Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Deaminative Carbonylative Thioesterification of Activated Alkylamines with Thiophenols under Transition-Metal-Free Conditions

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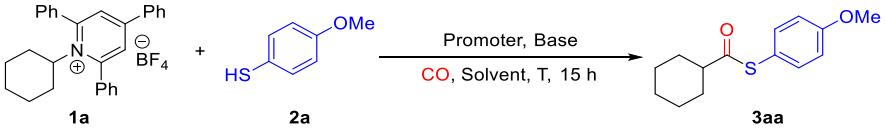
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All solvents were dried by standard techniques and distilled prior to use. Flash column chromatography was performed using 200-300 mesh silica gel. All NMR spectra were recorded at ambient temperature using Bruker Avance III HD 300 NMR (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75 MHz), Bruker ARX 400 NMR spectrometers (^{1}H, 400 MHz; ^{13}C{^{1}H}, 101 MHz). ^{1}H NMR chemical shifts were reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas ^{13}C{^{1}H} NMR spectra were reported relative to TMS via the carbon signals of the deuterated solvent ($CDCl_3$: 77.0 ppm). Data for ^{1}H were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), and integration. All ^{13}C NMR spectra were broad-band ^{1}H decoupled. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). High resolution mass spectra (HR-MS) were recorded on Agilent 6210. The data were given as mass units per charge (m/z). Gas chromatography (GC) analysis were performed on an Agilent HP-5890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using argon as carrier gas.

2. Optimization studies

Table S1 Optimization of the reaction conditions

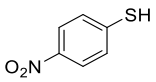


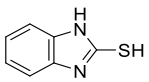
Entry	1a (mmol)	2a (mmol)	Promoter (equiv)	Base (equiv)	Solvent (mL)	T (°C)	CO (bar)	3aa (%)[a]
1	0.1	0.12	DBN (2.0)	/	MeCN (1.5)	r.t.	20	18
2	0.12	0.1	DBN (2.0)	/	MeCN (1.5)	r.t.	20	22
3	0.12	0.1	DBU (2.0)	/	MeCN (1.5)	r.t.	20	28
4	0.12	0.1	TBD (2.0)	/	MeCN (1.5)	r.t.	20	trace
5	0.12	0.1	DABCO (2.0)	/	MeCN (1.5)	r.t.	20	trace
6	0.12	0.1	DiPEA (2.0)	/	MeCN (1.5)	r.t.	20	trace
7	0.12	0.1	Et_3N (2.0)	/	MeCN (1.5)	r.t.	20	trace
8	0.12	0.1	DBU (2.0)	Li_2CO_3 (1.0)	MeCN (1.5)	r.t.	20	27
9	0.12	0.1	DBU (2.0)	K_2CO_3 (1.0)	MeCN (1.5)	r.t.	20	28

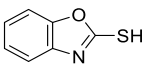
10	0.12	0.1	DBU (2.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	r.t.	20	38
11	0.12	0.1	DBU (2.0)	$NaHCO_3$ (1.0)	MeCN (1.5)	r.t.	20	24
12	0.12	0.1	DBU (2.0)	K_3PO_4 (1.0)	MeCN (1.5)	r.t.	20	35
13	0.12	0.1	DBU (2.0)	K_2HPO_4 (1.0)	MeCN (1.5)	r.t.	20	22
14	0.12	0.1	DBU (2.0)	LiOH (1.0)	MeCN (1.5)	r.t.	20	28
15	0.12	0.1	DBU (2.0)	$Cs(OAc)_2$ (1.0)	MeCN (1.5)	r.t.	20	25
16	0.12	0.1	DBU (2.0)	*t*-BuOK (1.0)	MeCN (1.5)	r.t.	20	32
17	0.12	0.1	DBU (2.0)	HCOOK (1.0)	MeCN (1.5)	r.t.	20	26
18	0.12	0.1	DBU (2.0)	LiOMe (1.0)	MeCN (1.5)	r.t.	20	11
19	0.12	0.1	DBU (2.0)	Cs_2CO_3 (0.5)	MeCN (1.5)	r.t.	20	34
20	0.12	0.1	DBU (2.0)	Cs_2CO_3 (2.0)	MeCN (1.5)	r.t.	20	40
21	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	r.t.	20	40
22	0.12	0.1	DBU (3.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	r.t.	20	39
23	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	THF (1.5)	r.t.	20	16
24	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	1,4-Dioxane (1.5)	r.t.	20	18
25	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	Toluene (1.5)	r.t.	20	9
26	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	50	20	52
27	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	60	20	64
28	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	80	20	61
29	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	100	20	39
30	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	60	10	48
31	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	60	30	70
32[b]	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	60	30	73
33[c]	0.12	0.1	DBU (1.0)	Cs_2CO_3 (1.0)	MeCN (1.5)	60	30	**74** (**73**)[d]

Reaction conditions: **1a** (0.12 mmol, 1.2 equiv), **2a** (0.1 mmol, 1.0 equiv), promoter (0.2 mmol, 2.0 equiv), base (0.1 mmol, 1.0 equiv), solvent (1.5 mL), CO (20 bar), r.t., 15 h; [a] Determined by GC using hexadecane as the internal standard; [b] 24 h; [c] 2.0 equiv H_2O was added; [d] isolated yield. DBN = 1,5-Diazabicyclo [4.3.0] non-5-ene. DBU = 1,8-Diazabicyclo [5.4.0] undec-7-ene. TBD = 1,3,4,6,7,8-Hexahydro-2*H*-pyrimido [1,2-*a*] pyrimidine. DABCO = triethylenediamine.

Unsuccessful thiophenols:

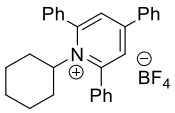




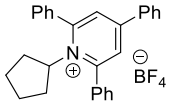


3. General procedure for the synthesis of Katritzky salts

Katritzky salts **1a-1i** were all synthesized as described previously.[1]



1a



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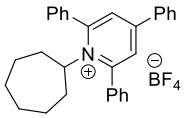

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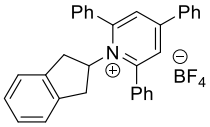

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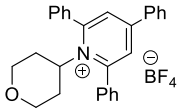

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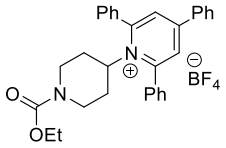

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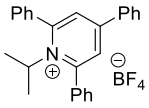

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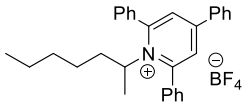

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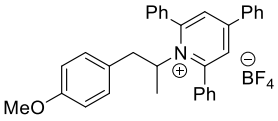
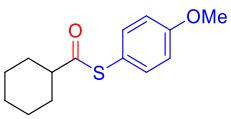


1i

4. General procedure for the synthesis of thioesters

A 4 mL screw-cap vial was charged with Katritzky salts (0.12 mmol), thiophenols (if solid, 0.1 mmol, 1.0 equiv) Cs_2CO_3 (0.1 mmol, 1.0 equiv) and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. After flashed the vials with argon and vacuum three times, DBU (0.1 mmol, 1.0 equiv), H_2O (0.2 mmol, 2.0 equiv), thiophenols (if liquid, 0.1 mmol, 1.0 equiv) and dry MeCN (1.5 mL) were injected by syringe. The vial was fixed in an alloy plate and put into Parr 4560 series autoclave (500 mL) under argon atmosphere. At room temperature, the autoclave was flushed with carbon monoxide for three times and 30 bar of carbon monoxide was charged. The autoclave was reacted at 60 °C for 24 h. Afterwards, the autoclave was cooled to room temperature and the pressure was carefully released. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (*n*-Pentane/EtOAc) to afford the corresponding thioesters.

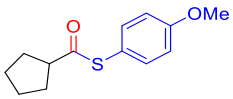
***S*-(4-Methoxyphenyl) cyclohexanecarbothioate (3aa):**



The title compound was prepared from 1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (57.2 mg, 0.12 mmol) and 4-methoxybenzenethiol (12.5 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 50:1, R_f = 0.3) to give the product as a colorless oil (18.2 mg, 73%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 6.95 – 6.90 (m, 2H), 3.82 (s, 3H), 2.59 (tt, *J* = 11.4, 3.5 Hz, 1H), 2.03 – 1.94 (m, 2H), 1.85 – 1.76 (m, 2H), 1.71 – 1.63 (m, 1H), 1.57 – 1.45 (m, 2H), 1.37 – 1.22 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.8, 160.4, 136.1, 118.6, 114.8, 55.3, 52.2, 29.5, 25.6, 25.5. **HRMS** (EI) calcd for $C_{14}H_{18}O_2S$ $[M]^+$: 250.1028, Found: 250.1022.

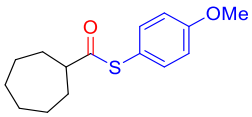
***S*-(4-Methoxyphenyl) cyclopentanecarbothioate (3ba):**



The title compound was prepared from 1-cyclopentyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (55.5 mg, 0.12 mmol) and 4-methoxybenzenethiol (12.5 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 50:1, R_f = 0.3) to give the product as a colorless oil (18.6 mg, 79%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 6.96 – 6.90 (m, 2H), 3.82 (s, 3H), 3.14 – 3.02 (m, 1H), 2.00 – 1.83 (m, 4H), 1.77 – 1.57 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.9, 160.5, 136.1, 118.9, 114.8, 55.3, 52.6, 30.6, 25.9. **HRMS** (ESI) calcd for $C_{13}H_{17}O_2S$ $[M+H]^+$: 237.0949, Found: 237.0952.

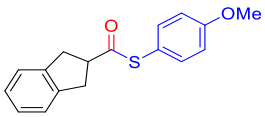
***S*-(4-Methoxyphenyl) cycloheptanecarbothioate (3ca):**



The title compound was prepared from 1-cycloheptyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (58.9 mg, 0.12 mmol) and 4-methoxybenzenethiol (12.5 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 50:1, R_f = 0.3) to give the product as a colorless oil (20.7 mg, 76%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 6.96 – 6.89 (m, 2H), 3.82 (s, 3H), 2.75 (tt, *J* = 9.4, 4.2 Hz, 1H), 2.07 – 1.94 (m, 2H), 1.83 – 1.67 (m, 4H), 1.61 – 1.45 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.4, 160.5, 136.1, 118.8, 114.8, 55.3, 53.9, 31.3, 28.2, 26.4. **HRMS** (EI) calcd for $C_{15}H_{20}O_2S$ $[M]^+$: 264.1184, Found: 264.1178.

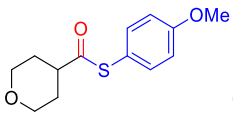
***S*-(4-Methoxyphenyl) 2,3-dihydro-1*H*-indene-2-carbothioate (3da):**



The title compound was prepared from 1-(2,3-dihydro-1*H*-inden-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (61.0 mg, 0.12 mmol) and 4-methoxybenzenethiol (12.5 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 50:1, R_f = 0.2) to give the product as a white solid (15.4 mg, 54%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.25 – 7.15 (m, 4H), 6.99 – 6.92 (m, 2H), 3.83 (s, 3H), 3.74 – 3.59 (m, 1H), 3.42 – 3.22 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 200.5, 160.6, 141.1, 136.2, 134.4, 126.7, 124.3, 118.3, 114.9, 114.6, 55.3, 52.2, 36.6. **HRMS** (ESI) calcd for $C_{17}H_{16}NaO_2S$ $[M+H]^+$: 307.0768, Found: 307.0775.

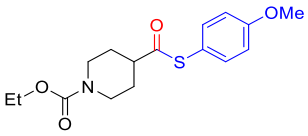
_S_-(4-Hethoxyphenyl) tetrahydro-2_H_-pyran-4-carbothioate (3ea):



The title compound was prepared from 2,4,6-triphenyl-1-(tetrahydro-2*H*-pyran-4-yl)pyridin-1-ium tetrafluoroborate (57.5 mg, 0.12 mmol) and 4-methoxybenzenethiol (12.5 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 10:1, R_f = 0.2) to give the product as a colorless oil (16.9 mg, 67%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 6.97 – 6.91 (m, 2H), 4.06 – 3.98 (m, 2H), 3.82 (s, 3H), 3.52 – 3.40 (m, 2H), 2.90 – 2.77 (m, 1H), 1.93 – 1.80 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 200.3, 160.7, 136.2, 117.9, 114.9, 67.0, 55.3, 48.9, 29.1. **HRMS** (EI) calcd for $C_{13}H_{16}O_3S$ $[M]^+$: 252.0820, Found: 252.0815.

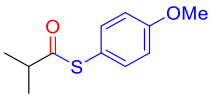
Ethyl 4-(((4-methoxyphenyl)thio)carbonyl)piperidine-1-carboxylate (3fa):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 4-methoxybenzenethiol (12.5 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.3) to give the product as a colorless oil (21.0 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 6.96 – 6.91 (m, 2H), 4.23 – 4.10 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 2.88 (t, *J* = 12.5 Hz, 2H), 2.75 (tt, *J* = 11.1, 3.8 Hz, 1H), 1.95 (d, *J* = 13.2 Hz, 2H), 1.77 – 1.67 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.3, 160.6, 155.4, 136.1, 117.8, 114.9, 61.4, 55.3, 49.7, 43.0, 28.4, 14.6. **HRMS** (EI) calcd for $C_{16}H_{21}NO_4S$ $[M]^+$: 323.1191, Found: 323.1186.

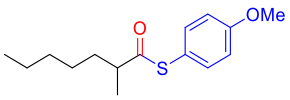
_S_-(4-Methoxyphenyl) 2-methylpropanethioate (3ga):



The title compound was prepared from 1-isopropyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (87.4 mg, 0.2 mmol) and 4-methoxybenzenethiol (12.5 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 50:1, R_f = 0.3) to give the product as a colorless oil (12.8 mg, 61%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 6.97 – 6.90 (m, 2H), 3.82 (s, 3H), 2.92 – 2.78 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.9, 160.5, 136.1, 118.5, 114.8, 55.3, 42.7, 19.4. **HRMS** (EI) calcd for $C_{11}H_{14}O_2S$ $[M]^+$: 210.0715, Found: 210.0709.

