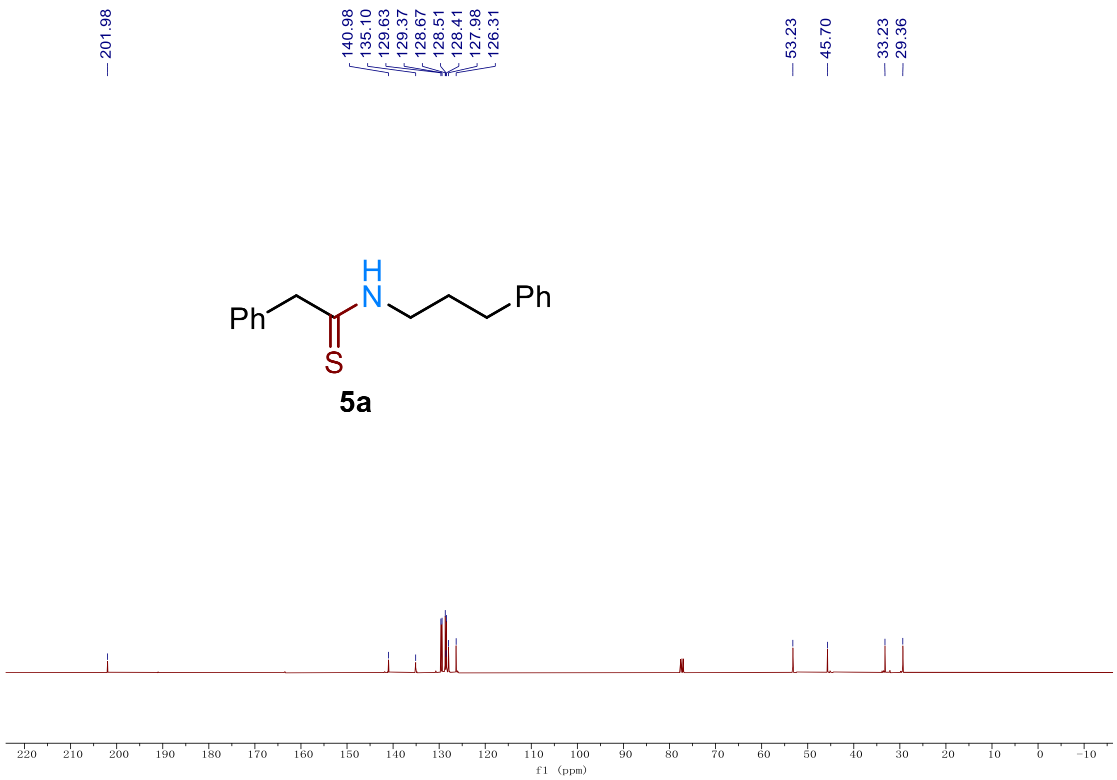
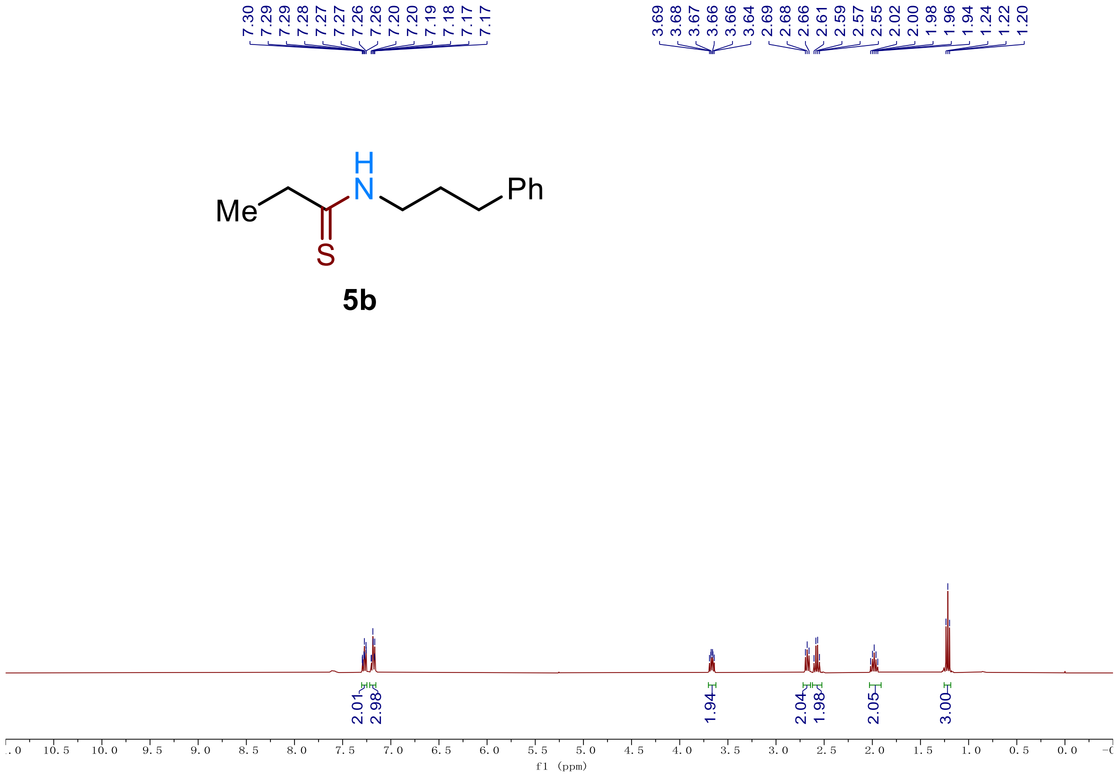
7.34
7.33
7.32
7.32
7.32
7.30
7.25
7.24
7.24
7.24
7.23
7.22
7.21
7.20
7.19
7.18
7.18
7.17
7.16
7.16
7.07
7.06
7.04
4.05
3.63
3.61
3.60
3.58
2.55
2.53
2.51
1.89
1.87
1.85
1.83
1.82
Ph
H
N
Ph
S
3.17
5.43
2.15
1.94
2.00
2.03
2.09
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

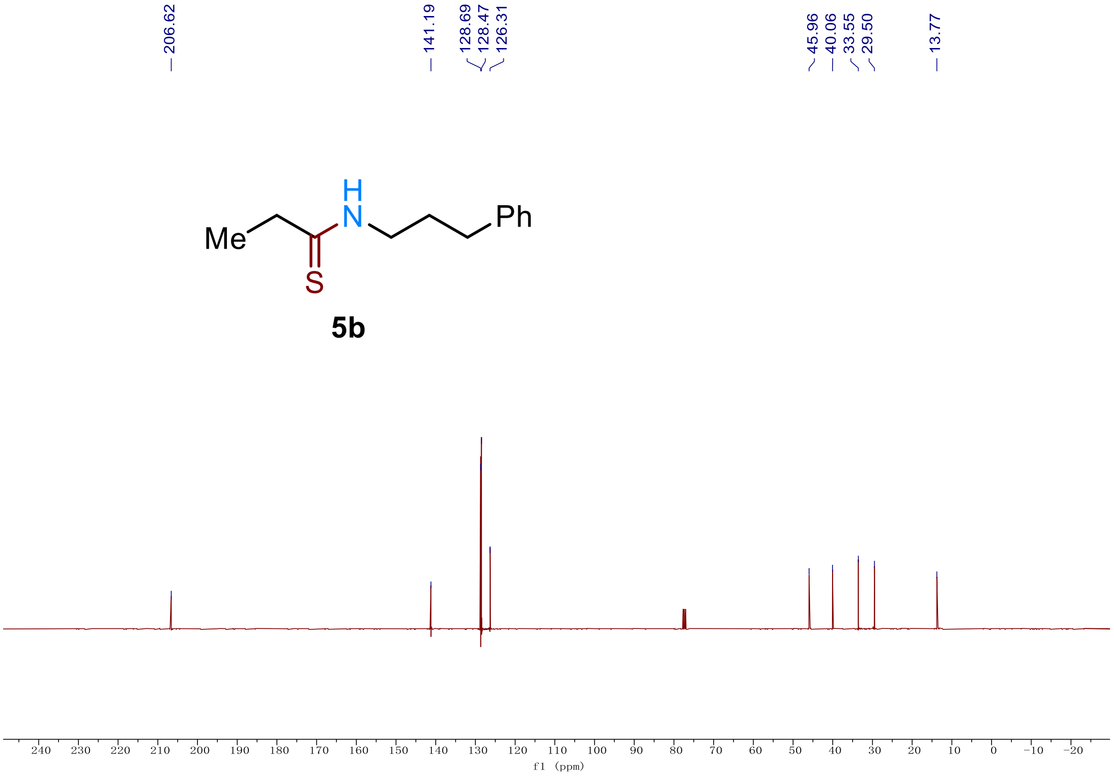
5a


201.98
140.98
135.10
129.63
129.37
128.67
128.51
128.41
127.98
126.31
53.23
45.70
33.23
29.36
Ph
H
N
Ph
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

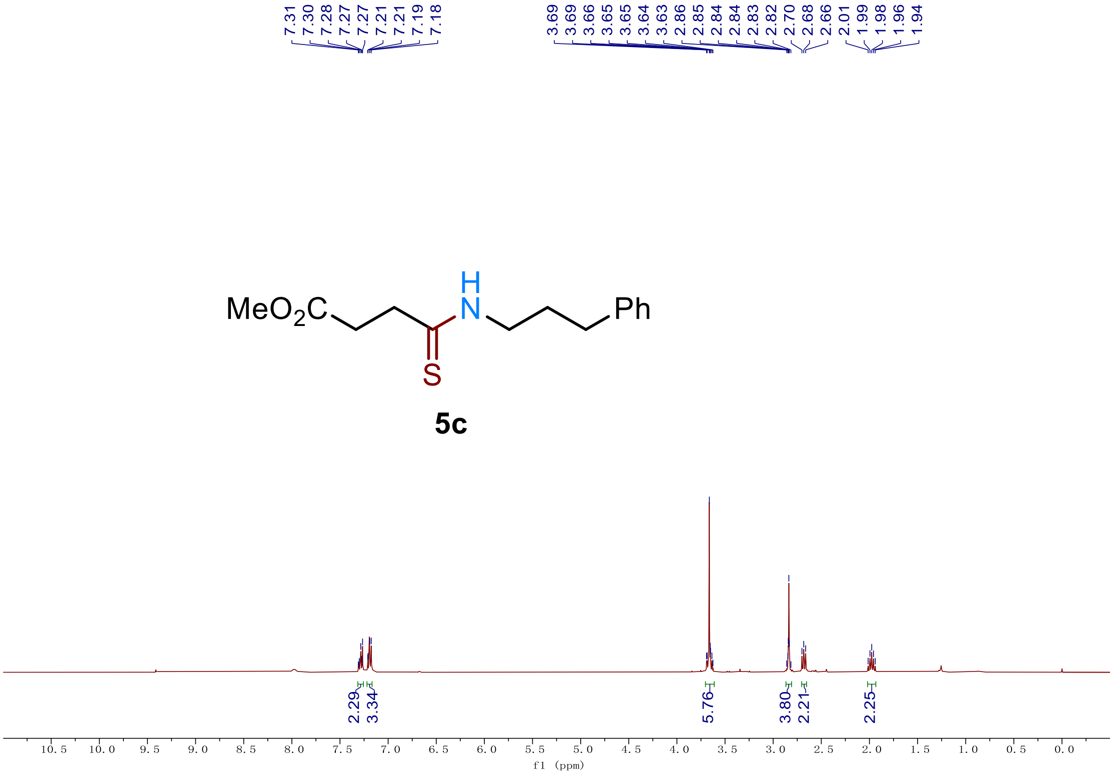
5a


7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.20
7.20
7.19
7.18
7.17
7.17
3.69
3.68
3.67
3.66
3.66
3.64
2.69
2.68
2.66
2.61
2.59
2.57
2.55
2.02
2.00
1.98
1.96
1.94
1.24
1.22
1.20
Me
H
N
Ph
S
2.01
2.98
1.94
2.04
1.98
2.05
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

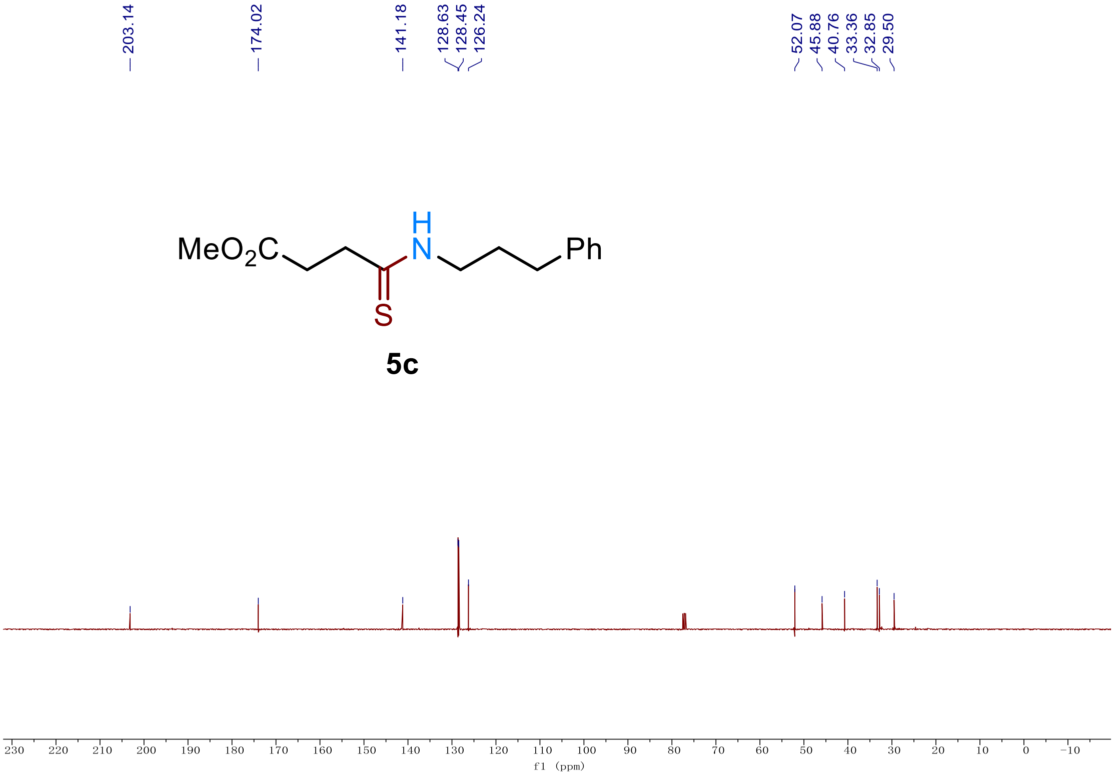
5b


206.62
141.19
128.69
128.47
126.31
45.96
40.06
33.55
29.50
13.77
H
N
Me
Ph
S
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

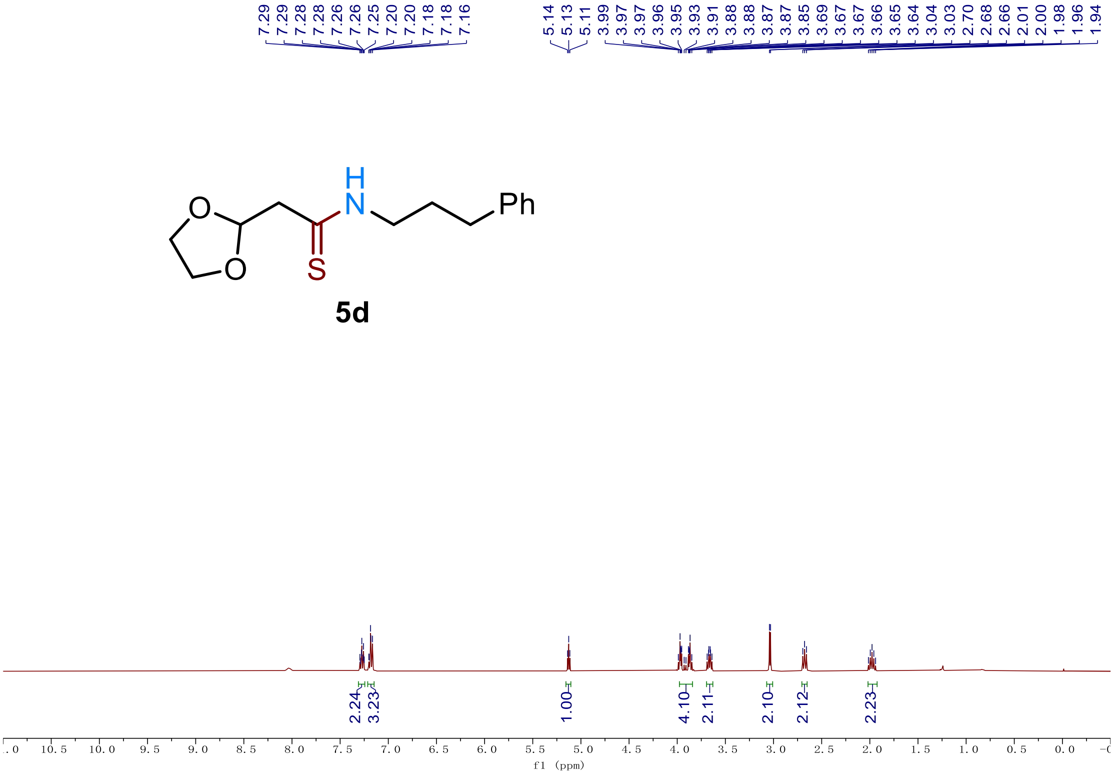
5b


7.31
7.30
7.28
7.27
7.27
7.21
7.21
7.19
7.18
3.69
3.69
3.66
3.65
3.65
3.64
3.63
2.86
2.85
2.84
2.84
2.83
2.82
2.70
2.68
2.66
2.01
1.99
1.98
1.96
1.94
MeO2C
H
N
Ph
S
2.29
3.34
5.76
3.80
2.21
2.25
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

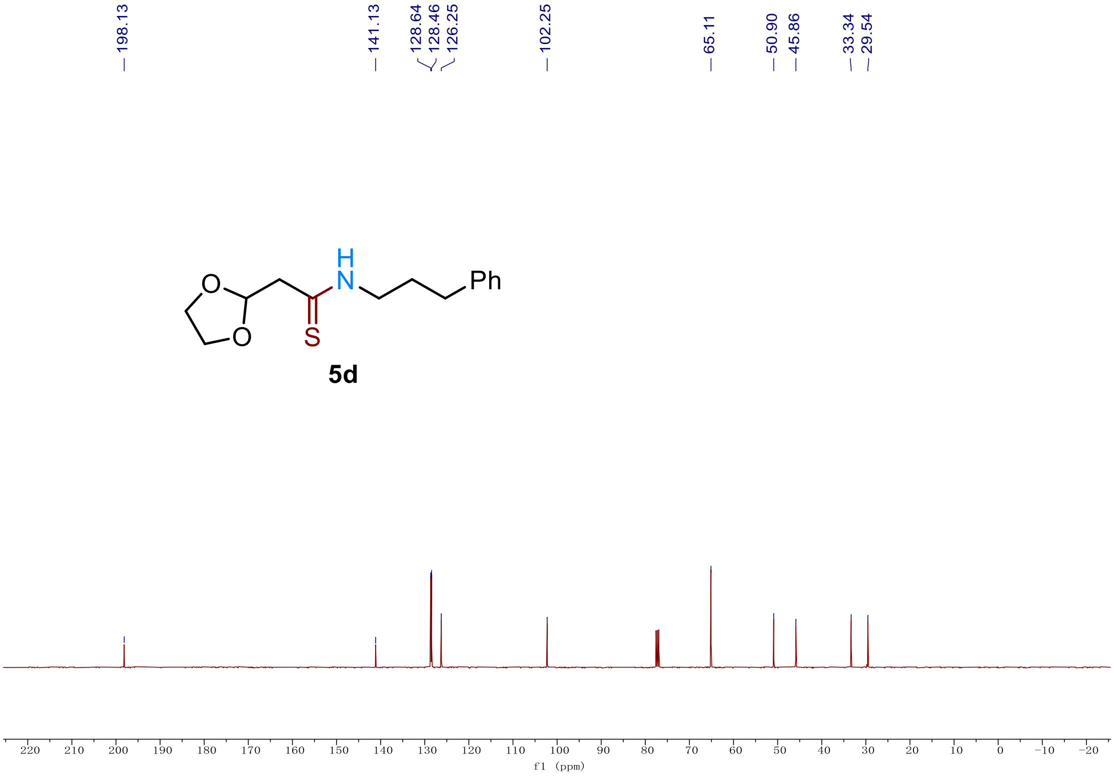
5c


203.14
174.02
141.18
128.63
128.45
126.24
52.07
45.88
40.76
33.36
32.85
29.50
MeO2C
H
N
Ph
S
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

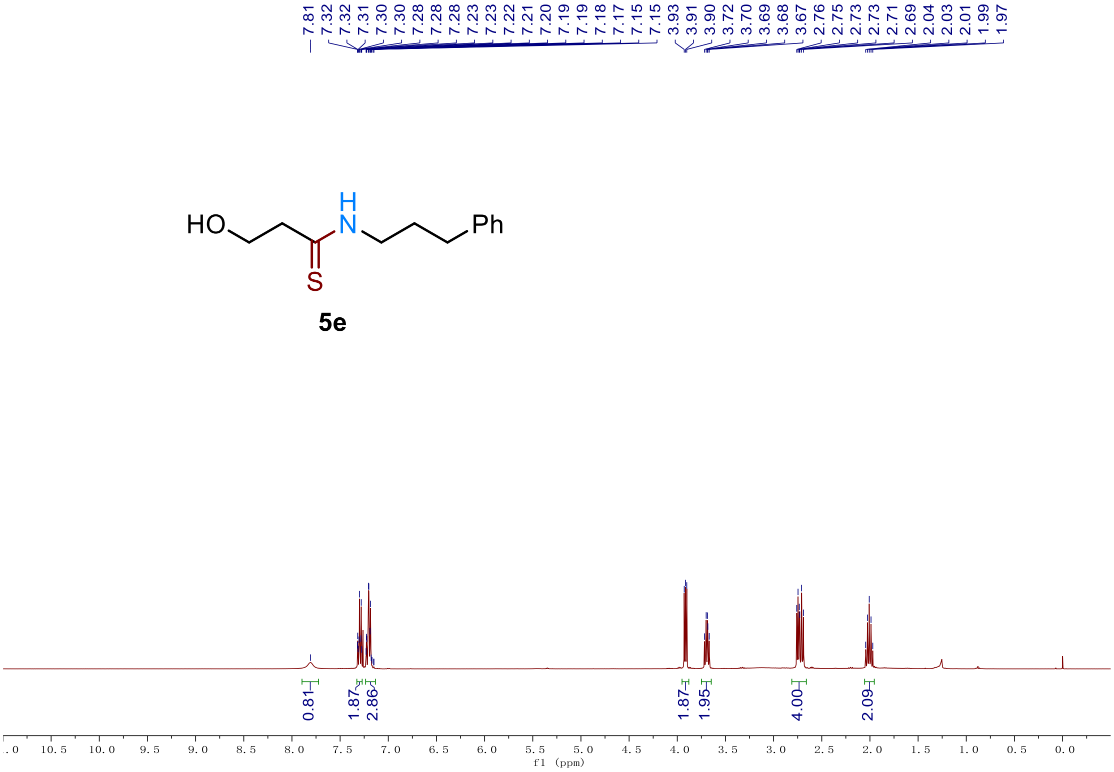
5c


7.29
7.29
7.28
7.28
7.26
7.26
7.25
7.20
7.20
7.18
7.18
7.16
5.14
5.13
5.11
3.99
3.97
3.97
3.96
3.95
3.93
3.91
3.88
3.88
3.87
3.87
3.85
3.69
3.67
3.67
3.66
3.65
3.64
3.04
3.03
2.70
2.68
2.66
2.01
2.00
1.98
1.96
1.94
O
O
H
N
Ph
S
2.24
3.23
1.00
4.10
2.11
2.10
2.12
2.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

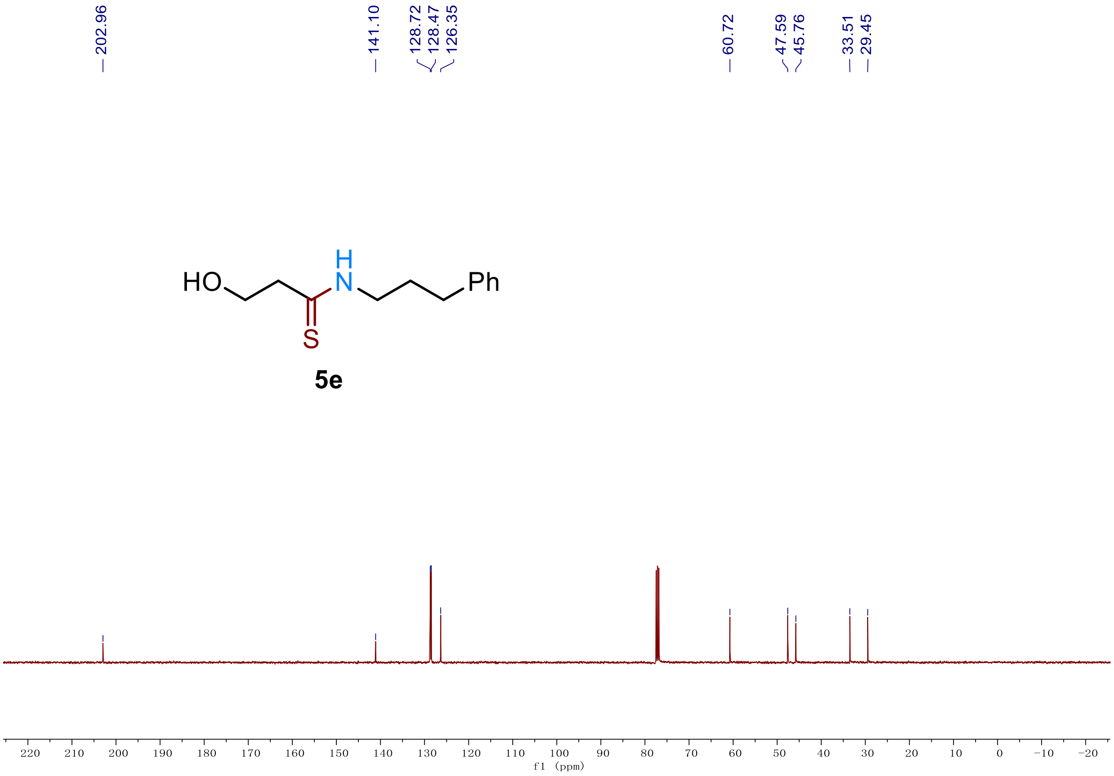
5d


198.13
141.13
128.64
128.46
126.25
102.25
65.11
50.90
45.86
33.34
29.54
O
O
H
N
S
Ph
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

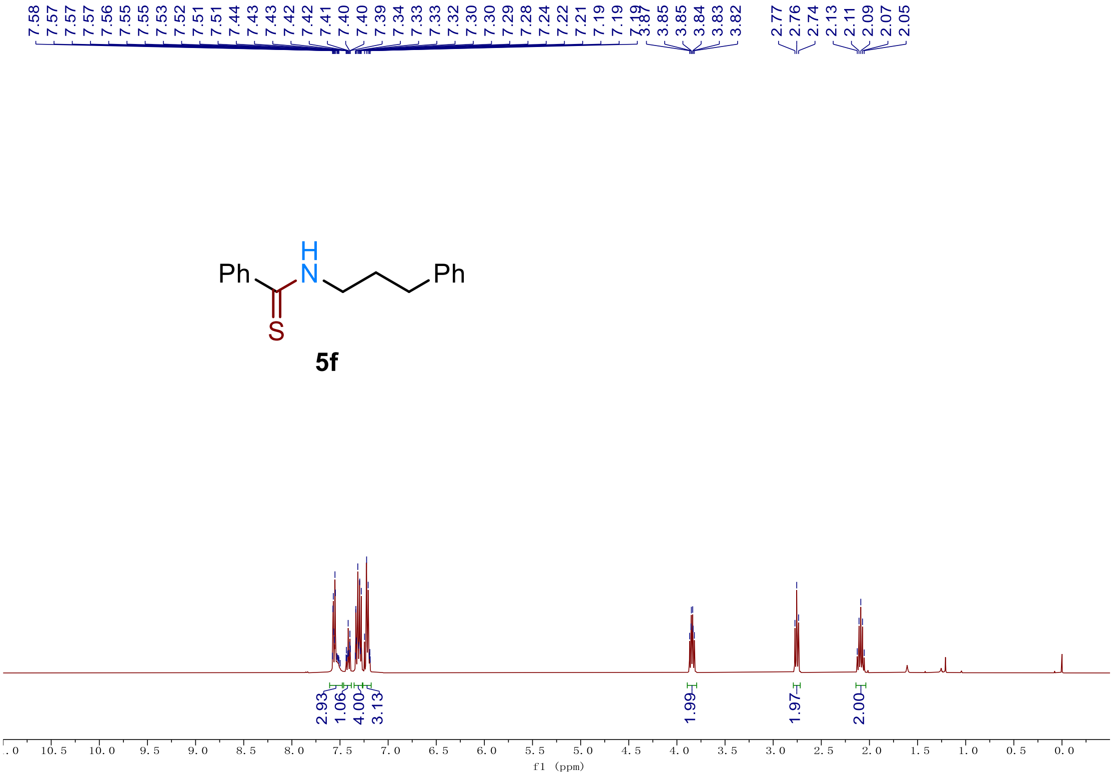
5d


7.81
7.32
7.32
7.31
7.30
7.30
7.28
7.28
7.28
7.23
7.23
7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.15
3.93
3.91
3.90
3.72
3.70
3.69
3.68
3.67
2.76
2.75
2.73
2.73
2.71
2.69
2.04
2.03
2.01
1.99
1.97
HO
H
N
S
Ph
0.81
1.87
2.86
1.87
1.95
4.00
2.09
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

5e


202.96
141.10
128.72
128.47
126.35
60.72
47.59
45.76
33.51
29.45
HO
H
N
S
Ph
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

5e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7.57
7.57
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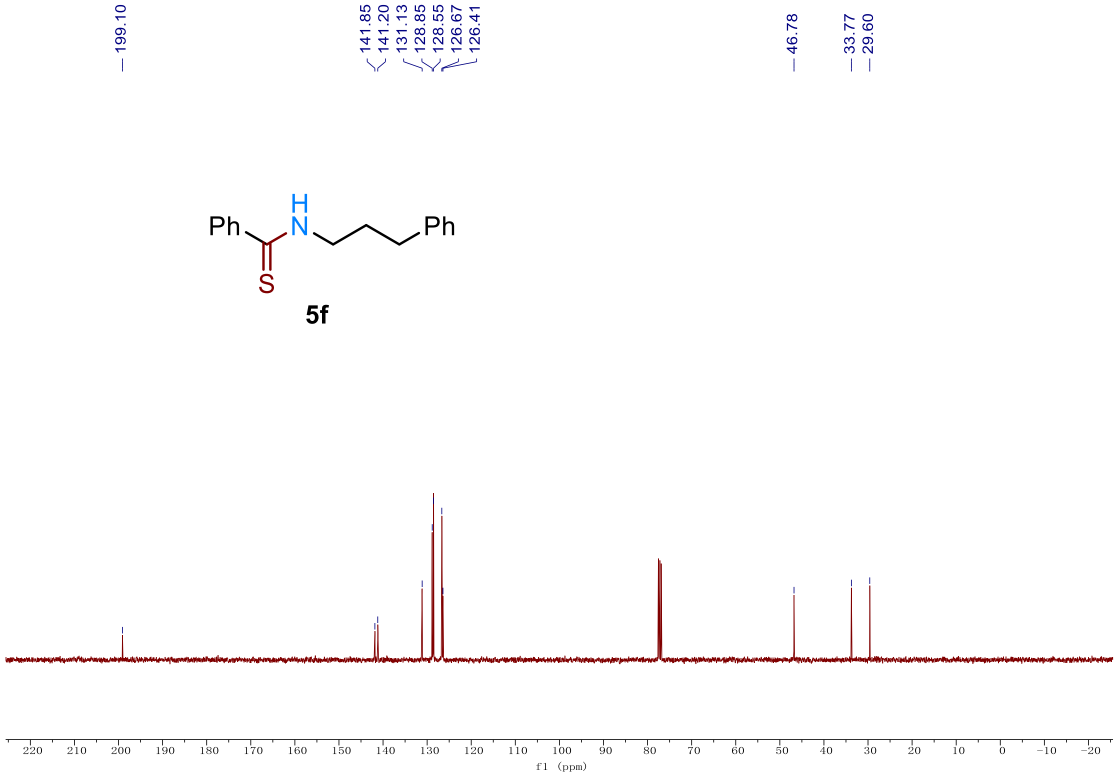
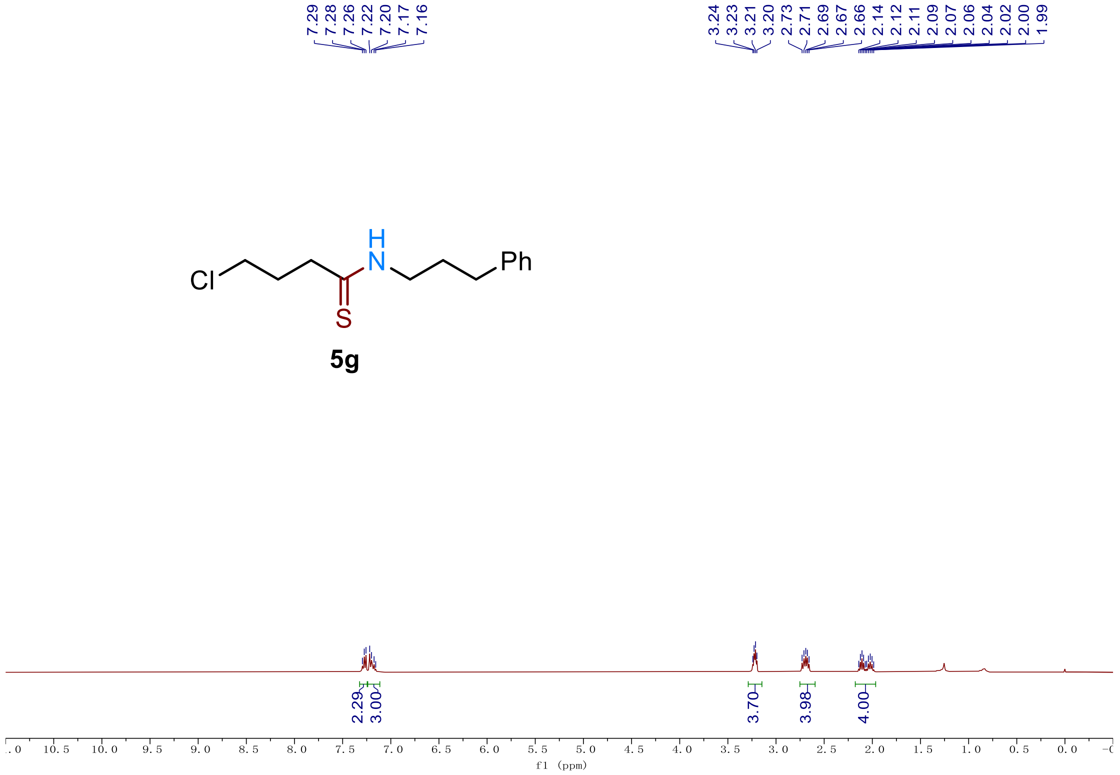
7.55
7.53
7.52
7.51
7.51
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.34
7.33
7.33
7.32
7.30
7.30
7.29
7.28
7.24
7.22
7.21
7.19
7.19
3.87
3.85
3.85
3.84
3.83
3.82
2.77
2.76
2.74
2.13
2.11
2.09
2.07
2.05
Ph
H
N
S
Ph
2.93
1.06
4.00
3.13
1.99
1.97
2.00
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

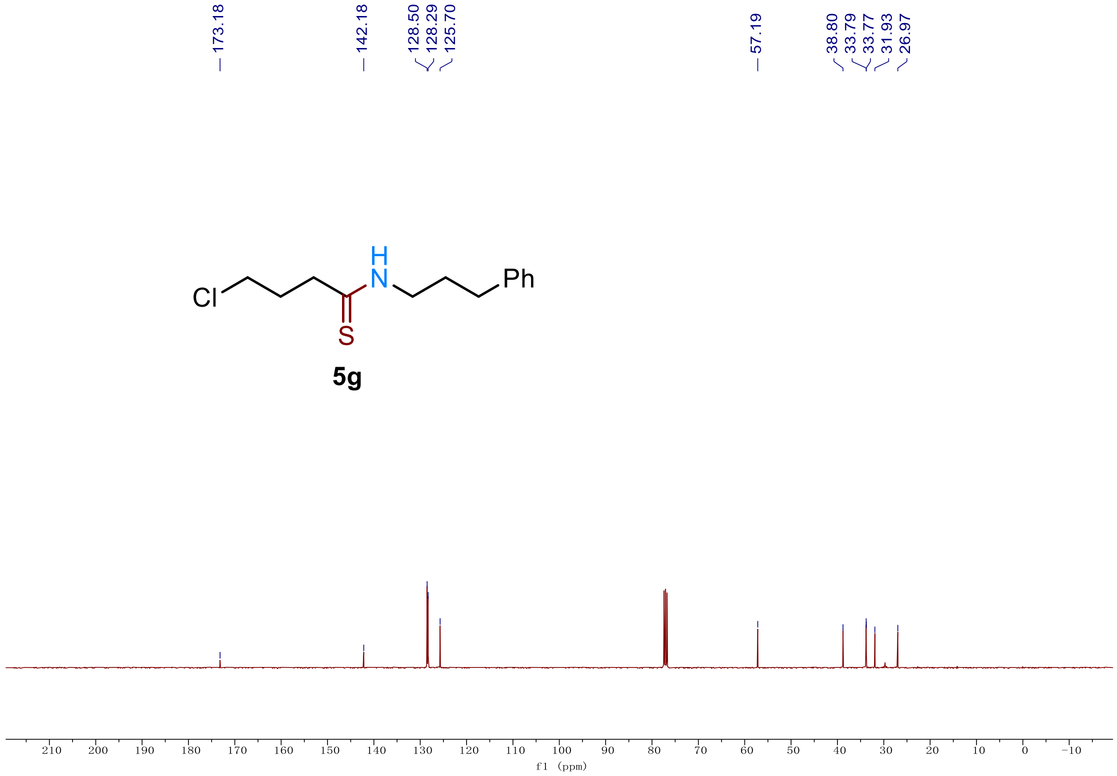
5f


199.10
141.85
141.20
131.13
128.85
128.55
126.67
126.41
46.78
33.77
29.60
Ph
H
N
Ph
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

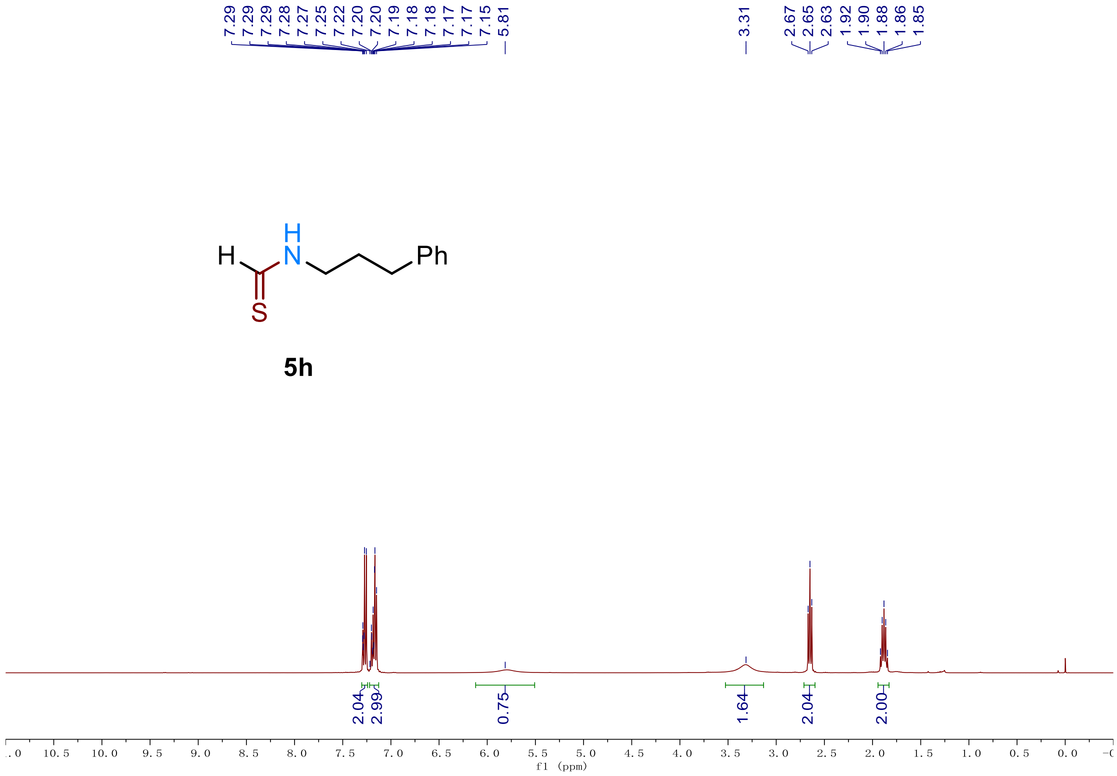
5f


7.29
7.28
7.26
7.22
7.20
7.17
7.16
3.24
3.23
3.21
3.20
2.73
2.71
2.69
2.67
2.66
2.14
2.12
2.11
2.09
2.07
2.06
2.04
2.02
2.00
1.99
Cl
H
N
Ph
S
2.29
3.00
3.70
3.98
4.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −(
f1 (ppm)

5g


173.18
142.18
128.50
128.29
125.70
57.19
38.80
33.79
33.77
31.93
26.97
Cl
H
N
Ph
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

5g


7.29
7.29
7.29
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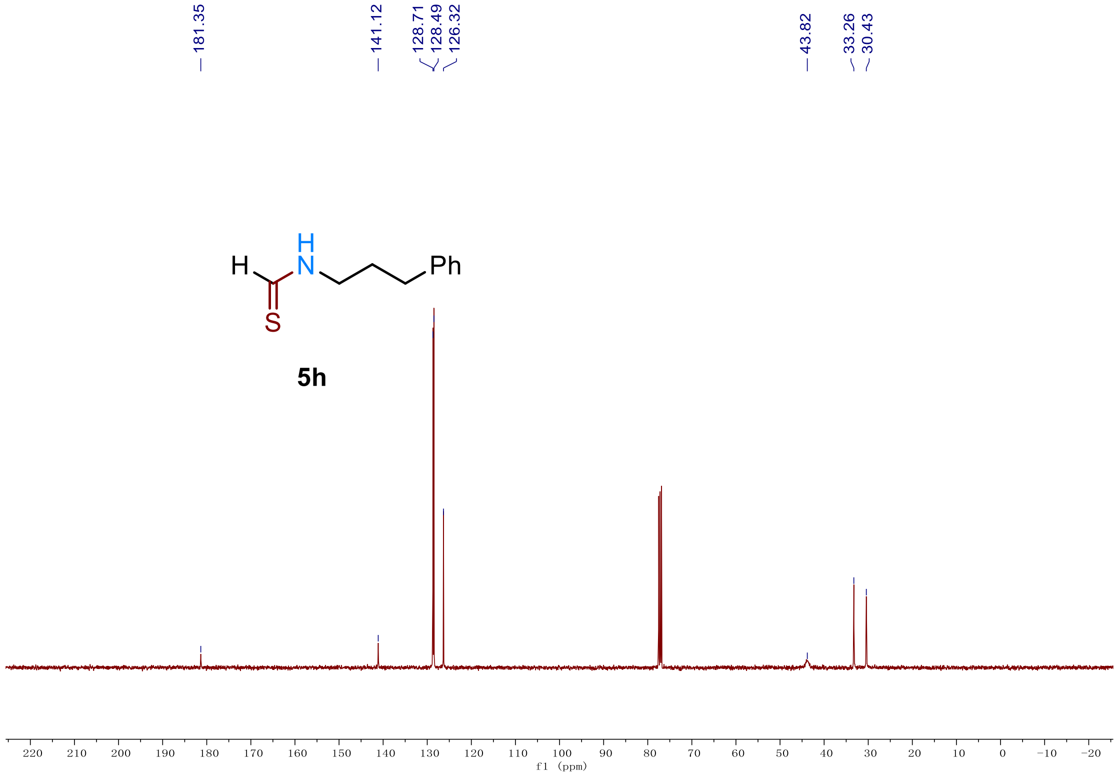
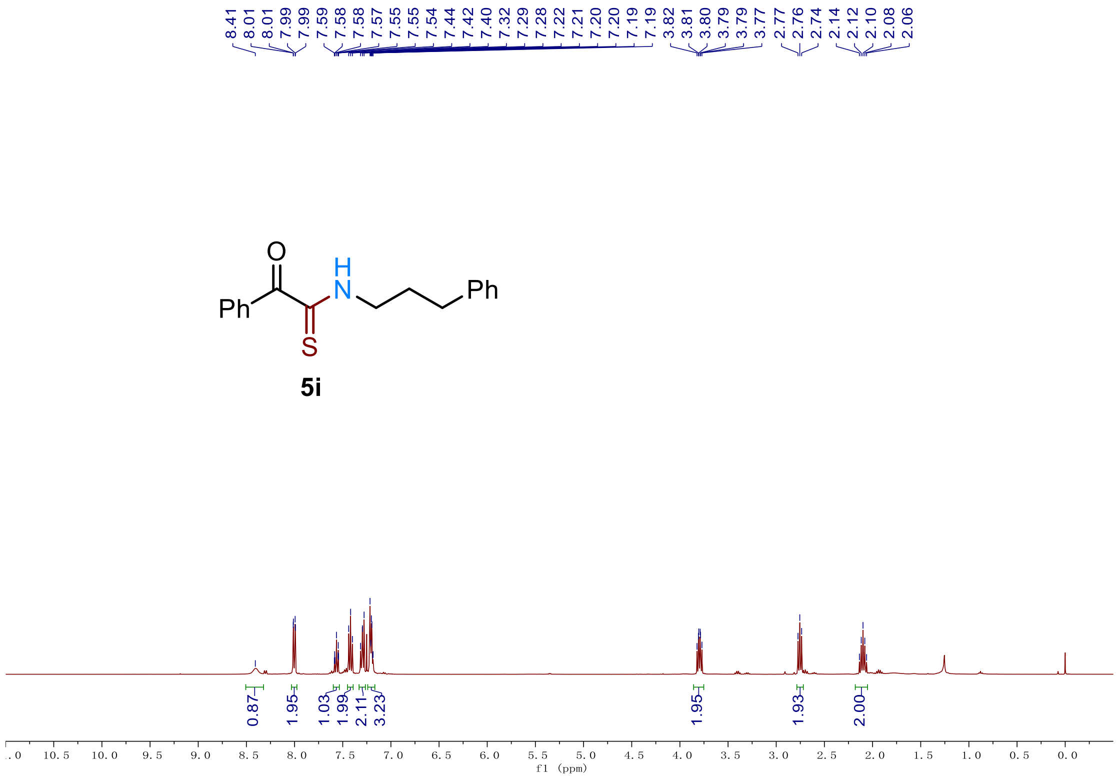
7.27
7.25
7.22
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.15
5.81
3.31
2.67
2.65
2.63
1.92
1.90
1.88
1.86
1.85
H
H
N
Ph
S
2.04
2.99
0.75
1.64
2.04
2.00
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

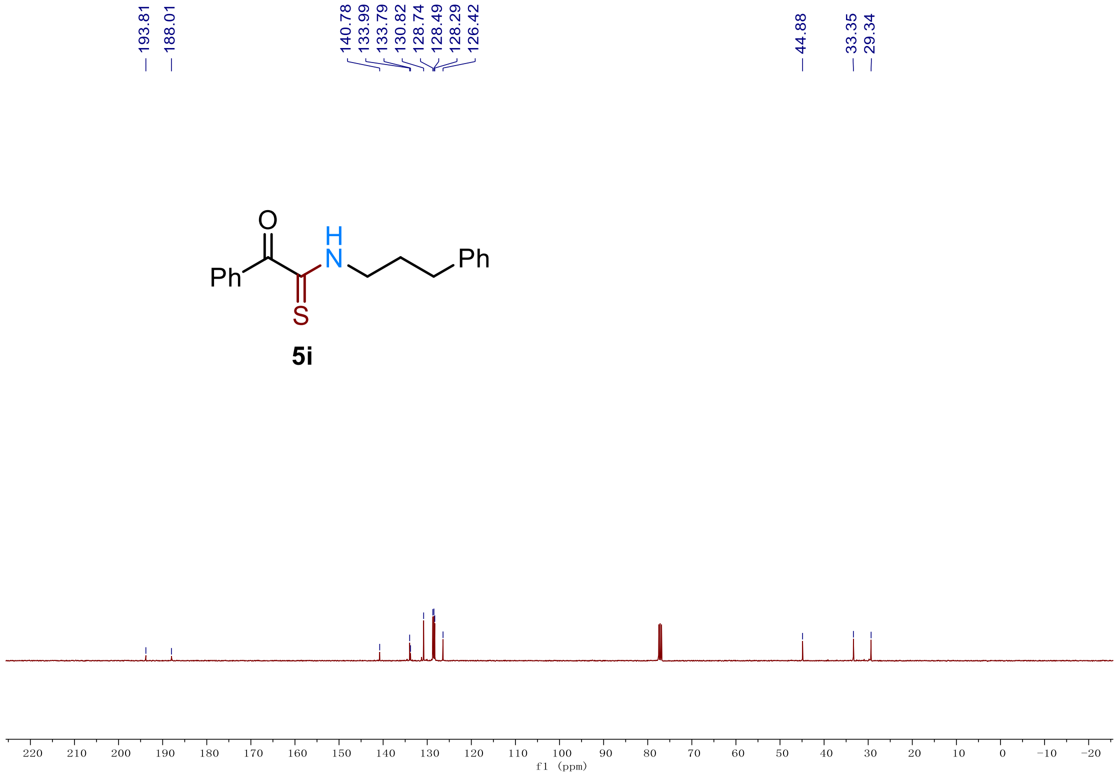
5h

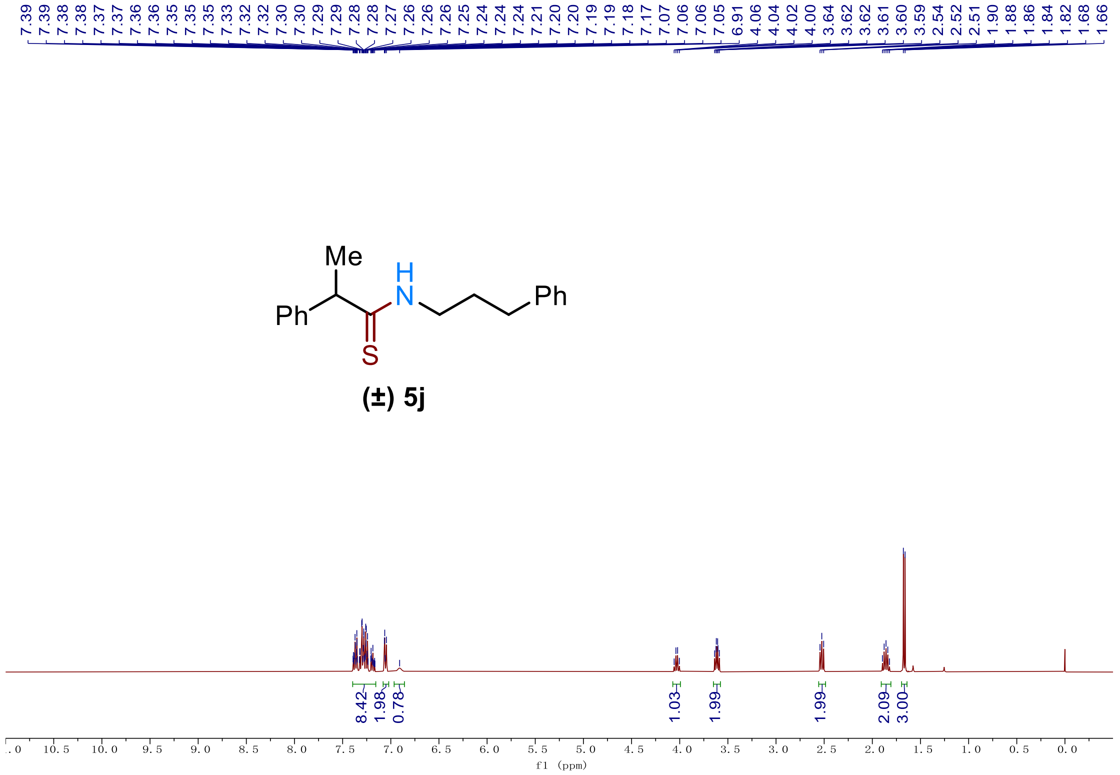

181.35
141.12
128.71
128.49
126.32
43.82
33.26
30.43
H
N
H
S
Ph
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

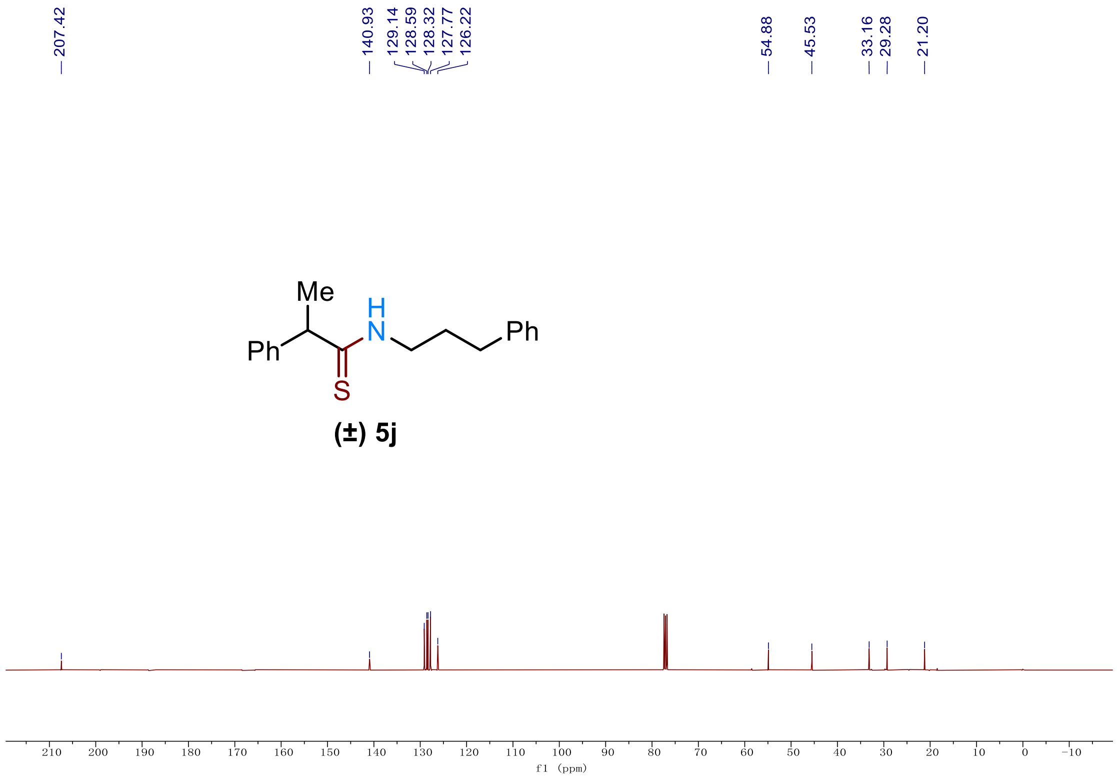
5h

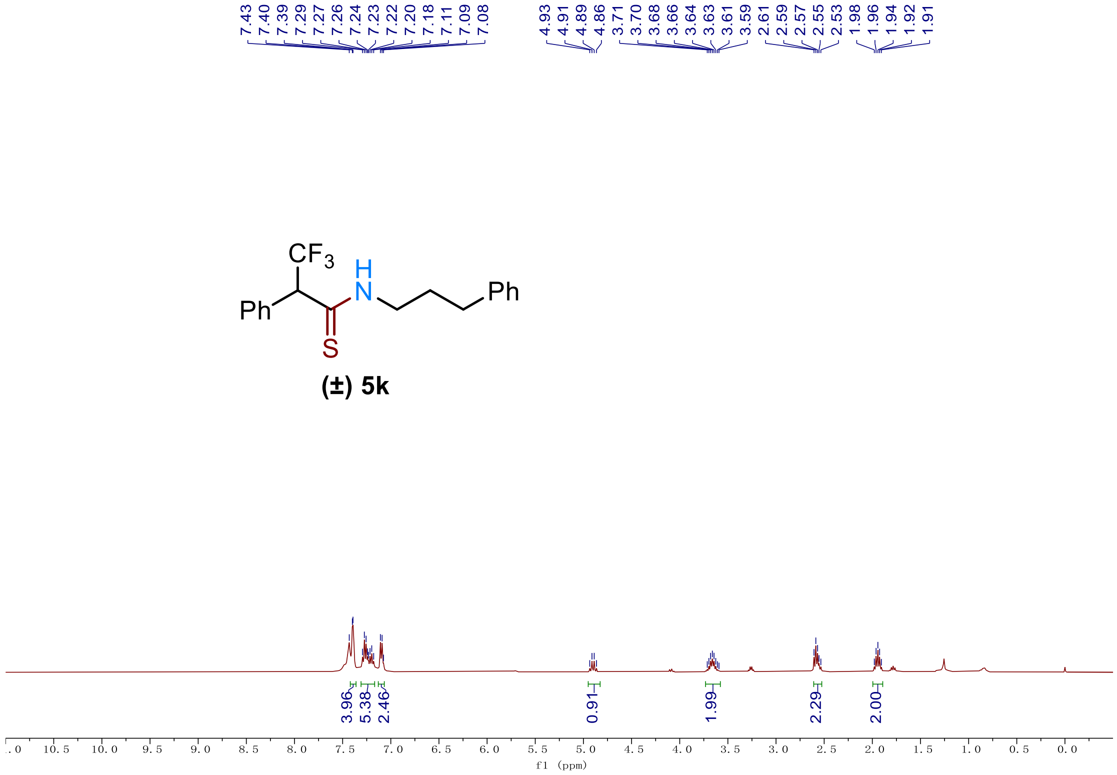

8.41
8.01
8.01
7.99
7.99
7.59
7.58
7.58
7.57
7.55
7.55
7.54
7.44
7.42
7.40
7.32
7.29
7.28
7.22
7.21
7.20
7.20
7.19
7.19
3.82
3.81
3.80
3.79
3.79
3.77
2.77
2.76
2.74
2.14
2.12
2.10
2.08
2.06
O
Ph
H
N
S
Ph
0.87
1.95
1.03
1.99
2.11
3.23
1.95
1.93
2.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

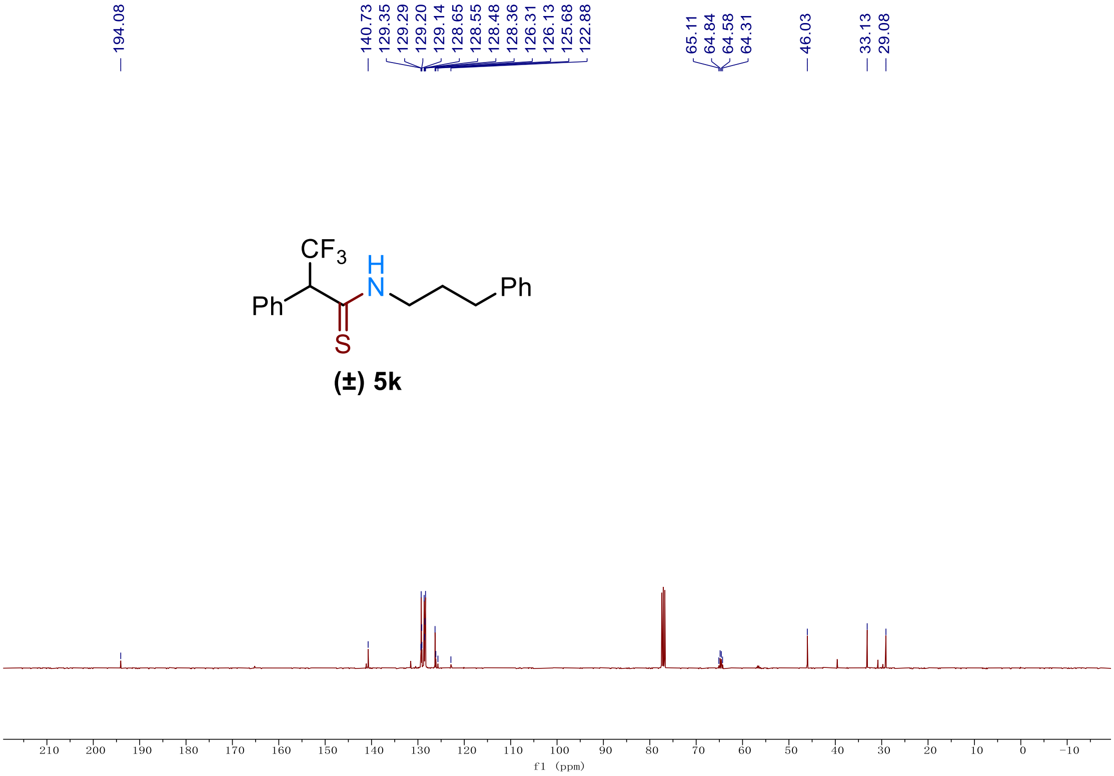
5i

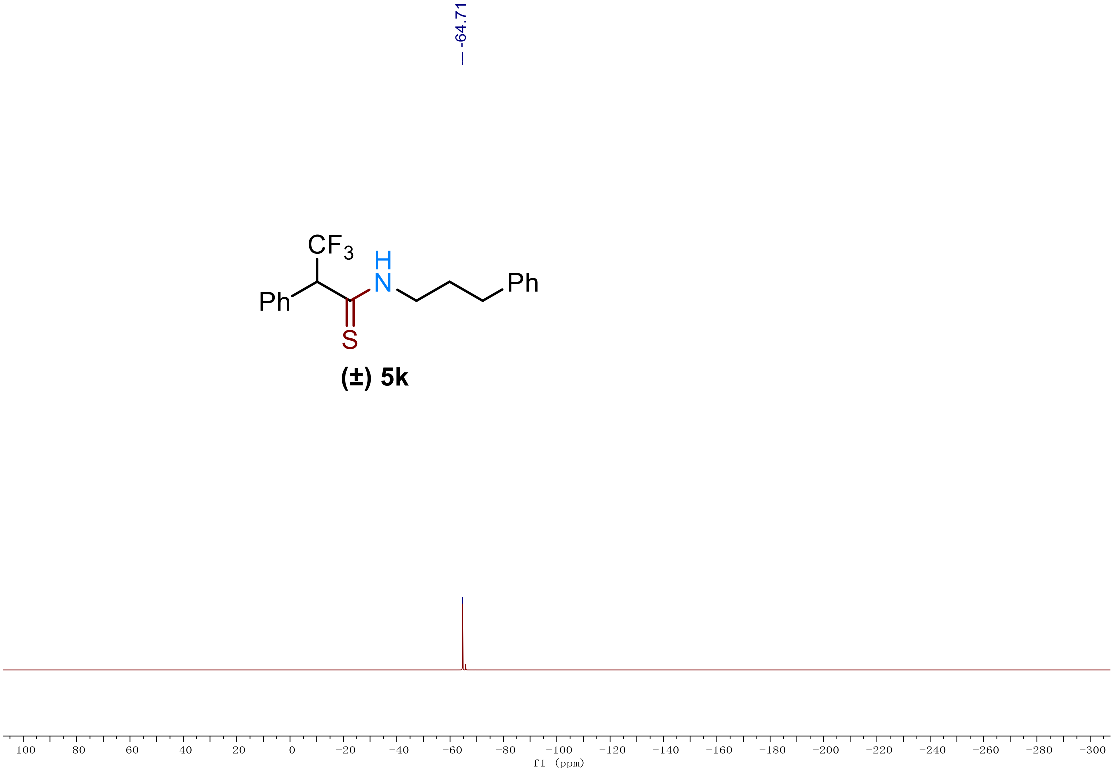

193.81
188.01
140.78
133.99
133.79
130.82
128.74
128.49
128.29
126.42
44.88
33.35
29.34
O
H
N
Ph
Ph
S
5i
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

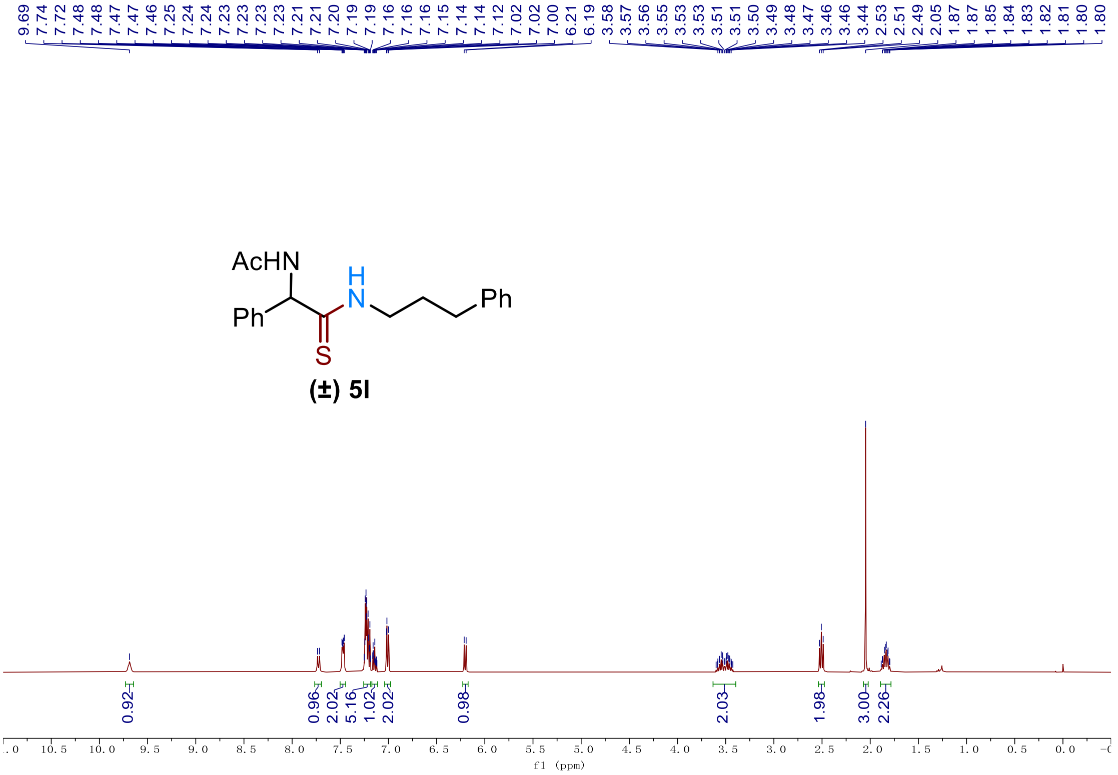

7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.35
7.33
7.32
7.32
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.24
7.21
7.20
7.20
7.19
7.18
7.17
7.07
7.06
7.06
7.05
6.91
4.06
4.04
4.02
4.00
3.64
3.62
3.61
3.60
3.59
2.54
2.52
2.51
1.90
1.88
1.86
1.84
1.82
1.68
1.66
Me
H
N
Ph
Ph
S
(±) 5j
8.42
1.98
0.78
1.03
1.99
1.99
2.09
3.00
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.42
140.93
129.14
128.59
128.32
127.77
126.22
54.88
45.53
33.16
29.28
21.20
Me
H
N
Ph
Ph
S
(±) 5j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

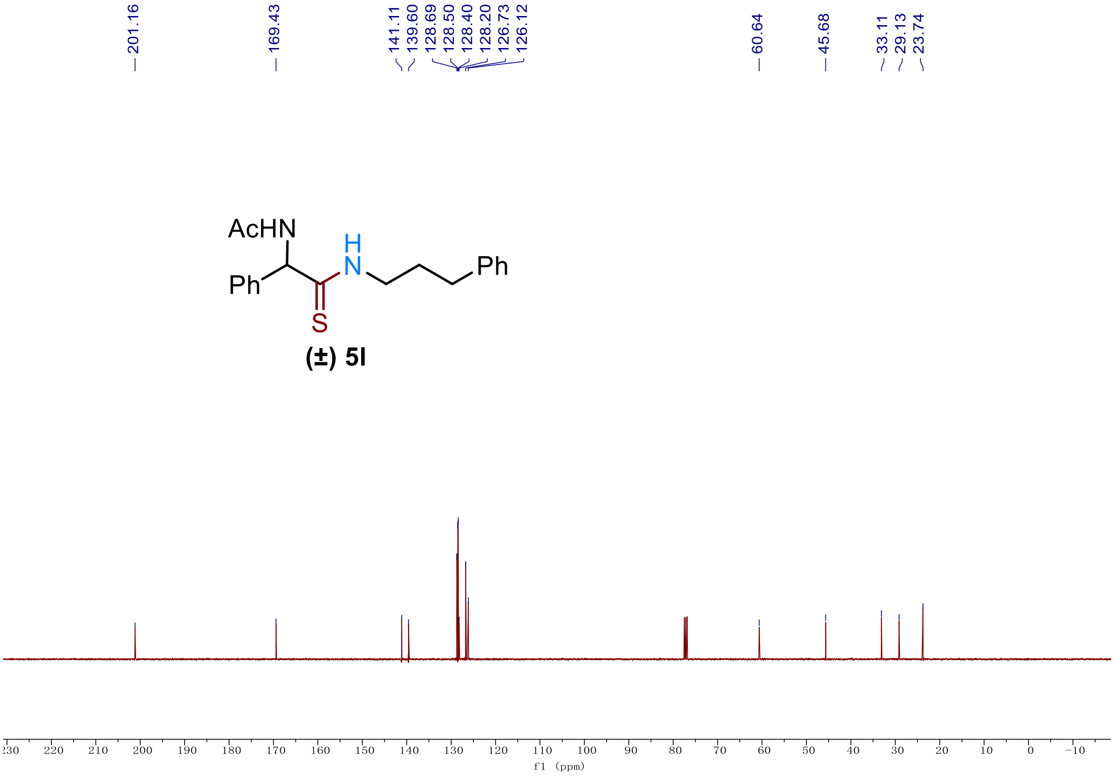

7.43
7.40
7.39
7.29
7.27
7.26
7.24
7.23
7.22
7.20
7.18
7.11
7.09
7.08
4.93
4.91
4.89
4.86
3.71
3.70
3.68
3.66
3.64
3.63
3.61
3.59
2.61
2.59
2.57
2.55
2.53
1.98
1.96
1.94
1.92
1.91
CF3
H
N
Ph
Ph
S
(±) 5k
3.96
5.38
2.46
0.91
1.99
2.29
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


194.08
140.73
129.35
129.29
129.20
129.14
128.65
128.55
128.48
128.36
126.31
126.13
125.68
122.88
65.11
64.84
64.58
64.31
46.03
33.13
29.08
CF3
H
N
Ph
Ph
S
(±) 5k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

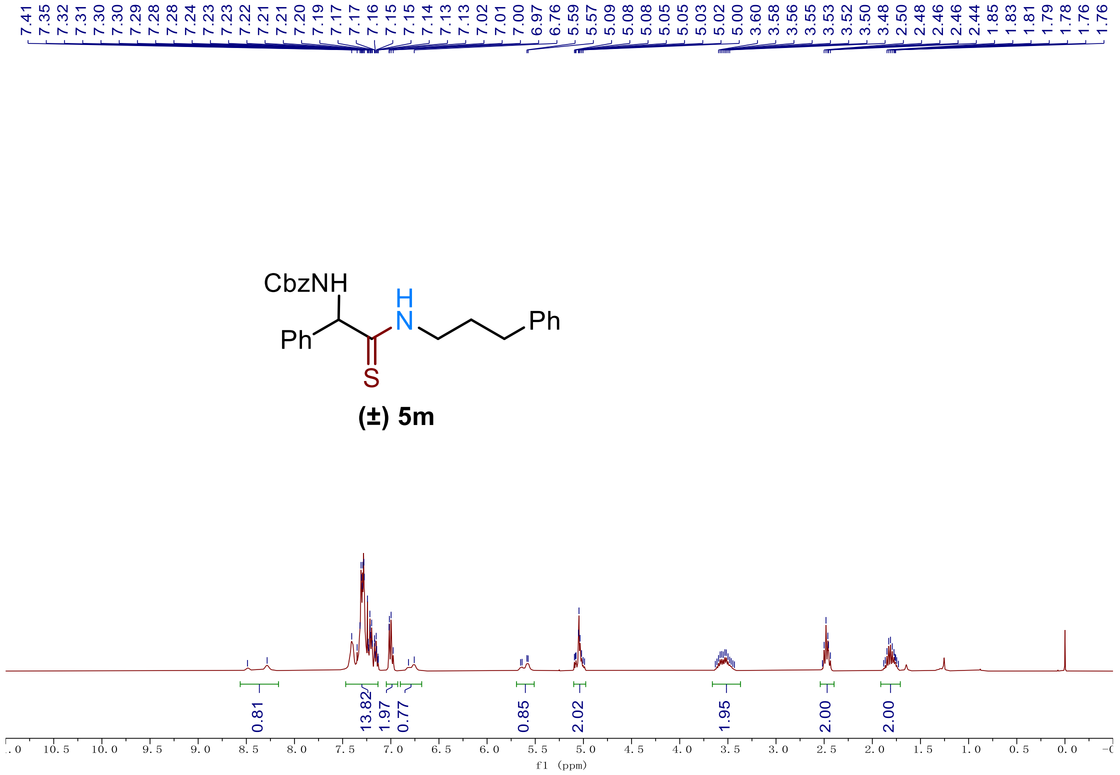

-64.71
CF3
H
N
Ph
Ph
S
(±) 5k
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)


9.69
7.74
7.72
7.48
7.48
7.47
7.47
7.46
7.25
7.24
7.24
7.23
7.23
7.23
7.21
7.21
7.20
7.19
7.19
7.16
7.16
7.15
7.14
7.14
7.12
7.02
7.02
7.00
6.21
6.19
3.58
3.57
3.56
3.55
3.53
3.53
3.51
3.51
3.50
3.49
3.48
3.47
3.46
3.46
3.44
2.53
2.51
2.49
2.05
1.87
1.87
1.85
1.84
1.83
1.82
1.81
1.80
1.80
AcHN
H
N
Ph
Ph
S
0.92
0.96
2.02
5.16
1.02
2.02
0.98
2.03
1.98
3.00
2.26
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

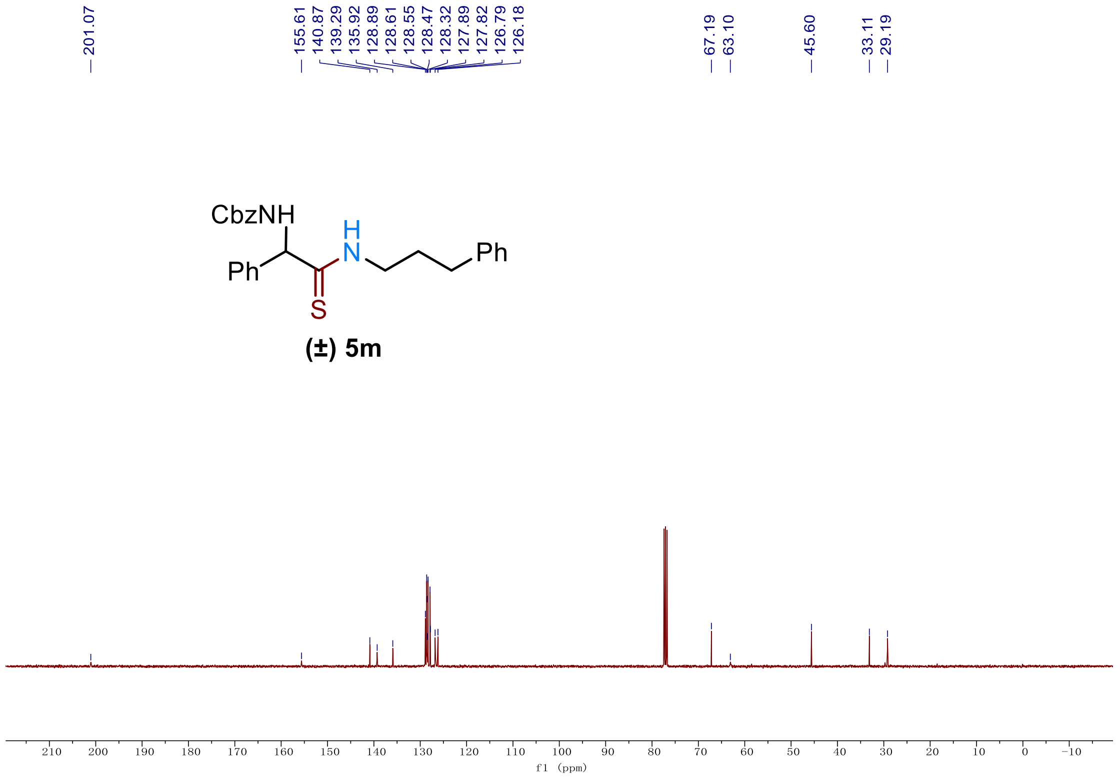
(±) 5l


201.16
169.43
141.11
139.60
128.69
128.50
128.40
128.20
126.73
126.12
60.64
45.68
33.11
29.13
23.74
AcHN
H
N
Ph
Ph
S
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

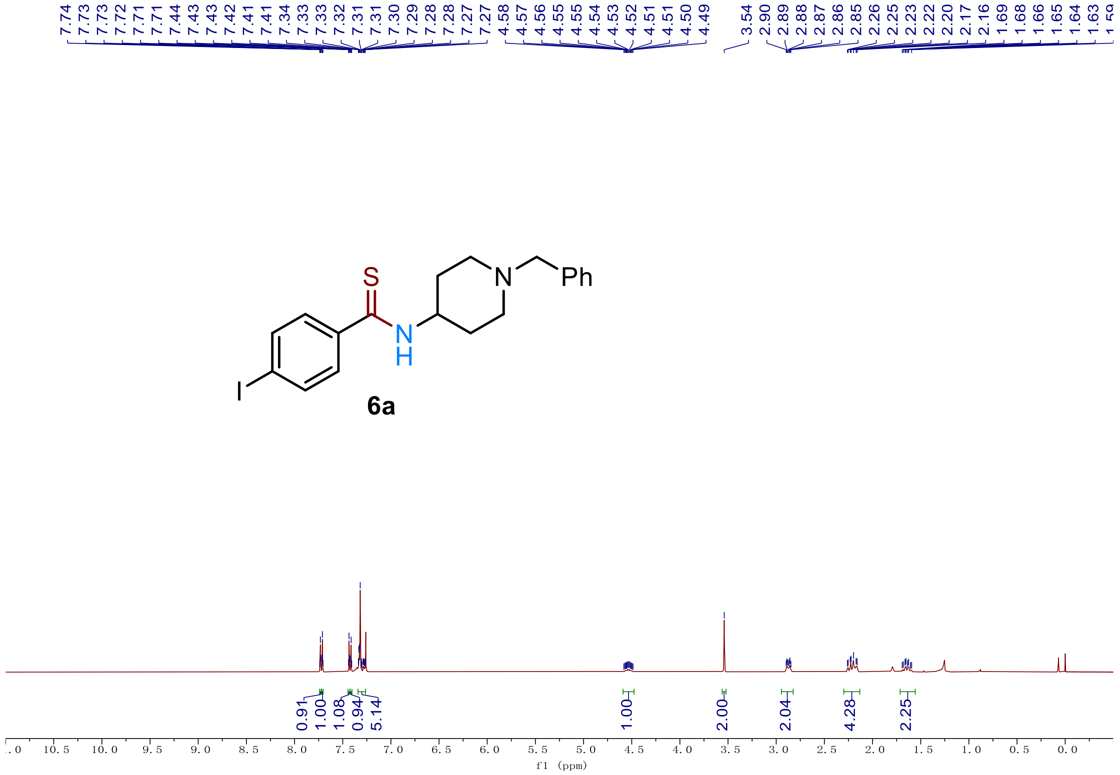
(±) 5l


7.41
7.35
7.32
7.31
7.30
7.29
7.28
7.28
7.24
7.23
7.22
7.21
7.21
7.20
7.19
7.17
7.17
7.16
7.15
7.15
7.14
7.13
7.13
7.02
7.01
7.00
6.97
6.76
5.59
5.57
5.09
5.08
5.08
5.05
5.05
5.03
5.02
5.00
3.60
3.58
3.56
3.55
3.53
3.52
3.50
3.48
2.50
2.48
2.46
2.46
2.44
1.85
1.83
1.81
1.79
1.78
1.76
1.76
CbzNH
H
N
Ph
Ph
S
0.81
13.82
1.97
0.77
0.85
2.02
1.95
2.00
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(±) 5m


201.07
155.61
140.87
139.29
135.92
128.89
128.61
128.55
128.47
128.32
127.89
127.82
126.79
126.18
67.19
63.10
45.60
33.11
29.19
CbzNH
H
N
Ph
Ph
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

(±) 5m


7.74
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7.71
7.44
7.43
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7.42
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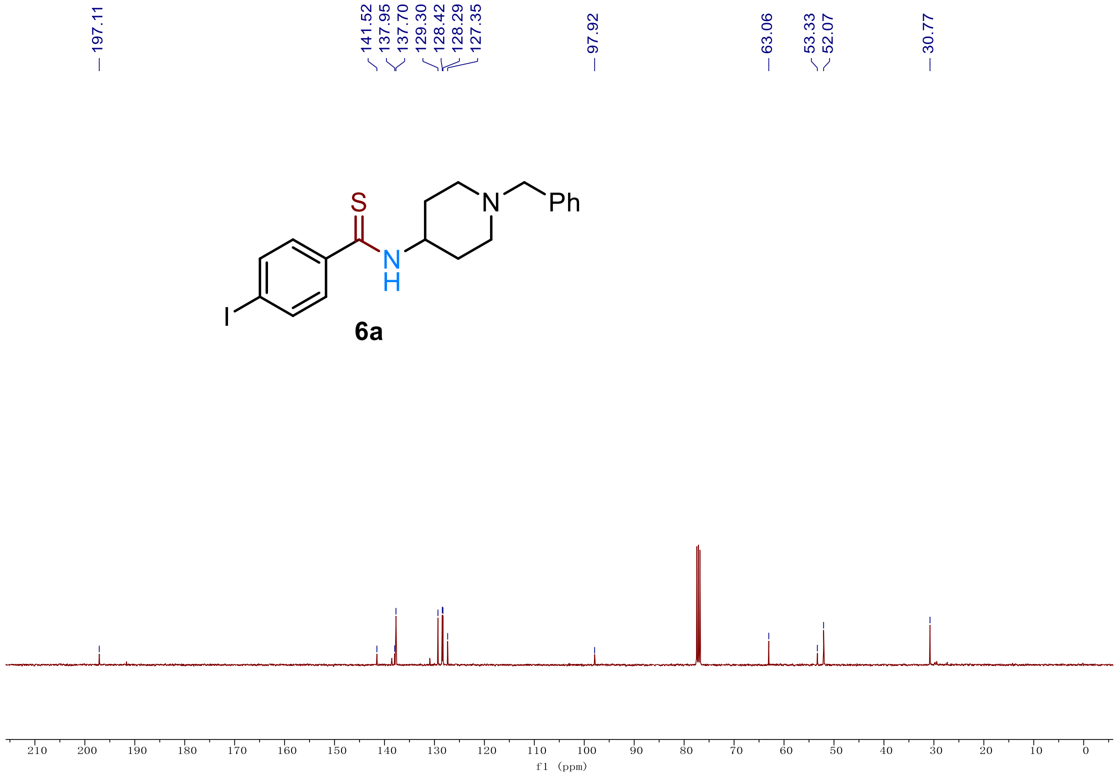
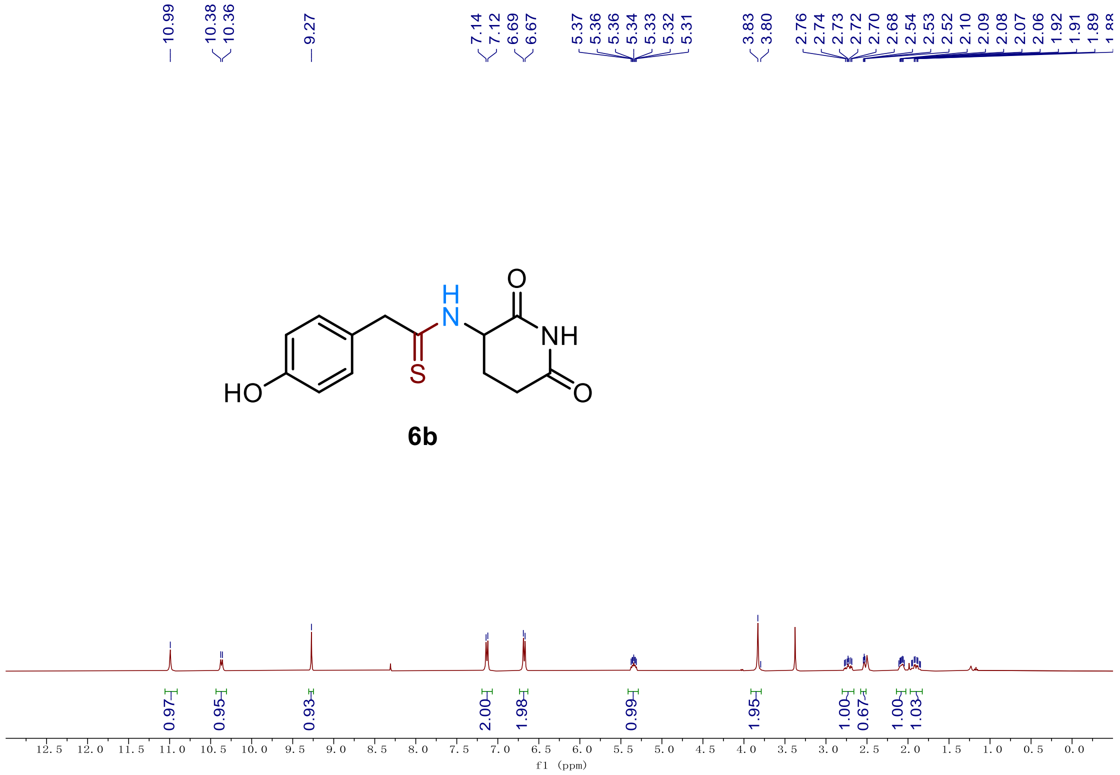
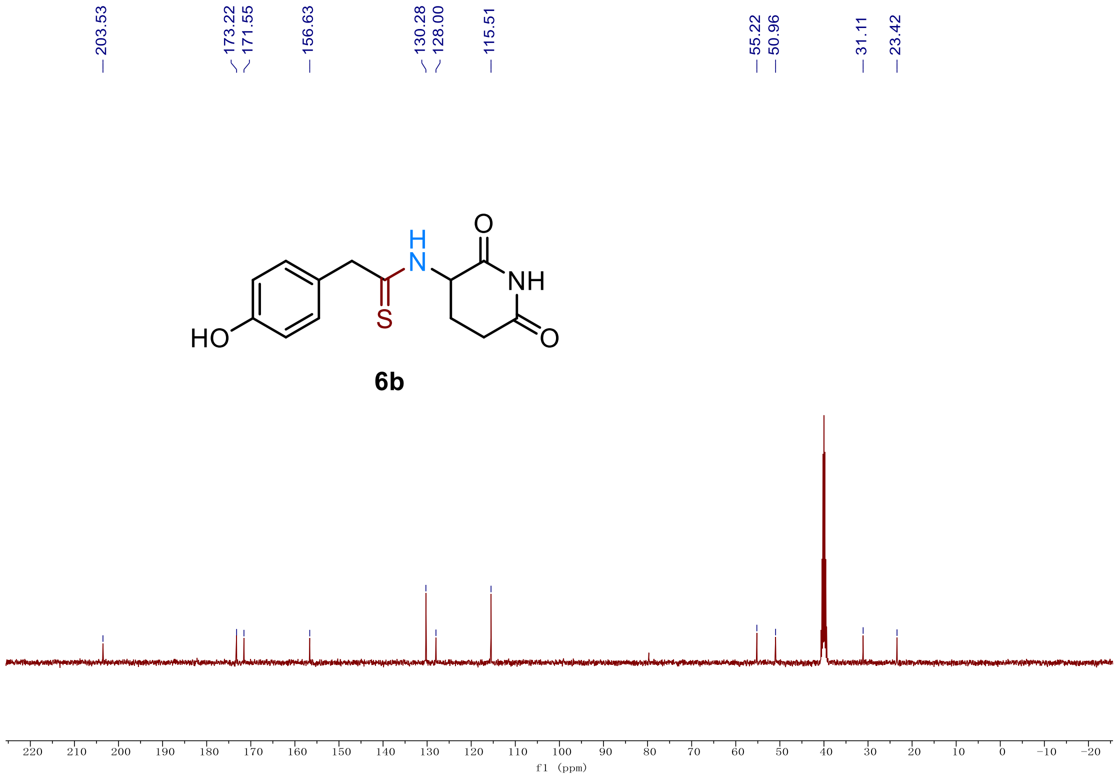
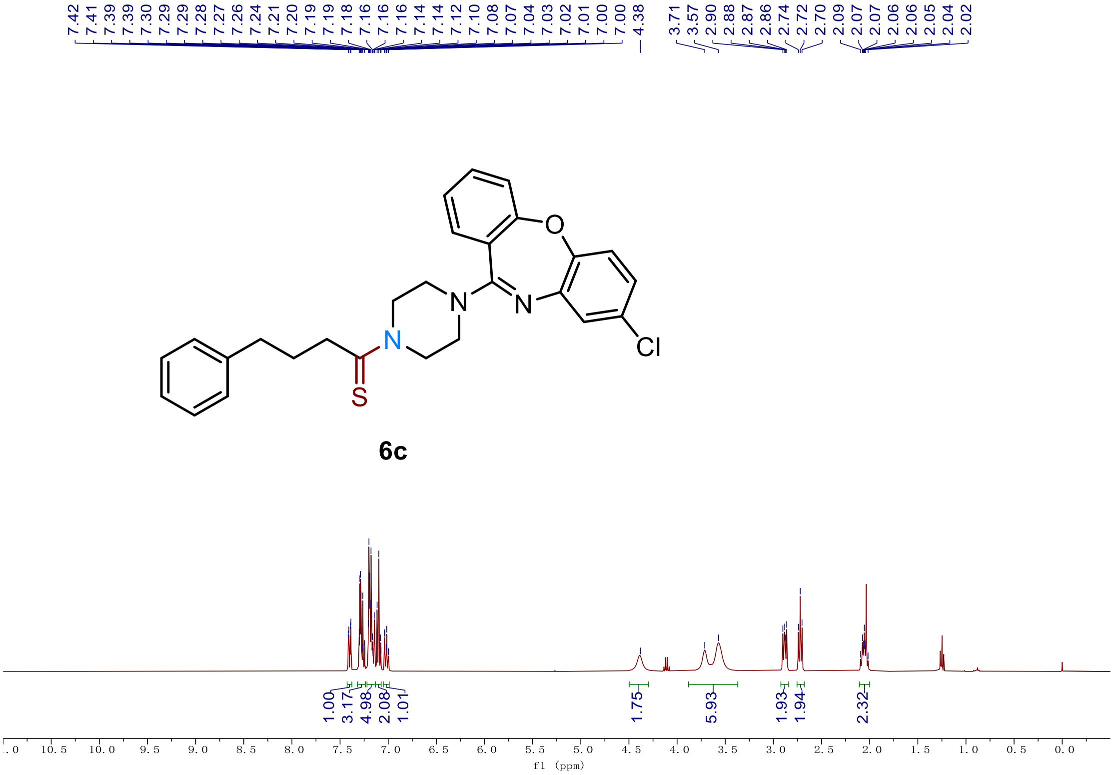
7.41
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.28
7.27
4.58
4.57
4.56
4.55
4.54
4.53
4.52
4.51
4.51
4.50
4.49
3.54
2.90
2.89
2.88
2.87
2.86
2.85
2.26
2.25
2.23
2.22
2.20
2.17
2.16
1.69
1.68
1.66
1.65
1.64
1.63
1.5
S
N
H
N
Ph
I
6a
0.91
1.00
1.08
0.94
5.14
1.00
2.00
2.04
4.28
2.25
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.11
141.52
137.95
137.70
129.30
128.42
128.29
127.35
97.92
63.06
53.33
52.07
30.77
S
N
H
N
Ph
I
6a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.99
10.38
10.36
9.27
7.14
7.12
6.69
6.67
5.37
5.36
5.36
5.34
5.33
5.32
5.31
3.83
3.80
2.76
2.74
2.73
2.72
2.70
2.68
2.54
2.53
2.52
2.10
2.09
2.08
2.07
2.06
1.92
1.91
1.89
1.88
H
N
O
NH
S
HO
O
6b
0.97
0.95
0.93
2.00
1.98
0.99
1.95
1.00
0.67
1.00
1.03
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