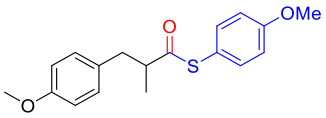
***S*-(4-Methoxyphenyl) 2-methylheptanethioate (3ha):**



The title compound was prepared from 1-(heptan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (59.2 mg, 0.12 mmol) and 4-methoxybenzenethiol (12.5 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 50:1, R_f = 0.4) to give the product as a colorless oil (14.2 mg, 53%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 6.96 – 6.90 (m, 2H), 3.82 (s, 3H), 2.81 – 2.66 (m, 1H), 1.82 – 1.70 (m, 1H), 1.48 – 1.40 (m, 1H), 1.37 – 1.26 (m, 6H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.7, 160.5, 136.1, 118.7, 114.8, 55.3, 48.2, 34.1, 31.7, 26.8, 22.5, 17.6, 14.0. **HRMS** (EI) calcd for $C_{15}H_{22}O_2S$ $[M]^+$: 266.1341, Found: 266.1335.

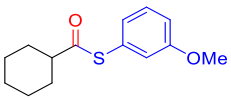
***S*-(4-Methoxyphenyl) 3-(4-methoxyphenyl)-2-methylpropanethioate (3ia):**



The title compound was prepared from 1-(1-(4-methoxyphenyl)propan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (65.0 mg, 0.12 mmol) and 4-methoxybenzenethiol (12.5 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 20:1, R_f = 0.2) to give the product as a colorless oil (16.2 mg, 51%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.13 – 7.07 (m, 2H), 6.96 – 6.89 (m, 2H), 6.87 – 6.81 (m, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.09 – 2.90 (m, 2H), 2.64 (dd, *J* = 12.9, 7.1 Hz, 1H), 1.21 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.1, 160.5, 158.2, 136.1, 131.0, 130.1, 118.5, 114.8, 113.8, 55.3, 55.2, 50.1, 39.1, 17.2. **HRMS** (EI) calcd for $C_{18}H_{20}O_3S$ $[M]^+$: 316.1133, Found: 316.1123.

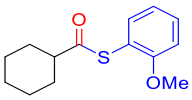
***S*-(3-Methoxyphenyl) cyclohexanecarbothioate (3ab):**



The title compound was prepared from 1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (57.2 mg, 0.12 mmol) and 3-methoxybenzenethiol (12.3 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 50:1, R_f = 0.3) to give the product as a colorless oil (16.0 mg, 64%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 1H), 7.02 – 6.90 (m, 3H), 3.81 (s, 3H), 2.60 (tt, *J* = 11.4, 3.5 Hz, 1H), 2.06 – 1.95 (m, 2H), 1.87 – 1.77 (m, 2H), 1.72 – 1.63 (m, 1H), 1.59 – 1.46 (m, 2H), 1.39 – 1.24 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 200.6, 159.8, 129.8, 128.9, 126.8, 119.6, 115.3, 55.3, 52.5, 29.5, 25.6, 25.5. **HRMS** (EI) calcd for $C_{14}H_{18}O_2S$ $[M]^+$: 250.1028, Found: 250.1022.

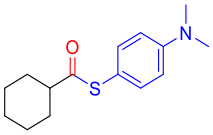
***S*-(2-Methoxyphenyl) cyclohexanecarbothioate (3ac):**



The title compound was prepared from 1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (57.2 mg, 0.12 mmol) and 2-methoxybenzenethiol (12.2 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 50:1, R_f = 0.3) to give the product as a colorless oil (20.9 mg, 84%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.01 – 6.93 (m, 2H), 3.83 (s, 3H), 2.63 (tt, *J* = 11.4, 3.6 Hz, 1H), 2.07 – 1.97 (m, 2H), 1.87 – 1.77 (m, 2H), 1.71 – 1.63 (m, 1H), 1.60 – 1.46 (m, 2H), 1.35 – 1.23 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 200.0, 159.2, 136.8, 131.3, 121.0, 116.2, 111.5, 56.0, 52.4, 29.5, 25.6, 25.5. **HRMS** (EI) calcd for $C_{14}H_{18}O_2S$ $[M]^+$: 250.1028, Found: 250.1022.

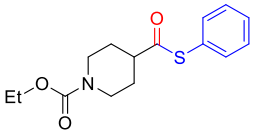
***S*-(4-(Dimethylamino)phenyl) cyclohexanecarbothioate (3ad):**



The title compound was prepared from 1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (57.2 mg, 0.12 mmol) and 4-(dimethylamino)benzenethiol (15.3 mg, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 50:1, R_f = 0.2) to give the product as a white solid (12.5 mg, 48%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 6.76 – 6.68 (m, 2H), 2.98 (s, 6H), 2.59 (tt, *J* = 11.4, 3.6 Hz, 1H), 2.03 – 1.93 (m, 2H), 1.85 – 1.76 (m, 2H), 1.71 – 1.62 (m, 1H), 1.58 – 1.44 (m, 2H), 1.37 – 1.19 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.7, 150.9, 135.7, 112.8, 52.0, 40.3, 29.5, 25.6, 25.5. **HRMS** (ESI) calcd for $C_{15}H_{22}NOS$ $[M+H]^+$: 264.1422, Found: 264.1423.

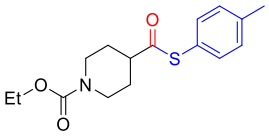
Ethyl 4-((phenylthio)carbonyl)piperidine-1-carboxylate (3fe):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and benzenethiol (10.3 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.3) to give the product as a colorless oil (19.5 mg, 67%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 5H), 4.20 – 4.05 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.94 – 2.84 (m, 2H), 2.77 (tt, *J* = 11.1, 3.8 Hz, 1H), 2.04 – 1.92 (m, 2H), 1.80 – 1.67 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.3, 155.4, 134.5, 129.4, 129.2, 127.2, 61.4, 50.0, 43.0, 28.4, 14.6. **HRMS** (ESI) calcd for $C_{15}H_{19}NNaO_3S$ $[M+Na]^+$: 316.0983, Found: 316.0980.

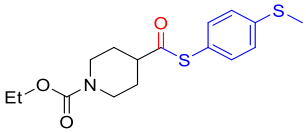
Ethyl 4-((*p*-tolylthio)carbonyl)piperidine-1-carboxylate (3ff):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 4-methylbenzenethiol (12.4 mg, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.3) to give the product as a colorless oil (18.5 mg, 60%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.24 – 7.19 (m, 2H), 4.21 – 4.10 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.94 – 2.84 (m, 2H), 2.76 (tt, *J* = 11.1, 3.8 Hz, 1H), 2.37 (s, 3H), 2.02 – 1.91 (m, 2H), 1.80 – 1.66 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.8, 155.4, 139.7, 134.5, 130.0, 123.6, 61.4, 49.9, 43.0, 28.4, 21.3, 14.6. **HRMS** (EI) calcd for $C_{16}H_{21}NO_3S$ $[M]^+$: 307.1242, Found: 307.1237.

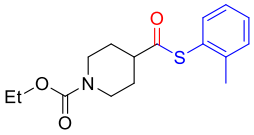
Ethyl 4-(((4-(methylthio)phenyl)thio)carbonyl)piperidine-1-carboxylate (3fg):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 4-(methylthio)benzenethiol (13.1 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.2) to give the product as a colorless oil (17.0 mg, 50%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 4.18 – 4.09 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.93 – 2.84 (m, 2H), 2.76 (tt, *J* = 11.0, 3.8 Hz, 1H), 2.48 (s, 3H), 2.03 – 1.87 (m, 2H), 1.79 – 1.65 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.5, 155.4, 141.1, 134.8, 126.6, 122.9, 61.4, 49.9, 43.0, 28.4, 15.3, 14.6. **HRMS** (ESI) calcd for $C_{16}H_{22}NO_3S_2$ $[M+H]^+$: 340.1041, Found: 340.1037.

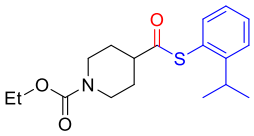
Ethyl 4-((*o*-tolylthio)carbonyl)piperidine-1-carboxylate (3fh):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 2-methylbenzenethiol (11.8 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.3) to give the product as a colorless oil (24.6 mg, 80%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 3H), 7.25 – 7.18 (m, 1H), 4.24 – 4.08 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.95 – 2.83 (m, 2H), 2.79 (tt, *J* = 11.0, 3.8 Hz, 1H), 2.32 (s, 3H), 2.04 – 1.91 (m, 2H), 1.81 – 1.68 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 198.8, 155.4, 141.9, 136.0, 130.8, 130.1, 126.7, 126.6, 61.4, 50.0, 43.0, 28.4, 20.6, 14.6. **HRMS** (EI) calcd for $C_{16}H_{21}NO_3S$ $[M]^+$: 307.1242, Found: 307.1237.

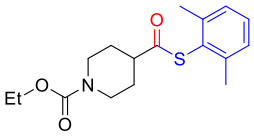
Ethyl 4-(((2-isopropylphenyl)thio)carbonyl)piperidine-1-carboxylate (3fi):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 2-isopropylbenzenethiol (15.1 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.3) to give the product as a colorless oil (19.0 mg, 57%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 3H), 7.24 – 7.18 (m, 1H), 4.20 – 4.09 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.34 – 3.21 (m, 1H), 2.96 – 2.84 (m, 2H), 2.84 – 2.75 (m, 1H), 2.04 – 1.91 (m, 2H), 1.81 – 1.68 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.3, 155.4, 151.8, 136.5, 130.5, 126.4, 126.2, 125.5, 61.4, 50.0, 43.1, 31.1, 28.5, 23.5, 14.7. **HRMS** (EI) calcd for $C_{18}H_{25}NO_3S$ $[M]^+$: 335.1555, Found: 335.1550.

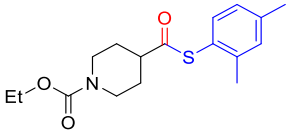
Ethyl 4-(((2,6-dimethylphenyl)thio)carbonyl)piperidine-1-carboxylate (3fj):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 2,6-dimethylbenzenethiol (13.3 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.2) to give the product as a colorless oil (21.4 mg, 67%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 1H), 7.16 – 7.13 (m, 2H), 4.22 – 4.09 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.98 – 2.86 (m, 2H), 2.86 – 2.77 (m, 1H), 2.32 (s, 6H), 2.02 – 1.96 (m, 2H), 1.83 – 1.69 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 198.3, 155.4, 142.6, 129.8, 128.3, 126.6, 61.4, 50.0, 43.0, 28.5, 21.6, 14.6. **HRMS** (EI) calcd for $C_{17}H_{23}NO_3S$ $[M]^+$: 321.1399, Found: 321.1393.

Ethyl 4-(((2,4-dimethylphenyl)thio)carbonyl)piperidine-1-carboxylate (3fk):

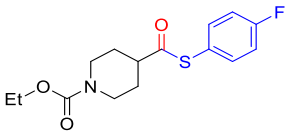


The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 2,4-dimethylbenzenethiol (13.4 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.3) to give the product as a colorless oil (19.7 mg, 61%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 1H), 7.14 – 7.12 (m, 1H), 7.05 – 7.01 (m, 1H), 4.20 – 4.08 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.95 – 2.85 (m, 2H), 2.78 (tt, *J* = 11.0, 3.8 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 1.99 – 1.94 (m, 2H), 1.81 – 1.67 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.3, 155.4, 141.7, 140.3,

135.8, 131.6, 127.5, 123.2, 61.4, 49.8, 43.0, 28.4, 21.2, 20.5, 14.6. **HRMS** (EI) calcd for $C_{17}H_{23}NO_3S$ $[M]^+$: 321.1399, Found: 321.1393.

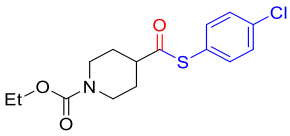
Ethyl 4-(((4-fluorophenyl)thio)carbonyl)piperidine-1-carboxylate (3fl):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 4-fluorobenzenethiol (10.7 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.3) to give the product as a colorless oil (18.2 mg, 59%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.15 – 7.06 (m, 2H), 4.22 – 4.10 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.94 – 2.84 (m, 2H), 2.76 (tt, *J* = 11.1, 3.8 Hz, 1H), 1.99 – 1.94 (m, 2H), 1.79 – 1.65 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.3, 163.5 (d, *J* = 249.8 Hz), 155.4, 136.6 (d, *J* = 8.6 Hz), 122.4, 116.5 (d, *J* = 22.1 Hz), 61.4, 49.9, 43.0, 28.4, 14.6. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -111.0. **HRMS** (EI) calcd for $C_{15}H_{18}FNO_3S$ $[M]^+$: 311.0991, Found: 311.0986.

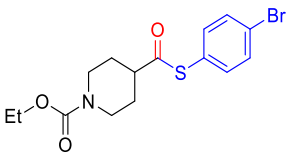
Ethyl 4-(((4-chlorophenyl)thio)carbonyl)piperidine-1-carboxylate (3fm):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 4-chlorobenzenethiol (12.2 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.3) to give the product as a colorless oil (17.7 mg, 54%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.35 – 7.27 (m, 2H), 4.22 – 4.08 (m, 4H), 2.95 – 2.83 (m, 2H), 2.76 (tt, *J* = 11.1, 3.9 Hz, 1H), 2.05 – 1.90 (m, 2H), 1.79 – 1.65 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 198.8, 155.4, 135.9, 135.8, 129.5, 125.6, 61.4, 50.1, 43.0, 28.4, 14.7. **HRMS** (EI) calcd for $C_{15}H_{18}ClNO_3S$ $[M]^+$: 327.0696, Found: 327.0690.