203.53
173.22
171.55
156.63
130.28
128.00
115.51
55.22
50.96
31.11
23.42
H
N
O
NH
S
HO
O
6b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.42
7.41
7.39
7.39
7.30
7.29
7.29
7.28
7.27
7.26
7.24
7.21
7.20
7.19
7.19
7.18
7.16
7.16
7.16
7.14
7.14
7.12
7.10
7.08
7.07
7.04
7.03
7.02
7.01
7.00
7.00
4.38
3.71
3.57
2.90
2.88
2.87
2.86
2.74
2.72
2.70
2.09
2.07
2.07
2.06
2.05
2.04
2.02
O
N
N
N
Cl
S
1.00
3.17
4.98
2.08
1.01
1.75
5.93
1.93
1.94
2.32
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
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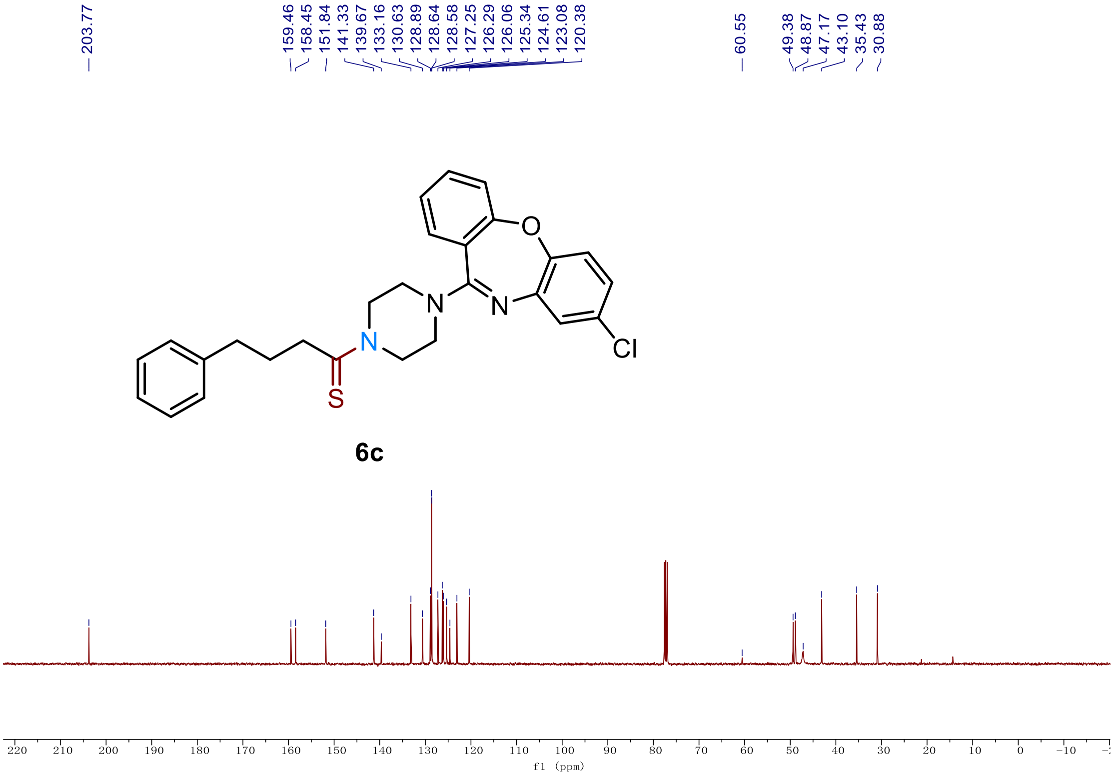
0.0
f1 (ppm)

6c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128.64
128.58
127.25
126.29
126.06
125.34
124.61
123.08
120.38
60.55
49.38
48.87
47.17
43.10
35.43
30.88
O
N
N
N
Cl
S
220
210
200
190
180
170
160
150
140
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100
90
80
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60
50
40
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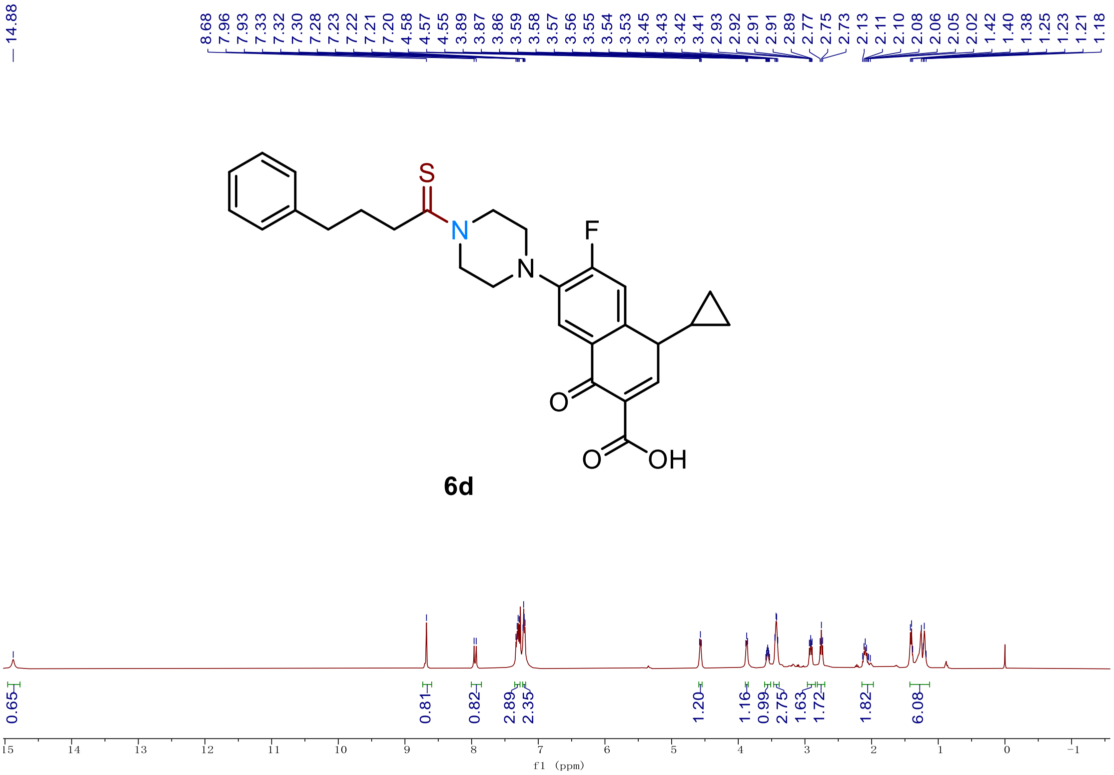
20
10
0
-10
f1 (ppm)

6c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7.20
4.58
4.57
4.55
3.89
3.87
3.86
3.59
3.58
3.57
3.56
3.55
3.54
3.53
3.45
3.43
3.42
3.41
2.93
2.92
2.91
2.91
2.89
2.77
2.75
2.73
2.13
2.11
2.10
2.08
2.06
2.05
2.02
1.42
1.40
1.38
1.25
1.23
1.21
1.18
S
N
N
F
O
O
OH
6d
0.65
0.81
0.82
2.89
2.35
1.20
1.16
0.99
2.75
1.63
1.72
1.82
6.08
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12
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8
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3
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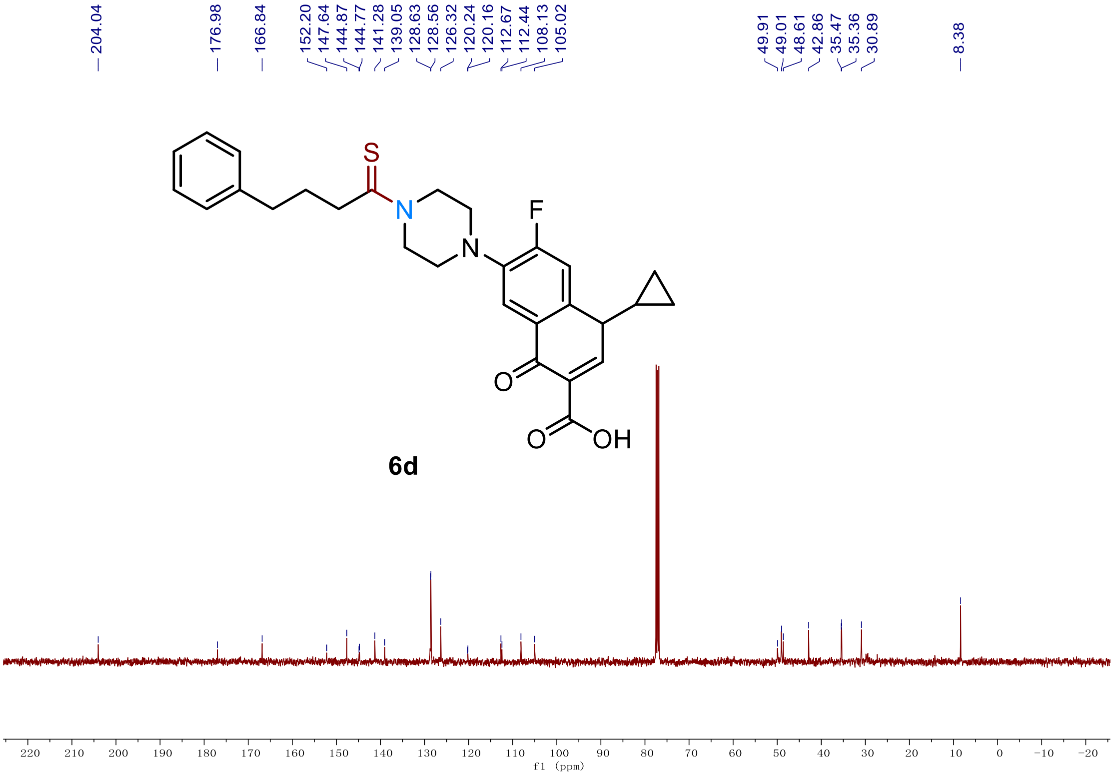
-1
f1 (ppm)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139.05
128.63
128.56
126.32
120.24
120.16
112.67
112.44
108.13
105.02
49.91
49.01
48.61
42.86
35.47
35.36
30.89
8.38
S
N
N
F
O
O
OH
6d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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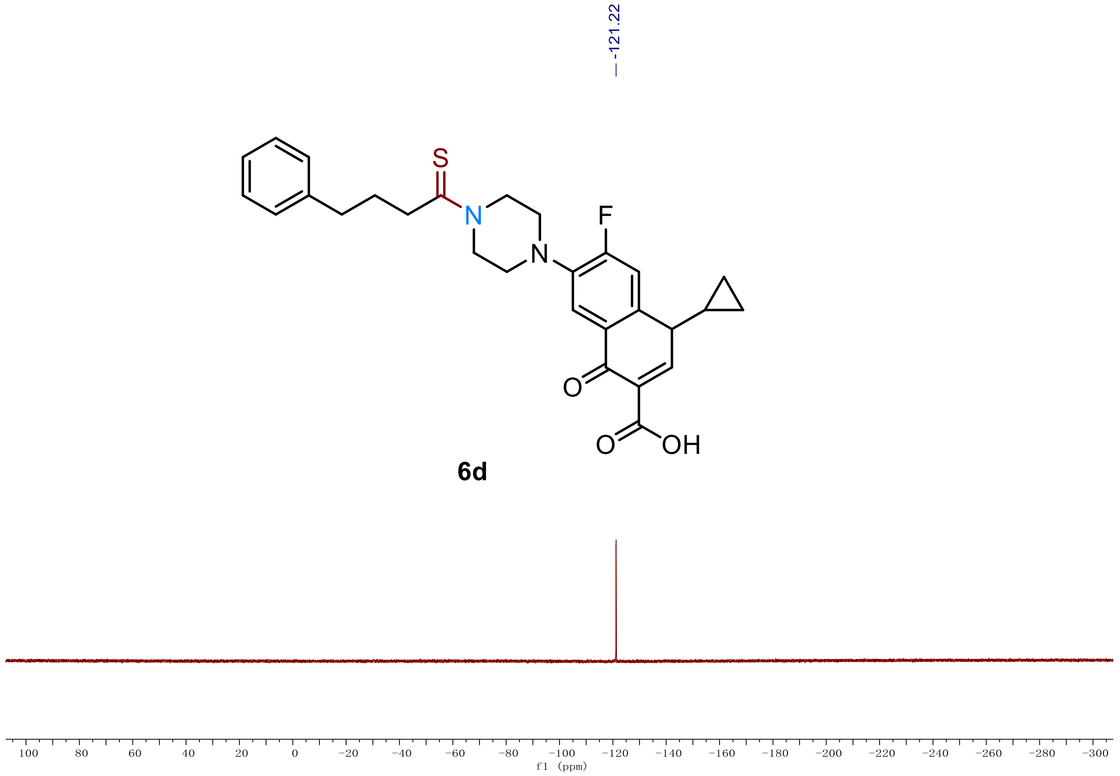
-10
-20
f1 (ppm)


-121.22
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N
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O
OH
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20
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−20
−40
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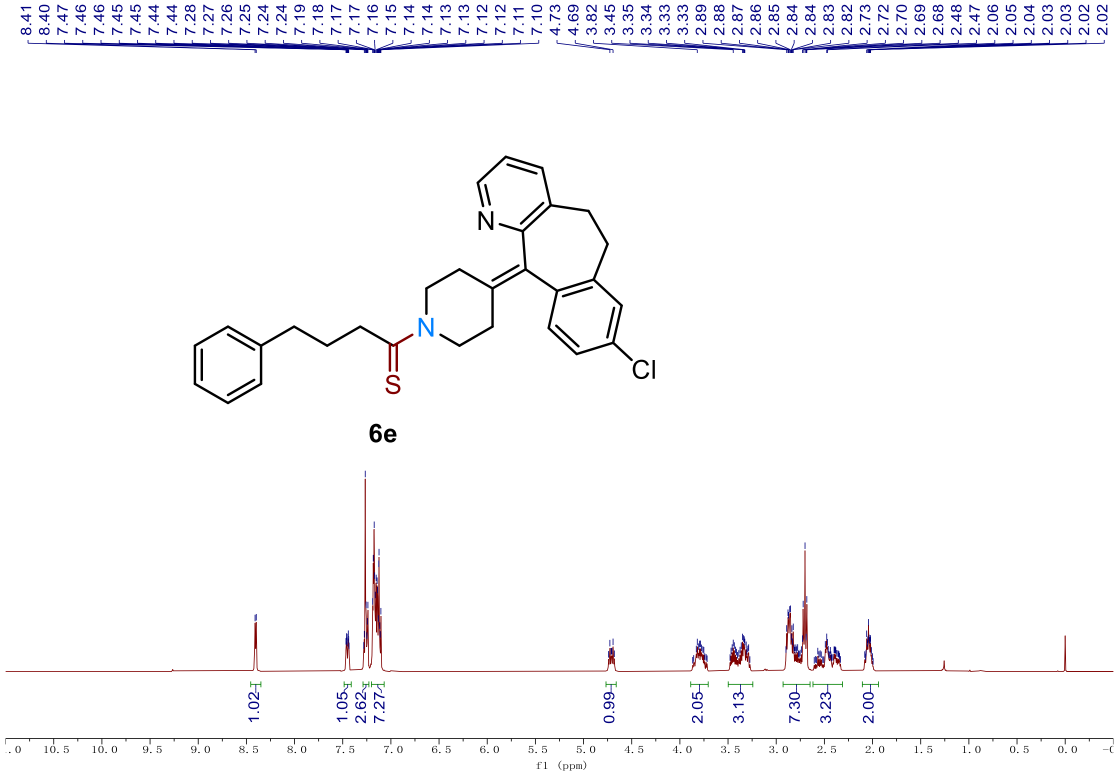
−140
−160
−180
−200
−220
−240
−260
−280
−300
f1 (ppm)

6d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8.40
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7.46
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7.44
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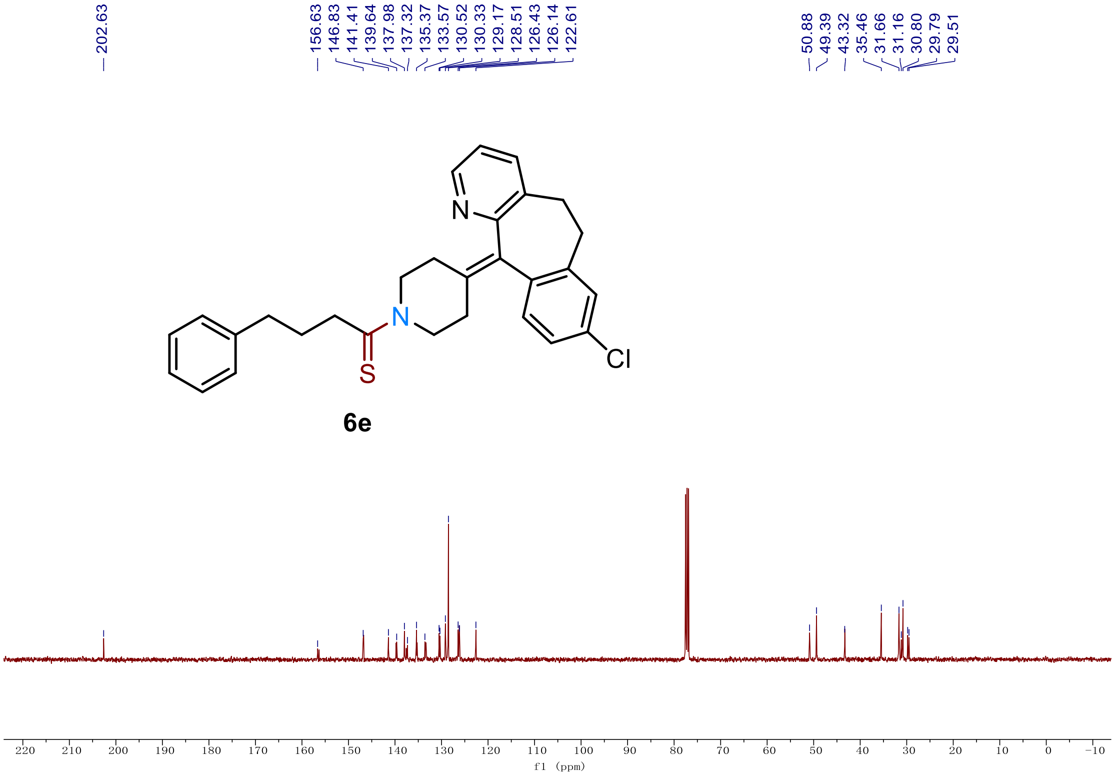
7.24
7.24
7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.10
4.73
4.69
3.82
3.45
3.35
3.34
3.33
3.33
2.89
2.88
2.87
2.86
2.85
2.84
2.84
2.83
2.82
2.73
2.72
2.70
2.69
2.68
2.48
2.47
2.06
2.05
2.04
2.03
2.02
2.02
N
N
S
Cl
1.02
1.05
2.62
7.27
0.99
2.05
3.13
7.30
3.23
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

6e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156.63
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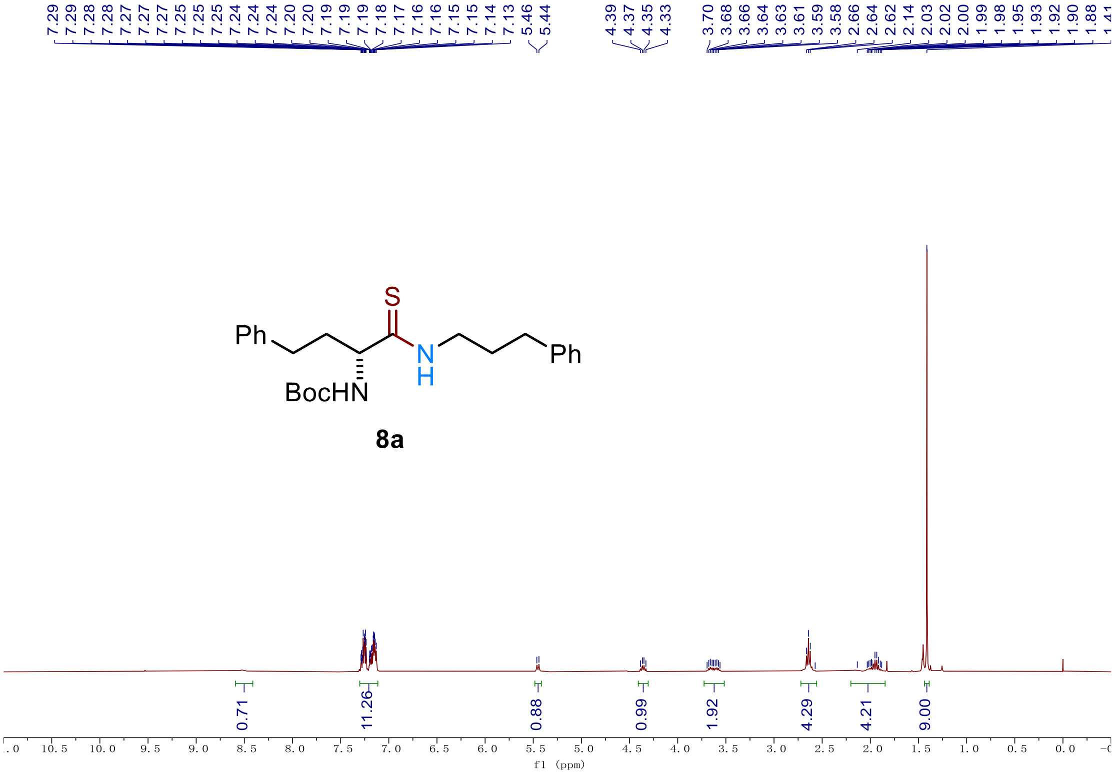
141.41
139.64
137.98
137.32
135.37
133.57
130.52
130.33
129.17
128.51
126.43
126.14
122.61
50.88
49.39
43.32
35.46
31.66
31.16
30.80
29.79
29.51
N
N
S
Cl
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

6e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7.27
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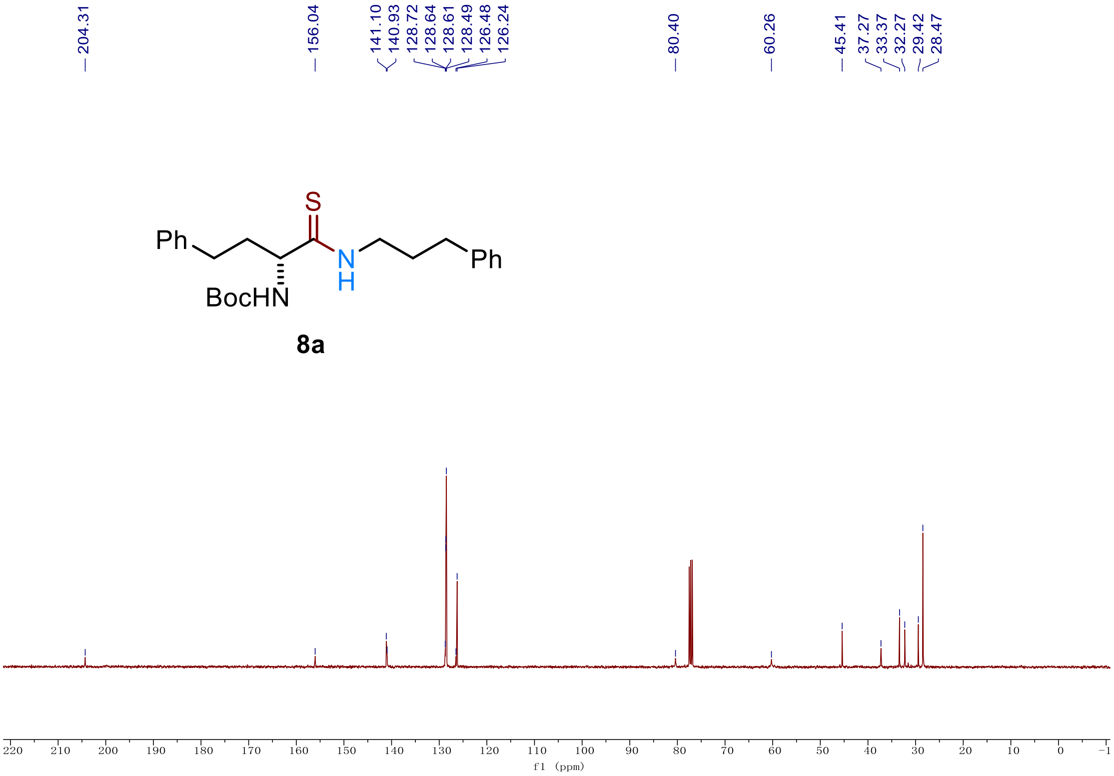
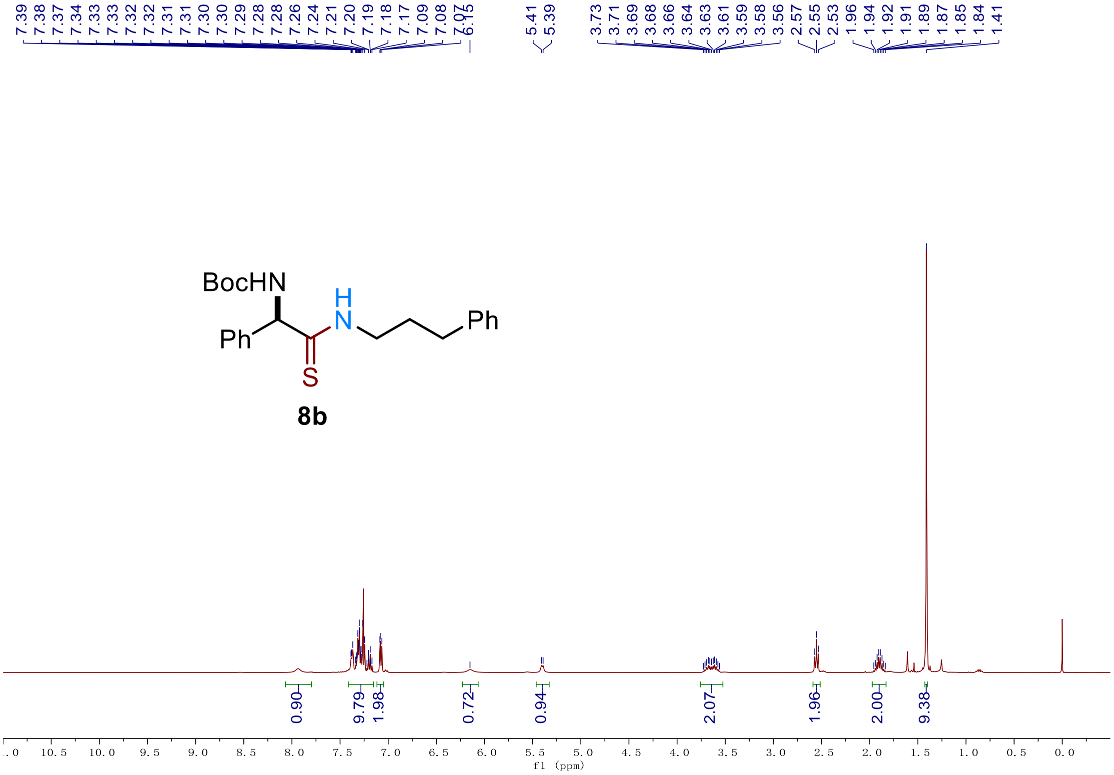
7.24
7.24
7.20
7.20
7.19
7.19
7.19
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.13
5.46
5.44
4.39
4.37
4.35
4.33
3.70
3.68
3.66
3.64
3.63
3.61
3.59
3.58
2.66
2.64
2.62
2.14
2.03
2.02
2.00
1.99
1.98
1.95
1.93
1.92
1.90
1.88
1.41
S
Ph
N
H
Ph
BocHN
0.71
11.26
0.88
0.99
1.92
4.29
4.21
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

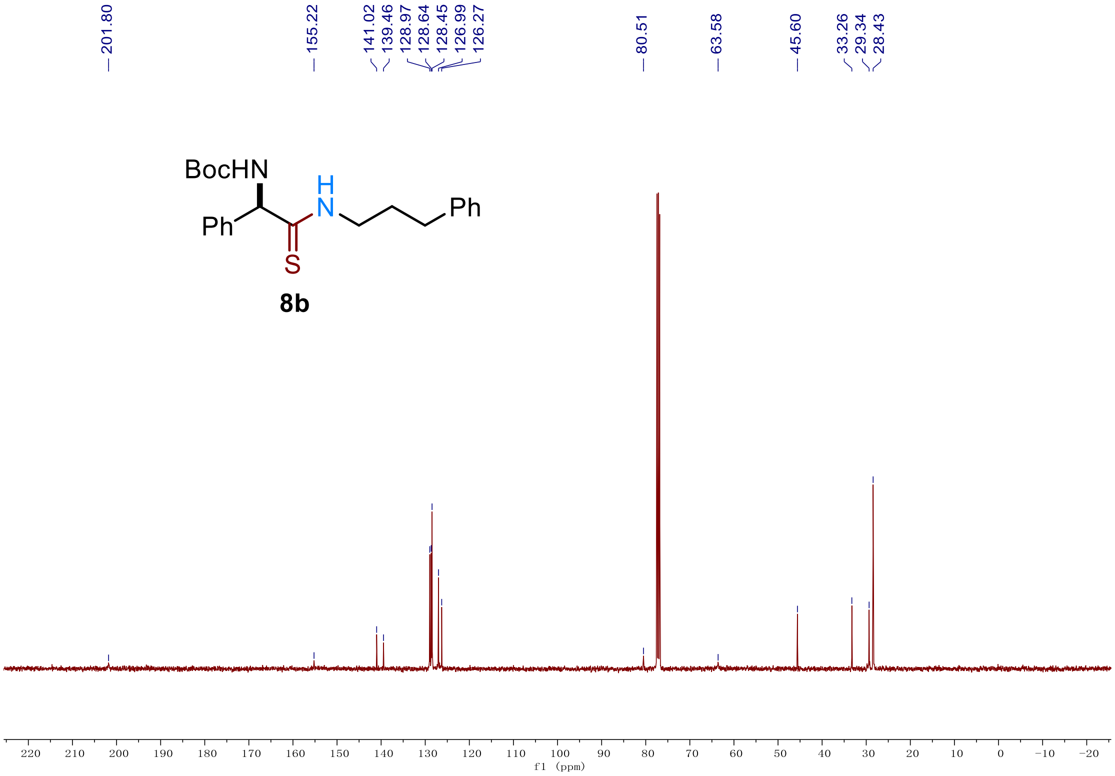
8a


204.31
156.04
141.10
140.93
128.72
128.64
128.61
128.49
126.48
126.24
80.40
60.26
45.41
37.27
33.37
32.27
29.42
28.47
S
Ph
N
H
Ph
BocHN
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

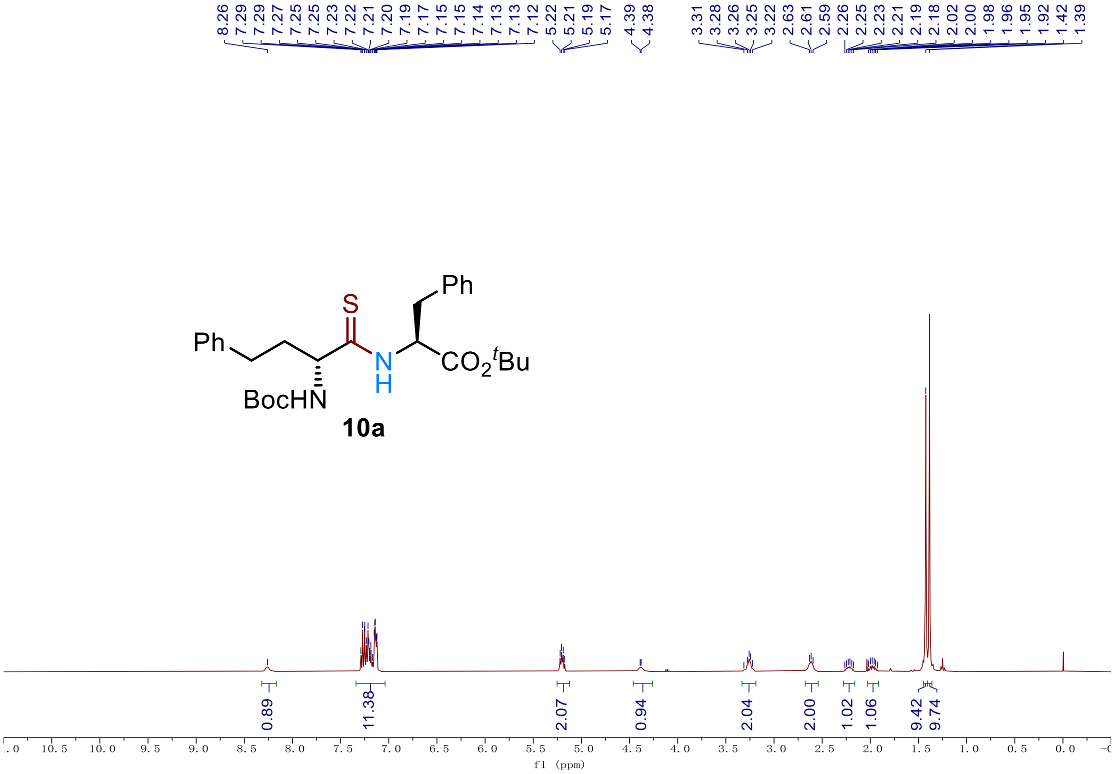
8a


7.39
7.38
7.37
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.28
7.28
7.26
7.24
7.21
7.20
7.19
7.18
7.17
7.09
7.08
7.07
6.15
5.41
5.39
3.73
3.71
3.69
3.68
3.66
3.64
3.63
3.61
3.59
3.58
3.56
2.57
2.55
2.53
1.96
1.94
1.92
1.91
1.89
1.87
1.85
1.84
1.41
BocHN
H
N
Ph
Ph
S
0.90
9.79
1.98
0.72
0.94
2.07
1.96
2.00
9.38
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

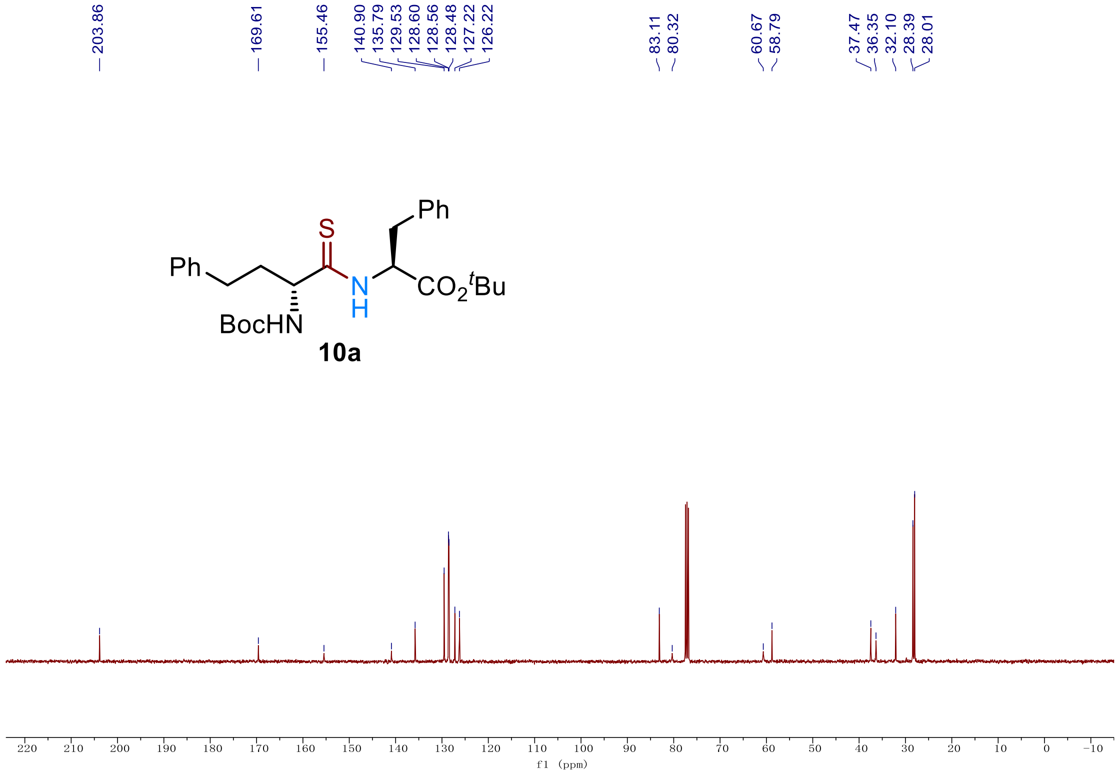
8b


201.80
155.22
141.02
139.46
128.97
128.64
128.45
126.99
126.27
80.51
63.58
45.60
33.26
29.34
28.43
BocHN
H
N
Ph
Ph
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

8b


8.26 7.29 7.29 7.27 7.25 7.25 7.23 7.23 7.22 7.21 7.20 7.19 7.17 7.15 7.15 7.14 7.13 7.13 7.12 5.22 5.21 5.19 5.17 4.39 4.38 3.31 3.28 3.26 3.25 3.22 2.63 2.61 2.59 2.26 2.25 2.23 2.21 2.19 2.18 2.02 2.00 1.98 1.96 1.95 1.92 1.42 1.39
Ph
S
Ph
N
H
CO2tBu
BocHN
0.89
11.38
2.07
0.94
2.04
2.00
1.02
1.06
9.42
9.74
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

10a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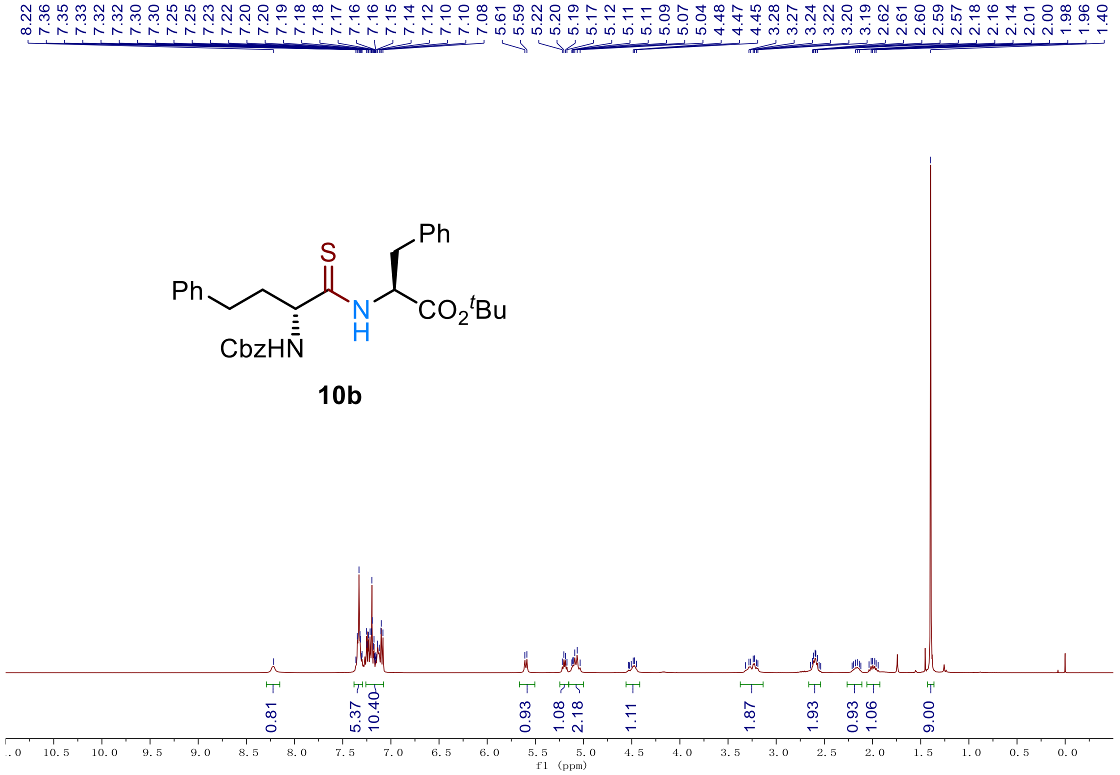
128.56
128.48
127.22
126.22
83.11
80.32
60.67
58.79
37.47
36.35
32.10
28.39
28.01
Ph
S
Ph
N
H
CO2tBu
BocHN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

10a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7.30
7.30
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7.25
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7.22
7.20
7.20
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.14
7.12
7.10
7.10
7.08
5.61
5.59
5.22
5.20
5.19
5.17
5.12
5.11
5.11
5.09
5.07
5.04
4.48
4.47
4.45
3.28
3.27
3.24
3.22
3.20
3.19
2.62
2.61
2.60
2.59
2.57
2.18
2.16
2.14
2.01
2.00
1.98
1.96
1.40
Ph
S
Ph
N
H
CO2tBu
CbzHN
0.81
5.37
10.40
0.93
1.08
2.18
1.11
1.87
1.93
0.93
1.06
9.00
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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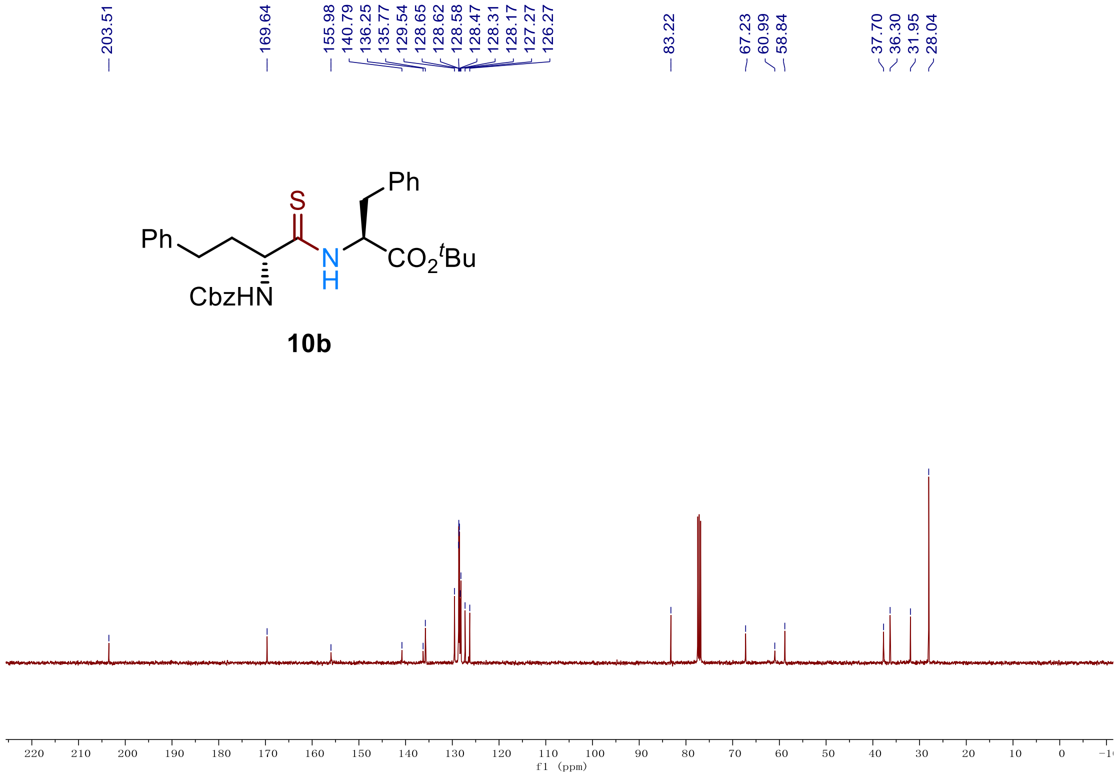
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

10b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136.25
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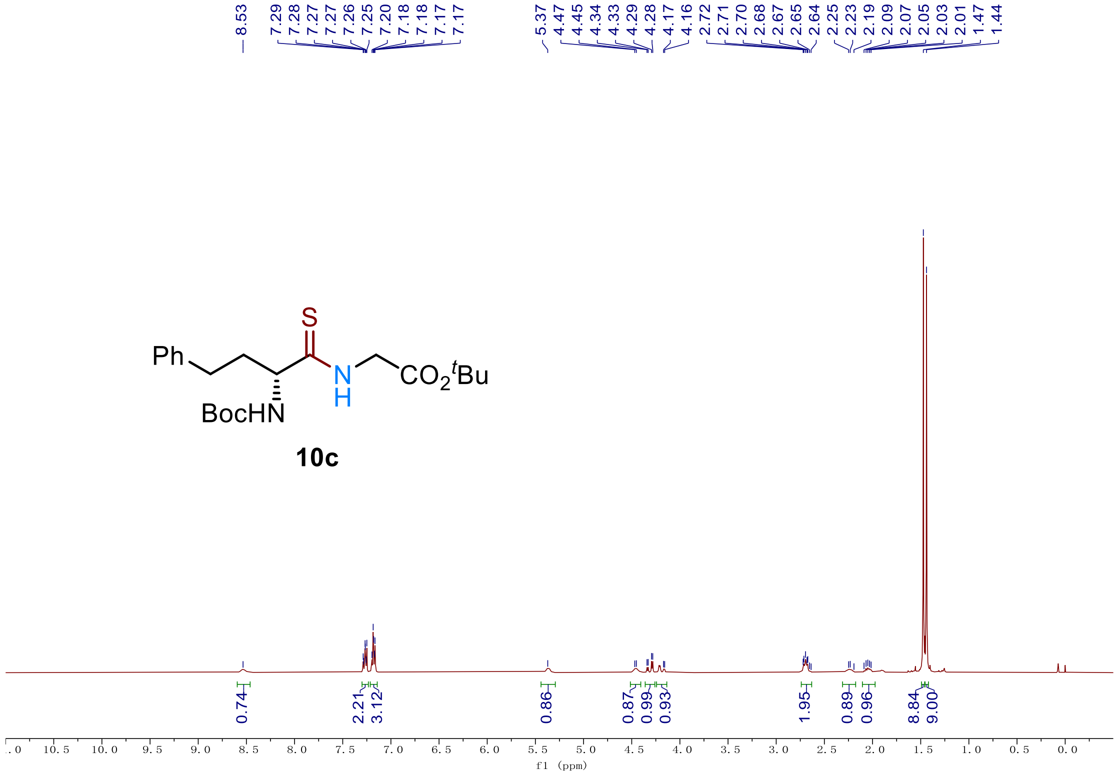
129.54
128.65
128.62
128.58
128.47
128.31
128.17
127.27
126.27
83.22
67.23
60.99
58.84
37.70
36.30
31.95
28.04
Ph
S
Ph
N
H
$CO_2{}^tBu$
CbzHN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

10b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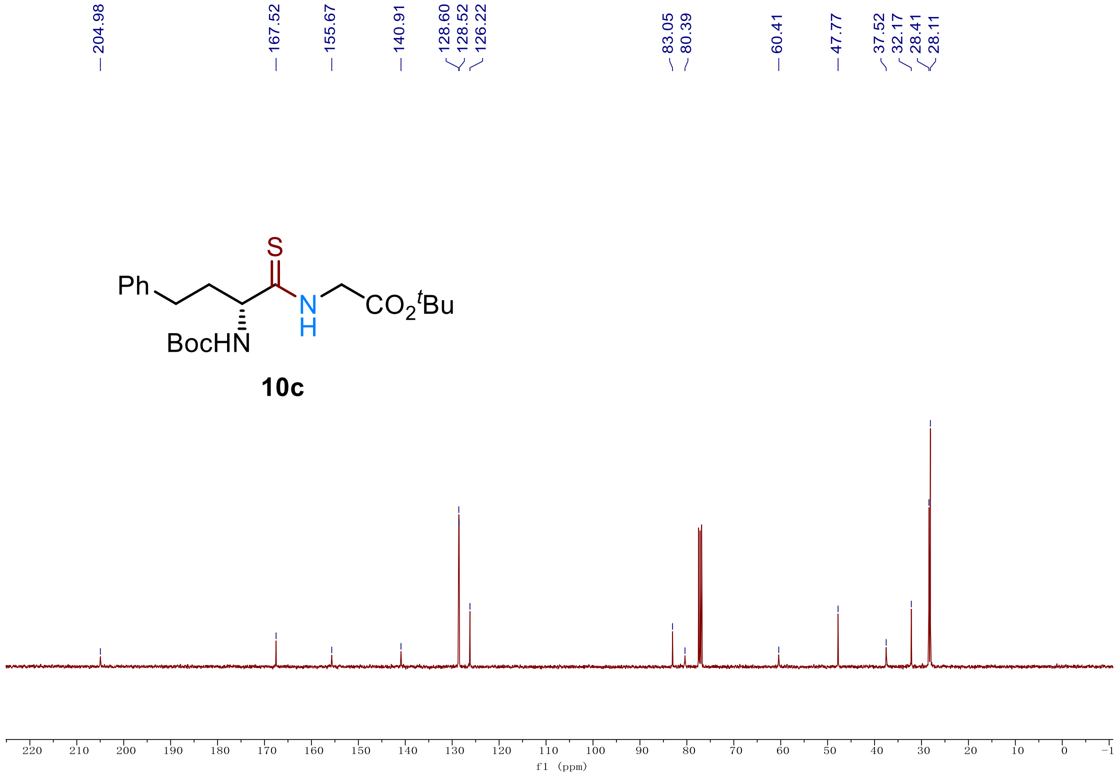
7.17
7.17
5.37
4.47
4.45
4.34
4.33
4.29
4.28
4.17
4.16
2.72
2.71
2.70
2.68
2.67
2.65
2.64
2.25
2.23
2.19
2.09
2.07
2.05
2.03
2.01
1.47
1.44
Ph
S
N
H
$CO_2{}^tBu$
BocHN
0.74
2.21
3.12
0.86
0.87
0.99
0.93
1.95
0.89
0.96
8.84
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

10c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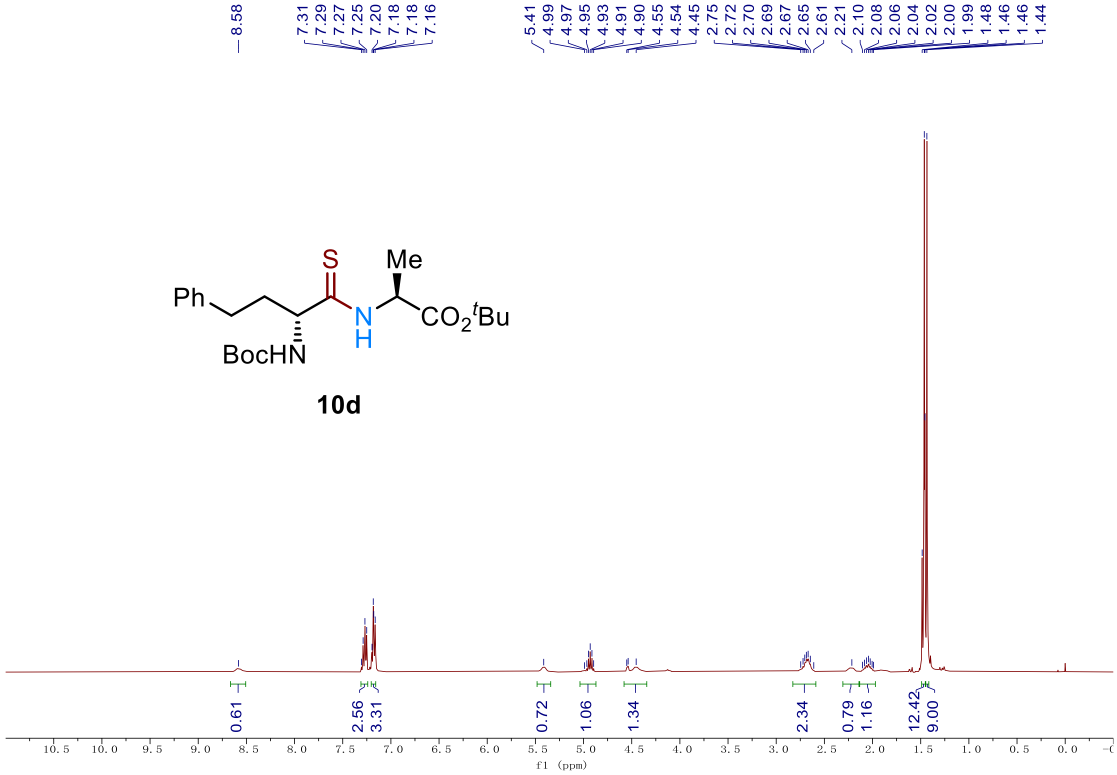
128.52
126.22
83.05
80.39
60.41
47.77
37.52
32.17
28.41
28.11
S
Ph
N
H
CO2tBu
BocHN
10c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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7.18
7.16
5.41
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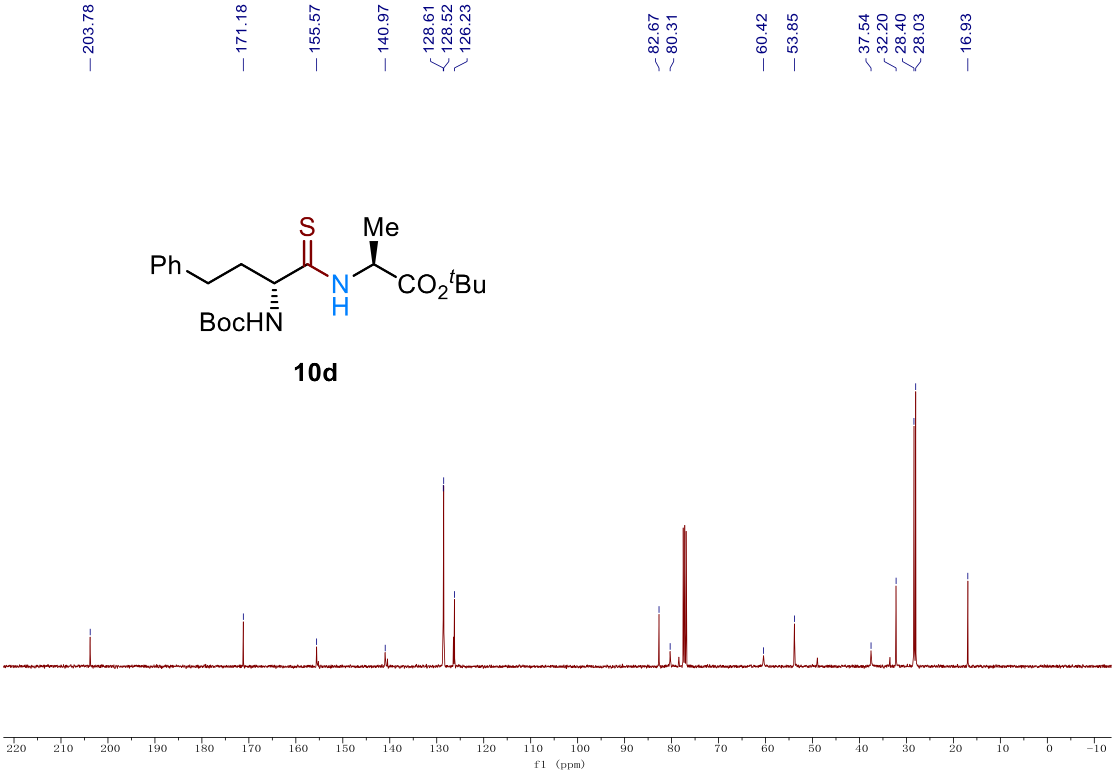
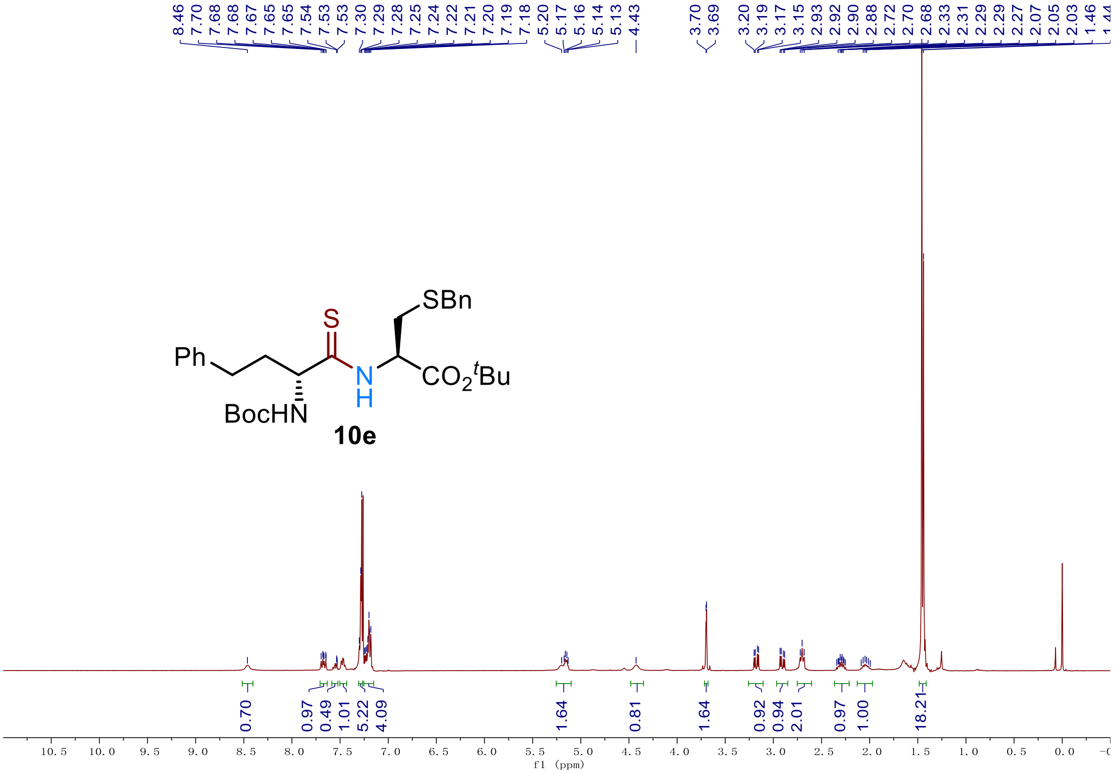
4.97
4.95
4.93
4.91
4.90
4.55
4.54
4.45
2.75
2.72
2.70
2.69
2.67
2.65
2.61
2.21
2.10
2.08
2.06
2.04
2.02
2.00
1.99
1.48
1.46
1.46
1.44
S
Me
Ph
N
H
CO2tBu
BocHN
10d
0.61
2.56
3.31
0.72
1.06
1.34
2.34
0.79
1.16
12.42
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


203.78
171.18
155.57
140.97
128.61
128.52
126.23
82.67
80.31
60.42
53.85
37.54
32.20
28.40
28.03
16.93
S
Me
Ph
N
H
$CO_2{}^tBu$
BocHN
10d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.68
7.67
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7.65
7.54
7.53
7.53
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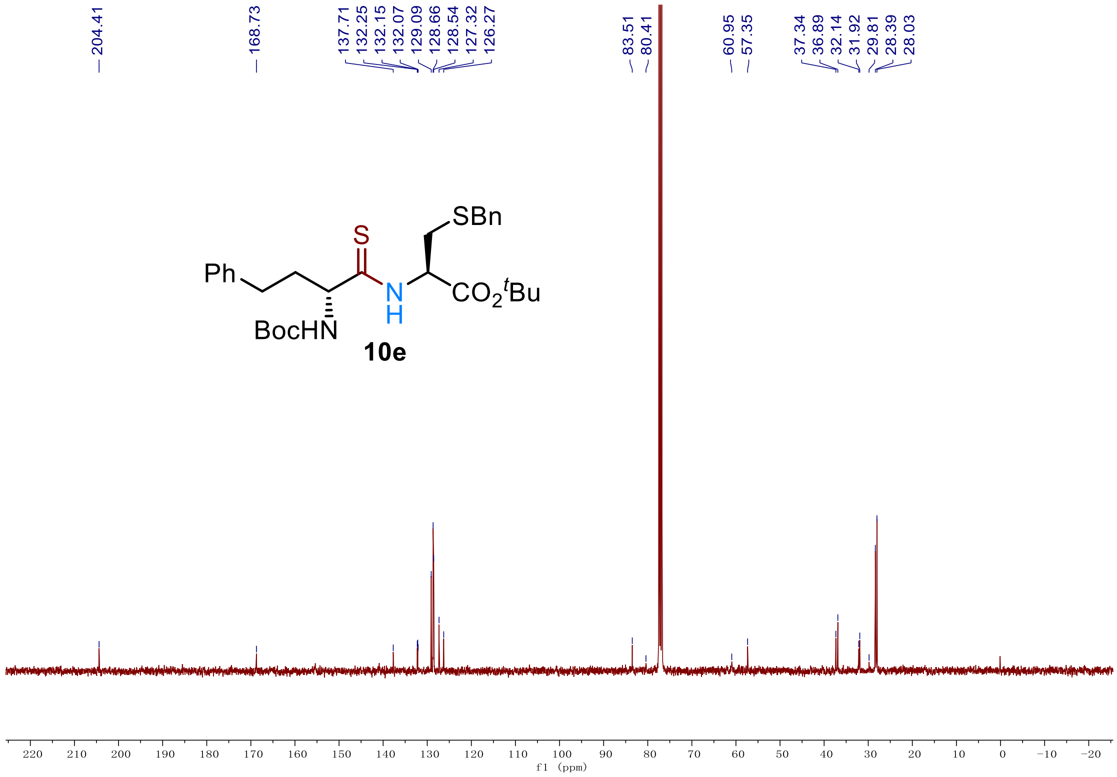
7.29
7.28
7.25
7.24
7.22
7.21
7.20
7.19
7.18
5.20
5.17
5.16
5.14
5.13
4.43
3.70
3.69
3.20
3.19
3.17
3.15
2.93
2.92
2.90
2.88
2.72
2.70
2.68
2.33
2.31
2.29
2.29
2.27
2.07
2.05
2.03
1.46
SBn
S
Ph
N
H
$CO_2{}^tBu$
BocHN
10e
0.70
0.97
0.49
1.01
5.22
4.09
1.64
0.81
1.64
0.92
0.94
2.01
0.97
1.00
18.21
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


204.41
168.73
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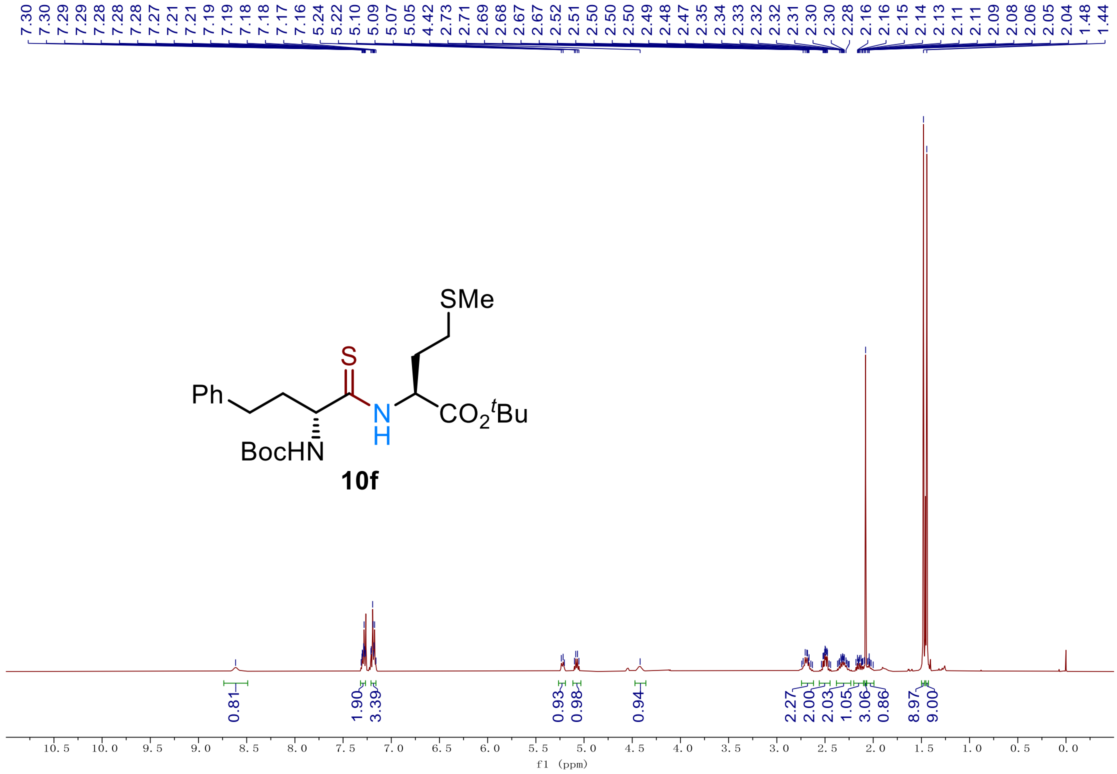
132.25
132.15
132.07
129.09
128.66
128.54
127.32
126.27
83.51
80.41
60.95
57.35
37.34
36.89
32.14
31.92
29.81
28.39
28.03
SBn
S
Ph
N
H
CO2tBu
BocHN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

10e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7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.21
7.21
7.19
7.18
7.18
7.17
7.16
5.24
5.22
5.10
5.09
5.07
5.05
4.42
2.73
2.71
2.69
2.68
2.67
2.52
2.51
2.50
2.50
2.50
2.49
2.48
2.47
2.35
2.34
2.33
2.32
2.32
2.31
2.30
2.30
2.28
2.16
2.16
2.15
2.14
2.13
2.11
2.11
2.09
2.08
2.06
2.05
2.04
1.48
1.44
SMe
S
Ph
N
H
CO2tBu
BocHN
0.81
1.90
3.39
0.93
0.98
0.94
2.27
2.00
2.03
1.05
3.06
0.86
8.97
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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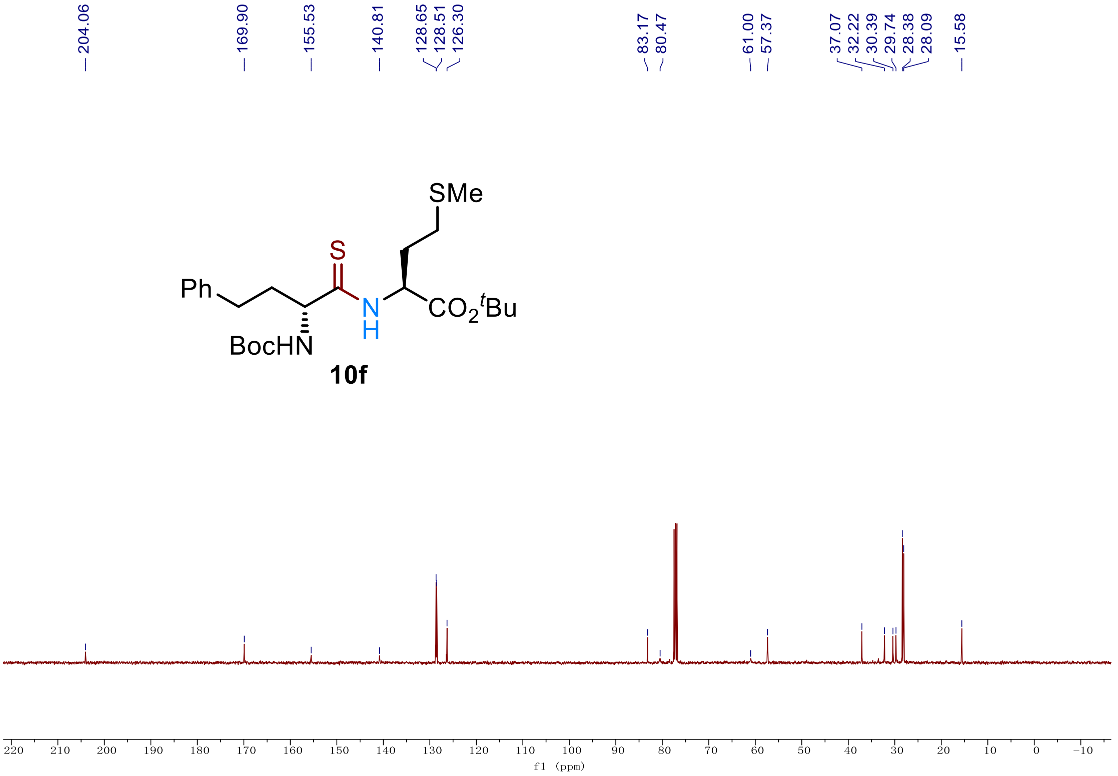
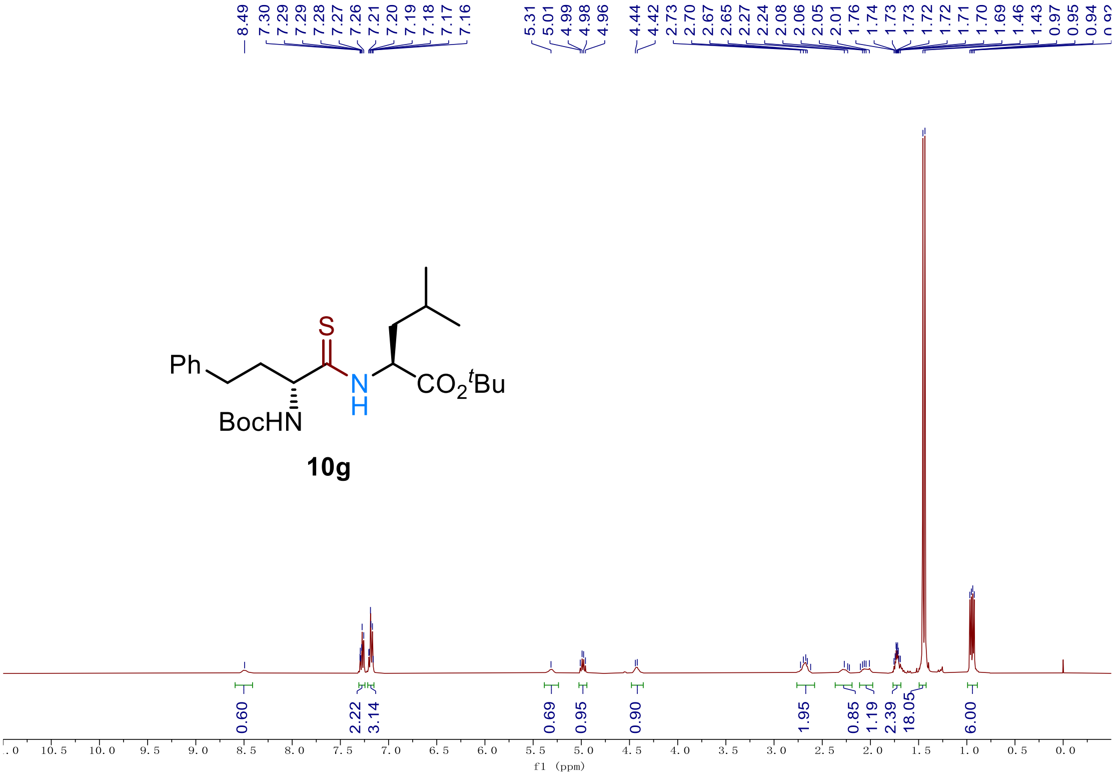
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

10f



10f

204.06
169.90
155.53
140.81
128.65
128.51
126.30
83.17
80.47
61.00
57.37
37.07
32.22
30.39
29.74
28.38
28.09
15.58
SMe
S
Ph
N
H
CO2tBu
BocHN
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



10g

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7.30
7.29
7.29
7.28
7.27
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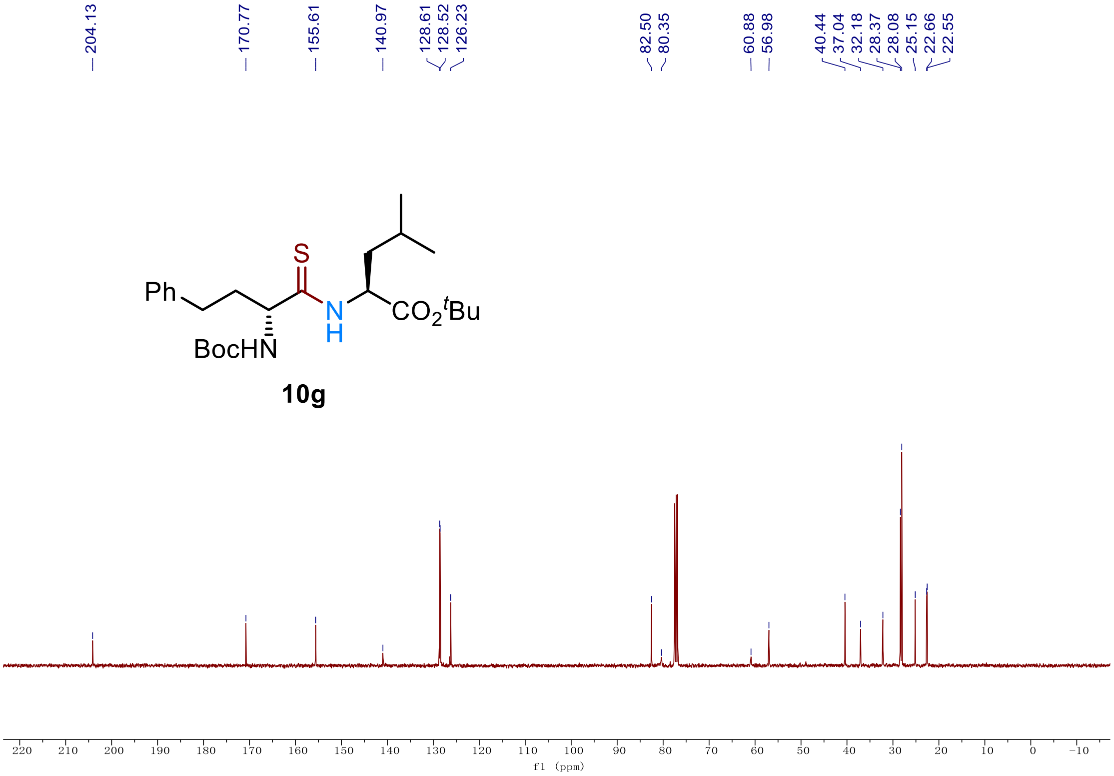
7.21
7.20
7.19
7.18
7.17
7.16
5.31
5.01
4.99
4.98
4.96
4.44
4.42
2.73
2.70
2.67
2.65
2.27
2.24
2.08
2.06
2.05
2.01
1.76
1.74
1.73
1.73
1.72
1.72
1.71
1.70
1.69
1.46
1.43
0.97
0.95
0.94
S
Ph
N
H
CO2tBu
BocHN
0.60
2.22
3.14
0.69
0.95
0.90
1.95
0.85
1.19
2.39
18.05
6.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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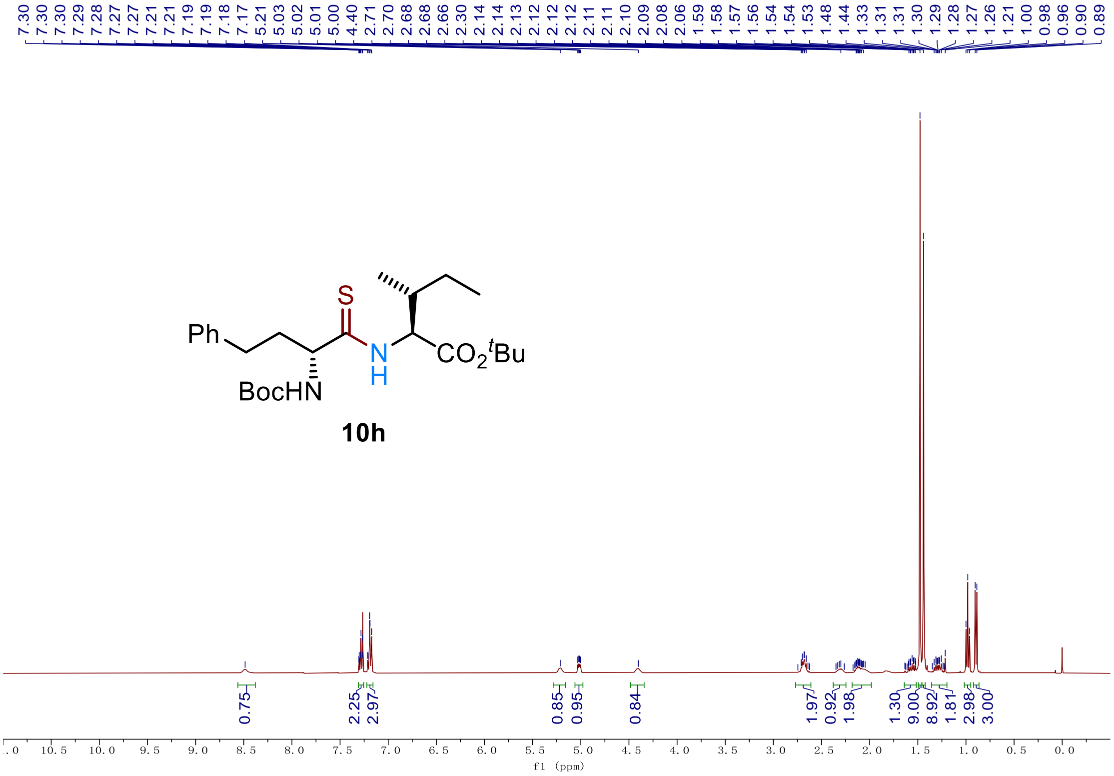
128.52
126.23
82.50
80.35
60.88
56.98
40.44
37.04
32.18
28.37
28.08
25.15
22.66
22.55
Ph
S
N
H
CO$_2$^{t}Bu
BocHN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

10g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7.30
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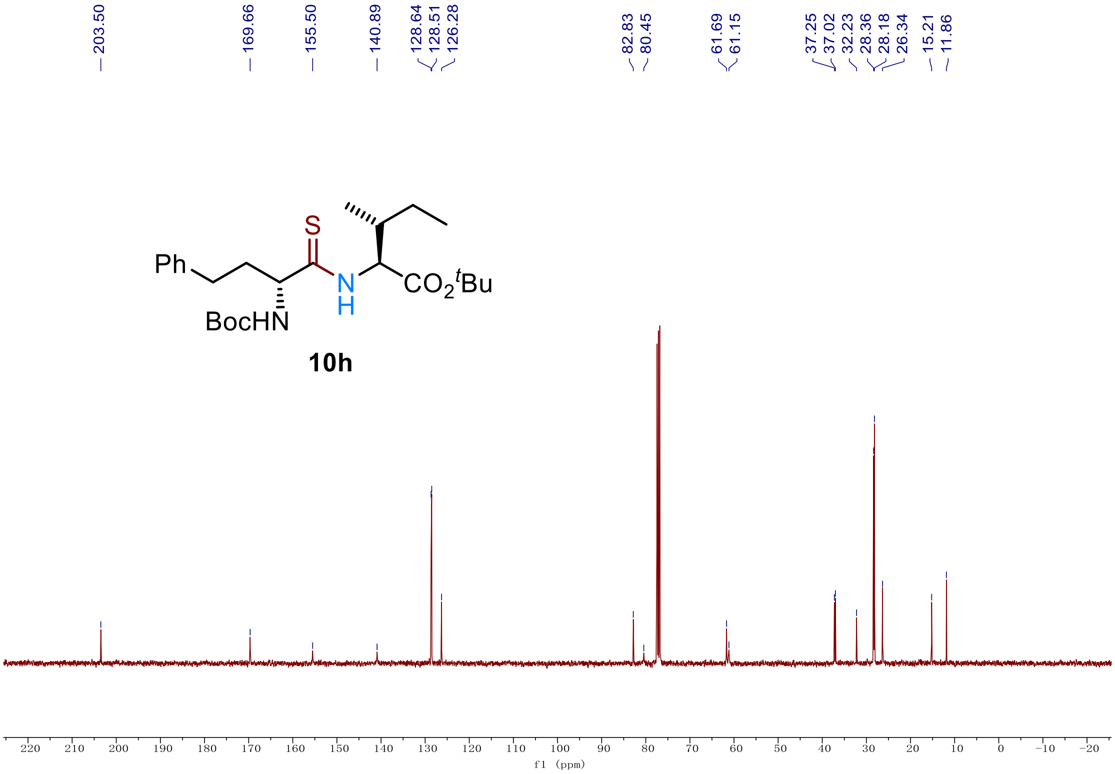
7.19
7.18
7.17
5.21
5.03
5.02
5.01
5.00
4.40
2.71
2.70
2.68
2.68
2.66
2.30
2.14
2.14
2.13
2.12
2.12
2.12
2.11
2.11
2.10
2.09
2.08
2.06
1.59
1.58
1.57
1.56
1.54
1.53
1.48
1.44
1.33
1.31
1.31
1.30
1.29
1.28
1.27
1.26
1.21
1.00
0.98
0.96
0.90
0.89
Ph
S
N
H
CO$_2$^{t}Bu
BocHN
0.75
2.25
2.97
0.85
0.95
0.84
1.97
0.92
1.98
1.30
9.00
8.92
1.81
2.98
3.00
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

10h


203.50
169.66
155.50
140.89
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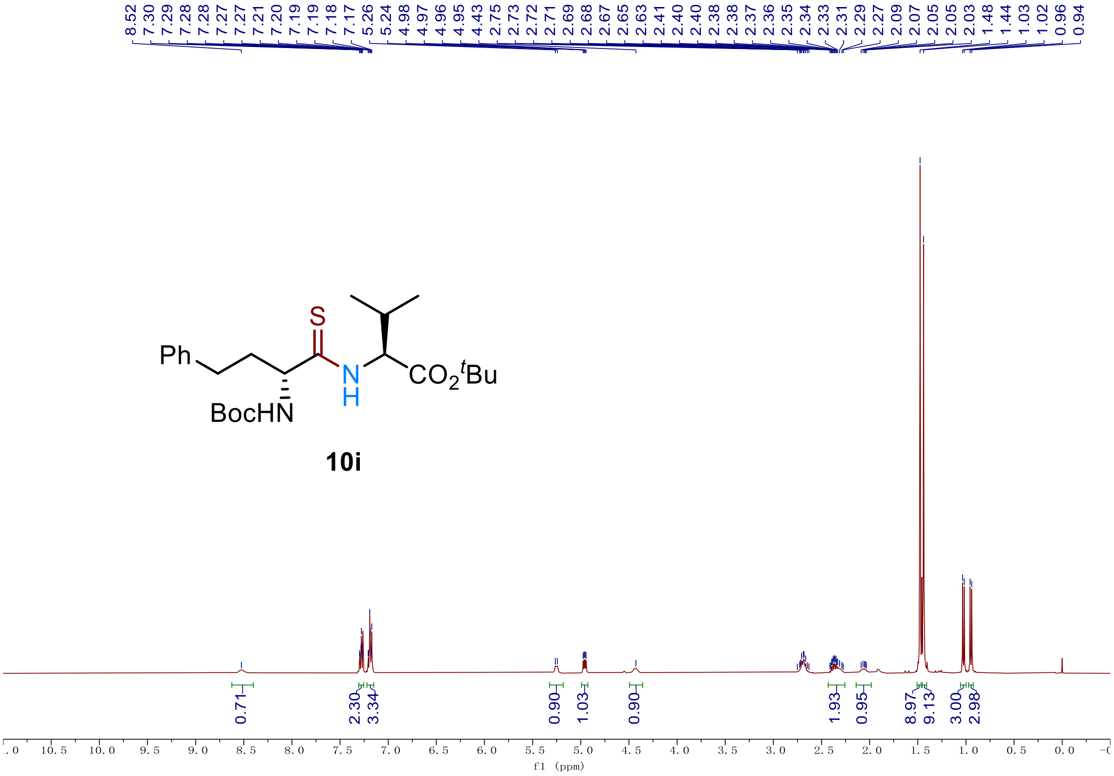
128.51
126.28
82.83
80.45
61.69
61.15
37.25
37.02
32.23
28.36
28.18
26.34
15.21
11.86
S
Ph
N
H
CO2tBu
BocHN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

10h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7.27
7.21
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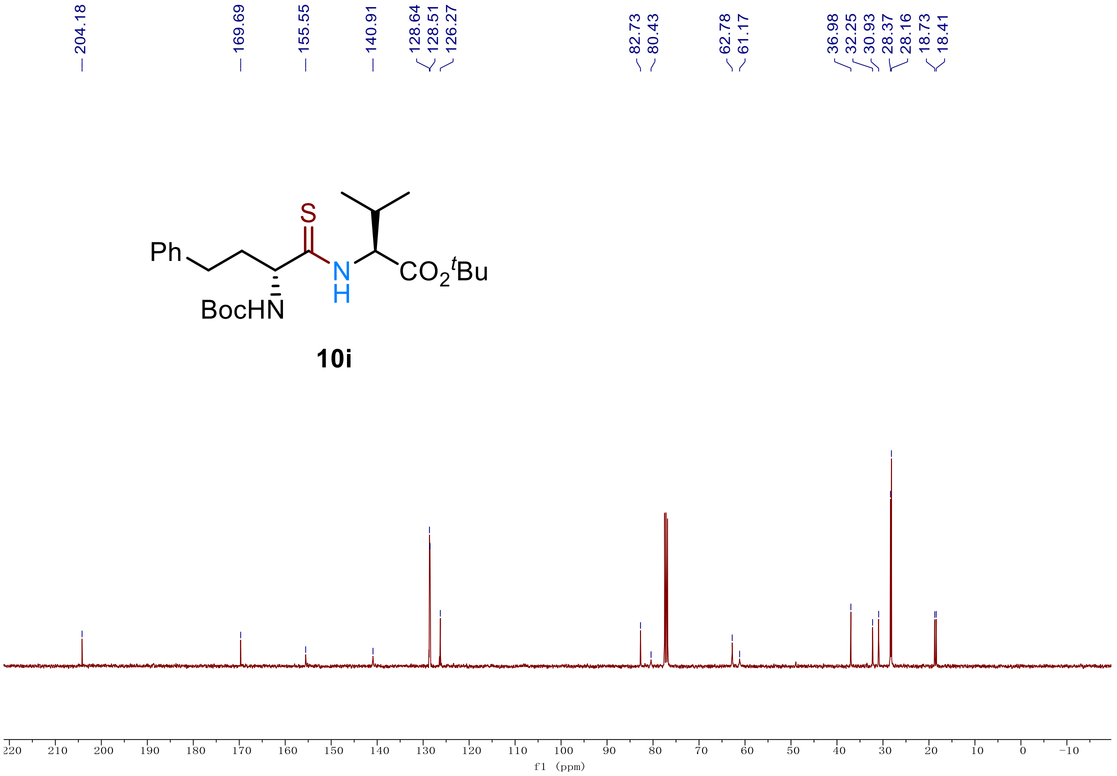
7.19
7.19
7.18
7.17
5.26
5.24
4.98
4.97
4.96
4.95
4.43
2.75
2.73
2.72
2.71
2.69
2.68
2.67
2.65
2.63
2.41
2.40
2.40
2.38
2.38
2.37
2.36
2.35
2.34
2.33
2.31
2.29
2.27
2.09
2.07
2.05
2.05
2.03
1.48
1.44
1.03
1.02
0.96
0.94
S
Ph
N
H
CO2tBu
BocHN
0.71
2.30
3.34
0.90
1.03
0.90
1.93
0.95
8.97
9.13
3.00
2.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

10i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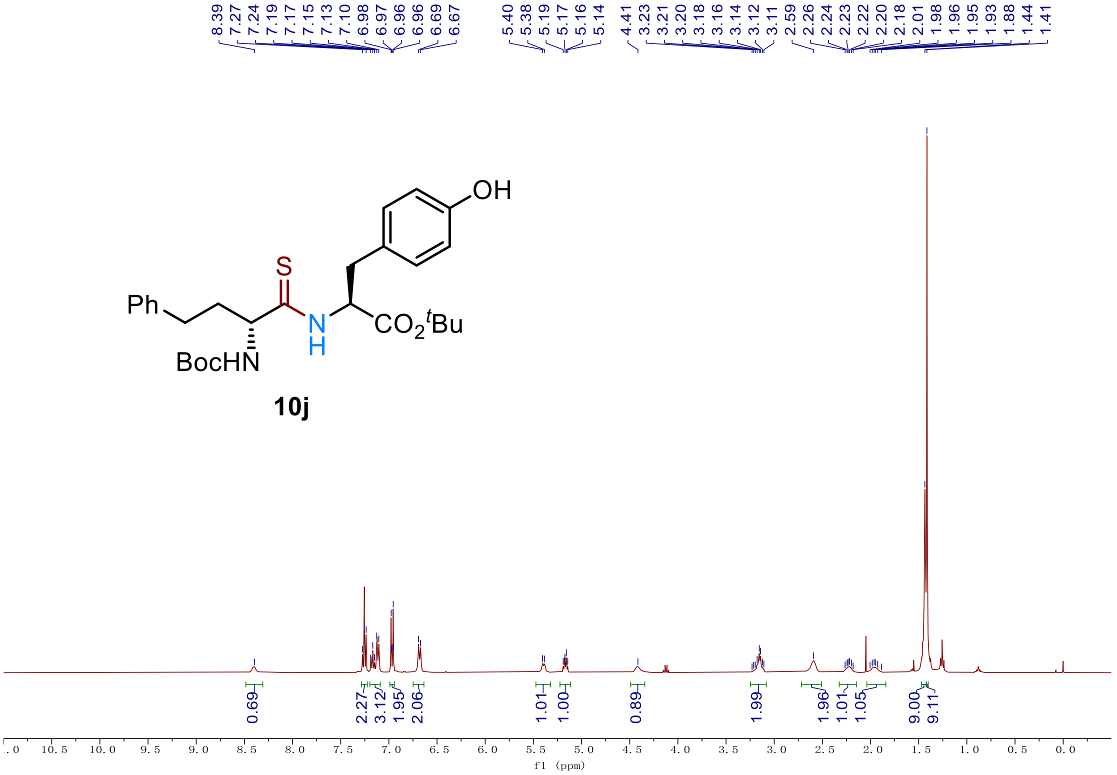
169.69
155.55
140.91
128.64
128.51
126.27
82.73
80.43
62.78
61.17
36.98
32.25
30.93
28.37
28.16
18.73
18.41
S
Ph
N
H
BocHN
CO2tBu
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

10i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7.27
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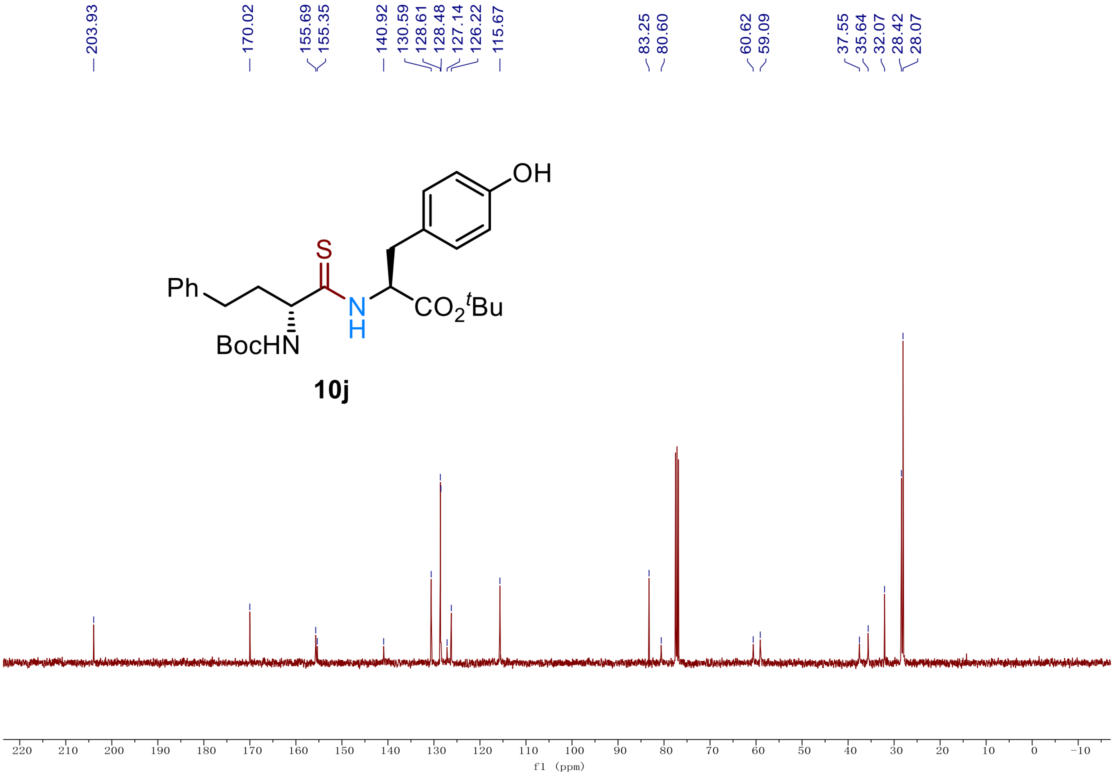
7.19
7.17
7.15
7.13
7.10
6.98
6.97
6.96
6.96
6.69
6.67
5.40
5.38
5.19
5.17
5.16
5.14
4.41
3.23
3.21
3.20
3.18
3.16
3.14
3.12
3.11
2.59
2.26
2.24
2.23
2.22
2.20
2.18
2.01
1.98
1.96
1.95
1.93
1.88
1.44
1.41
OH
S
Ph
N
H
BocHN
CO2tBu
0.69
2.27
3.12
1.95
2.06
1.01
1.00
0.89
1.99
1.96
1.01
1.05
9.00
9.11
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