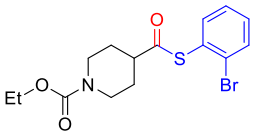
Ethyl 4-(((4-bromophenyl)thio)carbonyl)piperidine-1-carboxylate (3fn):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 4-bromobenzenethiol (18.9 mg, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.3) to give the product as a colorless oil (22.6 mg, 61%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.27 – 7.22 (m, 2H), 4.24 – 4.08 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.96 – 2.82 (m, 2H), 2.76 (tt, *J* = 11.1, 3.8 Hz, 1H), 2.02 – 1.90 (m, 2H), 1.79 – 1.65 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 198.6, 155.3, 136.0, 132.4, 126.3, 124.1, 61.4, 50.1, 43.0, 28.4, 14.6. **HRMS** (ESI) calcd for $C_{15}H_{19}BrNO_3S$ $[M+H]^+$: 372.0269, Found: 372.0269.

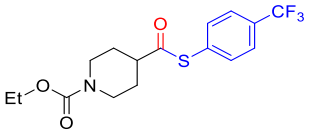
Ethyl 4-(((2-bromophenyl)thio)carbonyl)piperidine-1-carboxylate (3fo):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 2-bromobenzenethiol (11.8 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.2) to give the product as a colorless oil (19.5 mg, 52%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.35 (td, *J* = 7.5, 1.5 Hz, 1H), 7.27 (td, *J* = 8.1, 2.1 Hz, 1H), 4.18 – 4.09 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.99 – 2.87 (m, 2H), 2.81 (tt, *J* = 10.9, 3.9 Hz, 1H), 2.06 – 1.94 (m, 2H), 1.84 – 1.70 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.4, 155.4, 137.2, 133.6, 131.2, 129.5, 129.0, 128.0, 61.4, 50.0, 43.0, 28.3, 14.7. **HRMS** (ESI) calcd for $C_{15}H_{18}BrNNaO_3S$ $[M+Na]^+$: 394.0088, Found: 394.0086.

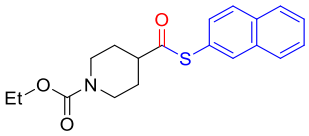
Ethyl 4-(((4-(trifluoromethyl)phenyl)thio)carbonyl)piperidine-1-carboxylate (3fp):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and 4-(trifluoromethyl)benzenethiol (13.5 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.2) to give the product as a colorless oil (10.0 mg, 28%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.55 – 7.50 (m, 2H), 4.24 – 4.08 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.97 – 2.84 (m, 2H), 2.79 (tt, *J* = 11.1, 3.8 Hz, 1H), 2.04 – 1.92 (m, 2H), 1.80 – 1.67 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 198.0, 155.3, 134.6, 131.9, 131.36 (d, *J* = 32.8 Hz), 125.94 (q, *J* = 3.8 Hz), 123.73 (d, *J* = 272.5 Hz), 61.4, 50.3, 43.0, 28.4, 14.6. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -62.9. **HRMS** (ESI) calcd for $C_{16}H_{19}F_3NO_3S$ $[M+H]^+$: 362.1038, Found: 362.1039.

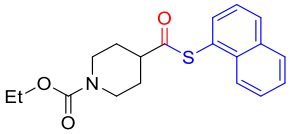
Ethyl 4-((naphthalen-2-ylthio)carbonyl)piperidine-1-carboxylate (3fq):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and naphthalene-2-thiol (16.0 mg, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.2) to give the product as a colorless oil (18.9 mg, 55%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 1H), 7.90 – 7.79 (m, 3H), 7.57 – 7.48 (m, 2H), 7.43 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.25 – 4.15 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.96 – 2.87 (m, 2H), 2.86 – 2.77 (m, 1H), 2.08 – 1.94 (m, 2H), 1.83 – 1.70 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.5, 155.4, 134.5, 133.5, 133.3, 130.9, 128.8, 127.9, 127.8, 127.2, 126.6, 124.5, 61.4, 50.0, 43.1, 28.5, 14.7. **HRMS** (EI) calcd for $C_{19}H_{21}NO_3S$ $[M]^+$: 343.1242, Found: 343.1237.

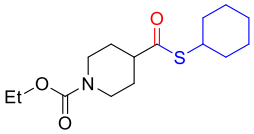
Ethyl 4-((naphthalen-1-ylthio)carbonyl)piperidine-1-carboxylate (3fr):



The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and naphthalene-1-thiol (13.9 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.2) to give the product as a colorless oil (18.6 mg, 54%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 – 8.08 (m, 1H), 7.98 – 7.85 (m, 2H), 7.68 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.59 – 7.48 (m, 3H), 4.25 – 4.11 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.99 – 2.84 (m, 3H), 2.10 – 1.95 (m, 2H), 1.86 – 1.73 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 198.9, 155.4, 135.1, 134.2, 134.2, 130.9, 128.7, 127.2, 126.4, 125.6, 125.0, 124.6, 61.4, 50.1, 43.1, 28.5, 14.7. **HRMS** (EI) calcd for $C_{19}H_{21}NO_3S$ $[M]^+$: 343.1242, Found: 343.1237.

Ethyl 4-((cyclohexylthio)carbonyl)piperidine-1-carboxylate (3fs):

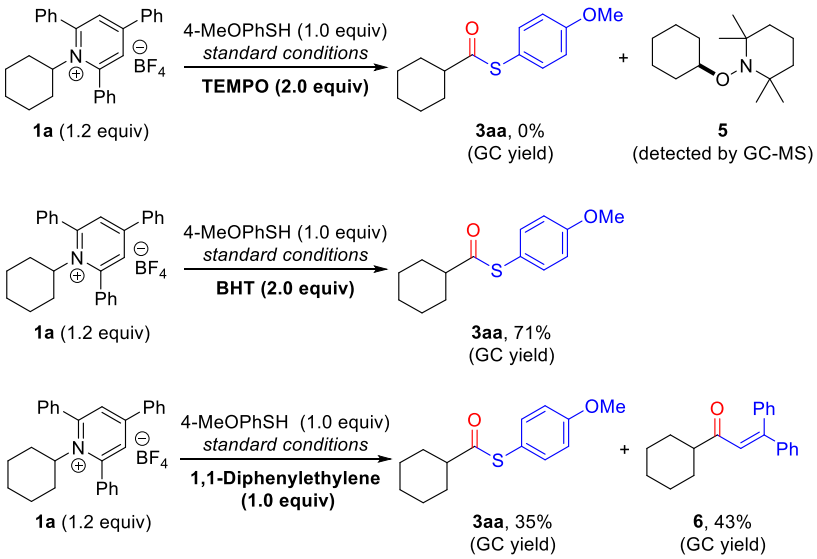


The title compound was prepared from 1-(1-(ethoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (66.0 mg, 0.12 mmol) and cyclohexanethiol (12.2 uL, 0.1 mmol), according to general carbonylation procedure. The crude residue was purified by flash chromatography (pentane/EA = 5:1, R_f = 0.4) to give the product as a colorless oil (12.1 mg, 40%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 – 4.08 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.54 – 3.46 (m, 1H), 2.87 – 2.78 (m, 2H), 2.58 (tt, *J* = 11.2, 3.8 Hz, 1H), 1.95 – 1.81 (m, 4H), 1.77 – 1.52 (m, 6H), 1.45 – 1.36 (m, 4H), 1.24 (d, *J* = 7.1

Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.3, 155.4, 61.3, 50.3, 43.1, 42.0, 33.0, 28.4, 25.9, 25.5, 14.7. **HRMS** (ESI) calcd for $C_{15}H_{26}NO_3S$ $[M+H]^+$: 300.1633, Found: 300.1639.

5. Mechanistic experiments



Scheme 1. Mechanistic experiments

A 4 mL screw-cap vial was charged with Katritzky salts **1a** (0.12 mmol), 4-methoxythiophenol **2a** (0.1 mmol, 1.0 equiv), Cs_2CO_3 (0.1 mmol, 1.0 equiv), radical scavenger (if solid, 1.0 or 2.0 equiv), and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. After flashed the vials with argon and vacuum three times, DBU (0.1 mmol, 1.0 equiv), H_2O (0.2 mmol, 2.0 equiv), radical scavenger (if liquid, 1.0 or 2.0 equiv), and dry MeCN (1.5 mL) were injected by syringe. The vial was fixed in an alloy plate and put into Parr 4560 series autoclave (500 mL) under argon atmosphere. At room temperature, the autoclave was flushed with carbon monoxide for three times and 30 bar of carbon monoxide was charged. The autoclave was reacted at 60 °C for 24 h. Afterwards, the autoclave was cooled to room temperature and the pressure was carefully released. Then a proper amount of solution was taken for GC and GC-MS analysis. The result is shown above (Scheme 1).

When TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was added into the system under the standard conditions, the reaction was inhibited completely, meanwhile the adduct of radical with TEMPO **5** was detected by GC-MS (Figure 1).However, when BHT (butylated hydroxytoluene) was added, the reaction was hardly affected and **3aa** was obtained in 71% yield. And the addition of 1,1-diphenylethylene lead to 35% yield of **3aa** and 43% yield of **6**. These results suggest that the alkyl radical and acyl radical were probably generated in this transformation.

```
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Instrument :    GCMS
Sample Name: ZF-34-17
Misc Info  :
Vial Number: 111
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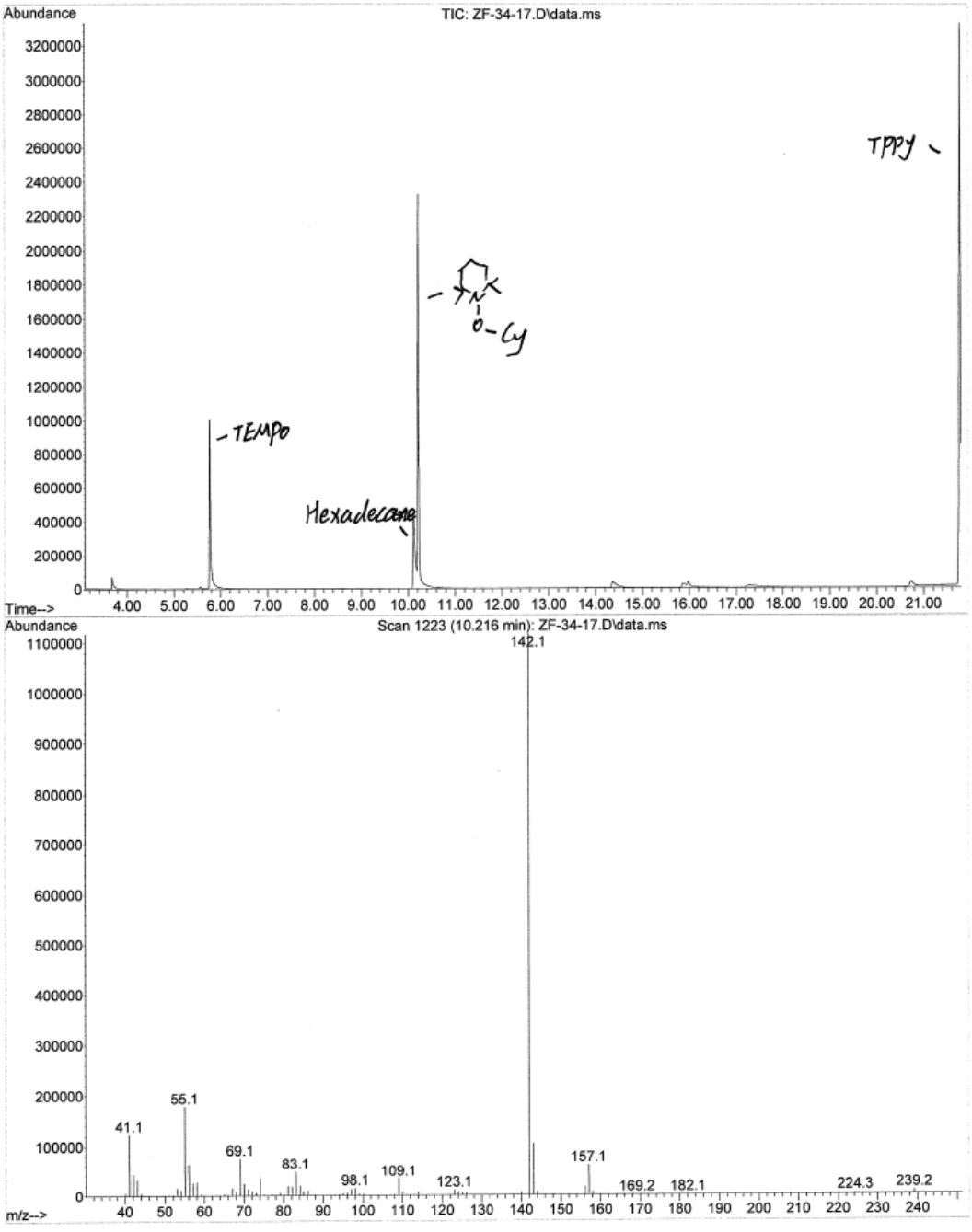
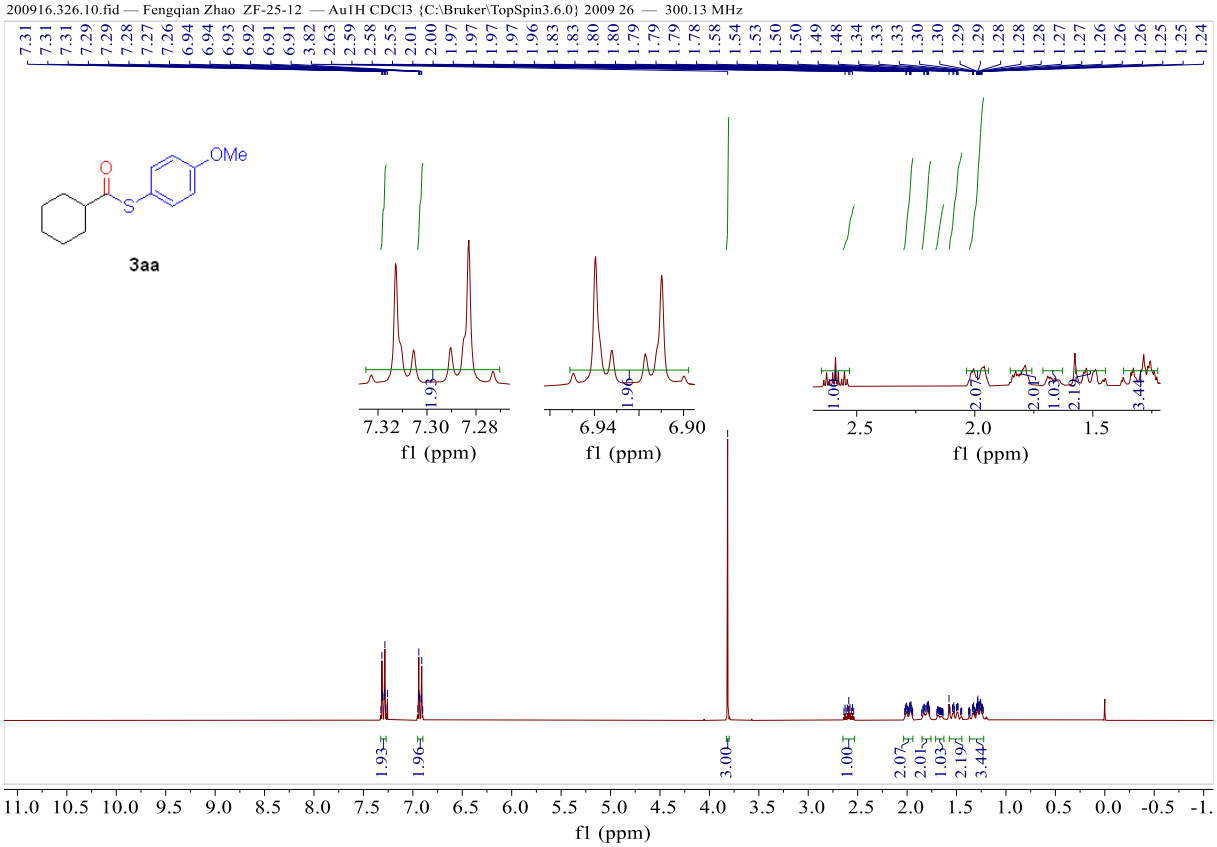