10j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170.02
155.69
155.35
140.92
130.59
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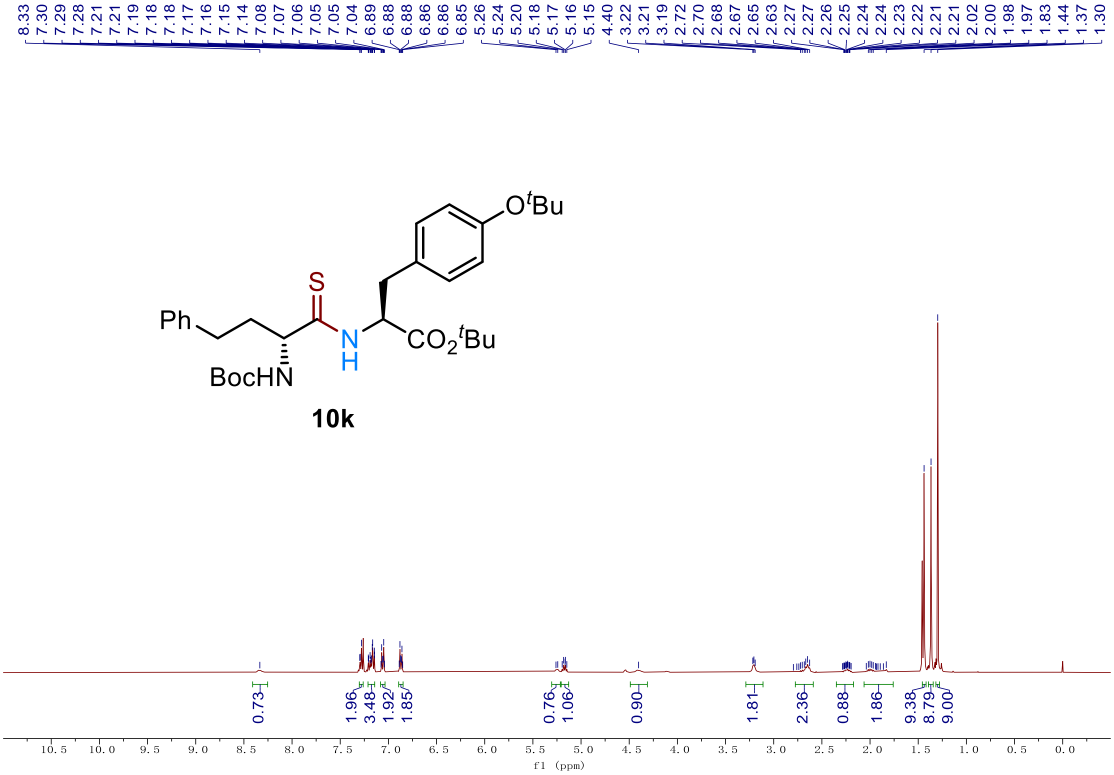
128.48
127.14
126.22
115.67
83.25
80.60
60.62
59.09
37.55
35.64
32.07
28.42
28.07
OH
S
Ph
N
H
CO2tBu
BocHN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

10j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7.30
7.29
7.28
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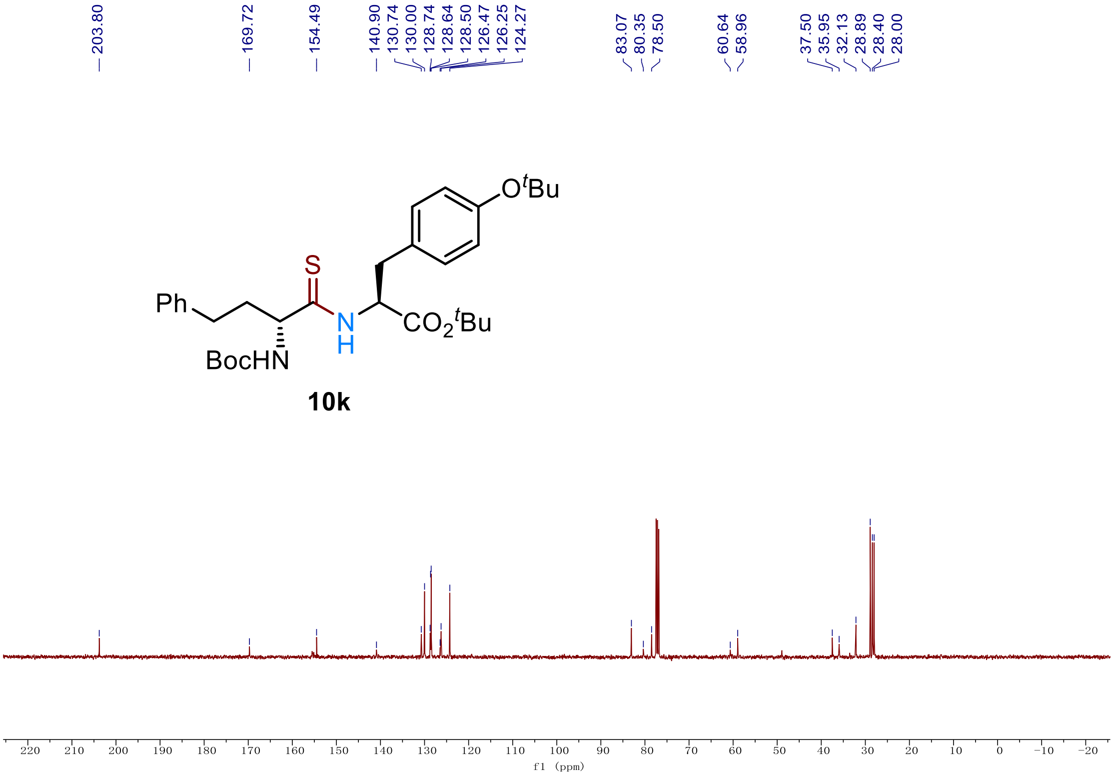
7.21
7.19
7.18
7.17
7.16
7.15
7.14
7.08
7.07
7.06
7.05
7.04
6.89
6.88
6.88
6.86
6.86
6.85
5.26
5.24
5.20
5.18
5.17
5.16
5.15
4.40
3.22
3.21
3.19
2.72
2.70
2.68
2.67
2.65
2.63
2.27
2.27
2.26
2.25
2.24
2.24
2.23
2.22
2.21
2.21
2.02
2.00
1.98
1.97
1.83
1.44
1.37
1.30
OtBu
S
Ph
N
H
CO2tBu
BocHN
0.73
1.96
3.48
1.92
1.85
0.76
1.06
0.90
1.81
2.36
0.88
1.86
9.38
8.79
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

10k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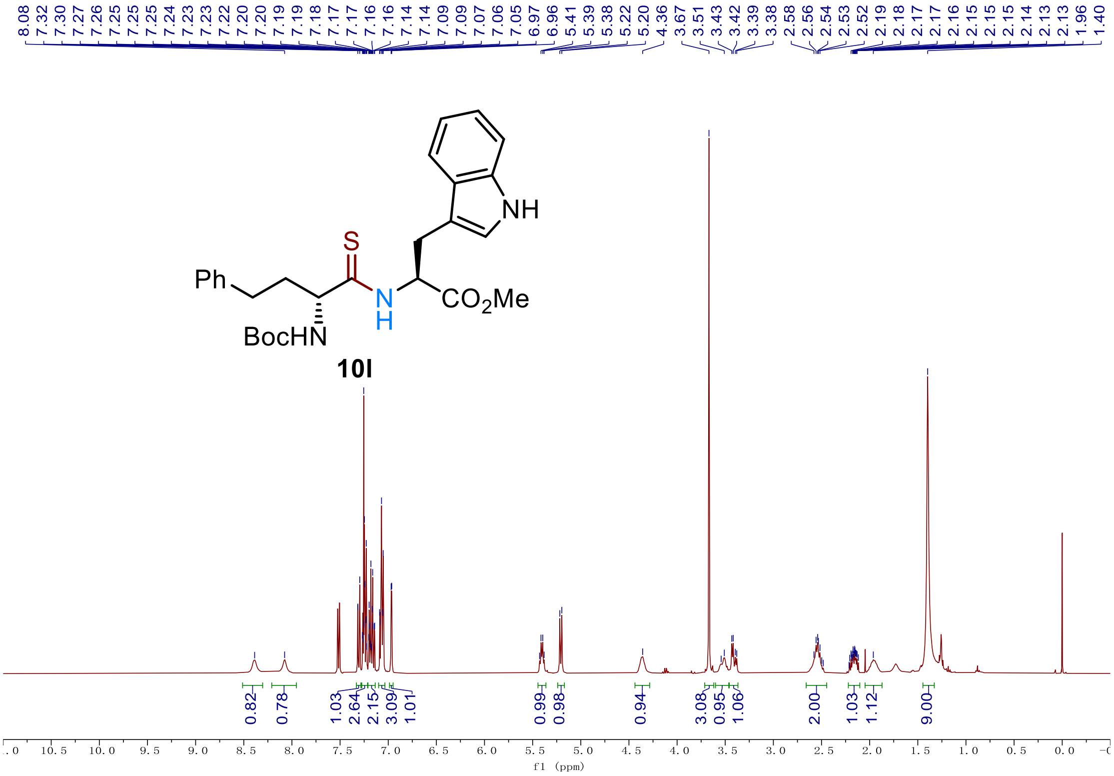
140.90
130.74
130.00
128.74
128.64
128.50
126.47
126.25
124.27
83.07
80.35
78.50
60.64
58.96
37.50
35.95
32.13
28.89
28.40
28.00
O^tBu
S
Ph
N
H
CO2tBu
BocHN
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

10k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7.32
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7.27
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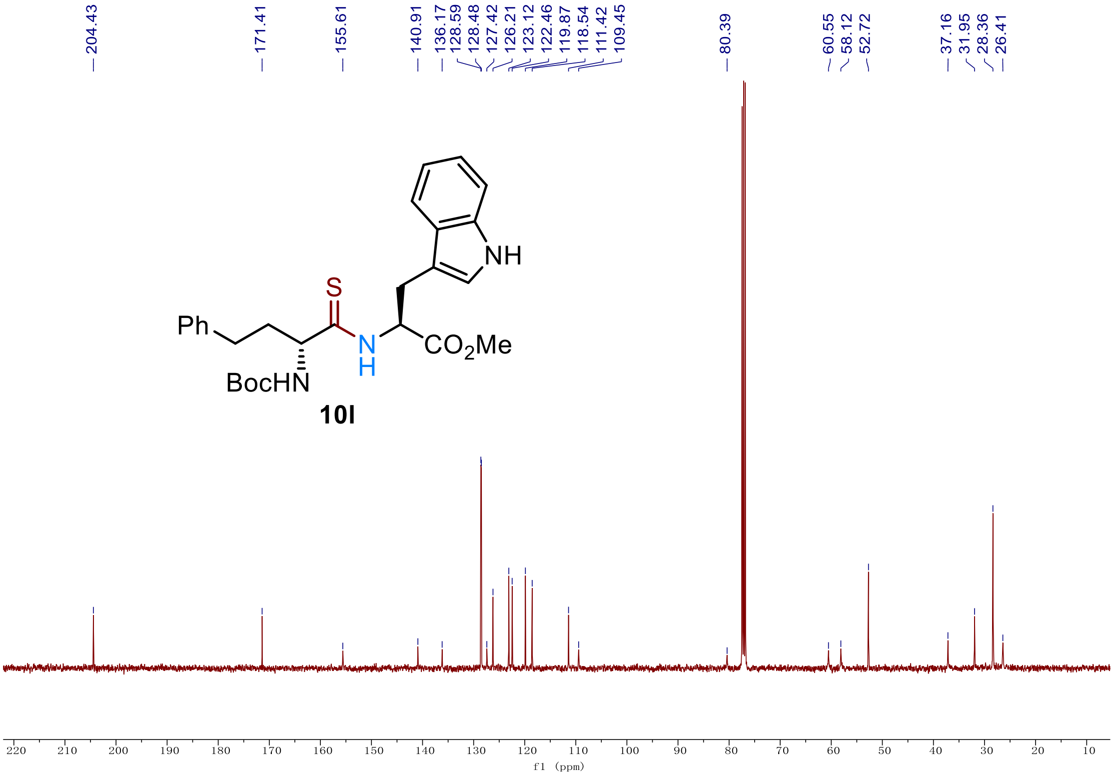
7.25
7.25
7.25
7.24
7.23
7.23
7.22
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.14
7.14
7.09
7.09
7.07
7.06
7.05
6.97
6.96
5.41
5.39
5.38
5.22
5.20
4.36
3.67
3.51
3.43
3.42
3.39
3.38
2.58
2.56
2.54
2.53
2.52
2.19
2.18
2.17
2.16
2.15
2.15
2.15
2.14
2.13
2.13
1.96
1.40
NH
S
Ph
N
H
CO2Me
BocHN
0.82
0.78
1.03
2.64
2.15
3.09
1.01
0.99
0.98
0.94
3.08
0.95
1.06
2.00
1.03
1.12
9.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

10l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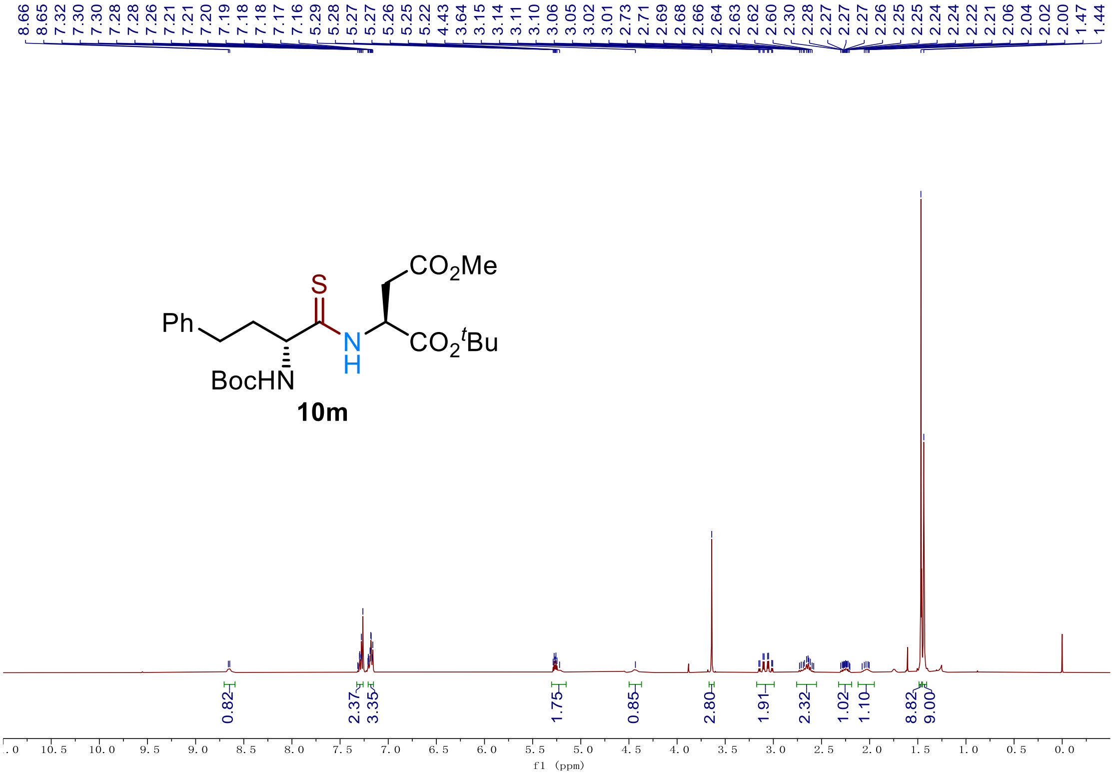
128.59
128.48
127.42
126.21
123.12
122.46
119.87
118.54
111.42
109.45
80.39
60.55
58.12
52.72
37.16
31.95
28.36
26.41
Ph
S
N
H
NH
CO2Me
BocHN
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

10l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8.65
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7.28
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7.26
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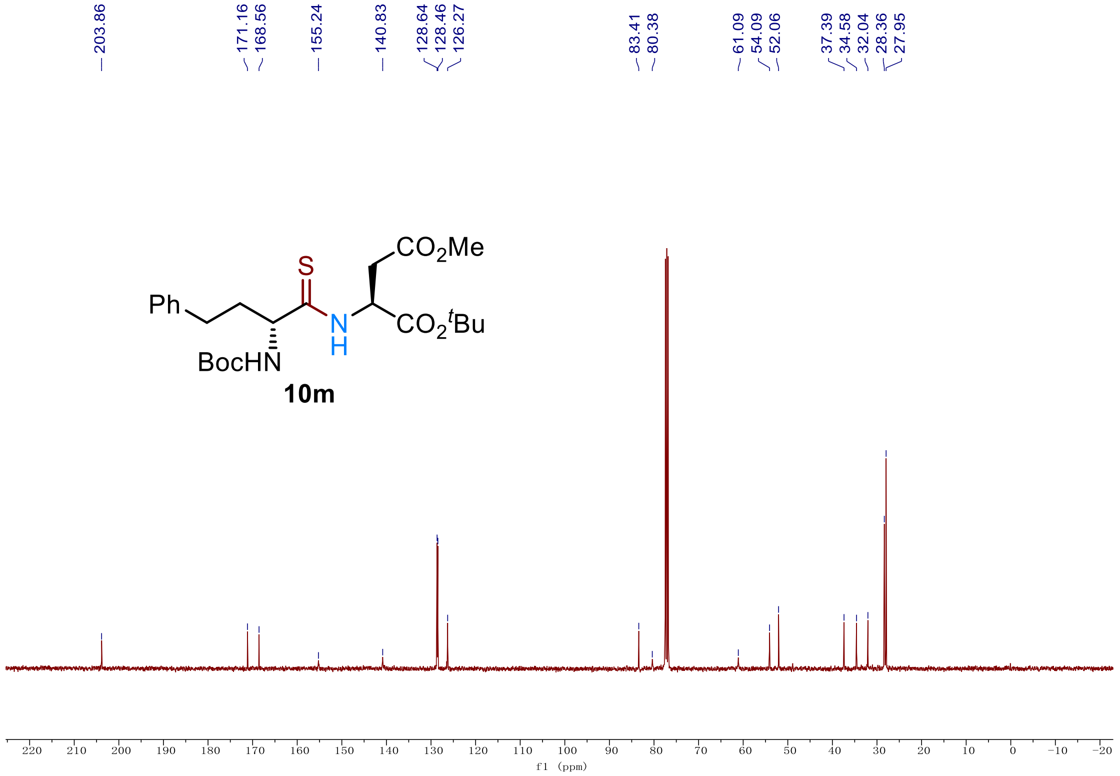
7.20
7.19
7.18
7.18
7.17
7.16
5.29
5.28
5.27
5.27
5.26
5.25
5.22
4.43
3.64
3.15
3.14
3.11
3.10
3.06
3.05
3.02
3.01
2.73
2.71
2.69
2.68
2.66
2.64
2.63
2.62
2.60
2.30
2.28
2.27
2.27
2.27
2.26
2.25
2.25
2.24
2.24
2.22
2.21
2.06
2.04
2.02
2.00
1.47
1.44
Ph
S
N
H
CO2Me
CO2tBu
BocHN
0.82
2.37
3.35
1.75
0.85
2.80
1.91
2.32
1.02
1.10
8.82
9.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

10m


203.86
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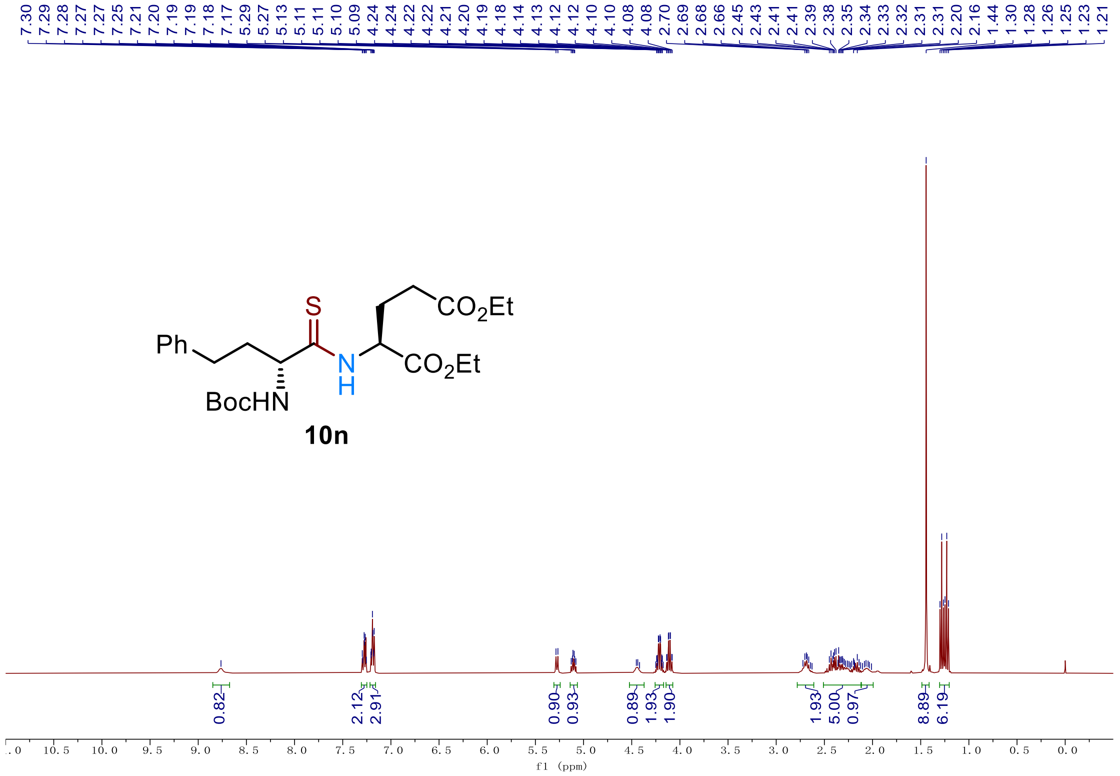
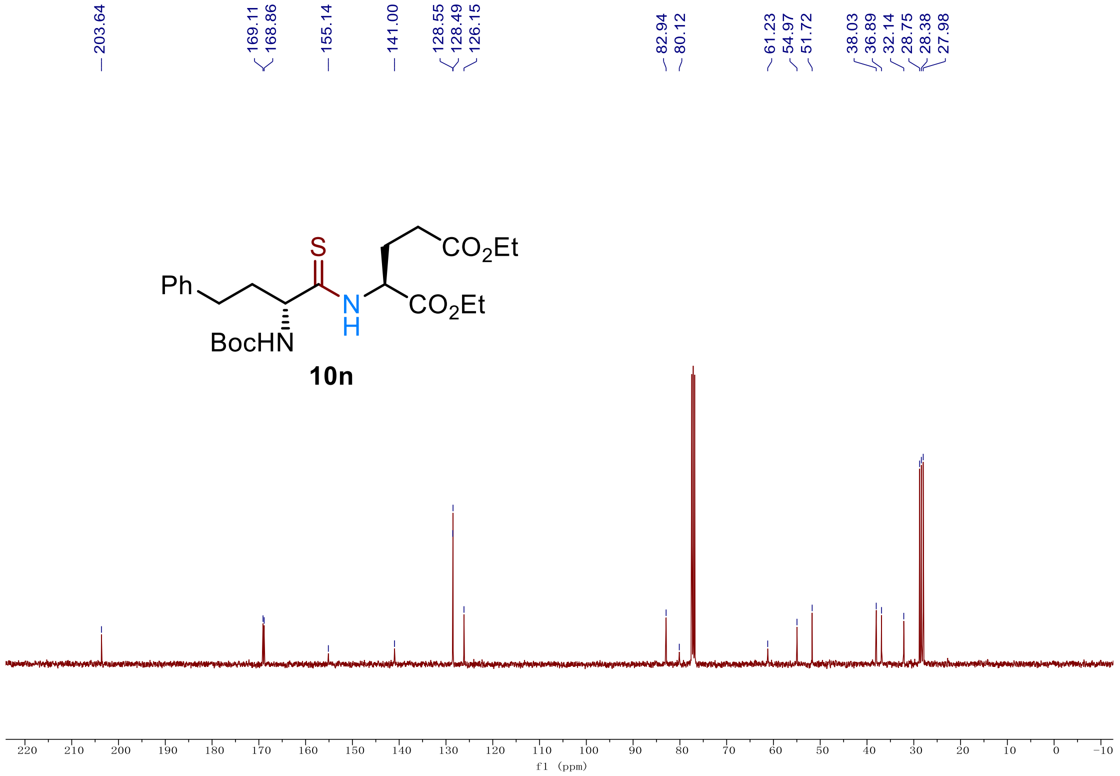
168.56
155.24
140.83
128.64
128.46
126.27
83.41
80.38
61.09
54.09
52.06
37.39
34.58
32.04
28.36
27.95
S
Ph
N
H
BocHN
CO$_2$Me
CO$_2{}^t$Bu
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

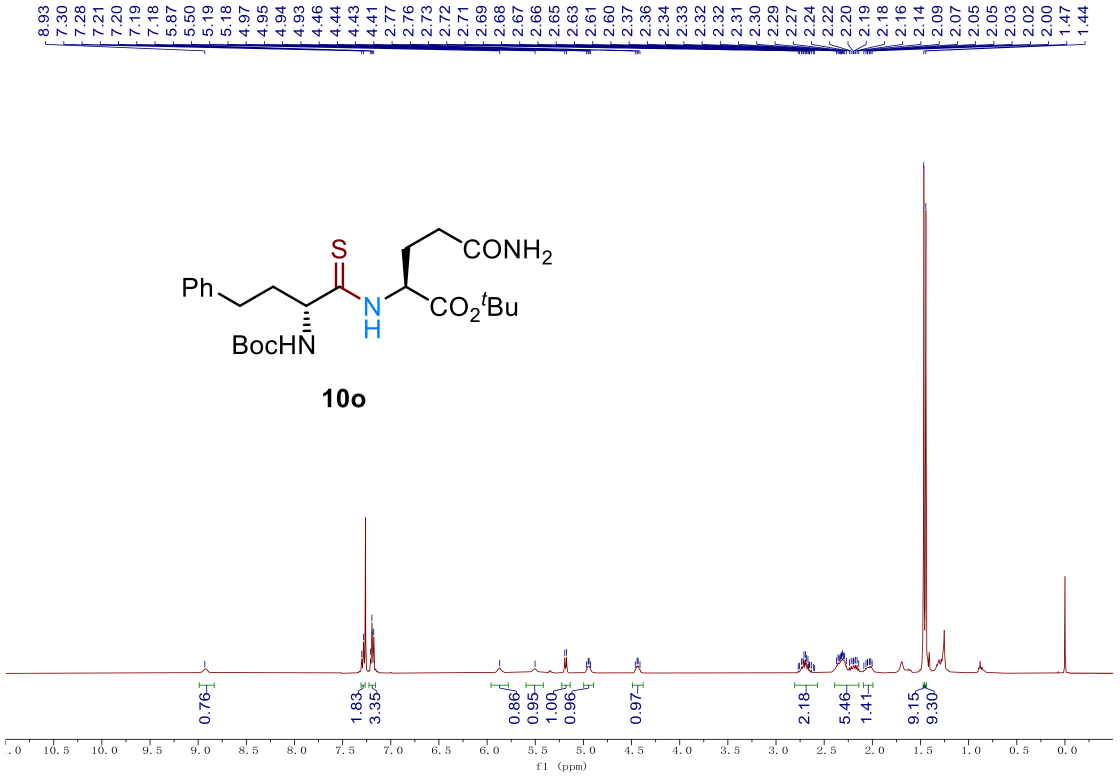
10m


7.30
7.29
7.28
7.27
7.27
7.25
7.21
7.20
7.19
7.19
7.18
7.17
5.29
5.27
5.13
5.11
5.11
5.10
5.09
4.24
4.24
4.22
4.22
4.21
4.21
4.20
4.19
4.18
4.14
4.13
4.12
4.12
4.10
4.10
4.08
4.08
2.70
2.69
2.68
2.66
2.45
2.43
2.41
2.41
2.39
2.38
2.35
2.34
2.33
2.32
2.31
2.31
2.20
2.16
1.44
1.30
1.28
1.26
1.25
1.23
1.21
S
Ph
N
H
BocHN
CO$_2$Et
CO$_2$Et
0.82
2.12
2.91
0.90
0.93
0.89
1.93
1.90
1.93
5.00
0.97
8.89
6.19
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

10n


203.64
169.11
168.86
155.14
141.00
128.55
128.49
126.15
82.94
80.12
61.23
54.97
51.72
38.03
36.89
32.14
28.75
28.38
27.98
Ph
S
N
H
BocHN
CO2Et
CO2Et
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

10n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7.30
7.28
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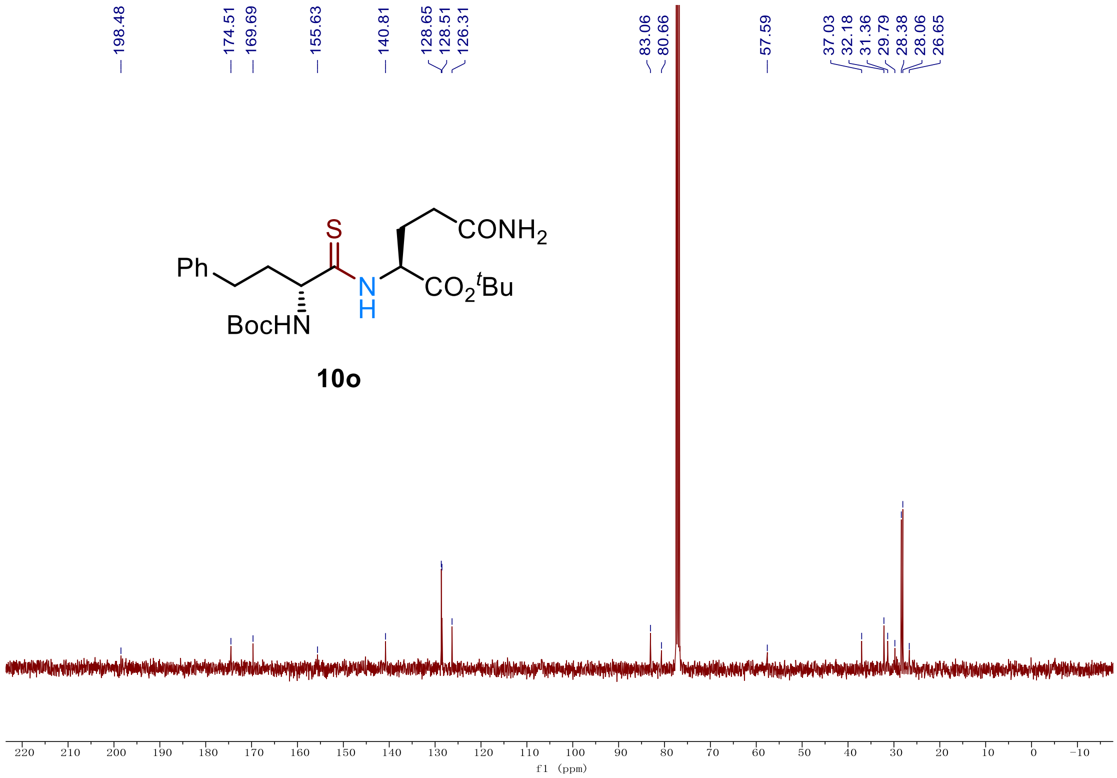
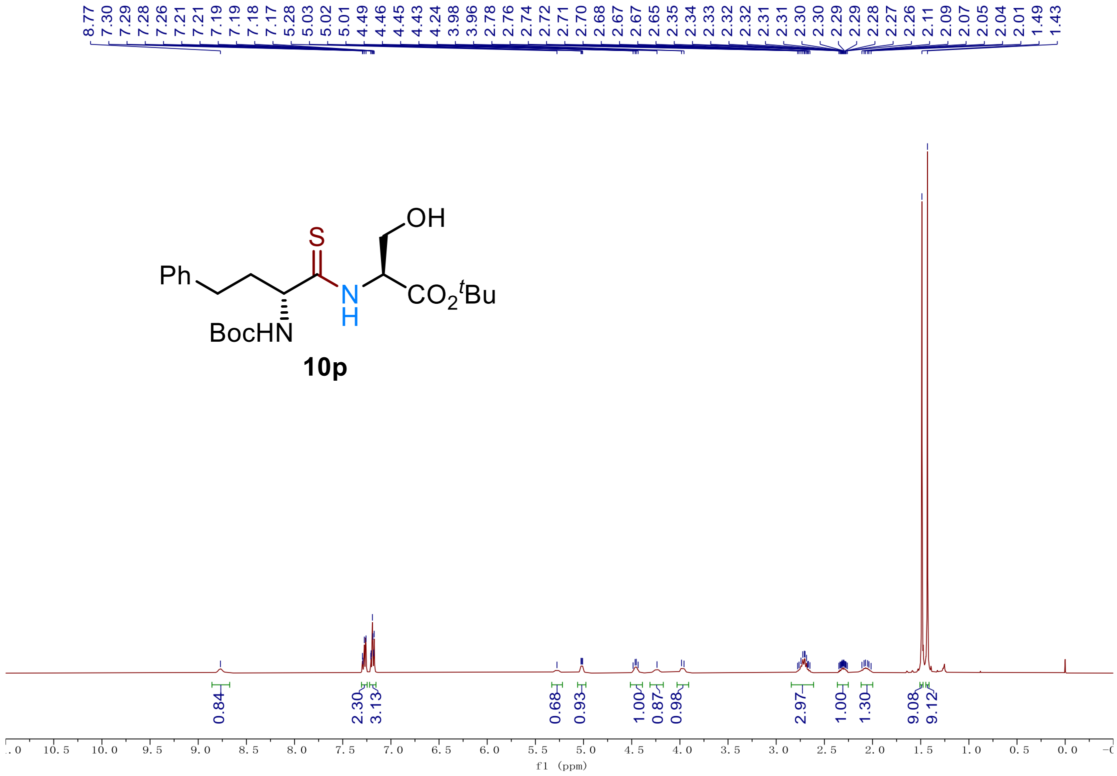
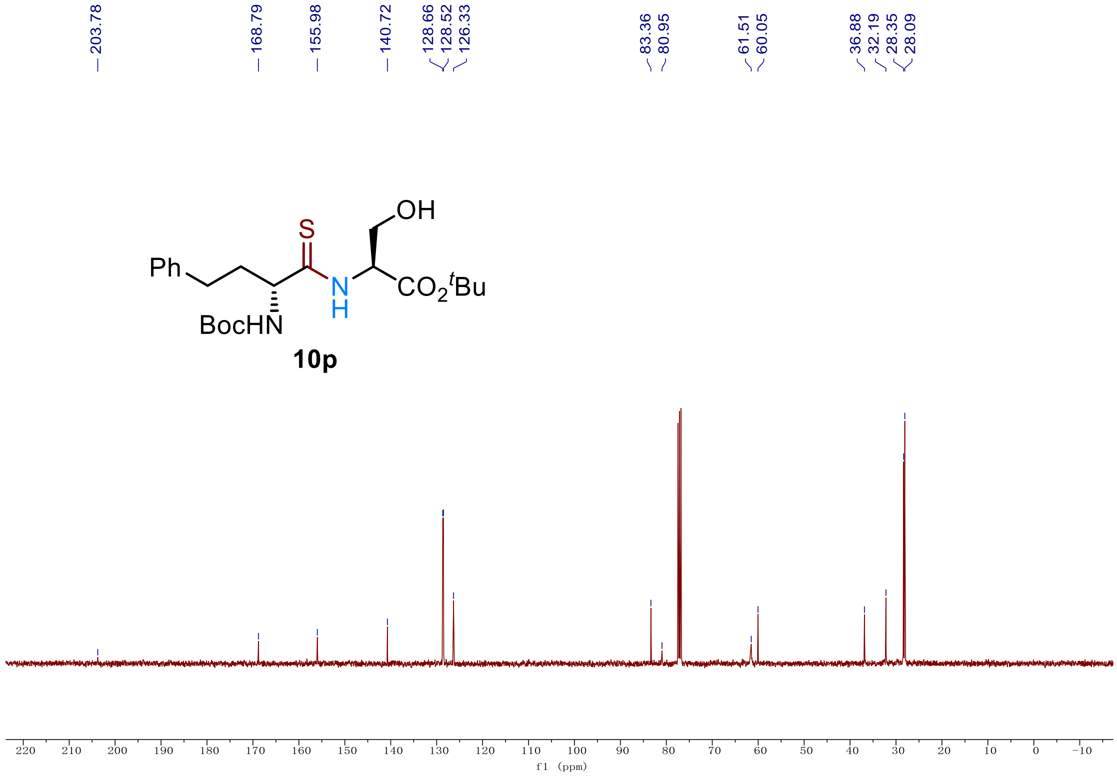
7.19
7.18
5.87
5.50
5.19
5.18
4.97
4.95
4.94
4.93
4.46
4.44
4.43
4.41
2.77
2.76
2.73
2.72
2.71
2.69
2.68
2.67
2.66
2.65
2.63
2.61
2.60
2.37
2.36
2.34
2.33
2.32
2.32
2.31
2.30
2.29
2.27
2.24
2.22
2.20
2.19
2.18
2.16
2.14
2.09
2.07
2.05
2.03
2.02
2.00
1.47
1.44
Ph
S
N
H
BocHN
CONH2
CO2tBu
0.76
1.83
3.35
0.86
0.95
1.00
0.96
0.97
2.18
5.46
1.41
9.15
9.30
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

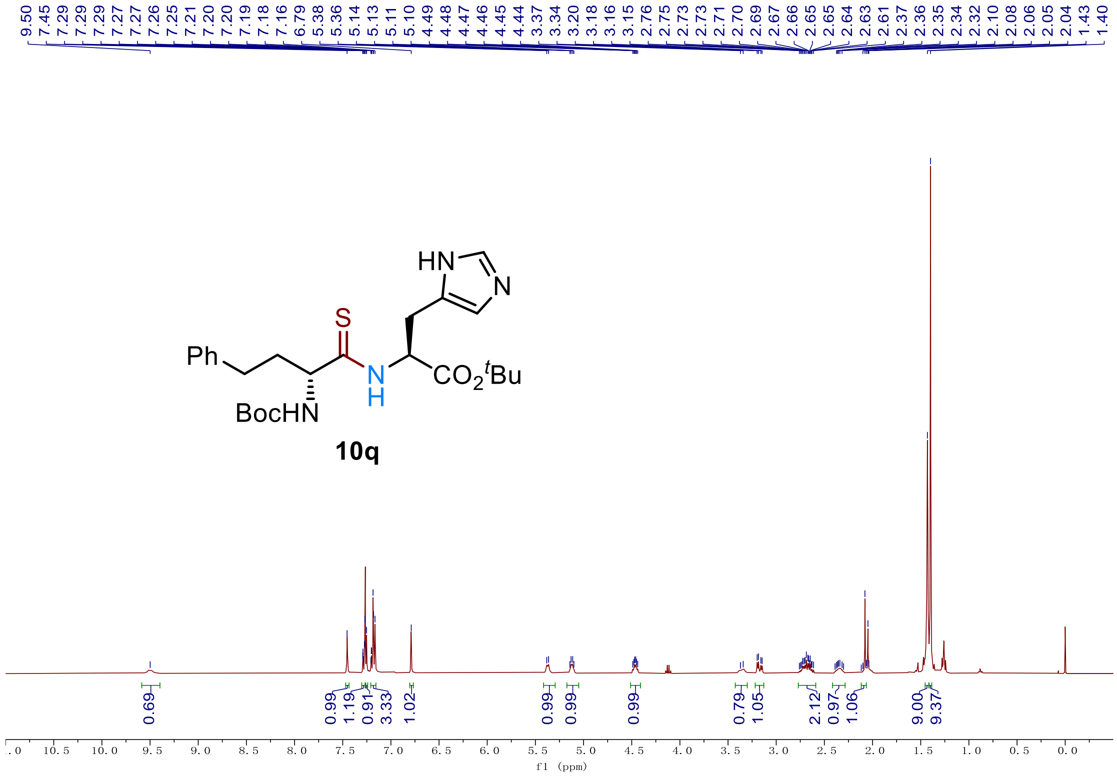
10o


198.48
174.51
169.69
155.63
140.81
128.65
128.51
126.31
83.06
80.66
57.59
37.03
32.18
31.36
29.79
28.38
28.06
26.65
S
Ph
CONH$_2$
N
H
CO$_2{}^t$Bu
BocHN
10o
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

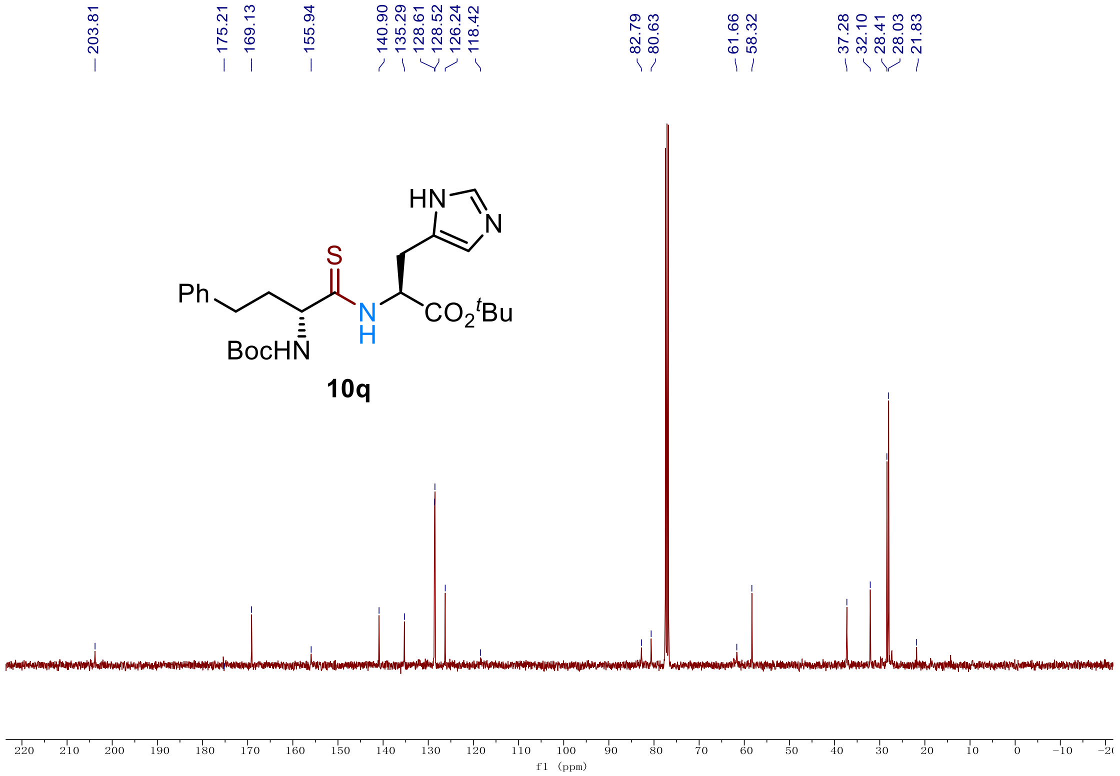

8.77
7.30
7.29
7.28
7.26
7.21
7.19
7.19
7.18
7.17
5.28
5.03
5.02
5.01
4.49
4.46
4.45
4.43
4.24
3.98
3.96
2.78
2.76
2.74
2.72
2.71
2.70
2.68
2.67
2.65
2.35
2.34
2.33
2.32
2.32
2.31
2.31
2.30
2.30
2.29
2.29
2.28
2.27
2.26
2.11
2.09
2.07
2.05
2.04
2.01
1.49
1.43
S
OH
Ph
N
H
CO$_2{}^t$Bu
BocHN
10p
0.84
2.30
3.13
0.68
0.93
1.00
0.87
0.98
2.97
1.00
1.30
9.08
9.12
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


203.78
168.79
155.98
140.72
128.66
128.52
126.33
83.36
80.95
61.51
60.05
36.88
32.19
28.35
28.09
OH
S
Ph
N
H
CO2tBu
BocHN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

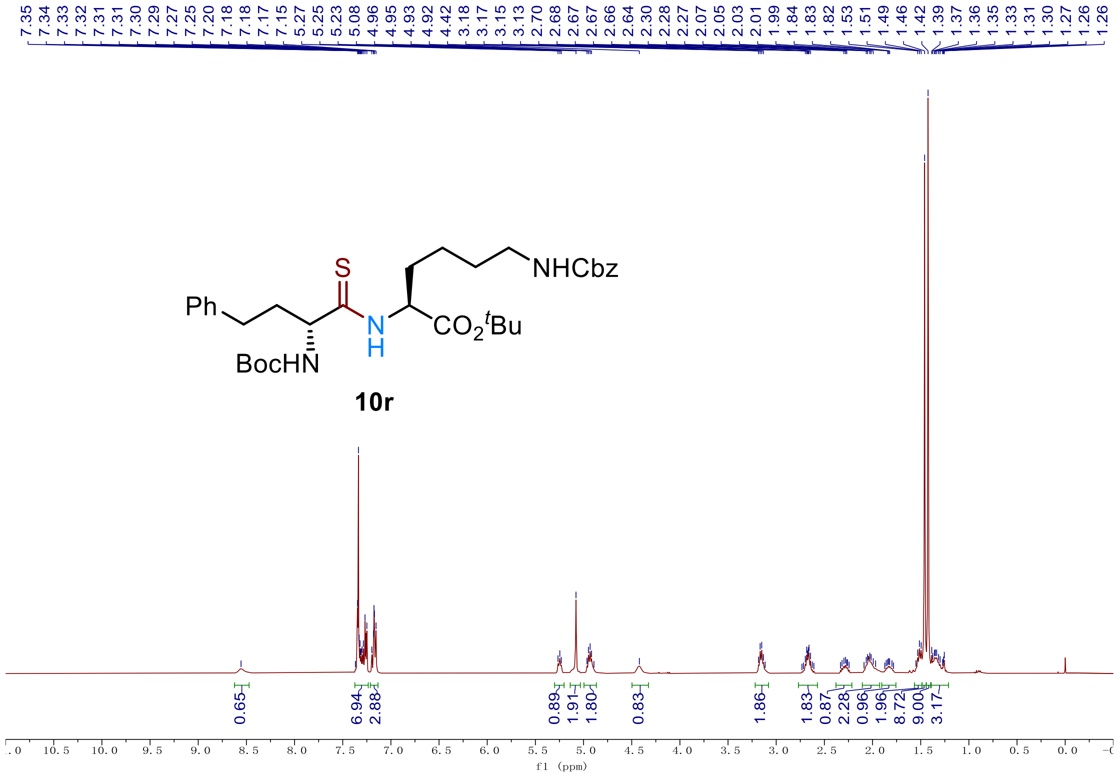
10p


9.50
7.45
7.29
7.29
7.29
7.27
7.27
7.26
7.25
7.21
7.20
7.20
7.19
7.18
7.16
6.79
5.38
5.36
5.14
5.13
5.11
5.10
4.49
4.48
4.47
4.46
4.45
4.44
3.37
3.34
3.20
3.18
3.16
3.15
2.76
2.75
2.73
2.73
2.71
2.70
2.69
2.67
2.66
2.65
2.65
2.64
2.63
2.61
2.37
2.36
2.35
2.34
2.32
2.10
2.08
2.06
2.05
2.04
1.43
1.40
HN
N
S
Ph
N
H
CO2tBu
BocHN
0.69
0.99
1.19
0.91
3.33
1.02
0.99
0.99
0.99
0.79
1.05
2.12
0.97
1.06
9.00
9.37
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

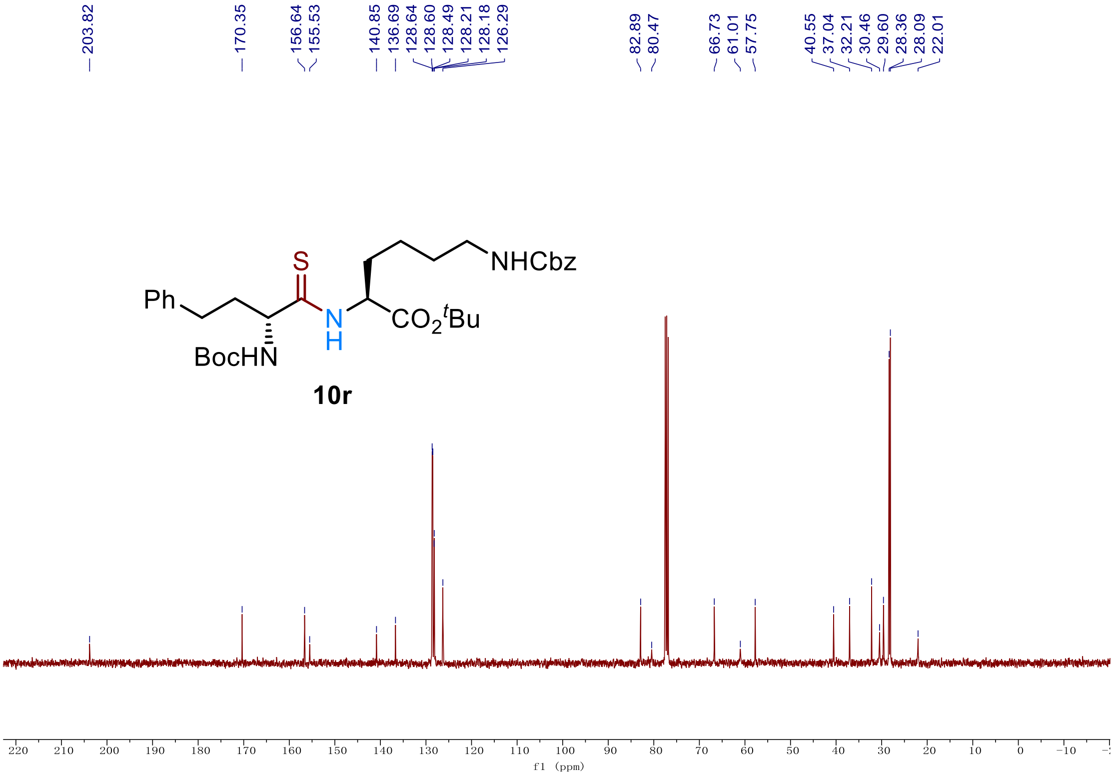
10q


203.81
175.21
169.13
155.94
140.90
135.29
128.61
128.52
126.24
118.42
82.79
80.63
61.66
58.32
37.28
32.10
28.41
28.03
21.83
Ph
S
N
H
HN
N
CO2tBu
BocHN
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

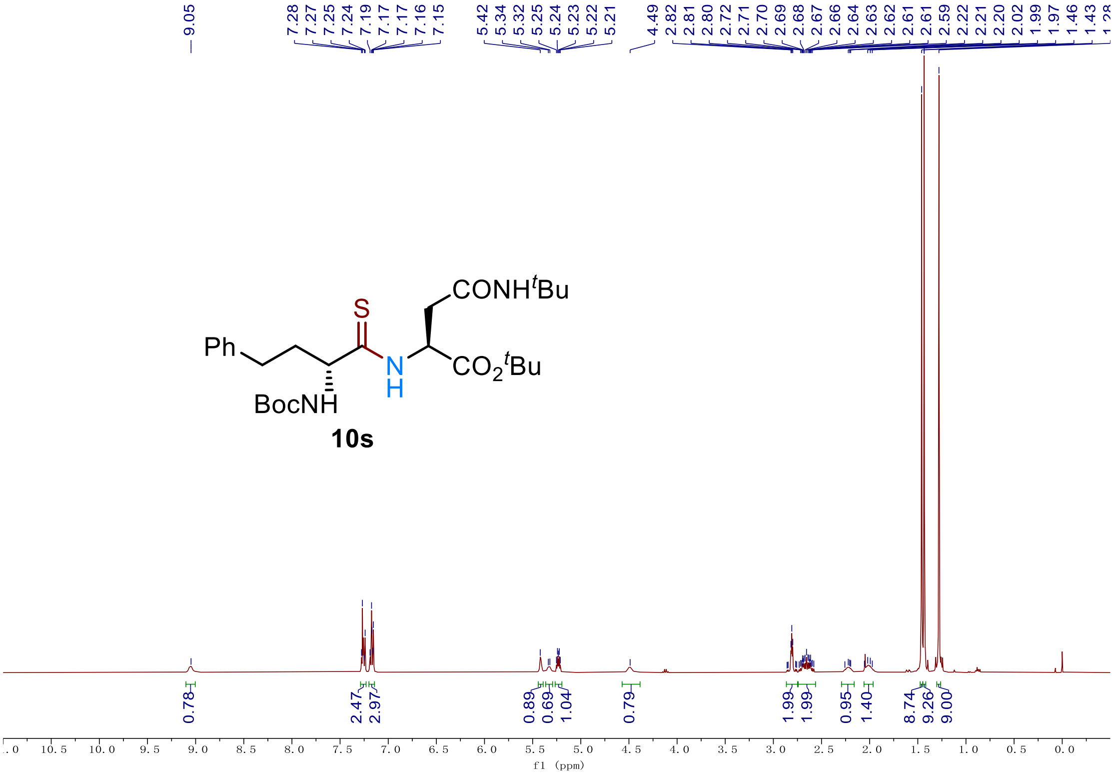
10q


7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.27 7.25 7.20 7.18 7.18 7.17 7.15 5.27 5.25 5.23 5.08 4.96 4.95 4.93 4.92 4.42 3.18 3.17 3.15 3.13 2.70 2.68 2.67 2.67 2.66 2.64 2.30 2.28 2.27 2.07 2.05 2.03 2.01 1.99 1.84 1.83 1.82 1.53 1.51 1.49 1.46 1.42 1.39 1.37 1.36 1.35 1.33 1.31 1.30 1.27 1.26 1.26
Ph
S
N
H
NHCbz
CO2tBu
BocHN
0.65
6.94
2.88
0.89
1.91
1.80
0.83
1.86
1.83
0.87
2.28
0.96
1.96
8.72
9.00
3.17
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

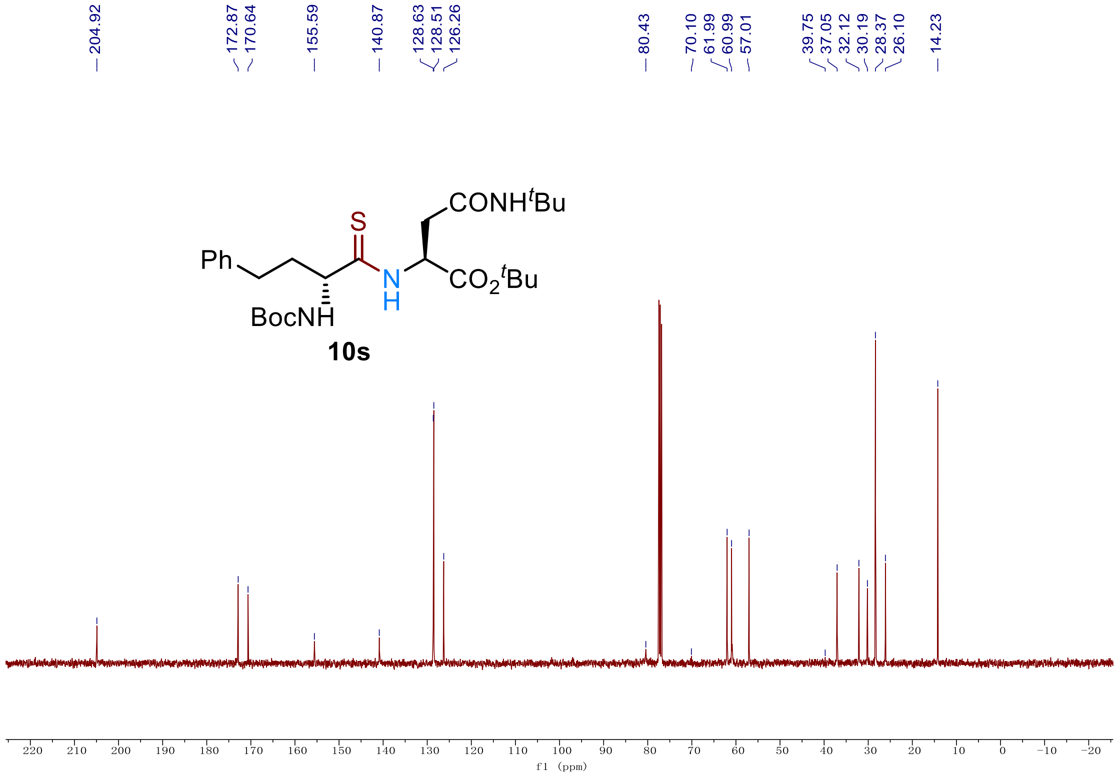
10r


203.82
170.35
156.64
155.53
140.85
136.69
128.64
128.60
128.49
128.21
128.18
126.29
82.89
80.47
66.73
61.01
57.75
40.55
37.04
32.21
30.46
29.60
28.36
28.09
22.01
Ph
S
N
H
NHCbz
CO$_2$^{t}Bu
BocHN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

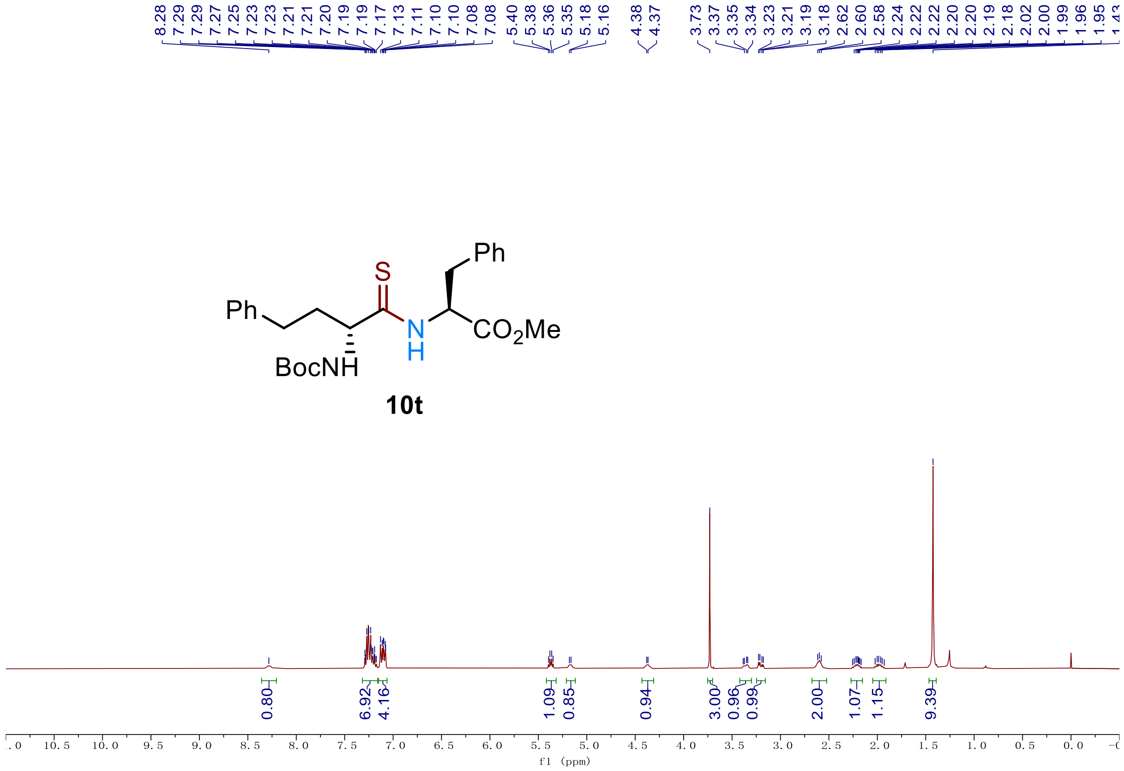
10r


9.05
7.28
7.27
7.25
7.24
7.19
7.17
7.17
7.16
7.15
5.42
5.34
5.32
5.25
5.24
5.23
5.22
5.21
4.49
2.82
2.81
2.80
2.72
2.71
2.70
2.69
2.68
2.67
2.66
2.64
2.63
2.62
2.61
2.61
2.59
2.22
2.21
2.20
2.02
1.99
1.97
1.46
1.43
Ph
S
N
H
CONH^{t}Bu
CO$_2$^{t}Bu
BocNH
0.78
2.47
2.97
0.89
0.69
1.04
0.79
1.99
1.99
0.95
1.40
8.74
9.26
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

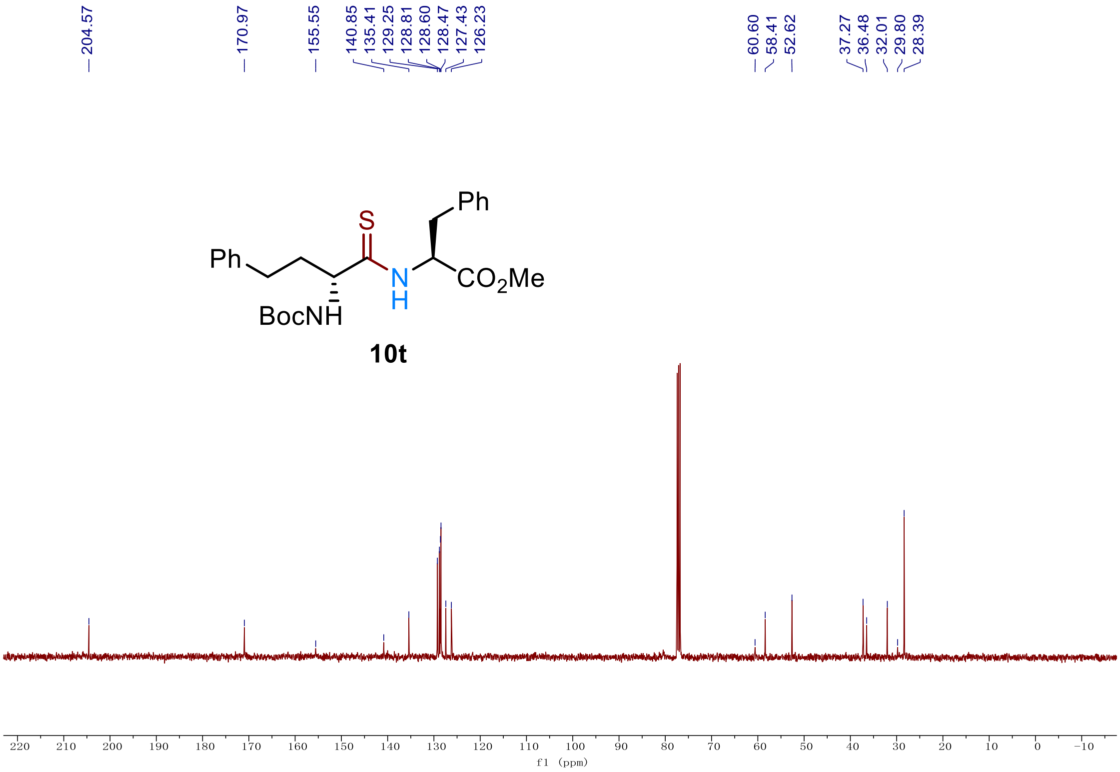
10s


204.92
172.87
170.64
155.59
140.87
128.63
128.51
126.26
80.43
70.10
61.99
60.99
57.01
39.75
37.05
32.12
30.19
28.37
26.10
14.23
S
CONH^{t}Bu
Ph
N
H
CO$_2$^{t}Bu
BocNH
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

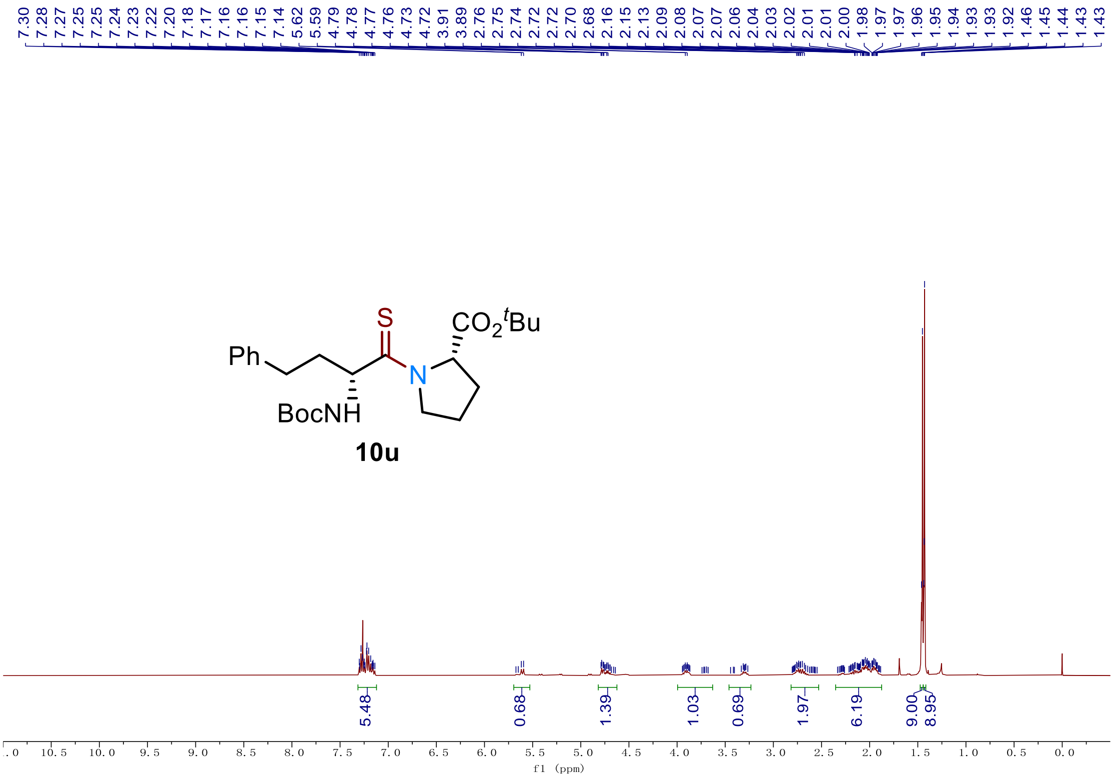
10s


8.28
7.29
7.29
7.27
7.25
7.23
7.23
7.21
7.21
7.20
7.19
7.19
7.17
7.13
7.11
7.10
7.10
7.08
7.08
5.40
5.38
5.36
5.35
5.18
5.16
4.38
4.37
3.73
3.37
3.35
3.34
3.23
3.21
3.19
3.18
2.62
2.60
2.58
2.24
2.22
2.22
2.20
2.20
2.19
2.18
2.02
2.00
1.99
1.96
1.95
S
Ph
Ph
N
H
CO$_2$Me
BocNH
0.80
6.92
4.16
1.09
0.85
0.94
3.00
0.96
0.99
2.00
1.07
1.15
9.39
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

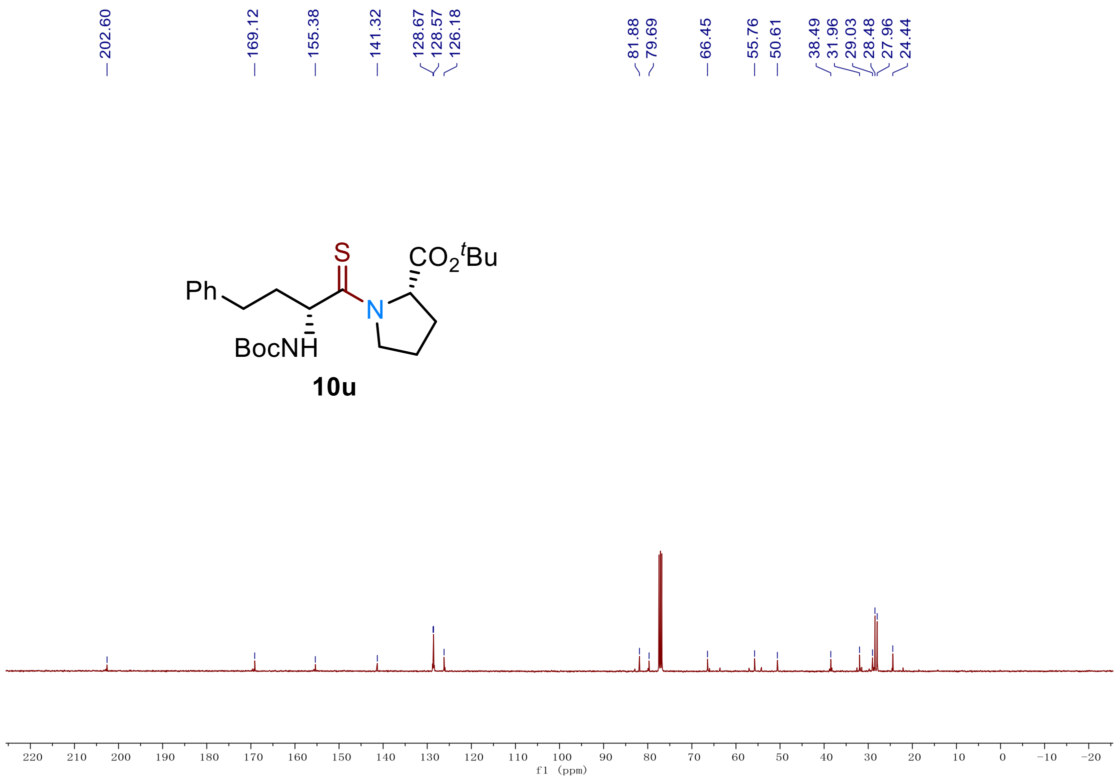
10t

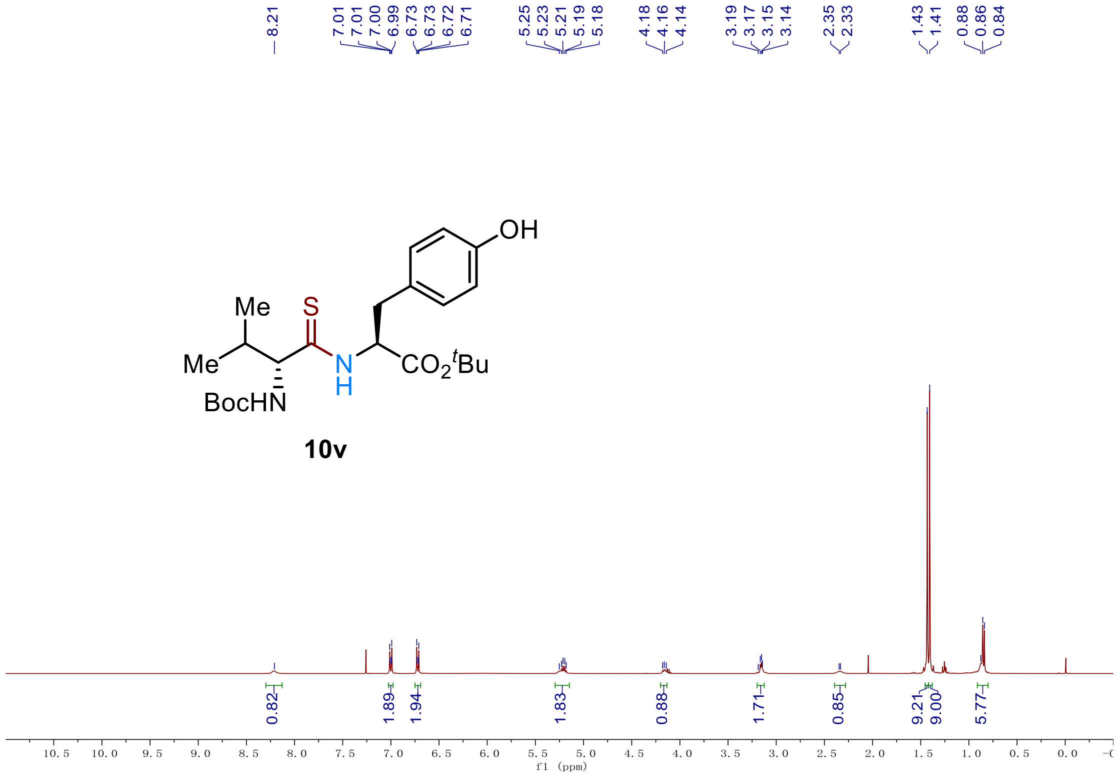

204.57
170.97
155.55
140.85
135.41
129.25
128.81
128.60
128.47
127.43
126.23
60.60
58.41
52.62
37.27
36.48
32.01
29.80
28.39
Ph
S
N
H
Ph
CO2Me
BocNH
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

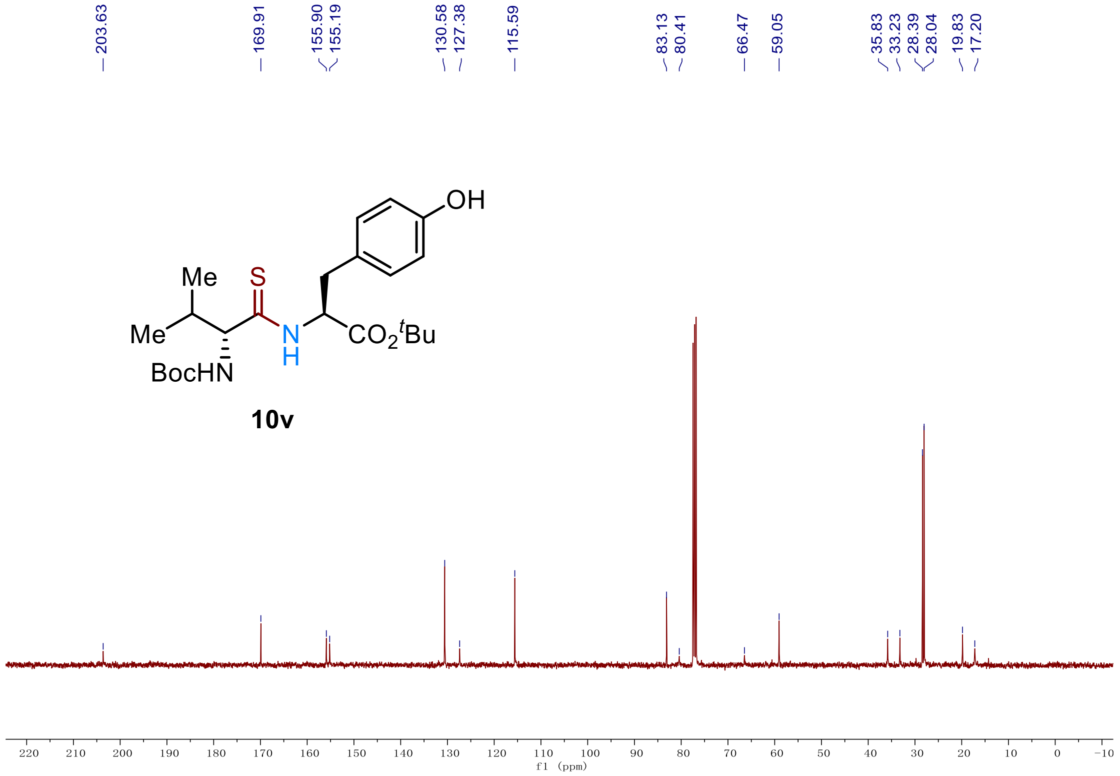
10t


7.30
7.28
7.27
7.25
7.25
7.24
7.23
7.22
7.20
7.18
7.17
7.16
7.16
7.15
7.14
5.62
5.59
4.79
4.78
4.77
4.76
4.73
4.72
3.91
3.89
2.76
2.75
2.74
2.72
2.72
2.70
2.68
2.16
2.15
2.13
2.09
2.08
2.07
2.07
2.06
2.04
2.03
2.02
2.01
2.01
2.00
1.98
1.97
1.97
1.96
1.95
1.94
1.93
1.93
1.92
1.46
1.45
1.44
1.43
1.43
S
CO2tBu
Ph
N
BocNH
5.48
0.68
1.39
1.03
0.69
1.97
6.19
9.00
8.95
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

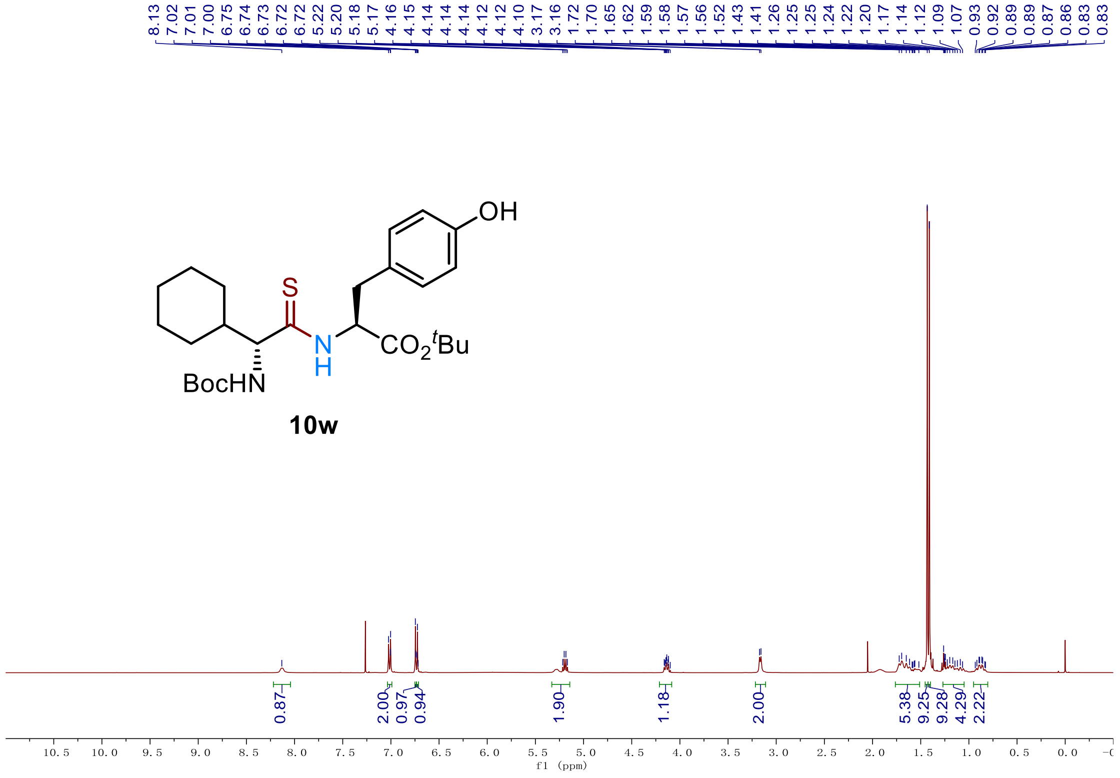
10u


10u
202.60
169.12
155.38
141.32
128.67
128.57
126.18
81.88
79.69
66.45
55.76
50.61
38.49
31.96
29.03
28.48
27.96
24.44
S
CO$_2$^{t}Bu
Ph
N
BocNH
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

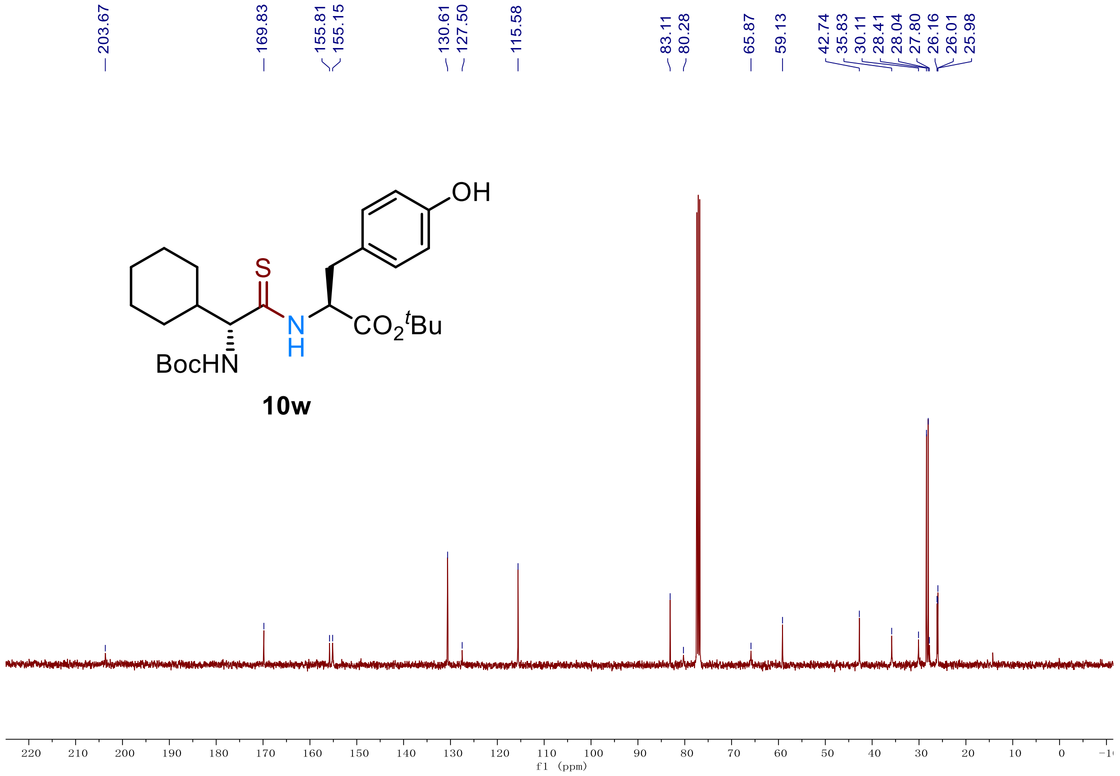

10v
8.21
7.01
7.01
7.00
6.99
6.73
6.73
6.72
6.71
5.25
5.23
5.21
5.19
5.18
4.18
4.16
4.14
3.19
3.17
3.15
3.14
2.35
2.33
1.43
1.41
0.88
0.86
0.84
OH
Me
S
Me
N
H
CO$_2$^{t}Bu
BocHN
0.82
1.89
1.94
1.83
0.88
1.71
0.85
9.21
9.00
5.77
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


203.63
169.91
155.90
155.19
130.58
127.38
115.59
83.13
80.41
66.47
59.05
35.83
33.23
28.39
28.04
19.83
17.20
OH
Me
S
Me
N
H
CO2tBu
BocHN
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

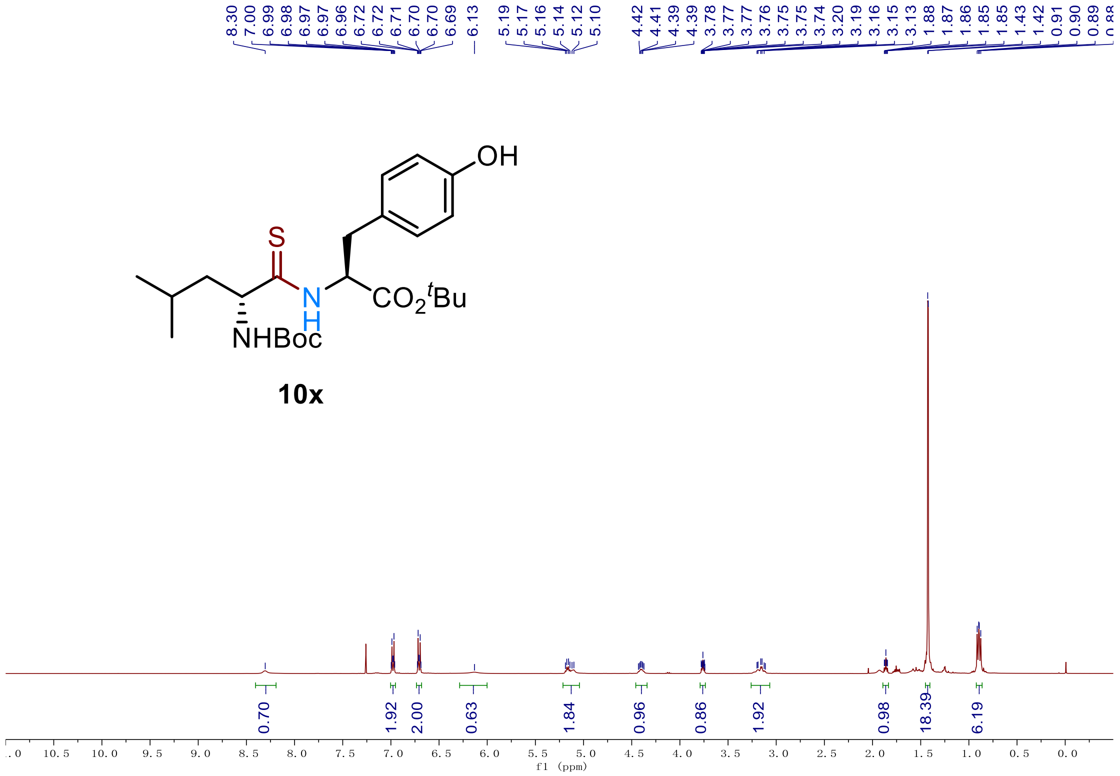
10v


8.13
7.02
7.01
7.00
6.75
6.74
6.73
6.72
6.72
5.22
5.20
5.18
5.17
4.16
4.15
4.14
4.14
4.14
4.12
4.12
4.10
3.17
3.16
1.72
1.70
1.65
1.62
1.59
1.58
1.57
1.56
1.52
1.43
1.41
1.26
1.25
1.25
1.24
1.22
1.20
1.17
1.14
1.12
1.09
1.07
0.93
0.92
0.89
0.89
0.87
0.86
0.83
0.83
OH
S
N
H
CO2tBu
BocHN
0.87
2.00
0.97
0.94
1.90
1.18
2.00
5.38
9.25
9.28
4.29
2.22
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

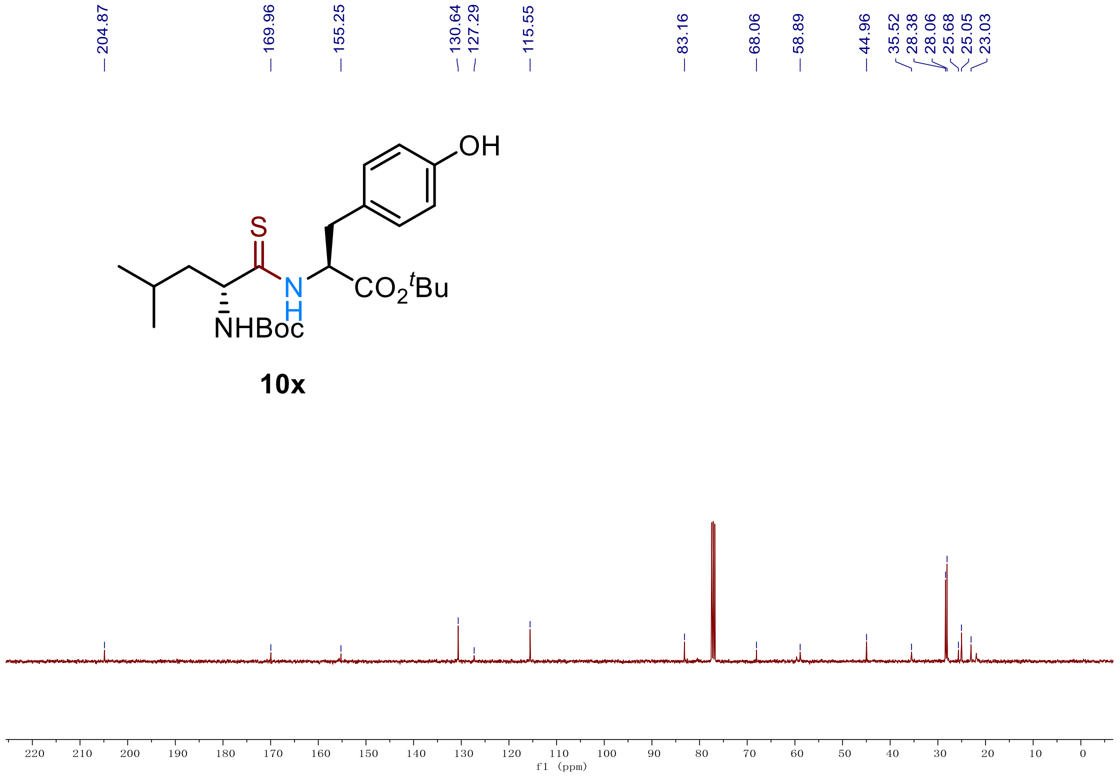
10w


203.67
169.83
155.81
155.15
130.61
127.50
115.58
83.11
80.28
65.87
59.13
42.74
35.83
30.11
28.41
28.04
27.80
26.16
26.01
25.98
OH
S
N
H
CO2tBu
BocHN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

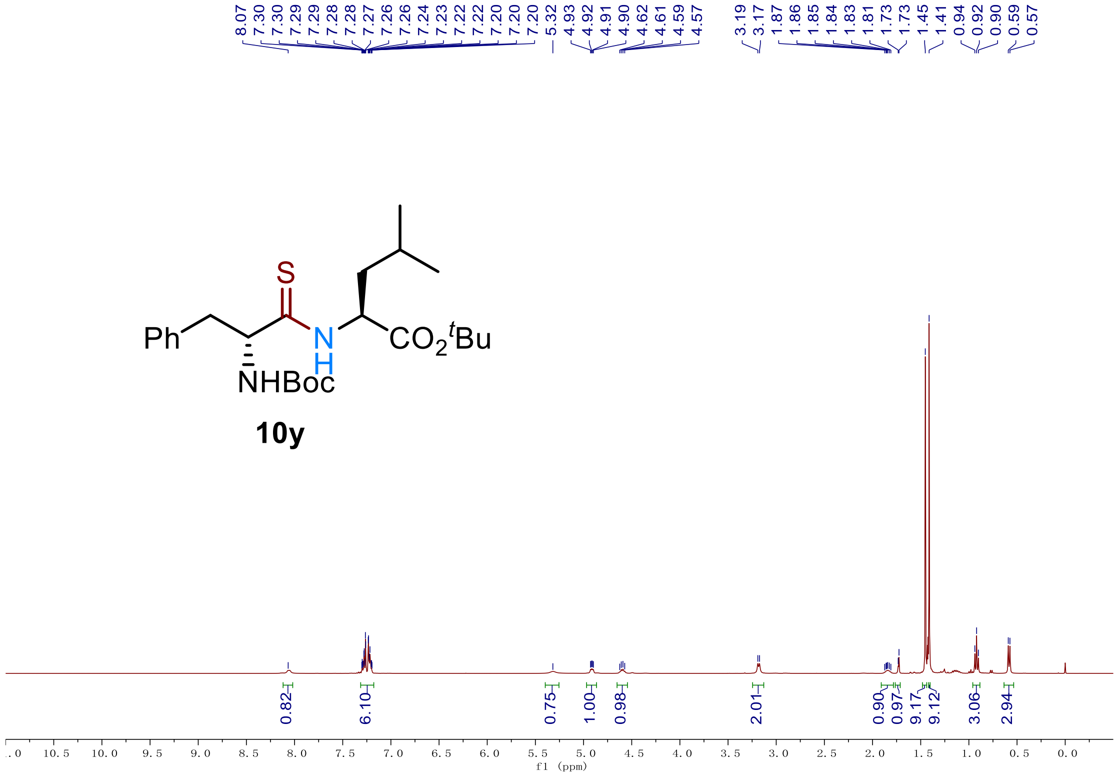
10w


8.30
7.00
6.99
6.98
6.97
6.97
6.96
6.72
6.72
6.71
6.70
6.70
6.69
6.13
5.19
5.17
5.16
5.14
5.12
5.10
4.42
4.41
4.39
4.39
3.78
3.77
3.77
3.76
3.75
3.75
3.74
3.20
3.19
3.16
3.15
3.13
1.88
1.87
1.86
1.85
1.85
1.43
1.42
0.91
0.90
0.89
OH
S
N
H
CO2tBu
NHBoc
0.70
1.92
2.00
0.63
1.84
0.96
0.86
1.92
0.98
18.39
6.19
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