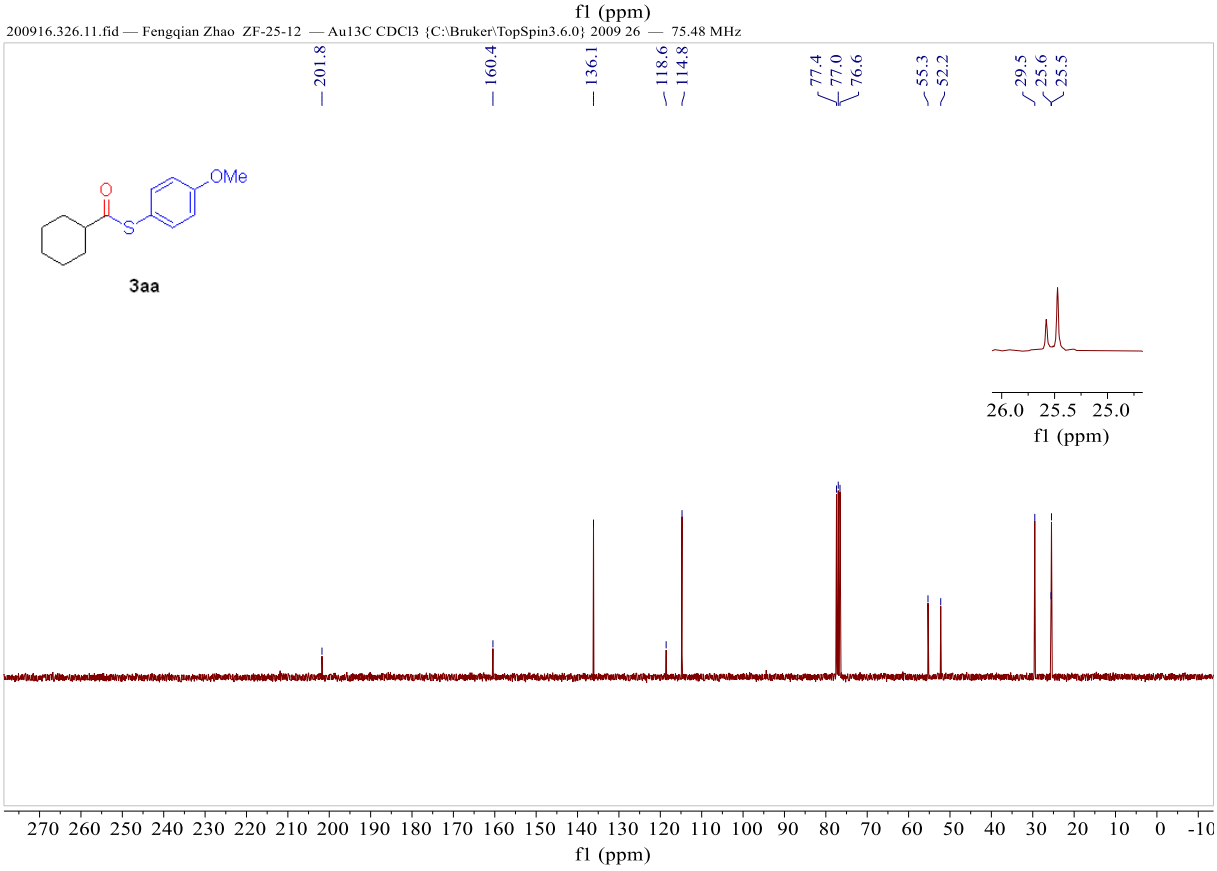
Figure 1. The GC-MS of the adduct of radical with TEMPO

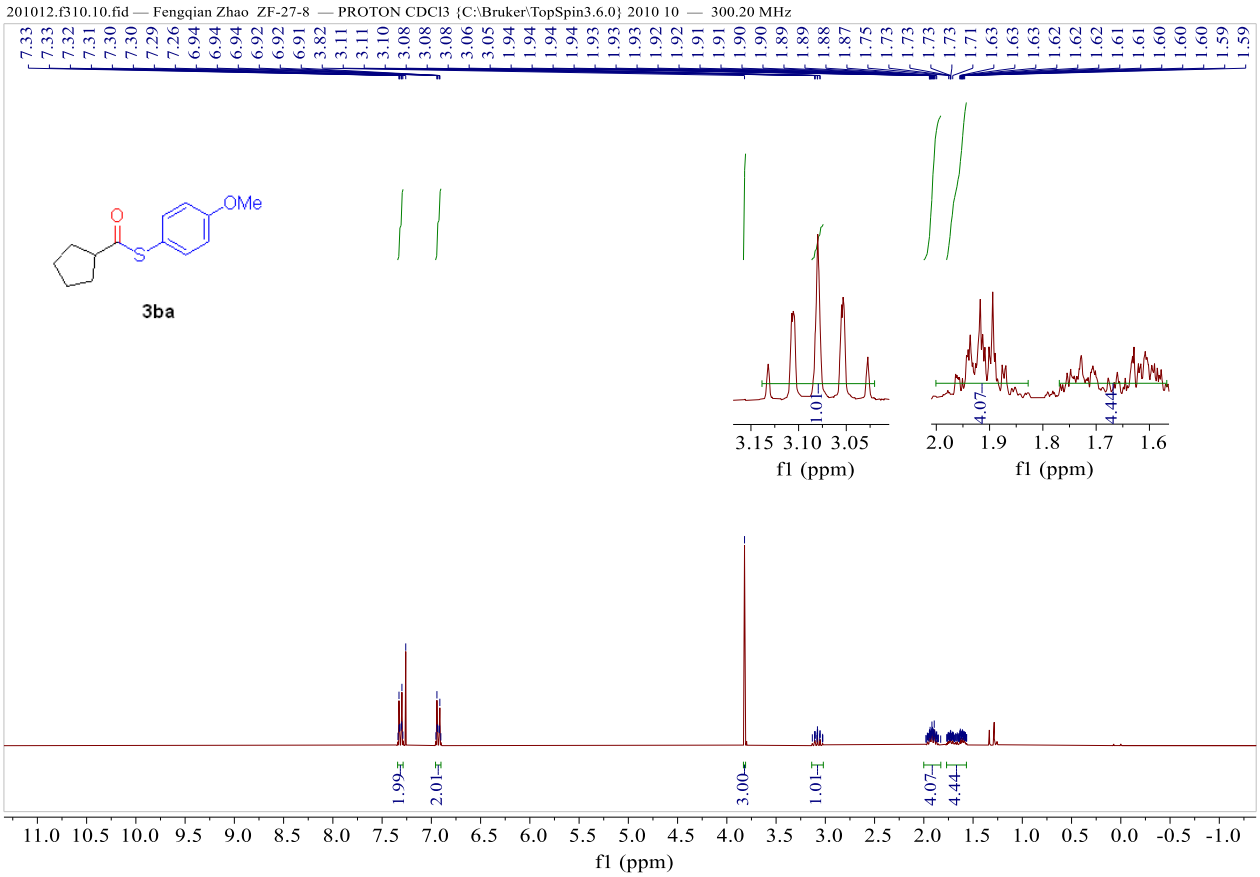
6. Reference:

1. a) C. H. Basch, J. Liao, J. Xu, J. J. Piane, M. P. Watson, *J. Am. Chem. Soc.* **2017**, *139*, 5313-5316; b) F. J. R. Klauck, M. J. James, F. Glorius, *Angew. Chem. Int. Ed.* **2017**, *56*, 12336-12339; c) S. Plunkett, C. H. Basch, S. O. Santana, M. P. Watson, *J. Am. Chem. Soc.* **2019**, *141*, 2257-2262; d) F. Sandfort, F. Strieth-Kalthoff, F. J. R. Klauck, M. J. James, F. Glorius, *Chem. Eur. J.* **2018**, *24*, 17210-17214; e) S. A. Said, A. Fiksdahl, *Tetrahedron Asymm.* **2001**, *12*, 1947-1951; f) F. Zhao, C. L. Li, X.-F. Wu, *Chem. Commun.* **2020**, *56*, 9182-9185; g) H. Yue, C. Zhu, L. Shen, Q. Geng, K. J. Hock, T. Yuan, L. Cavallo, M. Rueping, *Chem. Sci.* **2019**, *10*, 4430-4435.