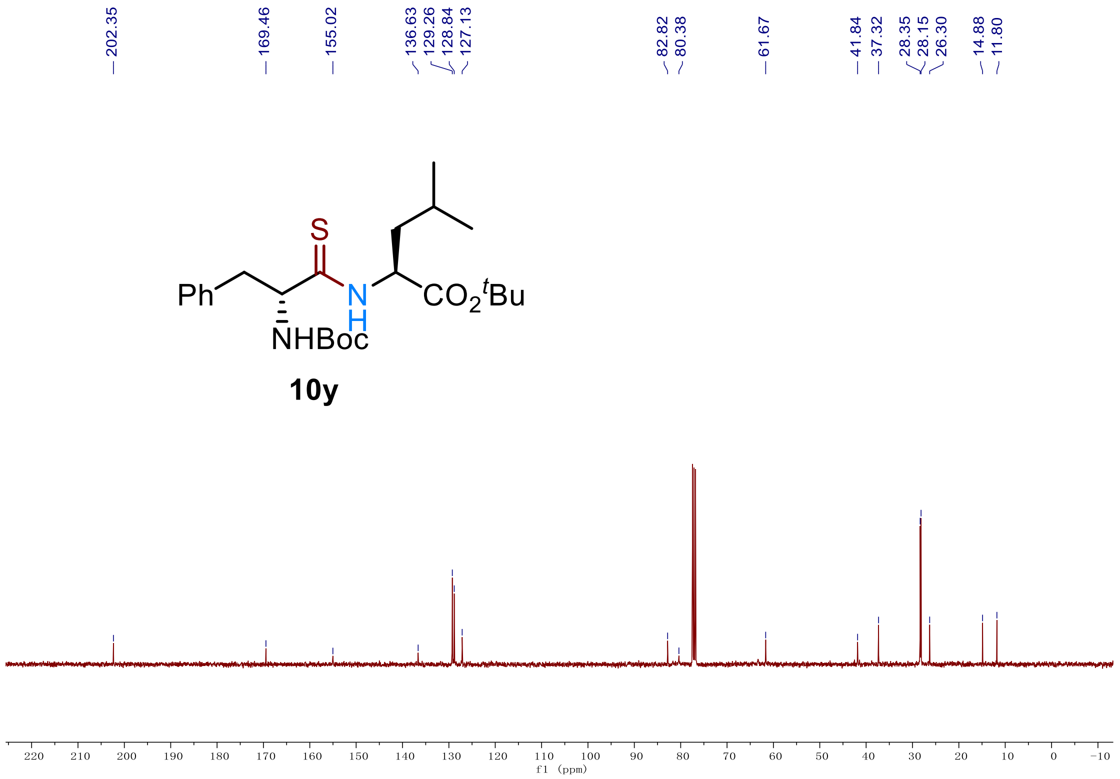
10x


204.87
169.96
155.25
130.64
127.29
115.55
83.16
68.06
58.89
44.96
35.52
28.38
28.06
25.68
25.05
23.03
OH
S
N
H
CO2tBu
NHBoc
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

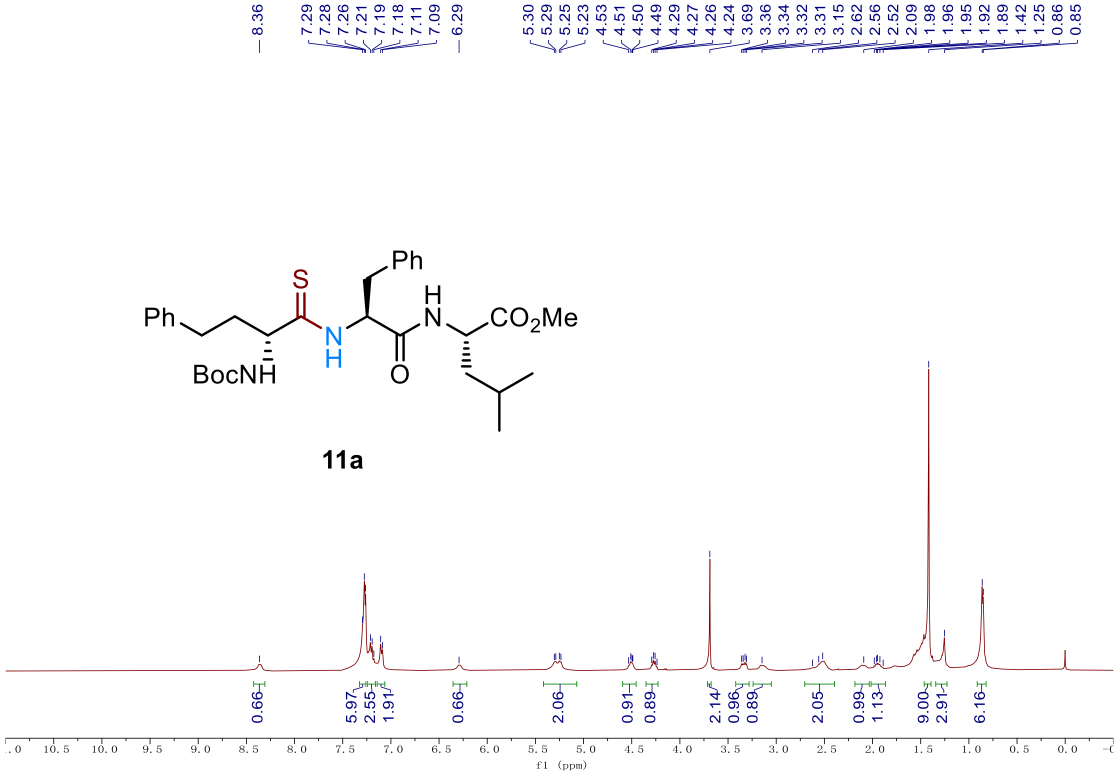
10x


8.07
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.24
7.23
7.22
7.22
7.20
7.20
7.20
5.32
4.93
4.92
4.91
4.90
4.62
4.61
4.59
4.57
3.19
3.17
1.87
1.86
1.85
1.84
1.83
1.81
1.73
1.73
1.45
1.41
0.94
0.92
0.90
0.59
0.57
S
Ph
N
H
CO2tBu
NHBoc
0.82
6.10
0.75
1.00
0.98
2.01
0.90
0.97
9.17
9.12
3.06
2.94
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

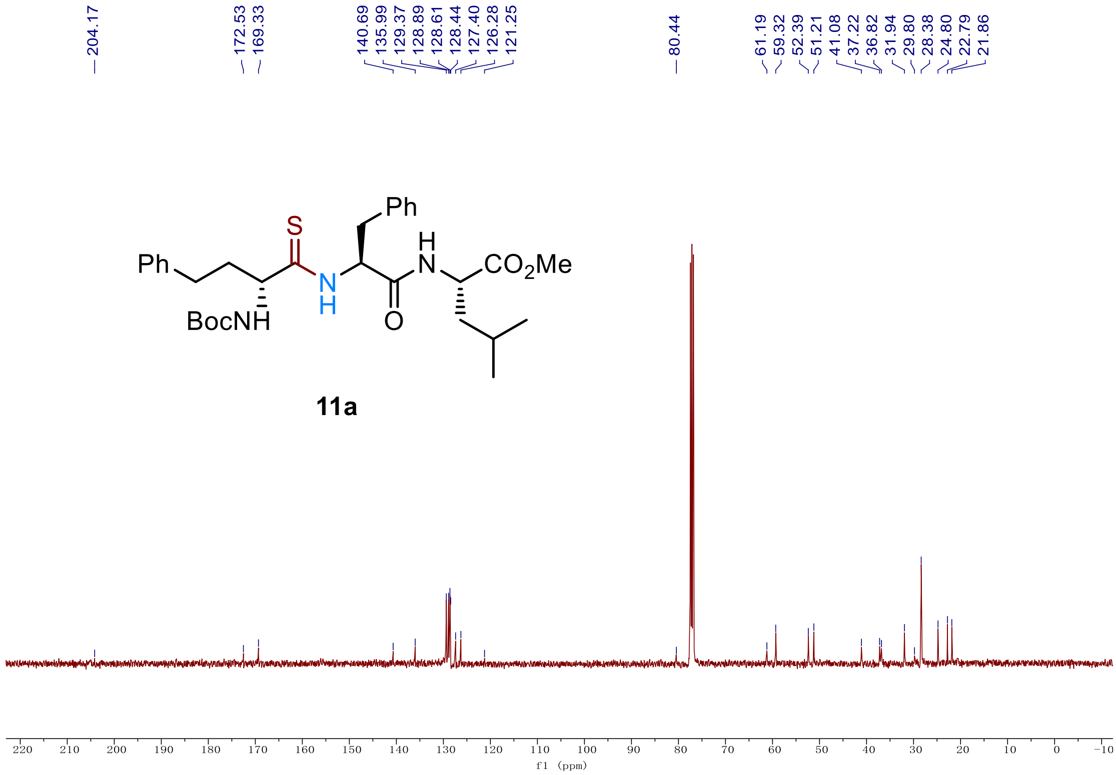
10y


202.35
169.46
155.02
136.63
129.26
128.84
127.13
82.82
80.38
61.67
41.84
37.32
28.35
28.15
26.30
14.88
11.80
Ph
S
N
H
NHBoc
$CO_2{}^tBu$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

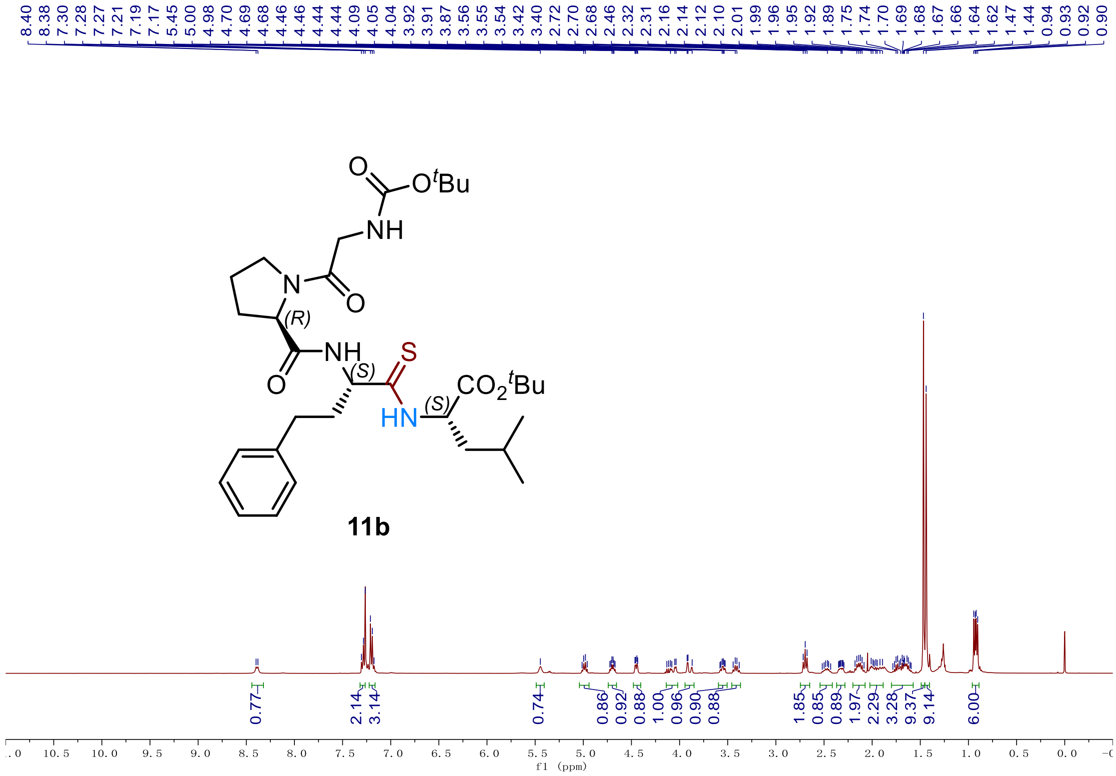
10y


8.36
7.29
7.28
7.26
7.21
7.19
7.18
7.11
7.09
6.29
5.30
5.29
5.25
5.23
4.53
4.51
4.50
4.49
4.29
4.27
4.26
4.24
3.69
3.36
3.34
3.32
3.31
3.15
2.62
2.56
2.52
2.09
1.98
1.96
1.95
1.92
1.89
1.42
1.25
0.86
0.85
Ph
S
Ph
H
N
CO_2Me
BocNH
N
H
O
0.66
5.97
2.55
1.91
0.66
2.06
0.91
0.89
2.14
0.96
0.89
2.05
0.99
1.13
9.00
2.91
6.16
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

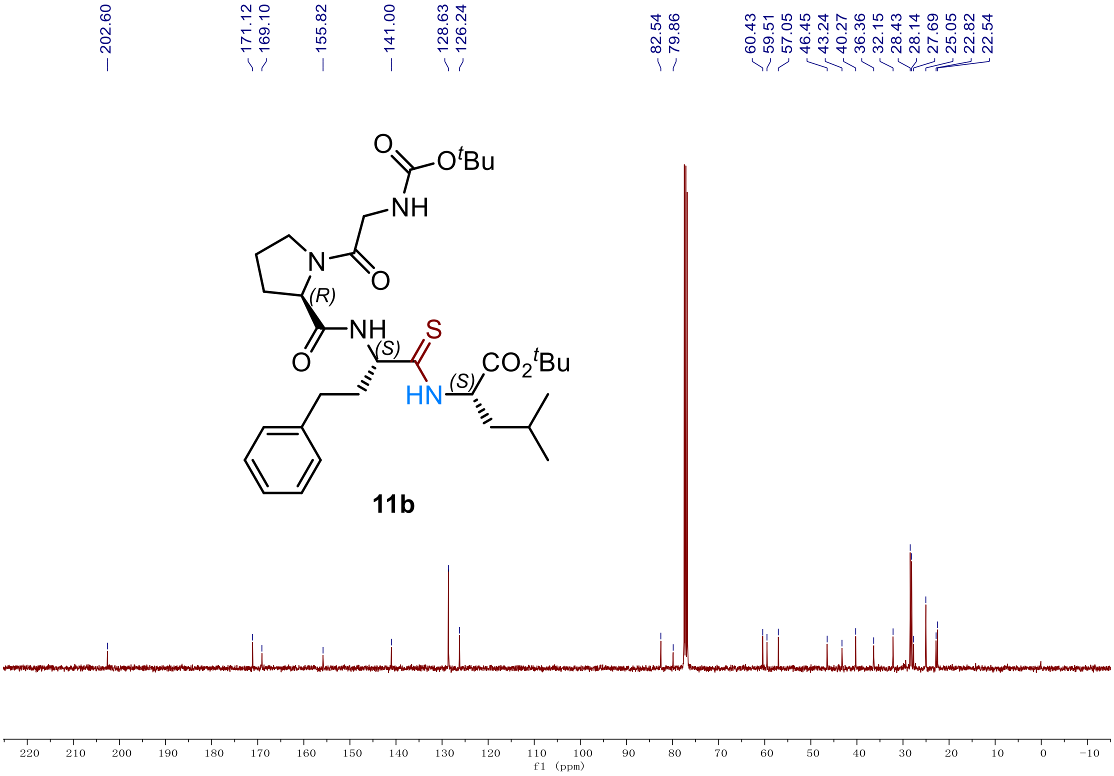
11a


204.17
172.53
169.33
140.69
135.99
129.37
128.89
128.61
128.44
127.40
126.28
121.25
80.44
61.19
59.32
52.39
51.21
41.08
37.22
36.82
31.94
29.80
28.38
24.80
22.79
21.86
Ph
S
Ph
H
N
CO2Me
N
H
BocNH
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

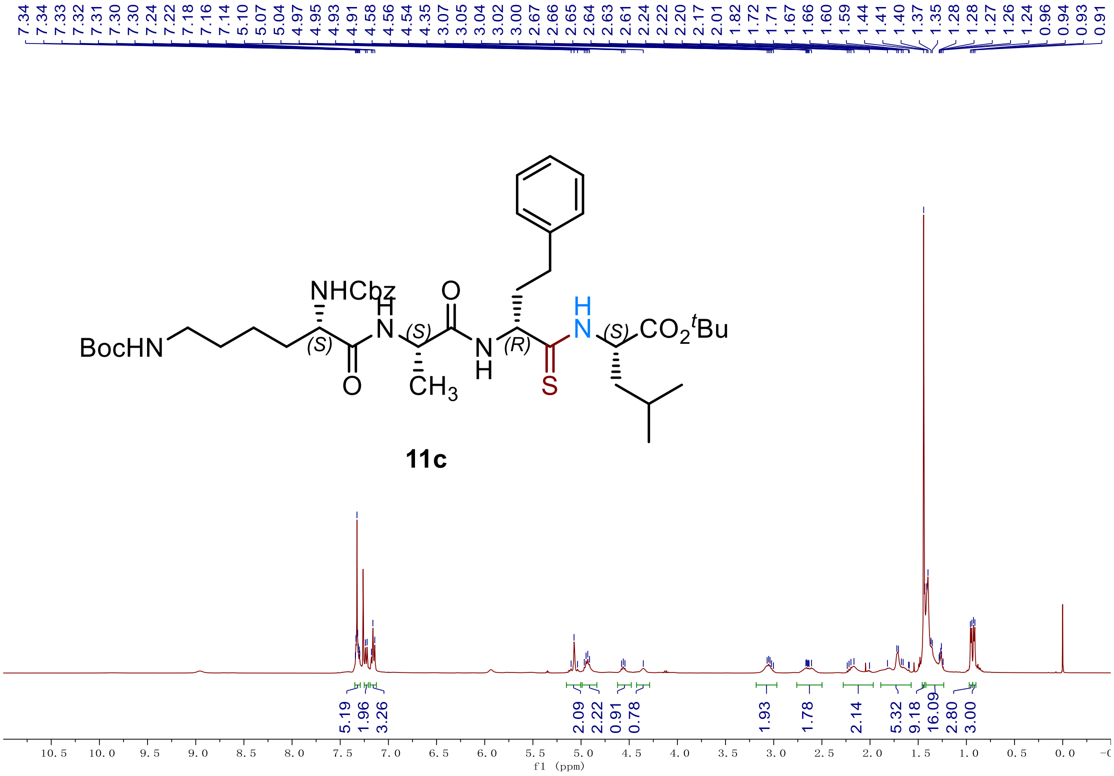
11a


8.40
8.38
7.30
7.28
7.27
7.21
7.19
7.17
5.45
5.00
4.98
4.70
4.69
4.68
4.46
4.46
4.44
4.44
4.09
4.05
4.04
3.92
3.91
3.87
3.56
3.55
3.54
3.42
3.40
2.72
2.70
2.68
2.46
2.32
2.31
2.16
2.14
2.12
2.10
2.01
1.99
1.96
1.95
1.92
1.89
1.75
1.74
1.70
1.69
1.68
1.67
1.66
1.64
1.62
1.47
1.44
0.94
0.93
0.92
0.90
O
O^tBu
NH
N
O
(R)
NH
(S)
S
CO2^tBu
O
HN
(S)
0.77
2.14
3.14
0.74
0.86
0.92
0.88
1.00
0.96
0.90
0.88
1.85
0.85
0.89
1.97
2.29
3.28
9.37
9.14
6.00
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−(
f1 (ppm)

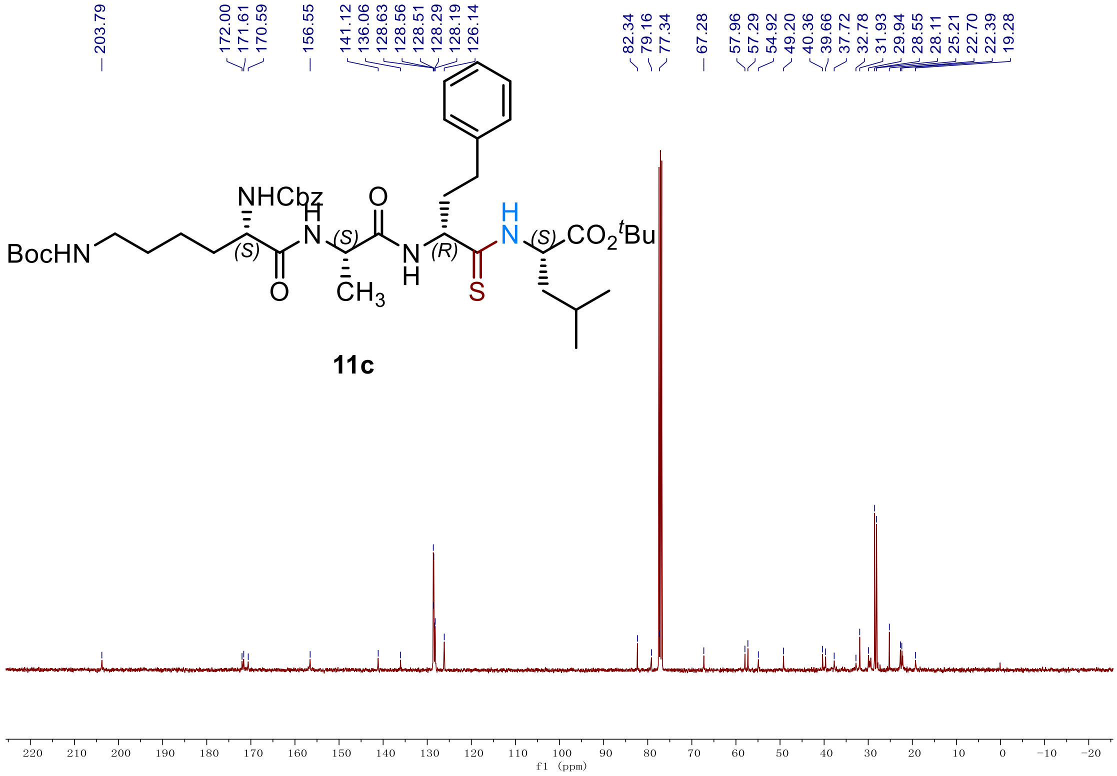
11b


202.60
171.12
169.10
155.82
141.00
128.63
126.24
82.54
79.86
60.43
59.51
57.05
46.45
43.24
40.27
36.36
32.15
28.43
28.14
27.69
25.05
22.82
22.54
O
O^tBu
NH
N
O
(R)
NH
(S)
S
O
CO2tBu
HN
(S)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

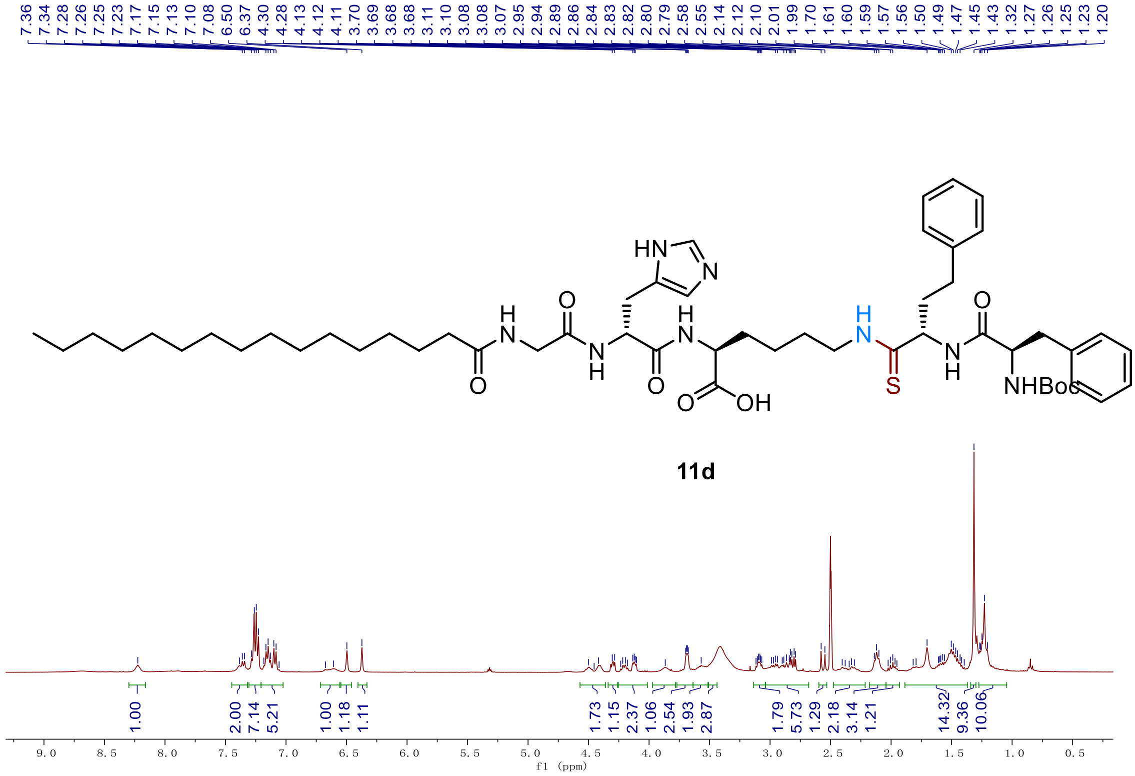
11b


7.34
7.34
7.33
7.32
7.31
7.30
7.30
7.24
7.22
7.18
7.16
7.14
5.10
5.07
5.04
4.97
4.95
4.93
4.91
4.58
4.56
4.54
4.35
3.07
3.05
3.04
3.02
3.00
2.67
2.66
2.65
2.64
2.63
2.61
2.24
2.22
2.20
2.17
2.01
1.82
1.72
1.71
1.67
1.66
1.60
1.59
1.44
1.41
1.40
1.37
1.35
1.28
1.28
1.27
1.26
1.24
0.96
0.94
0.93
0.91
NHCbz
O
H
N
(S)
N
H
(R)
H
N
(S)
CO2tBu
BocHN
(S)
O
CH3
S
5.19
1.96
3.26
2.09
2.22
0.91
0.78
1.93
1.78
2.14
5.32
9.18
16.09
2.80
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

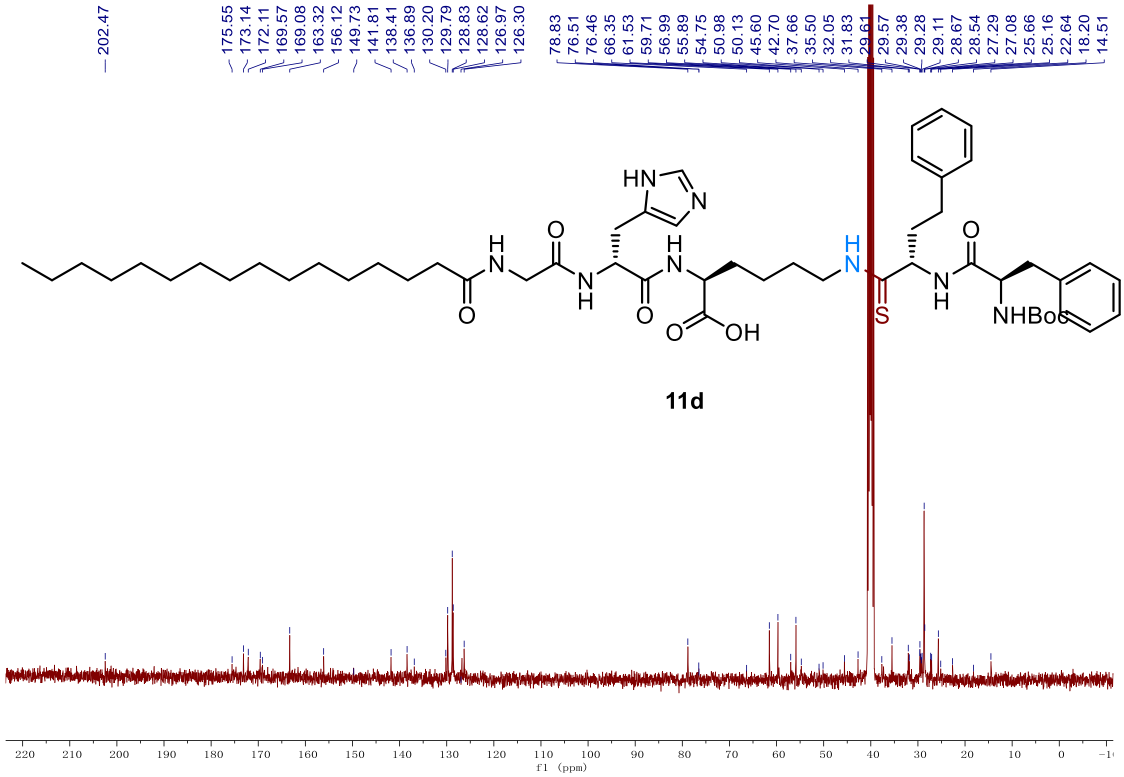
11c


203.79
172.00
171.61
170.59
156.55
141.12
136.06
128.63
128.56
128.51
128.29
128.19
126.14
82.34
79.16
77.34
67.28
57.96
57.29
54.92
49.20
40.36
39.66
37.72
32.78
31.93
29.94
28.55
28.11
25.21
22.70
22.39
19.28
BocHN
NHCbz
(S)
O
H
N
(S)
CH3
O
N
H
(R)
S
H
N
(S)
CO2tBu
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

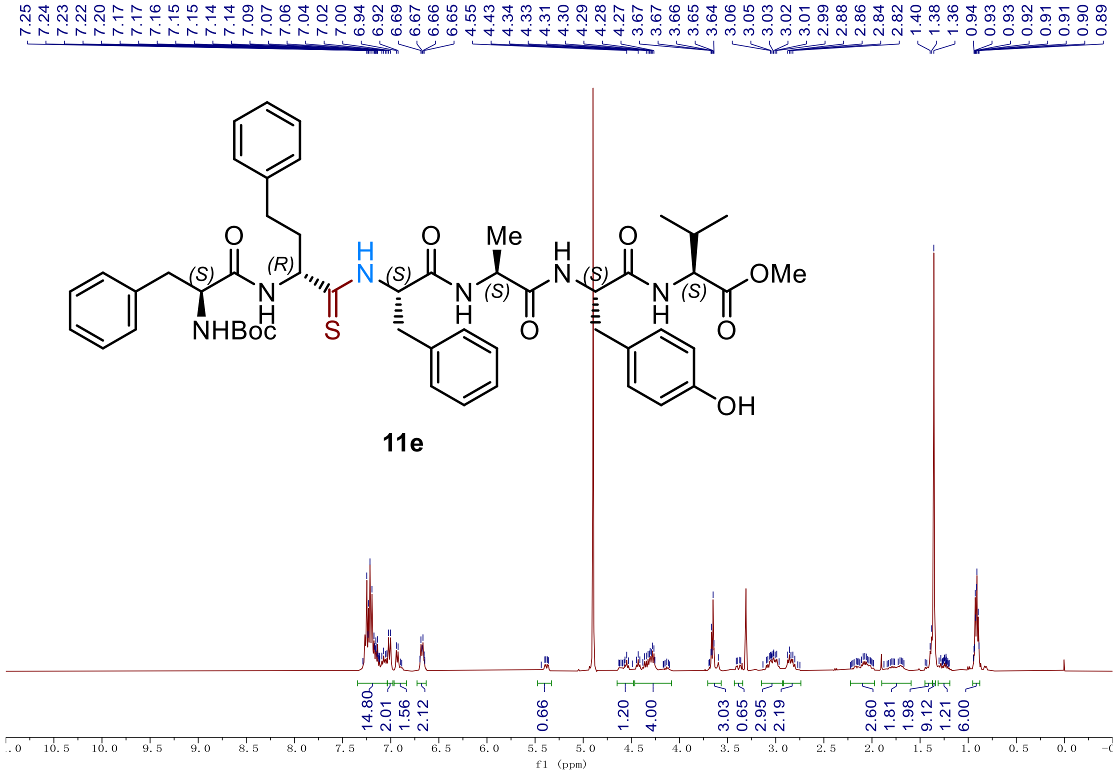
11c


7.36
7.34
7.28
7.26
7.25
7.23
7.17
7.15
7.13
7.10
7.08
6.50
6.37
4.30
4.28
4.13
4.12
4.11
3.70
3.69
3.68
3.68
3.11
3.10
3.08
3.08
3.07
2.95
2.94
2.89
2.86
2.84
2.83
2.82
2.80
2.79
2.58
2.55
2.14
2.12
2.10
2.01
1.99
1.70
1.61
1.60
1.59
1.57
1.56
1.50
1.49
1.47
1.45
1.43
1.32
1.27
1.26
1.25
1.23
1.20
H
N
O
O
N
H
HN
N
O
H
N
O
OH
H
N
S
N
H
O
NHBoc
1.00
2.00
7.14
5.21
1.00
1.18
1.11
1.73
1.15
2.37
1.06
2.54
1.93
2.87
1.79
5.73
1.29
2.18
3.14
1.21
14.32
9.36
10.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

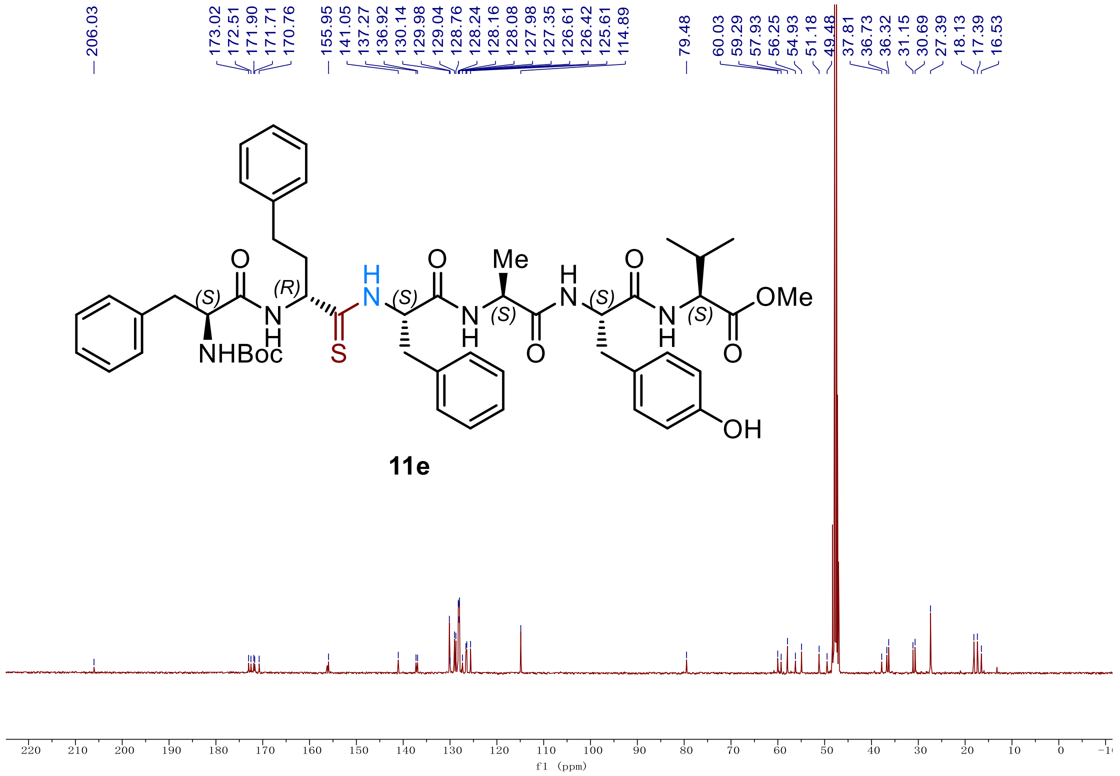
11d


202.47
175.55
173.14
172.11
169.57
169.08
163.32
156.12
149.73
141.81
138.41
136.89
130.20
129.79
128.83
128.62
126.97
126.30
78.83
76.51
76.46
66.35
61.53
59.71
56.99
55.89
54.75
50.98
50.13
45.60
42.70
37.66
35.50
32.05
31.83
29.61
29.57
29.38
29.28
29.11
28.67
28.54
27.29
27.08
25.66
25.16
22.64
18.20
14.51
HN
N
H
N
O
N
H
O
H
N
O
OH
H
N
S
N
H
O
NHBoc
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

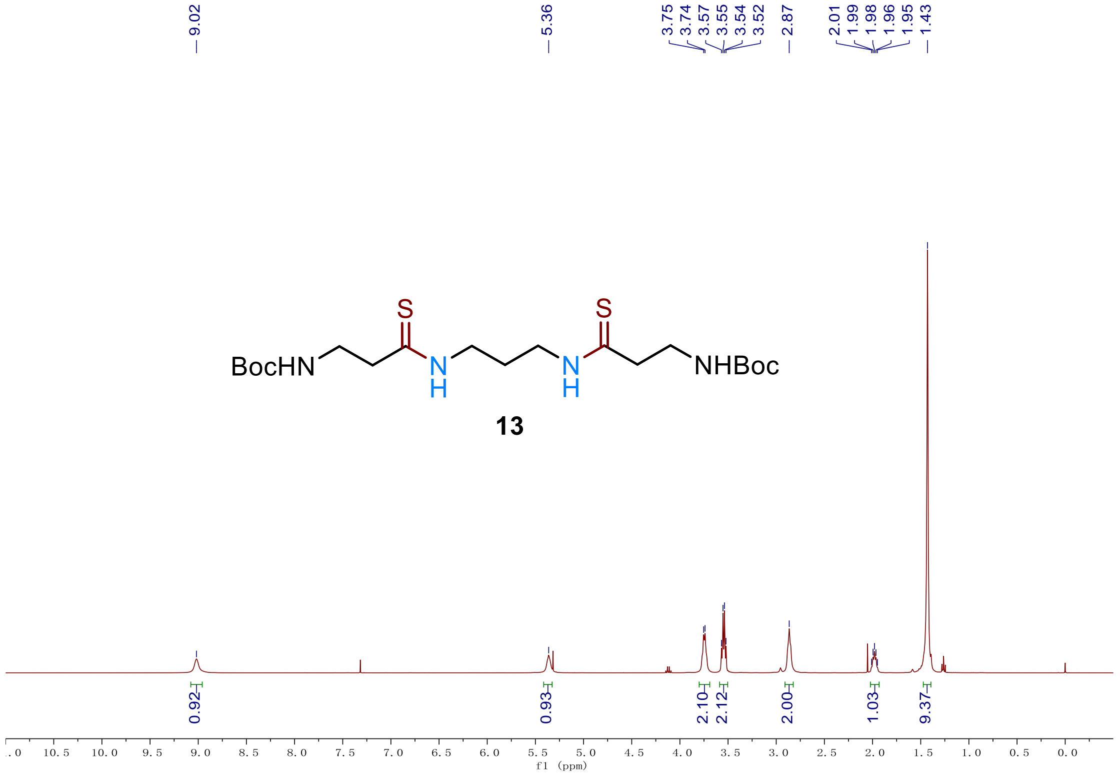
11d


7.25
7.24
7.23
7.22
7.20
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.09
7.07
7.06
7.04
7.02
7.00
6.94
6.92
6.69
6.67
6.66
6.65
4.55
4.43
4.34
4.33
4.31
4.30
4.29
4.28
4.27
3.67
3.67
3.66
3.65
3.64
3.06
3.05
3.03
3.02
3.01
2.99
2.88
2.86
2.84
2.82
1.40
1.38
1.36
0.94
0.93
0.93
0.92
0.91
0.91
0.90
0.89
O
(S)
(R)
N
H
NHBoc
S
H
N
(S)
O
Me
N
H
(S)
O
H
N
(S)
O
N
H
(S)
OMe
O
OH
14.80
2.01
1.56
2.12
0.66
1.20
4.00
3.03
0.65
2.95
2.19
2.60
1.81
1.98
9.12
1.21
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

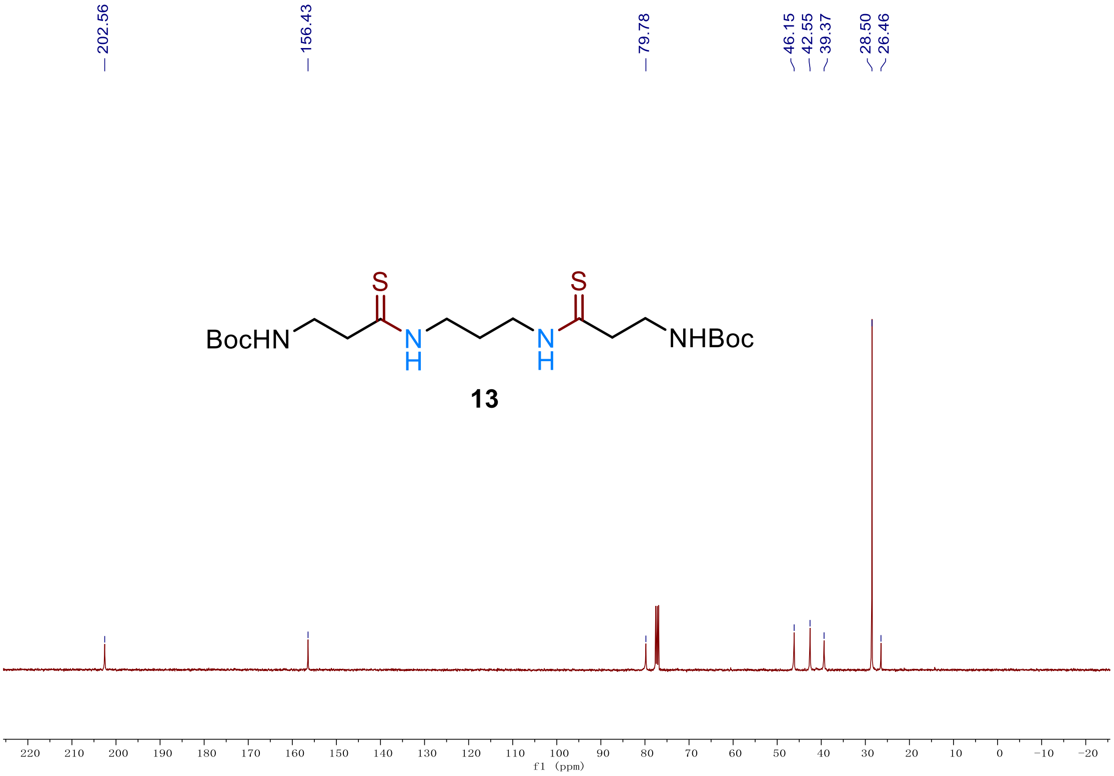
11e


206.03
173.02
172.51
171.90
171.71
170.76
155.95
141.05
137.27
136.92
130.14
129.98
129.04
128.76
128.24
128.16
128.08
127.98
127.35
126.61
126.42
125.61
114.89
79.48
60.03
59.29
57.93
56.25
54.93
51.18
49.48
37.81
36.73
36.32
31.15
30.69
27.39
18.13
17.39
16.53
O
Me
H
N
(S)
(R)
NHBoc
S
OMe
OH
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

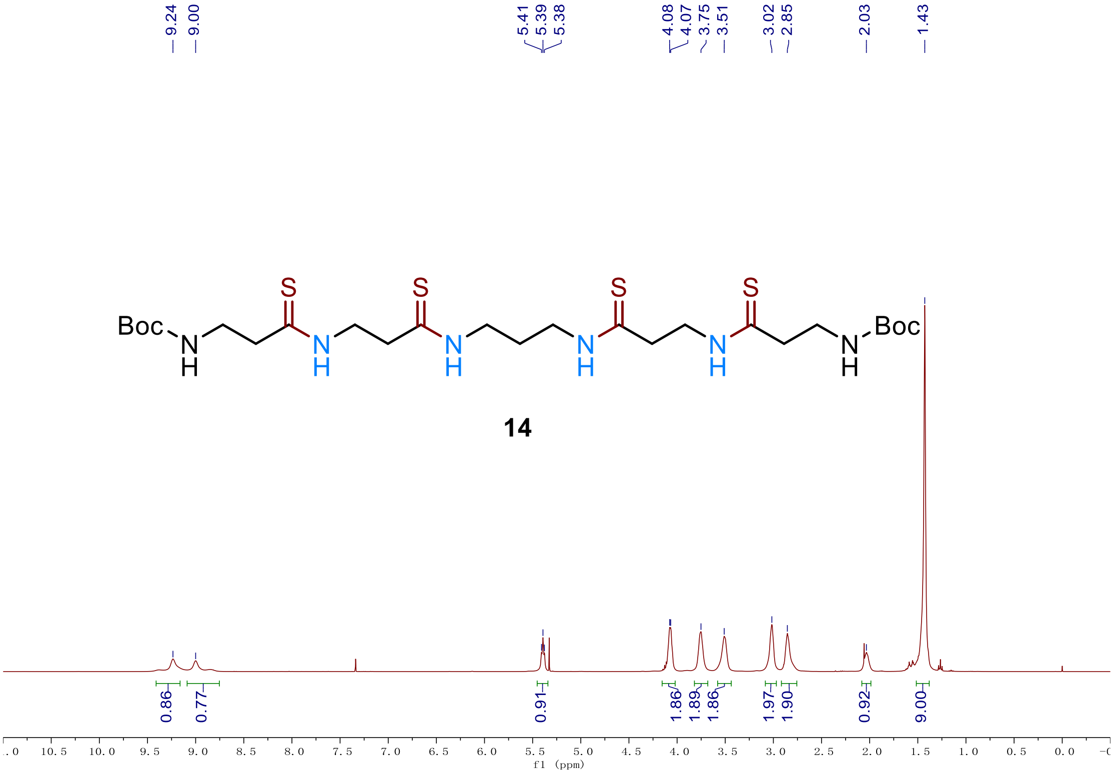
11e


9.02
5.36
3.75
3.74
3.57
3.55
3.54
3.52
2.87
2.01
1.99
1.98
1.96
1.95
1.43
S
BocHN
N
H
NHBoc
0.92
0.93
2.10
2.12
2.00
1.03
9.37
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

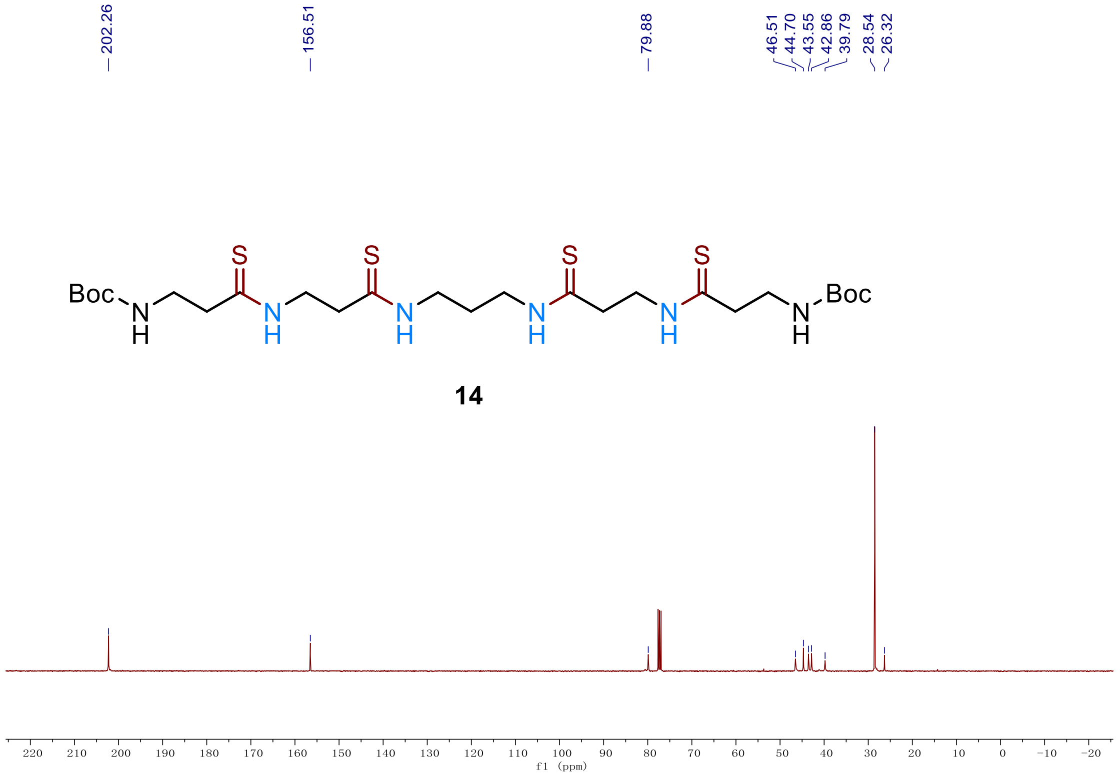
13


202.56
156.43
79.78
46.15
42.55
39.37
28.50
26.46
BocHN
S
N
H
S
N
H
NHBoc
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

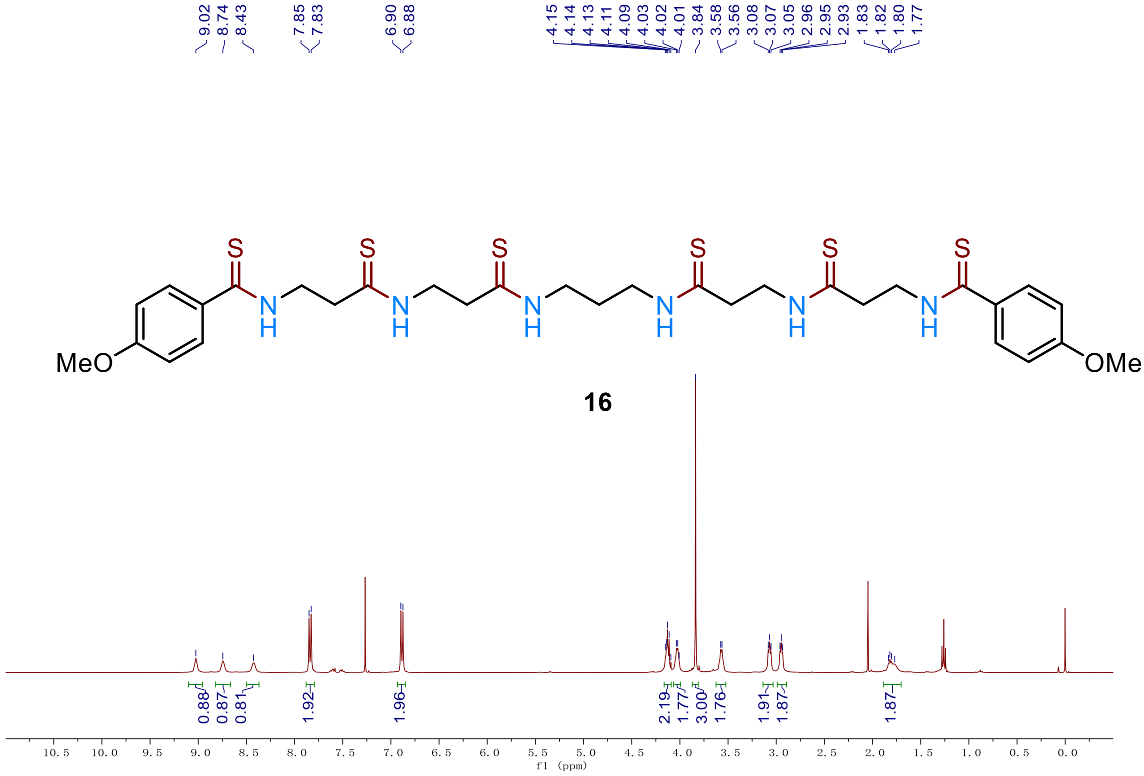
13


9.24
9.00
5.41
5.39
5.38
4.08
4.07
3.75
3.51
3.02
2.85
2.03
1.43
Boc
N
H
S
N
H
S
N
H
S
N
H
S
N
H
N
H
Boc
0.86
0.77
0.91
1.86
1.89
1.86
1.97
1.90
0.92
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

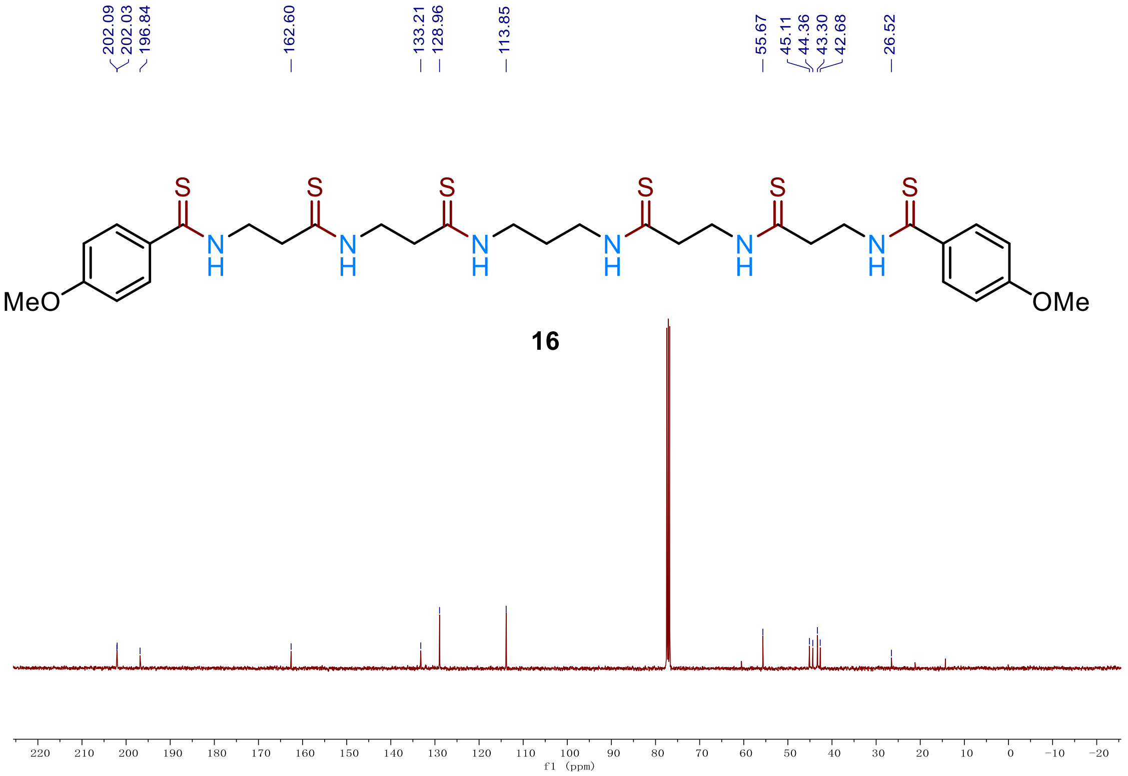
14


202.26
156.51
79.88
46.51
44.70
43.55
42.86
39.79
28.54
26.32
Boc
N
H
S
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20

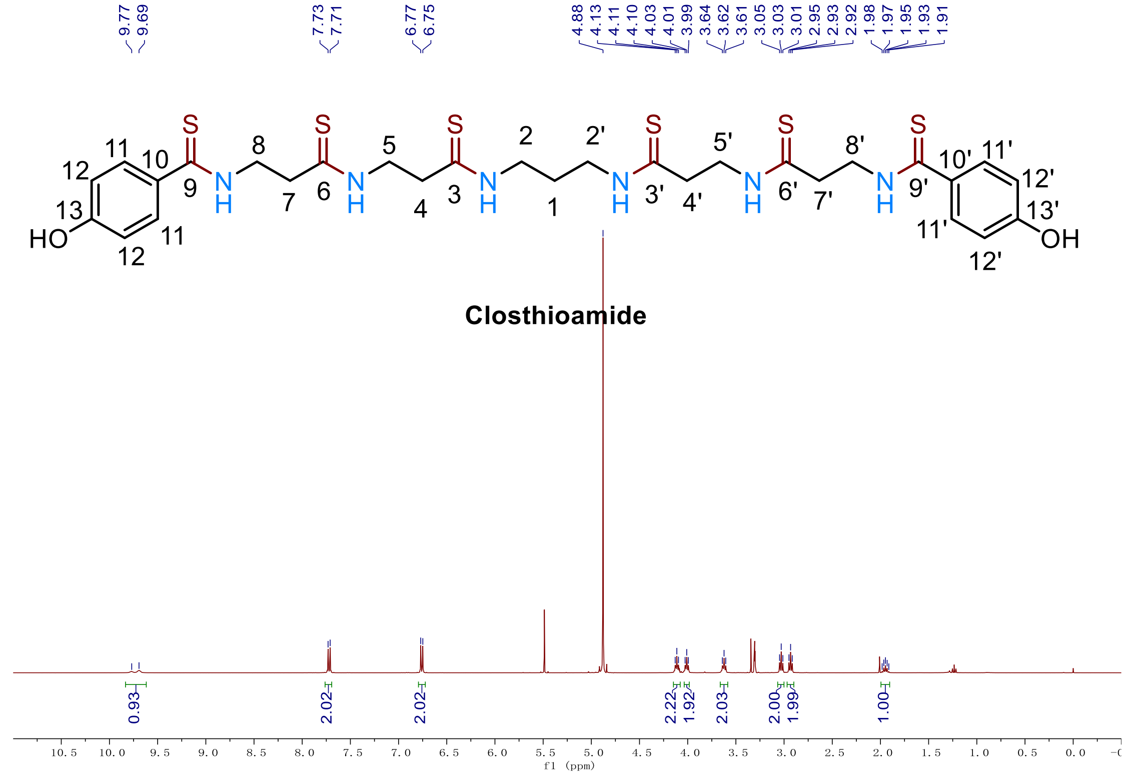
14


9.02
8.74
8.43
7.85
7.83
6.90
6.88
4.15
4.14
4.13
4.11
4.09
4.03
4.02
4.01
3.84
3.58
3.56
3.08
3.07
3.05
2.96
2.95
2.93
1.83
1.82
1.80
1.77
MeO
OMe
N
H
S
0.88
0.87
0.81
1.92
1.96
2.19
1.77
3.00
1.76
1.91
1.87
1.87
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

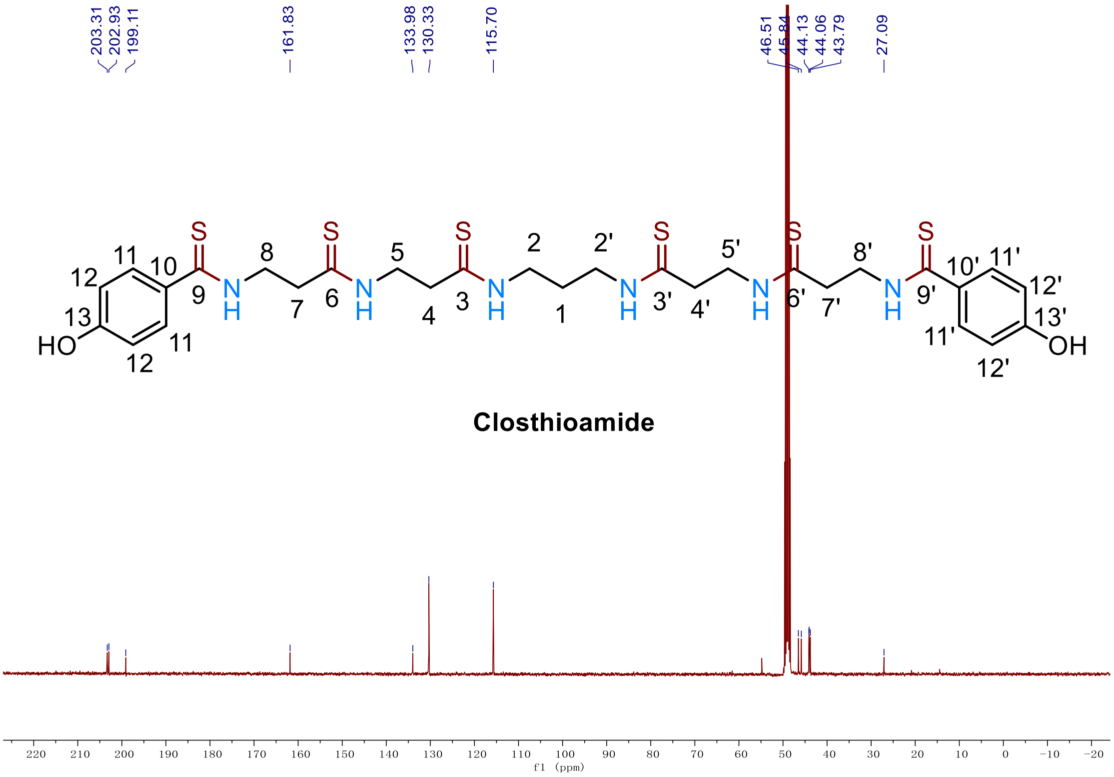
16



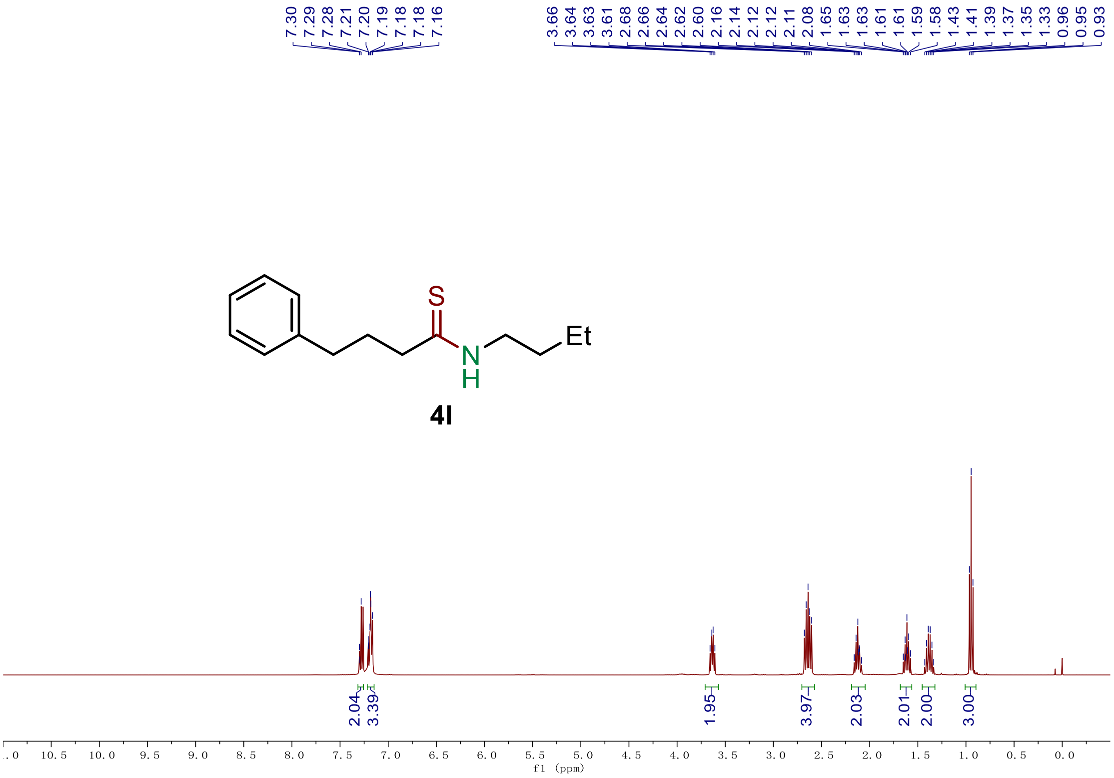
16



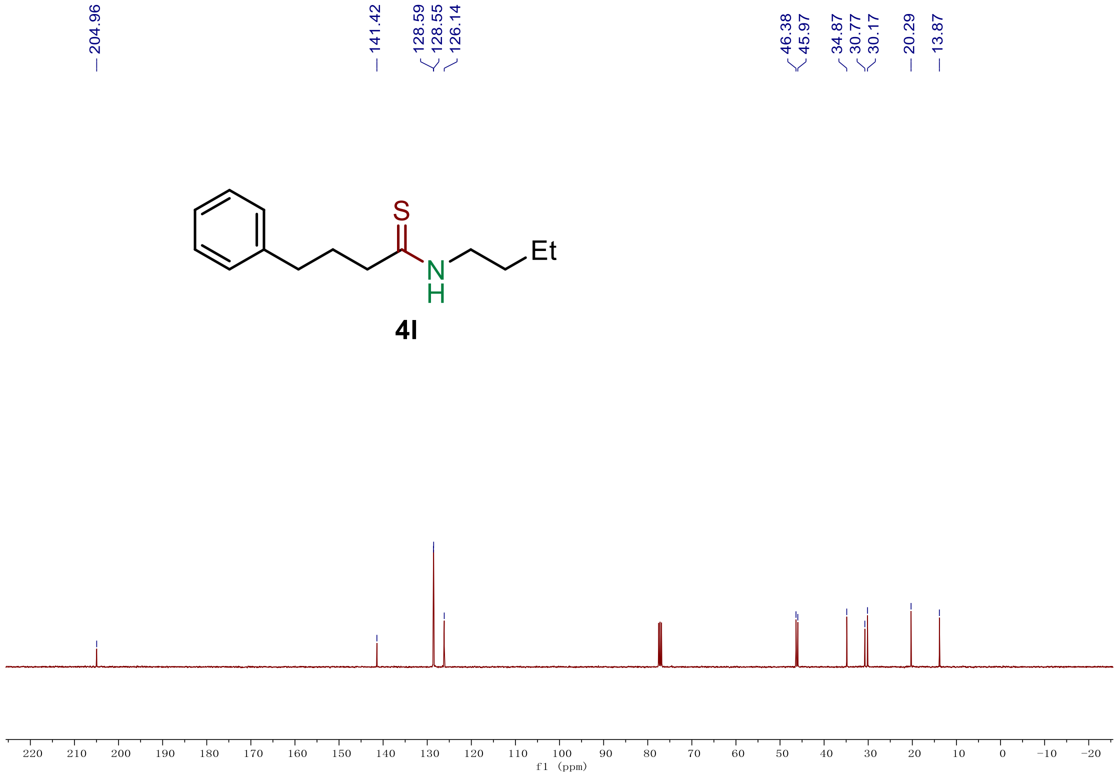
Closthioamide



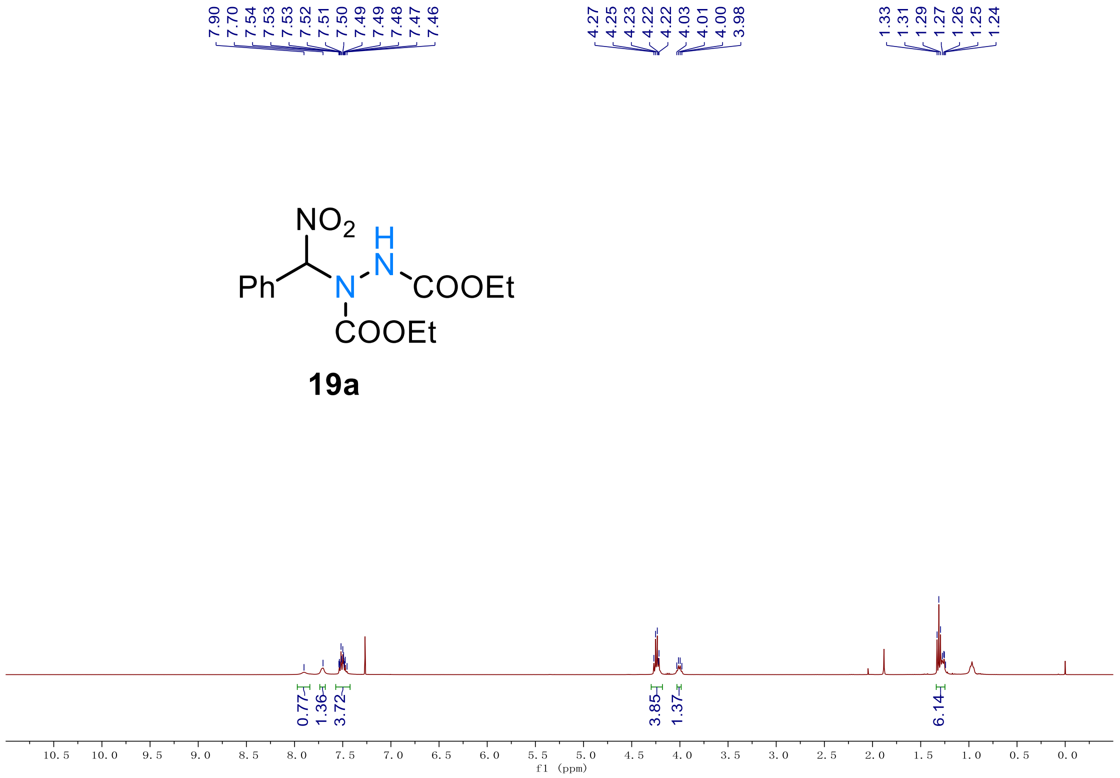
Closthioamide



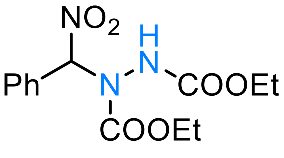
4l


204.96
141.42
128.59
128.55
126.14
46.38
45.97
34.87
30.77
30.17
20.29
13.87
S
N
H
Et
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

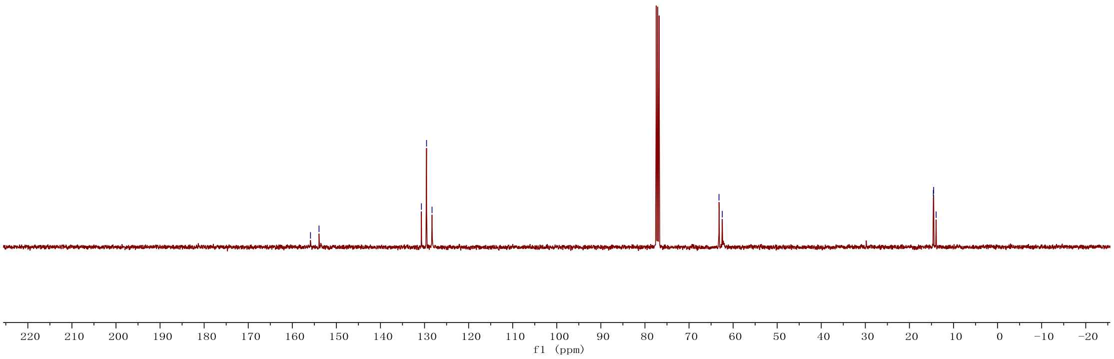
4l

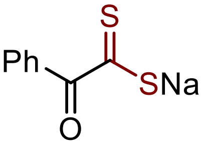

7.90
7.70
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.49
7.48
7.47
7.46
4.27
4.25
4.23
4.22
4.22
4.03
4.01
4.00
3.98
1.33
1.31
1.29
1.27
1.26
1.25
1.24
NO2
H
N
Ph
N
COOEt
COOEt
0.77
1.36
3.72
3.85
1.37
6.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

19a

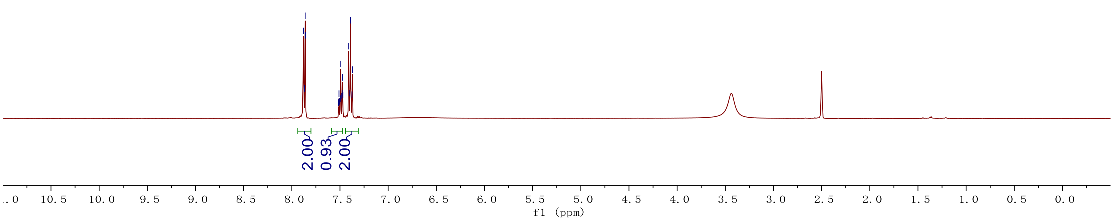


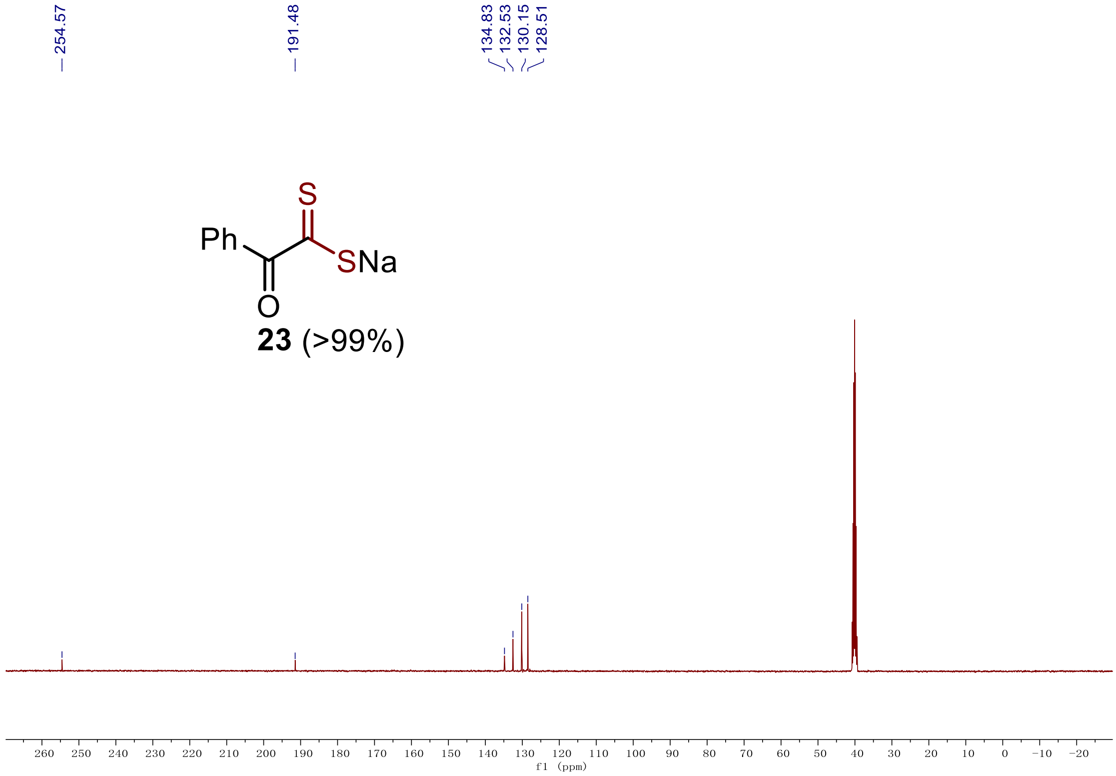
19a


155.87
153.94
130.71
129.55
128.30
63.20
62.45
14.57
14.50
13.94
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

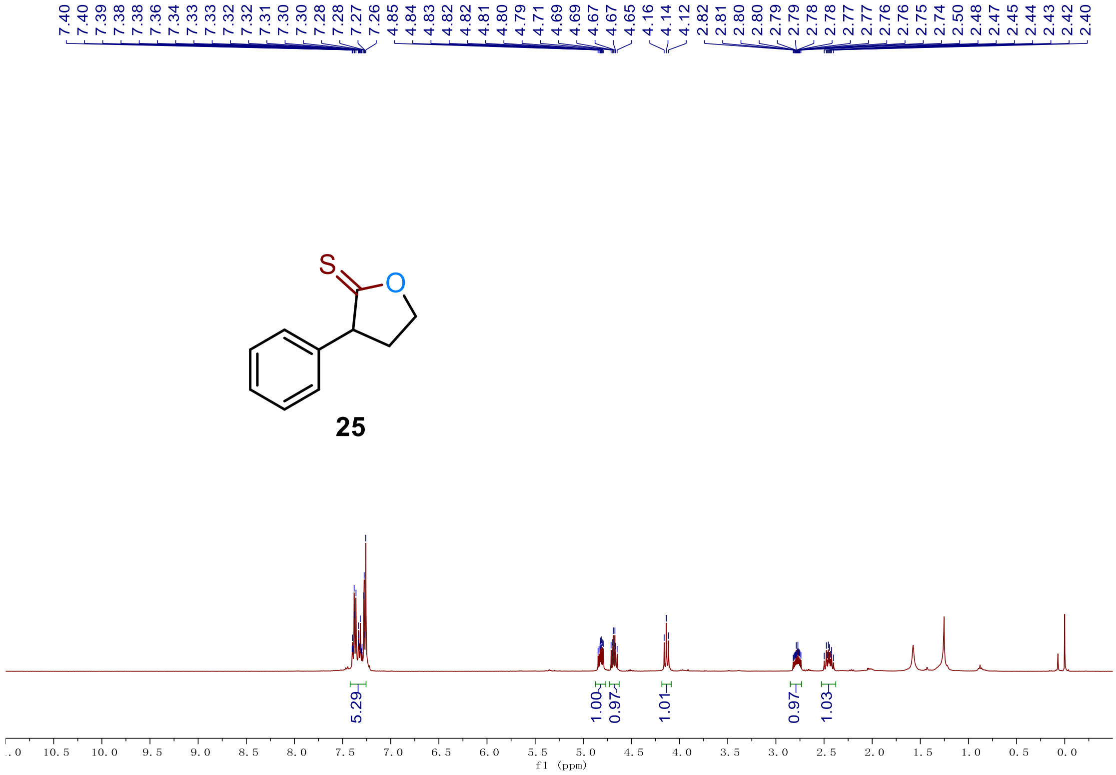


23 (>99%)

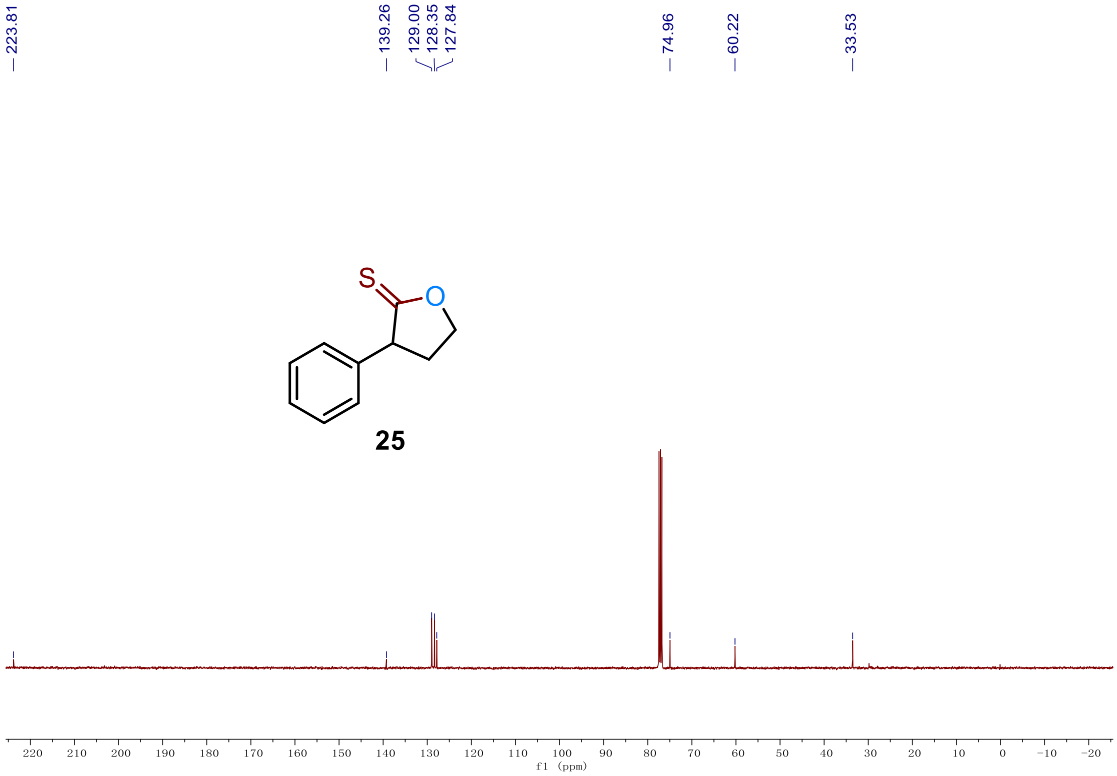

7.88
7.87
7.86
7.86
7.51
7.51
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.41
7.40
7.39
7.38
7.37
2.00
0.93
2.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


254.57
191.48
134.83
132.53
130.15
128.51
S
Ph
SNa
O
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

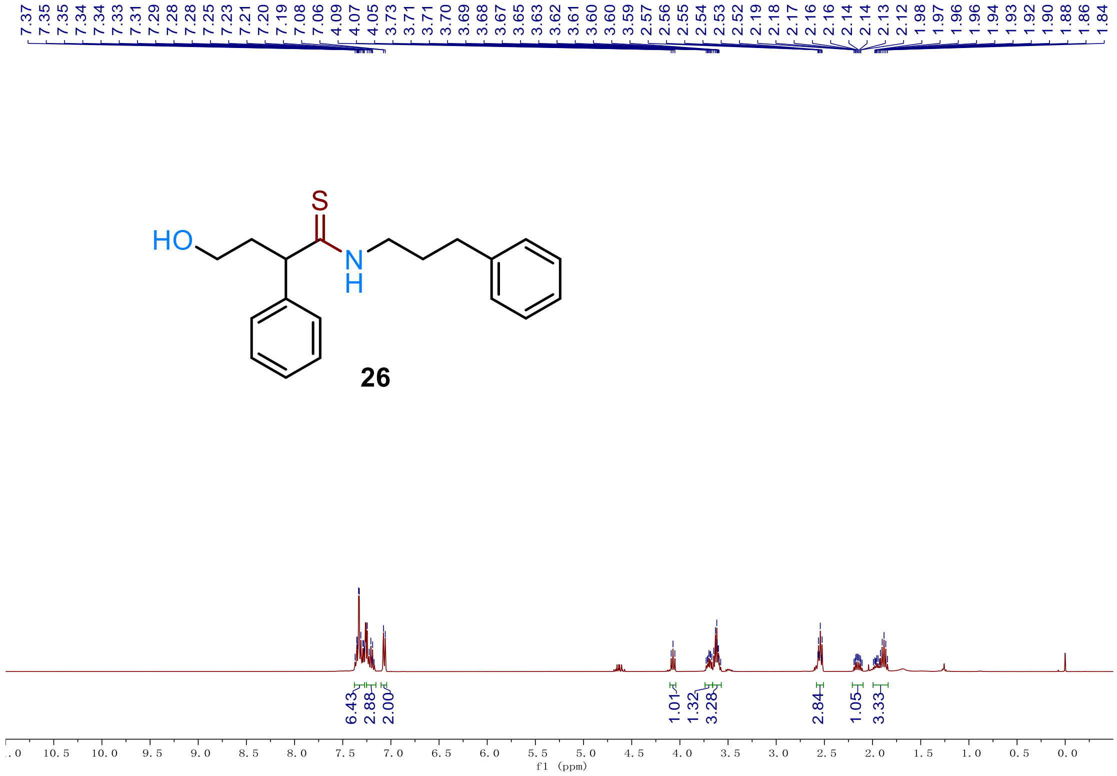
23 (>99%)


7.40 7.40 7.39 7.38 7.38 7.36 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.30 7.28 7.28 7.27 7.26 4.85 4.84 4.83 4.82 4.82 4.81 4.80 4.79 4.71 4.69 4.69 4.67 4.67 4.65 4.16 4.14 4.12 2.82 2.81 2.80 2.80 2.79 2.79 2.78 2.78 2.77 2.77 2.76 2.76 2.75 2.74 2.50 2.48 2.47 2.45 2.44 2.43 2.42 2.40
S
O
5.29
1.00
0.97
1.01
0.97
1.03
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

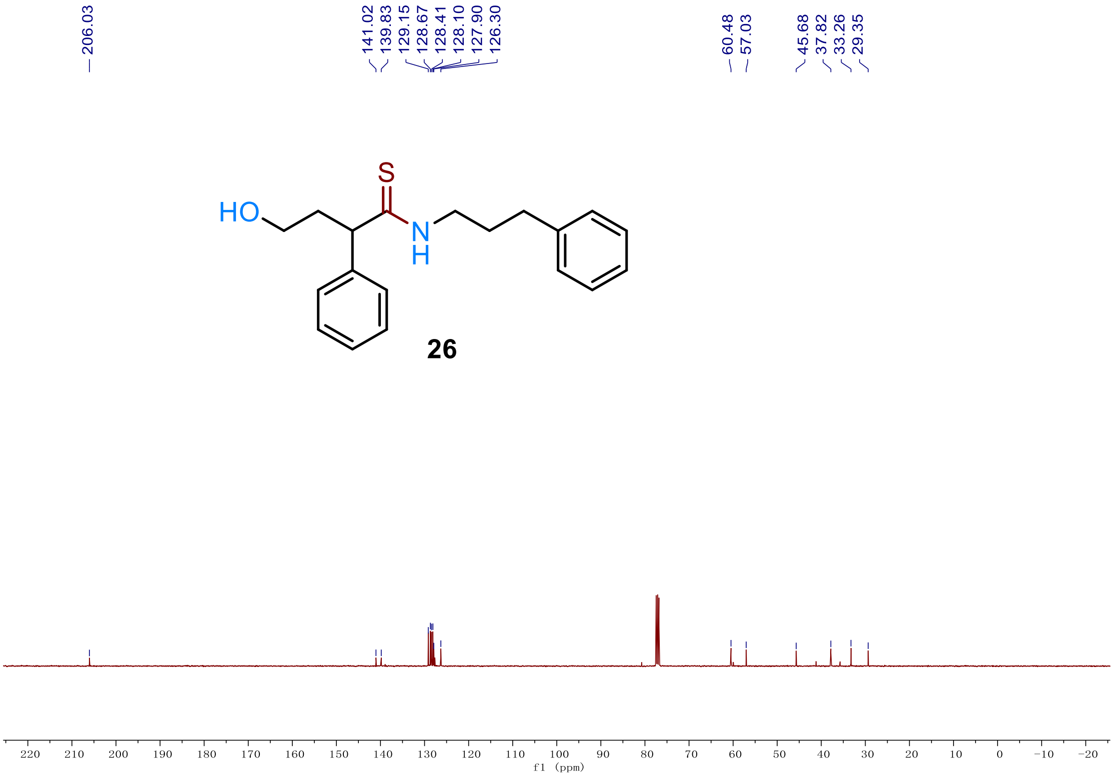
25


223.81
139.26
129.00
128.35
127.84
74.96
60.22
33.53
S
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

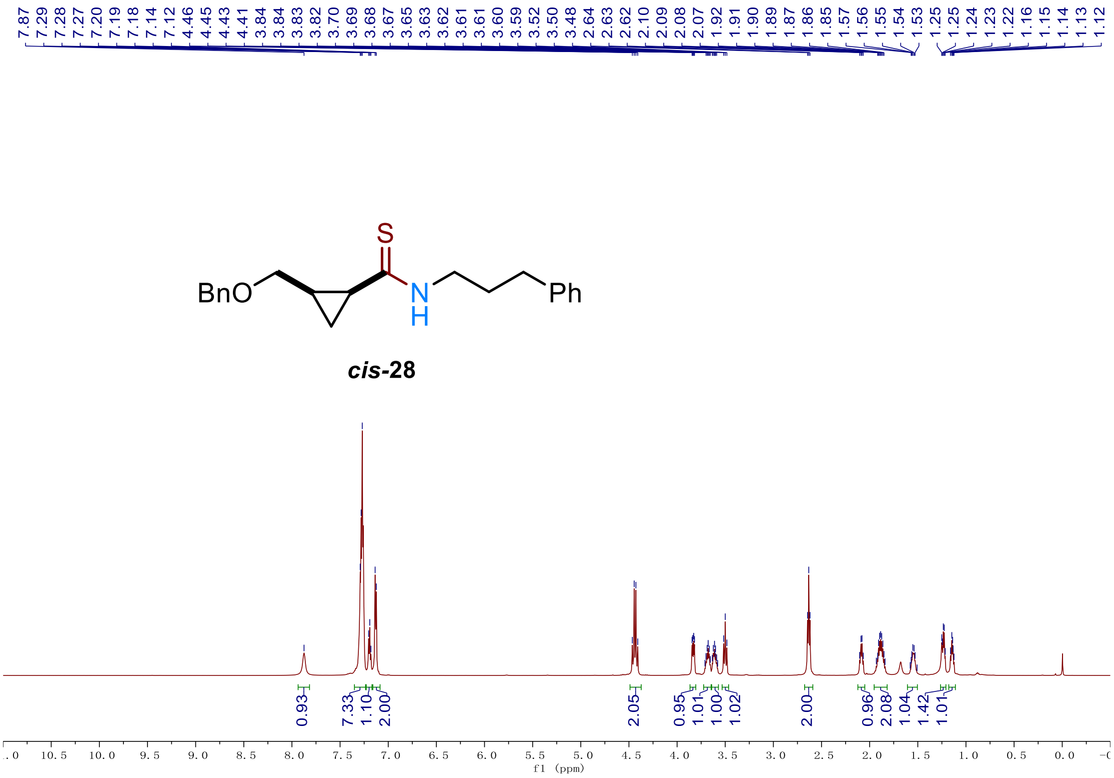
25


7.37 7.35 7.35 7.34 7.34 7.33 7.31 7.29 7.28 7.28 7.25 7.23 7.21 7.20 7.19 7.08 7.06 4.09 4.07 4.05 3.73 3.71 3.71 3.70 3.69 3.68 3.67 3.65 3.63 3.62 3.61 3.60 3.60 3.59 2.57 2.56 2.55 2.54 2.53 2.52 2.19 2.18 2.17 2.16 2.16 2.14 2.14 2.13 2.12 1.98 1.97 1.96 1.96 1.94 1.93 1.92 1.90 1.88 1.86 1.84
S
HO
N
H
6.43
2.88
2.00
1.01
1.32
3.28
2.84
1.05
3.33
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

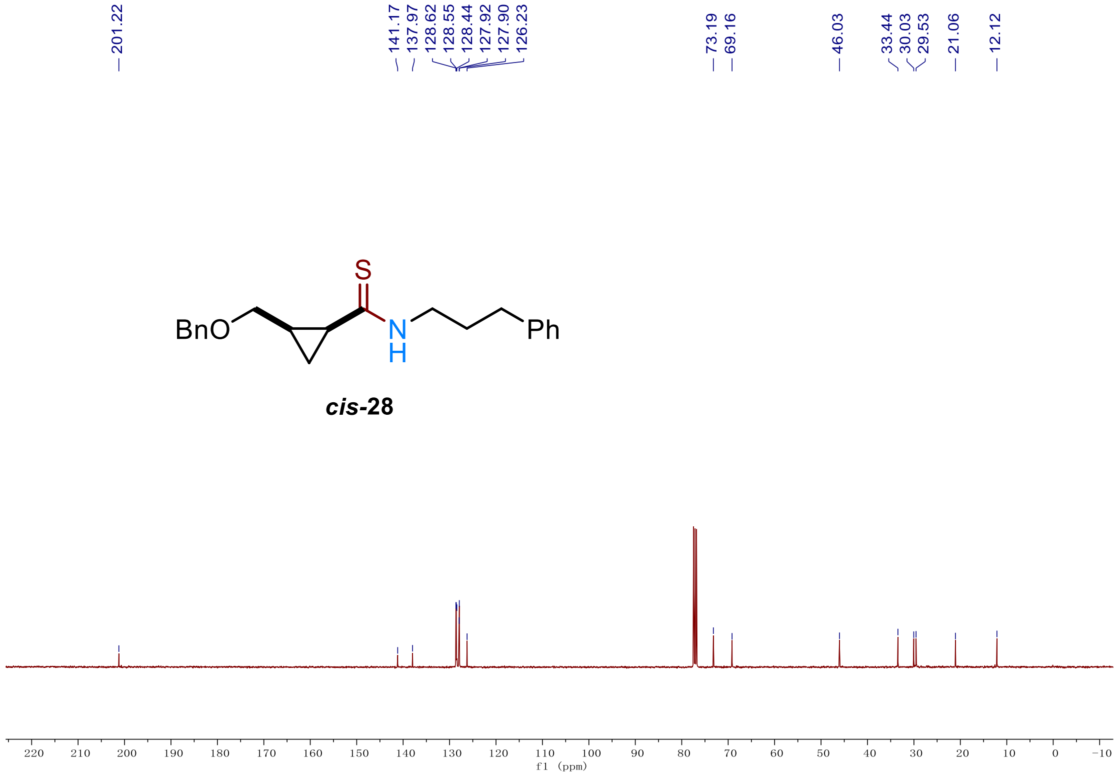
26


206.03
141.02
139.83
129.15
128.67
128.41
128.10
127.90
126.30
60.48
57.03
45.68
37.82
33.26
29.35
S
HO
N
H
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

26


7.87
7.29
7.28
7.27
7.20
7.19
7.18
7.14
7.12
4.46
4.45
4.43
4.41
3.84
3.84
3.83
3.82
3.70
3.69
3.68
3.67
3.65
3.63
3.62
3.61
3.61
3.60
3.59
3.52
3.50
3.48
2.64
2.63
2.62
2.10
2.09
2.08
2.07
1.92
1.91
1.90
1.89
1.87
1.86
1.85
1.57
1.56
1.55
1.54
1.53
1.25
1.25
1.24
1.23
1.22
1.16
1.15
1.14
1.13
1.12
S
BnO
N
H
Ph
0.93
7.33
1.10
2.00
2.05
0.95
1.01
1.00
1.02
2.00
0.96
2.08
1.04
1.42
1.01
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−(
f1 (ppm)

***cis*-28**


201.22
141.17
137.97
128.62
128.55
128.44
127.92
127.90
126.23
73.19
69.16
46.03
33.44
30.03
29.53
21.06
12.12
S
BnO
N
H
Ph
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

***cis*-28**