7. NMR Spectra of products: ^{1}H, ^{13}C and ^{19}F NMR



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S
3ba
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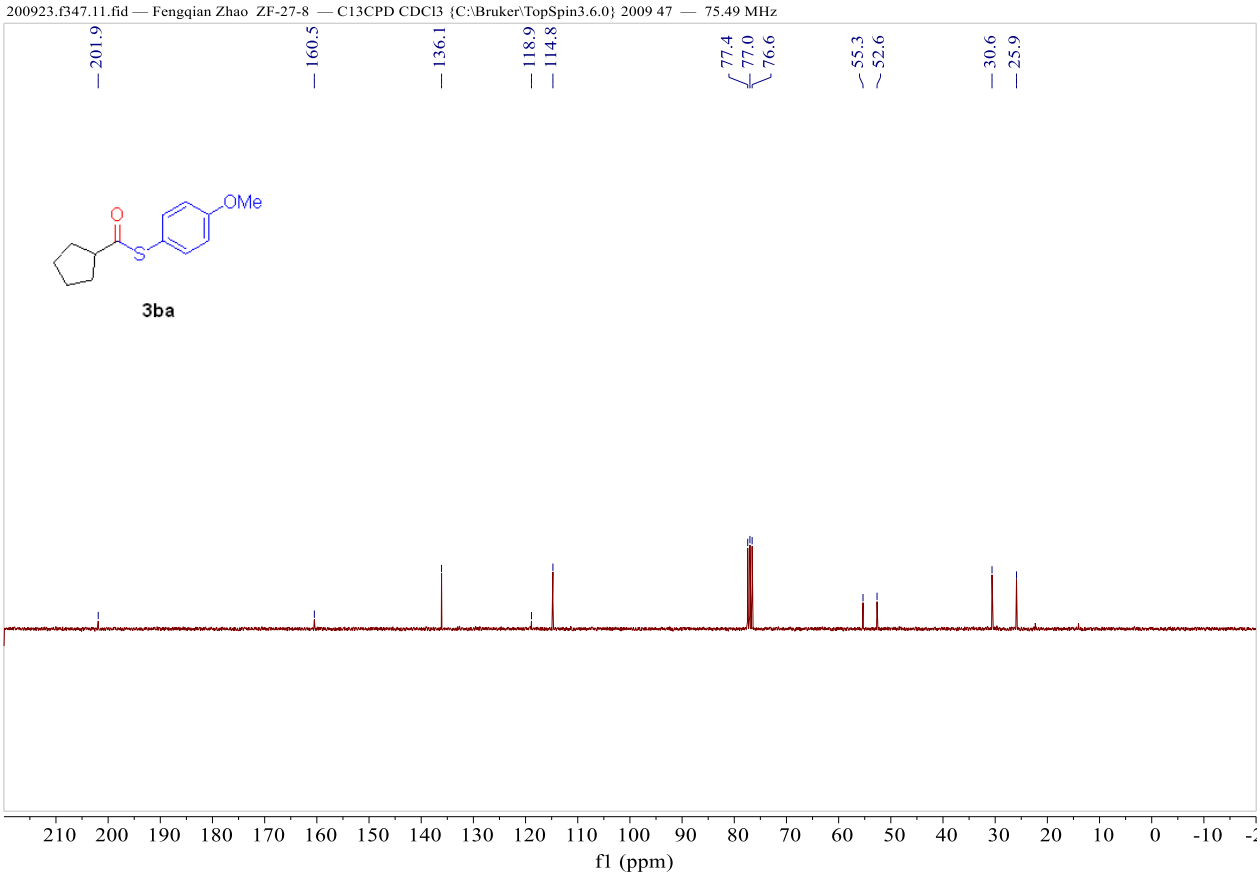
2.01
3.00
1.01
4.07
4.44
f1 (ppm)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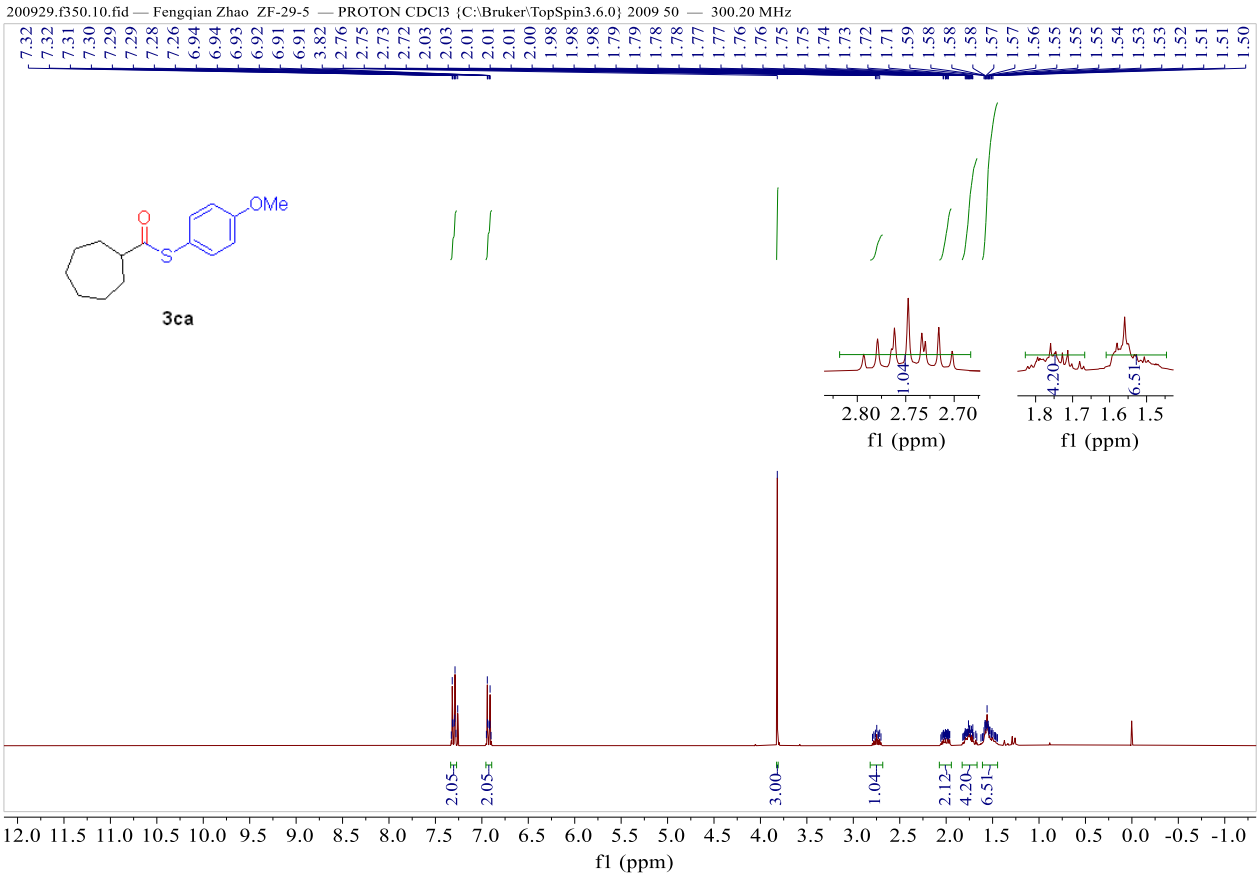
160.5
136.1
118.9
114.8
77.4
77.0
76.6
55.3
52.6
30.6
25.9
OMe
O
S
3ba
f1 (ppm)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S
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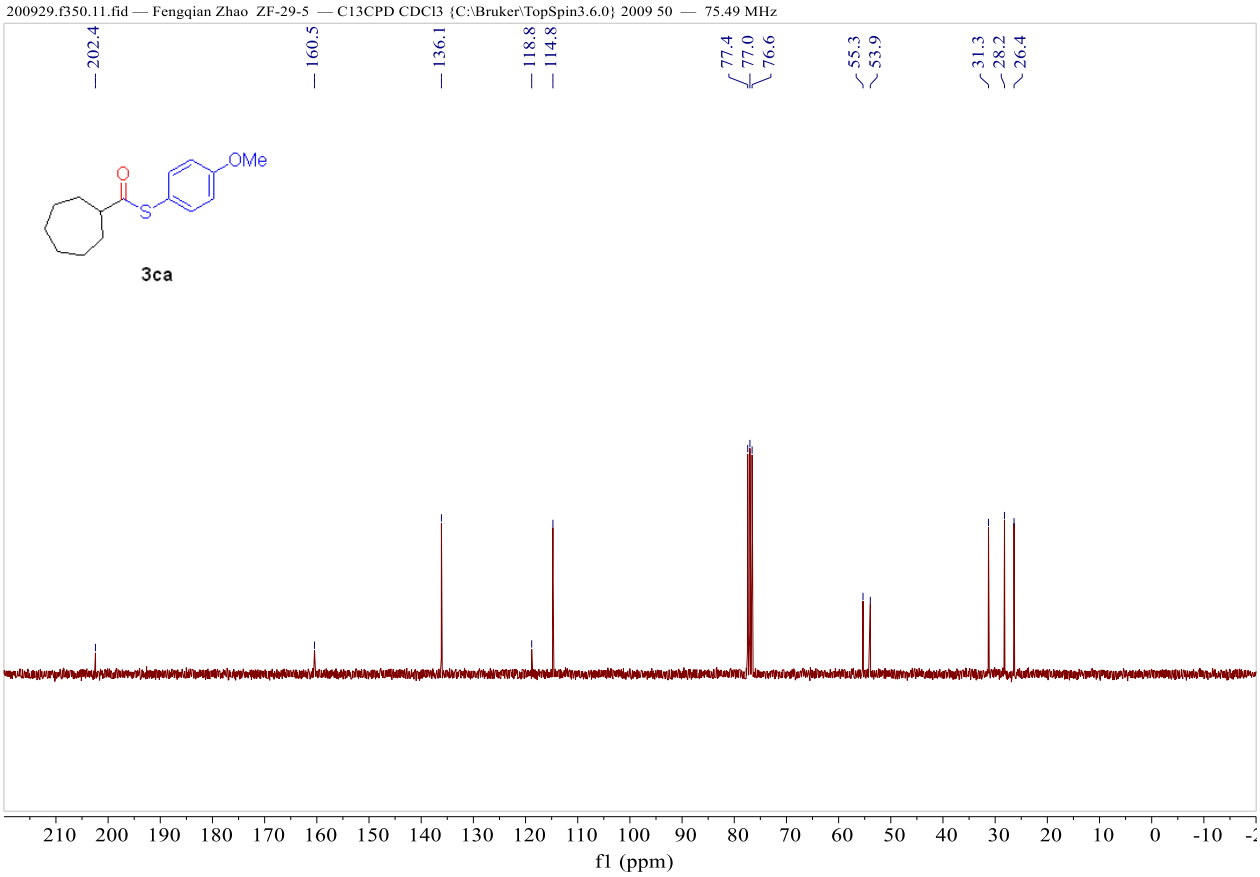
2.05
3.00
1.04
2.12
4.20
6.51
f1 (ppm)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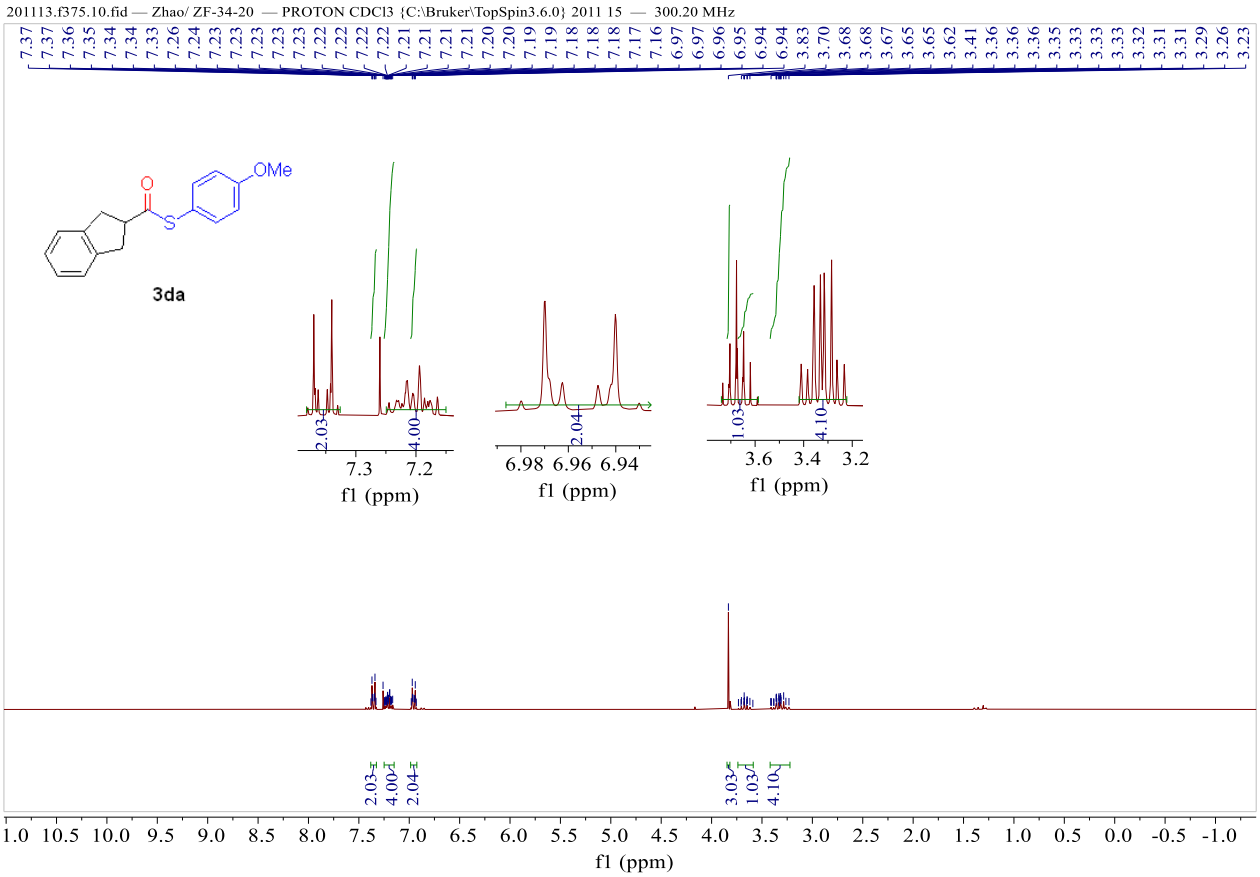
136.1
118.8
114.8
77.4
77.0
76.6
55.3
53.9
31.3
28.2
26.4
OMe
O
S
3ca
f1 (ppm)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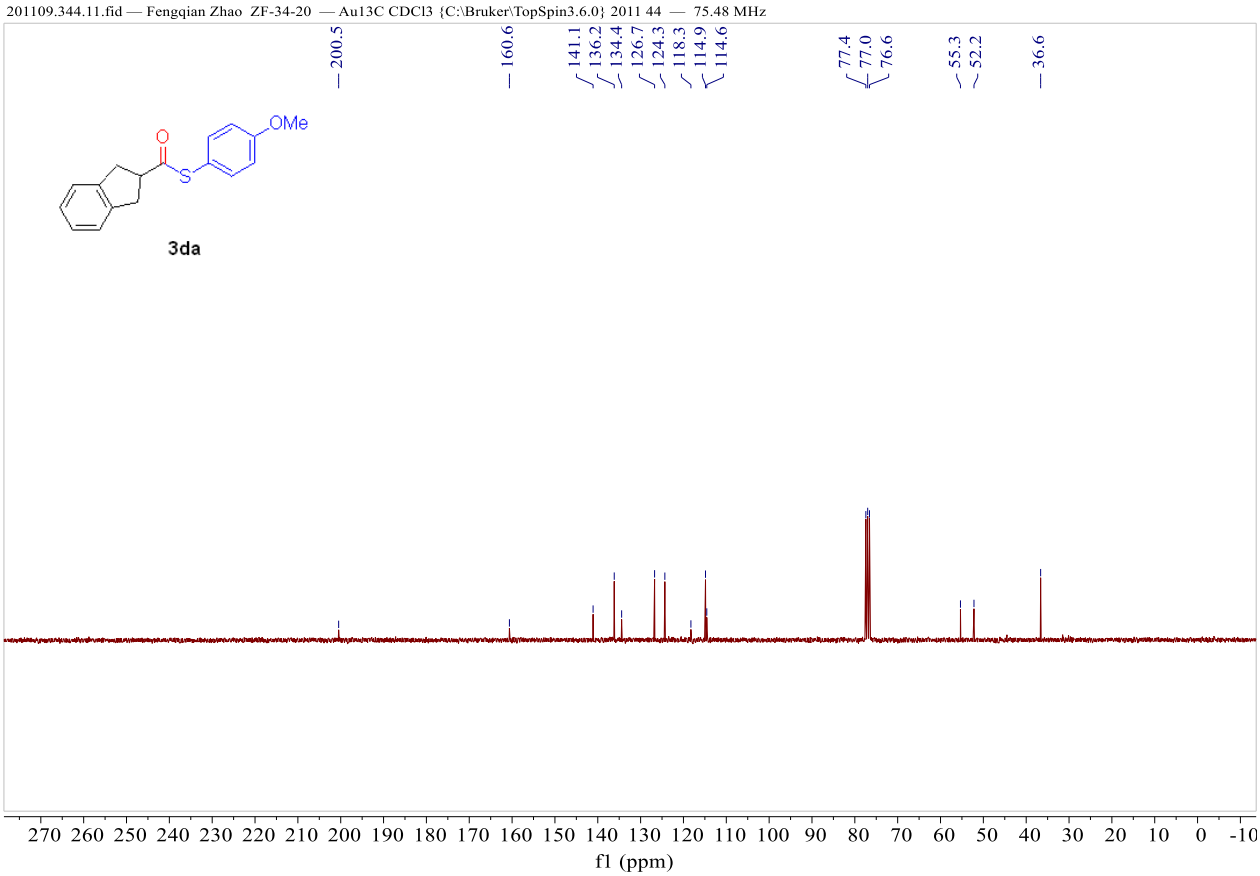
OMe
O
S
3da
f1 (ppm)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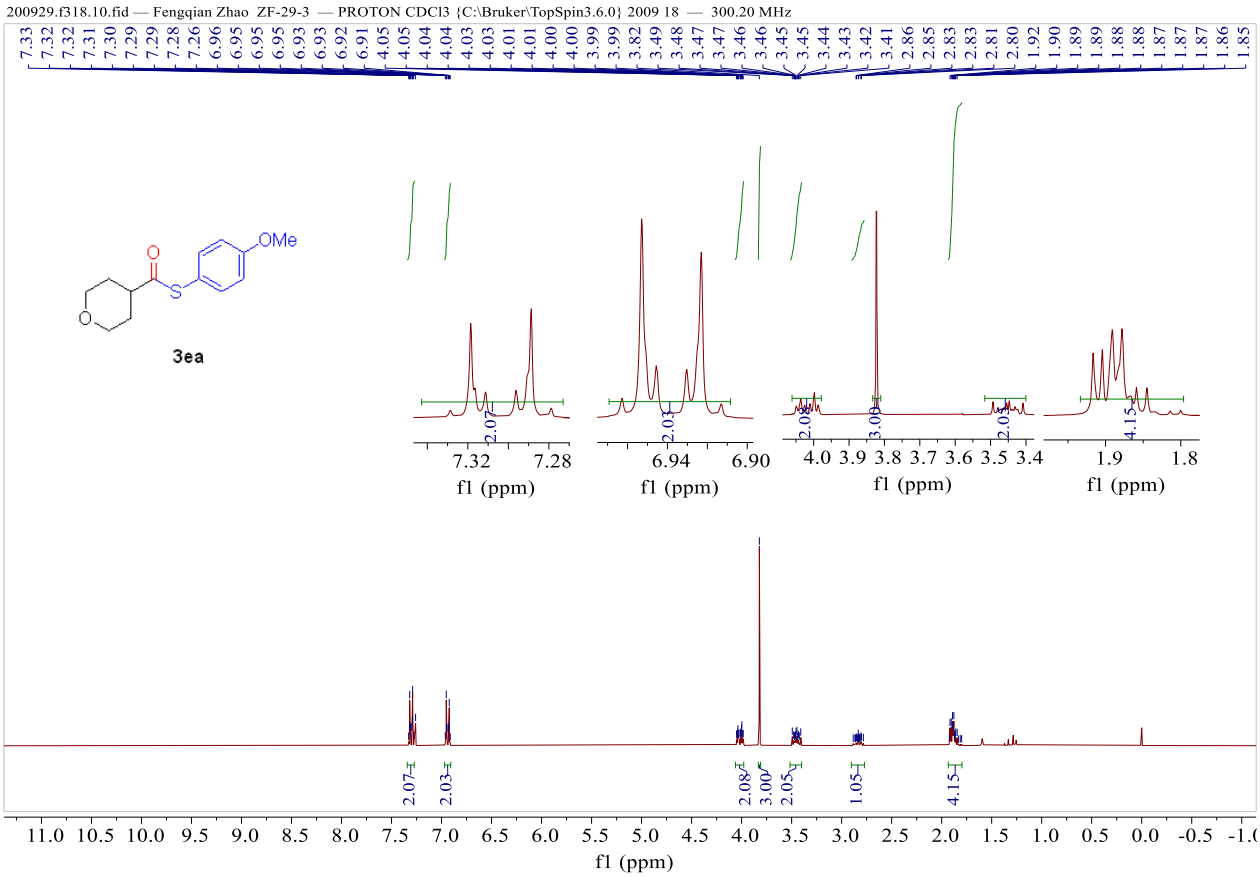
O
S
3da
f1 (ppm)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O
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O
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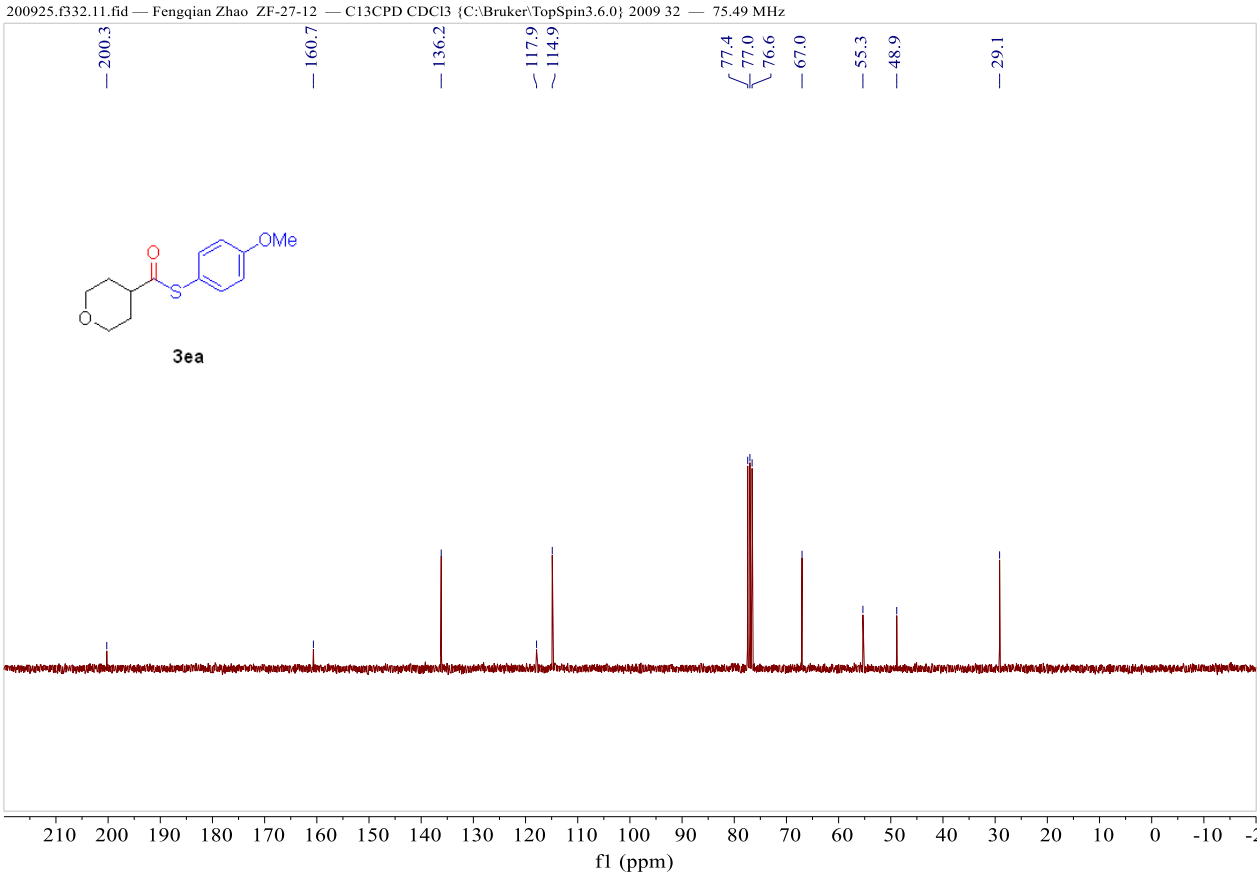
f1 (ppm)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48.9
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O
S
O
3ea
f1 (ppm)

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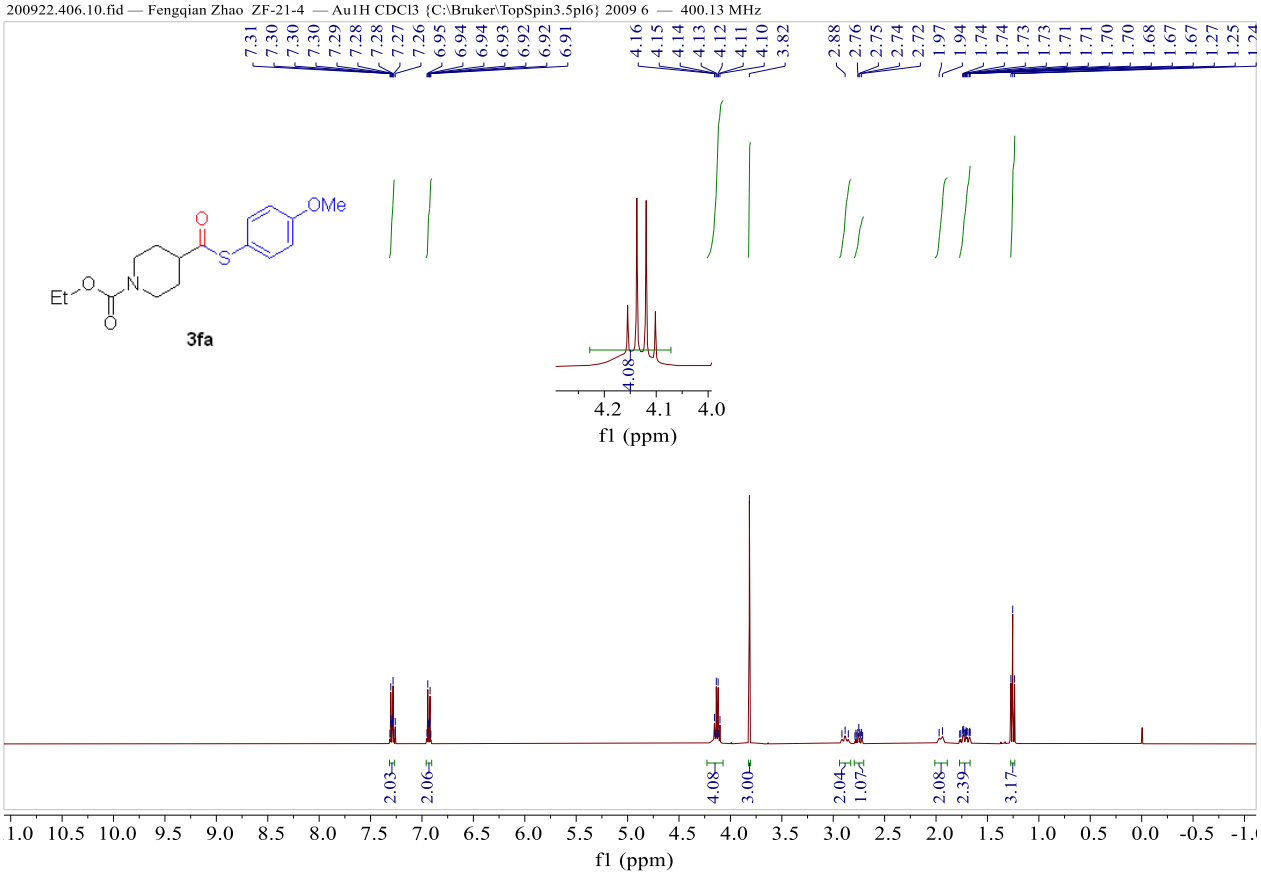

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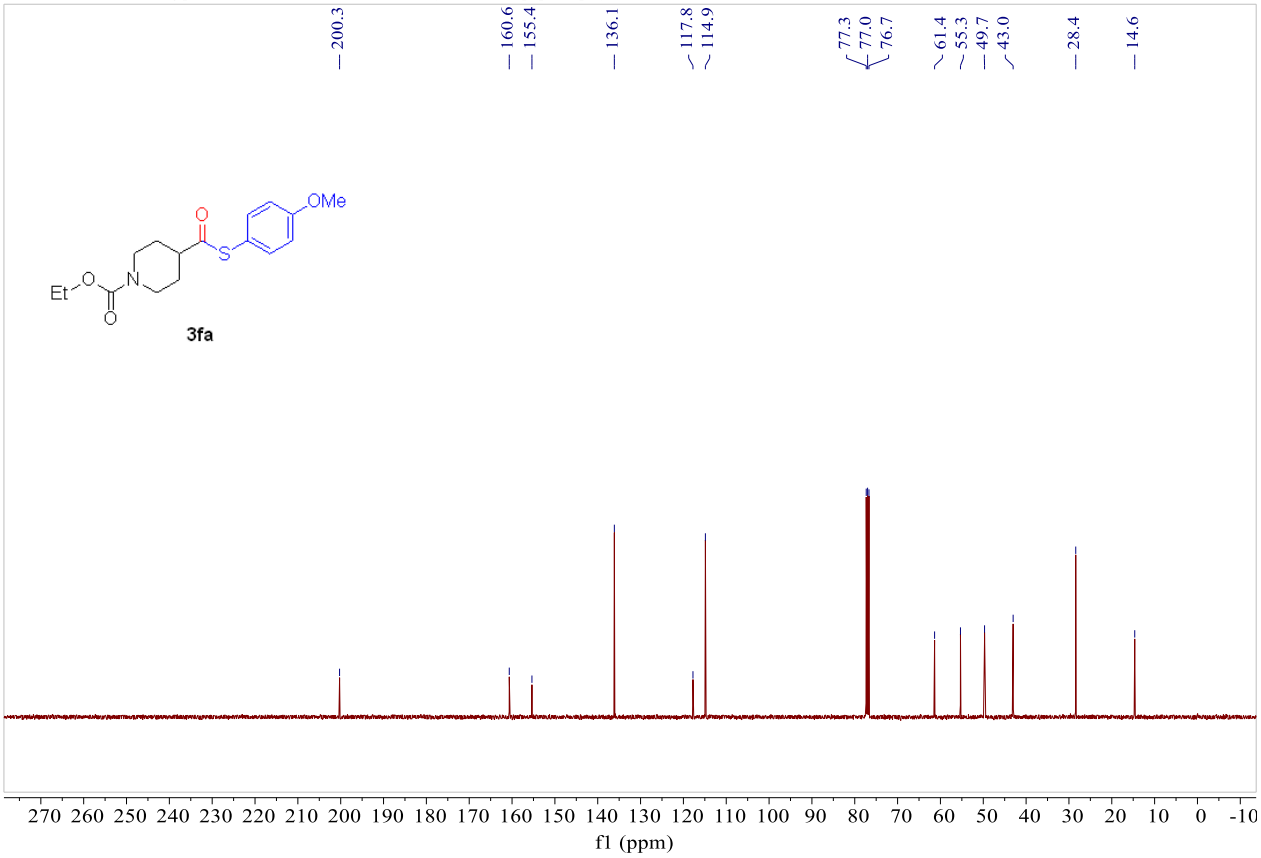

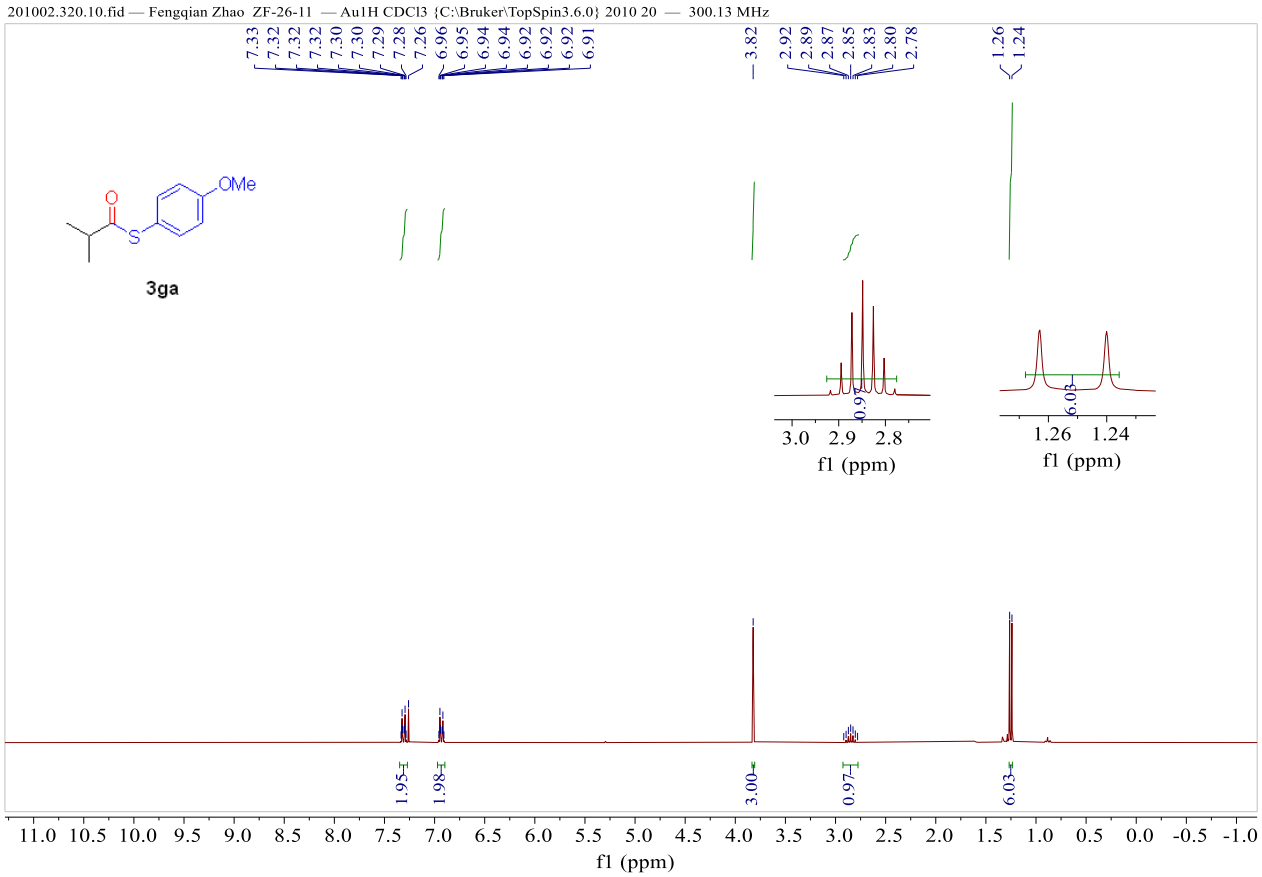
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7.30
7.29
7.28
7.26
6.96
6.95
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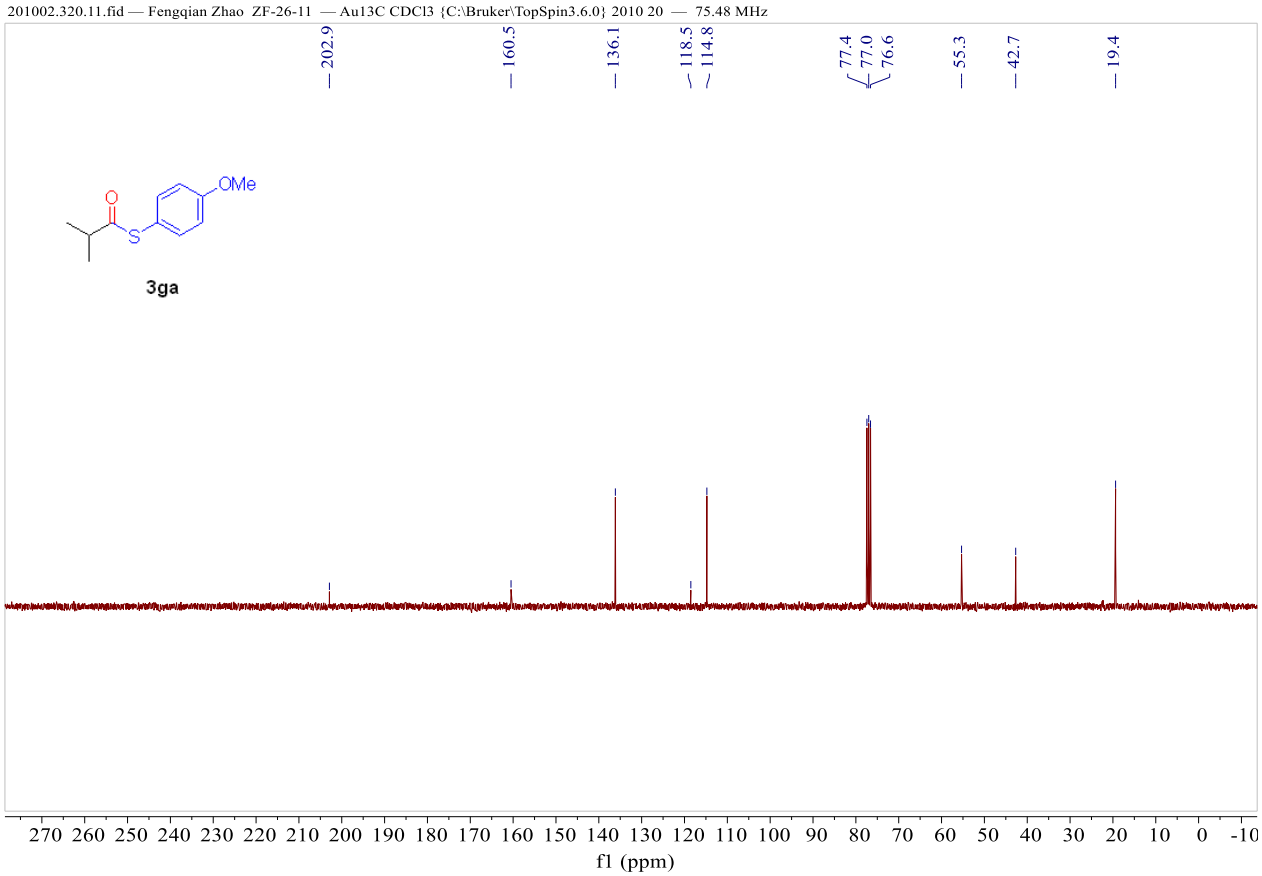
6.92
6.92
6.92
6.91
3.82
2.92
2.89
2.87
2.85
2.83
2.80
2.78
1.26
1.24
OMe
O
S
3ga
0.97
6.03
3.0 2.9 2.8
f1 (ppm)
1.26 1.24
f1 (ppm)
1.95
1.98
3.00
0.97
6.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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118.5
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77.4
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76.6
55.3
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O
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3ga
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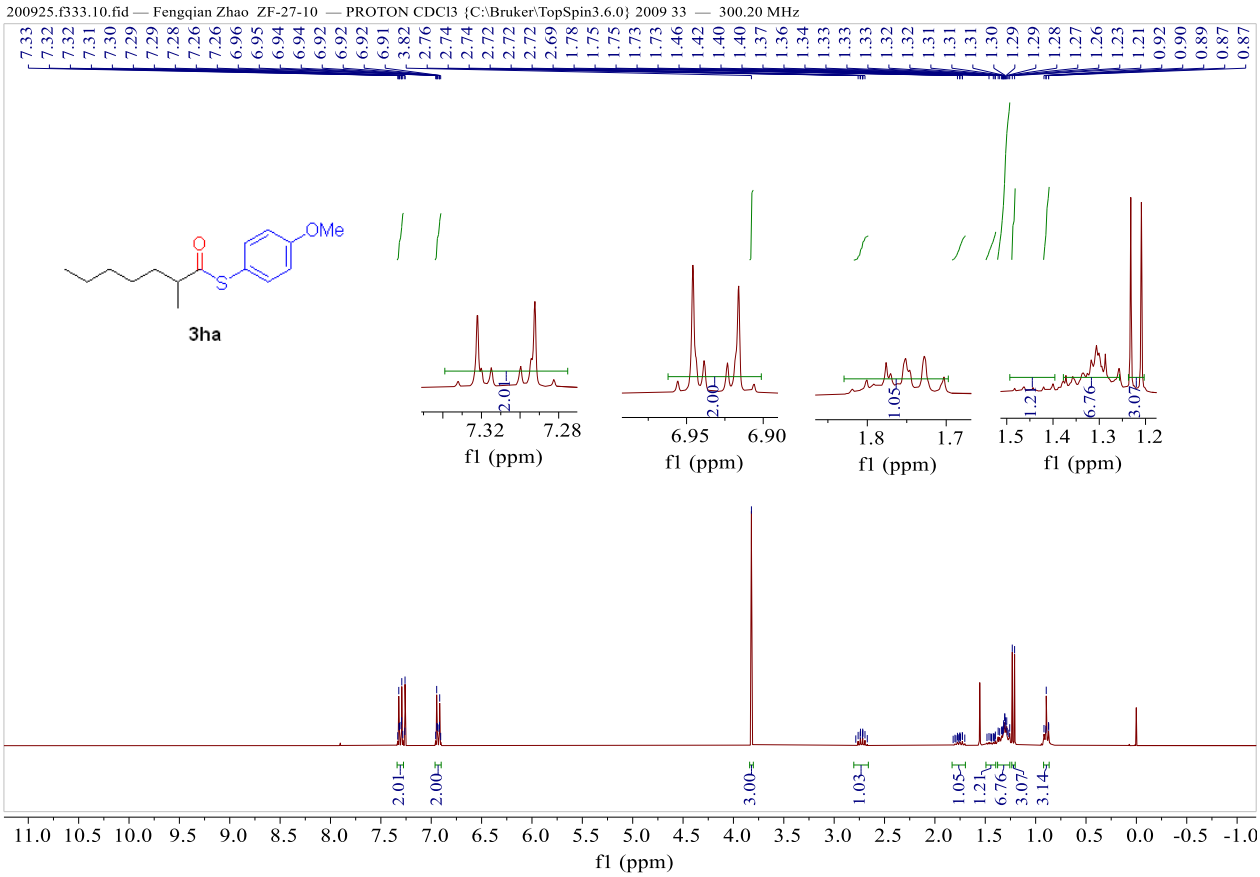
f1 (ppm)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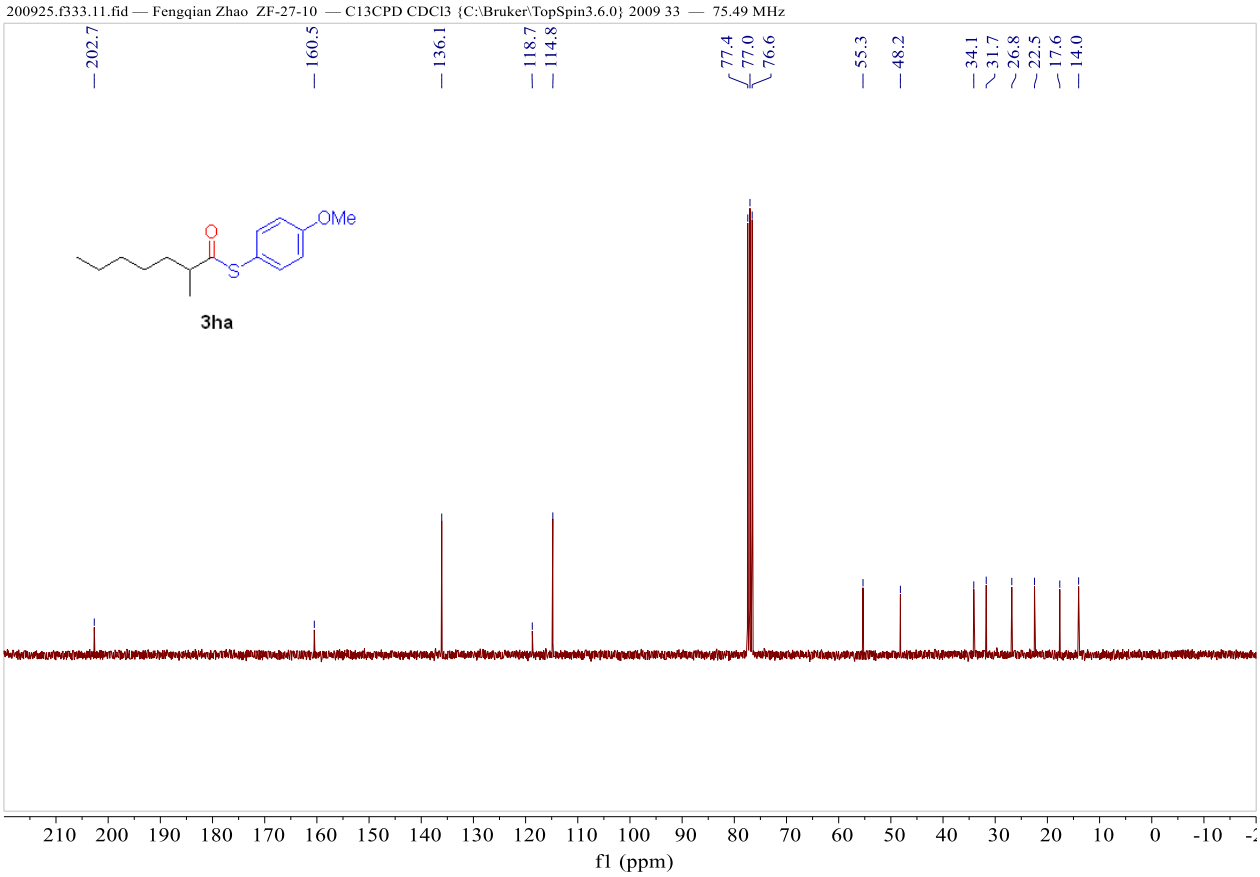
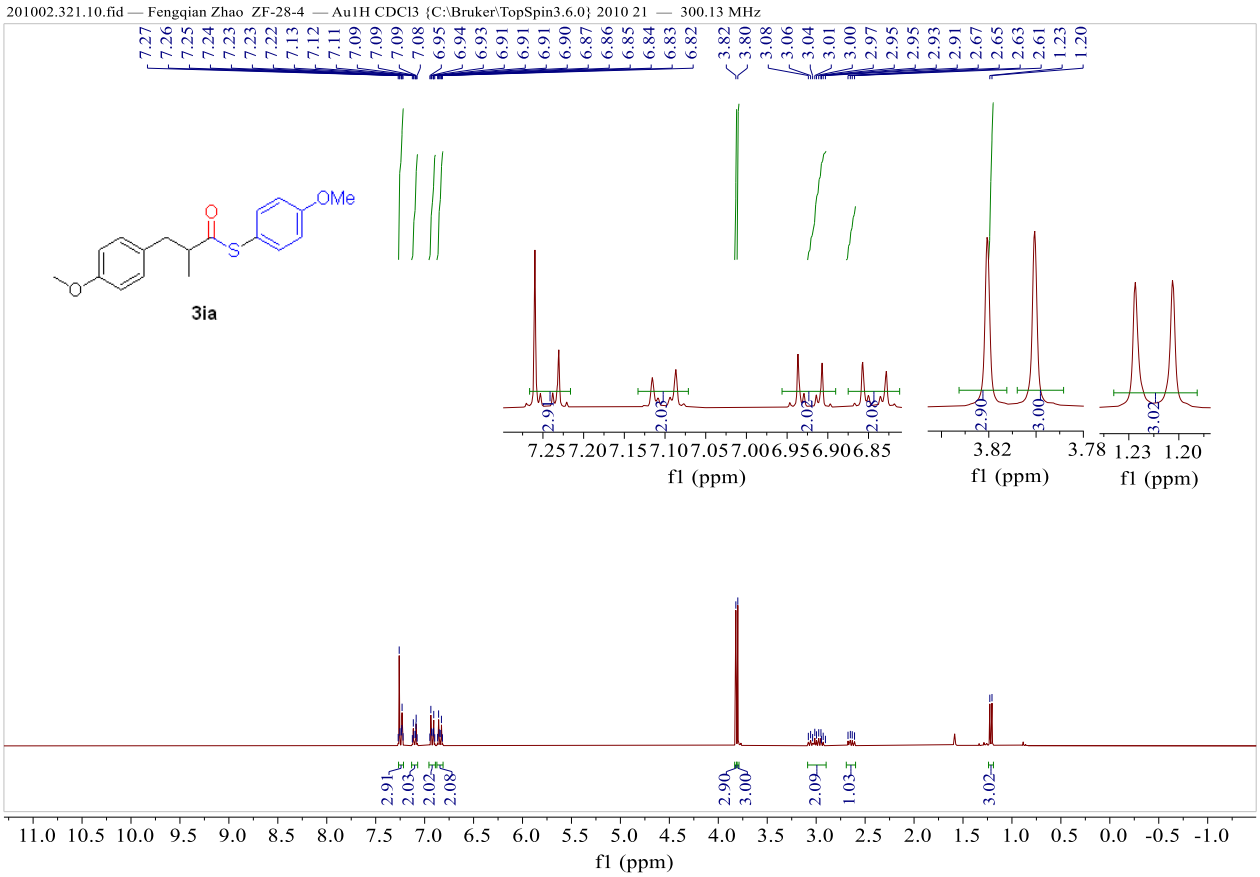
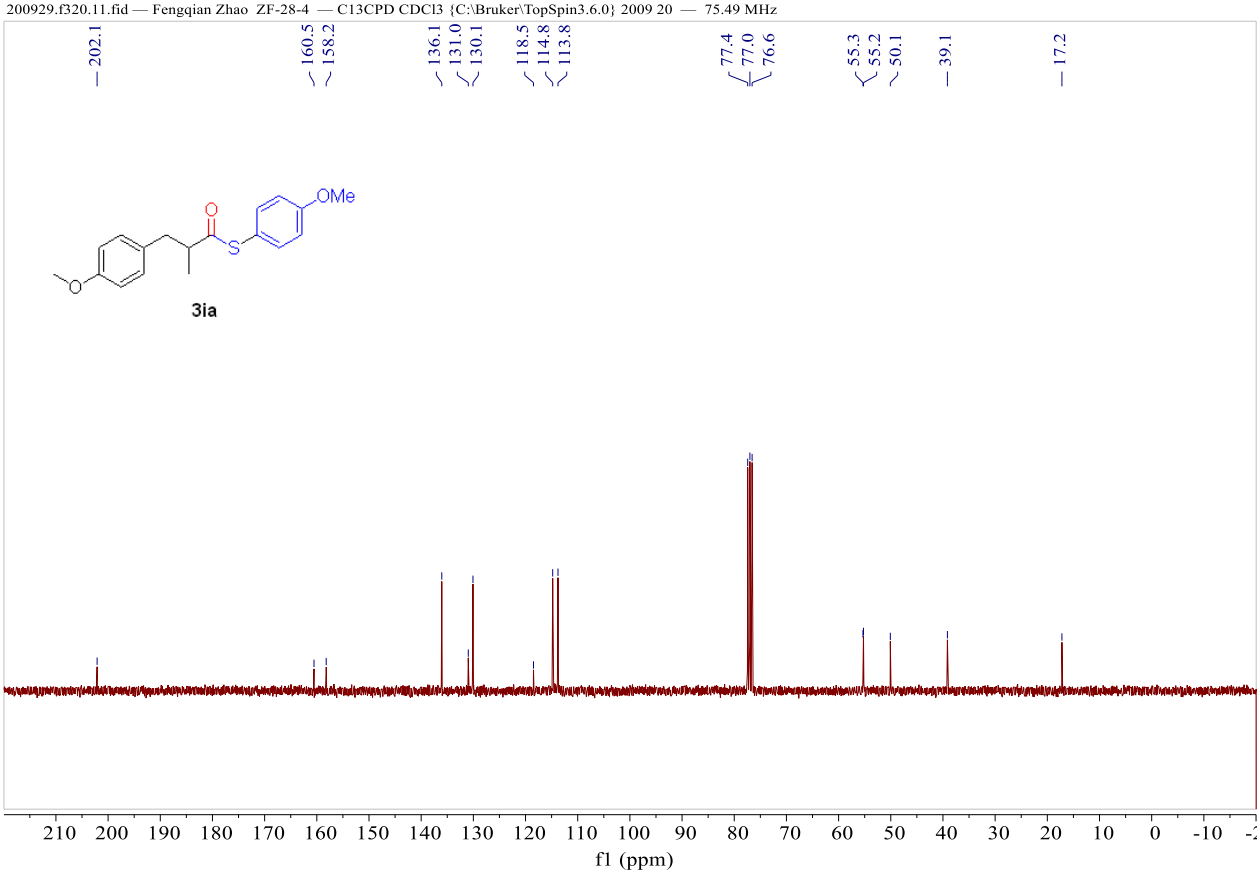
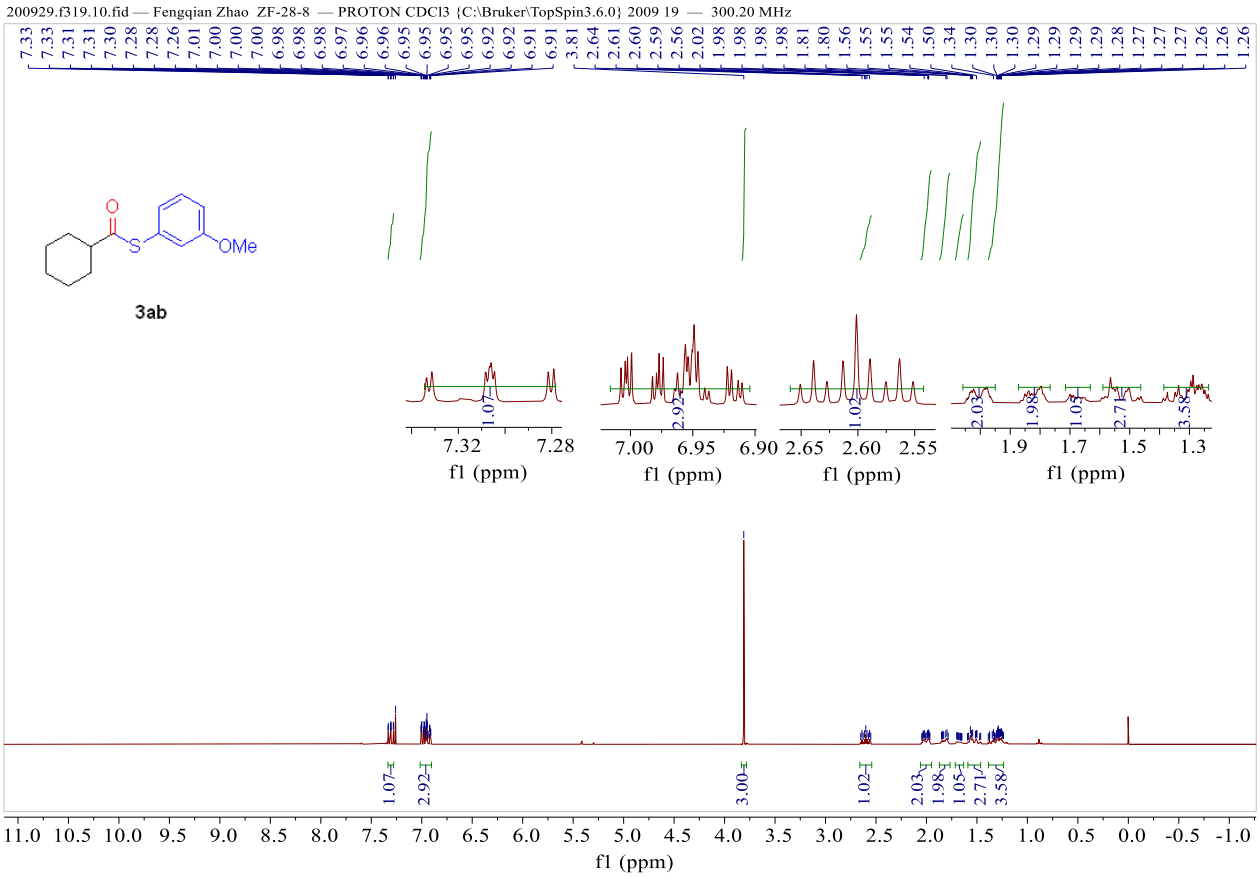
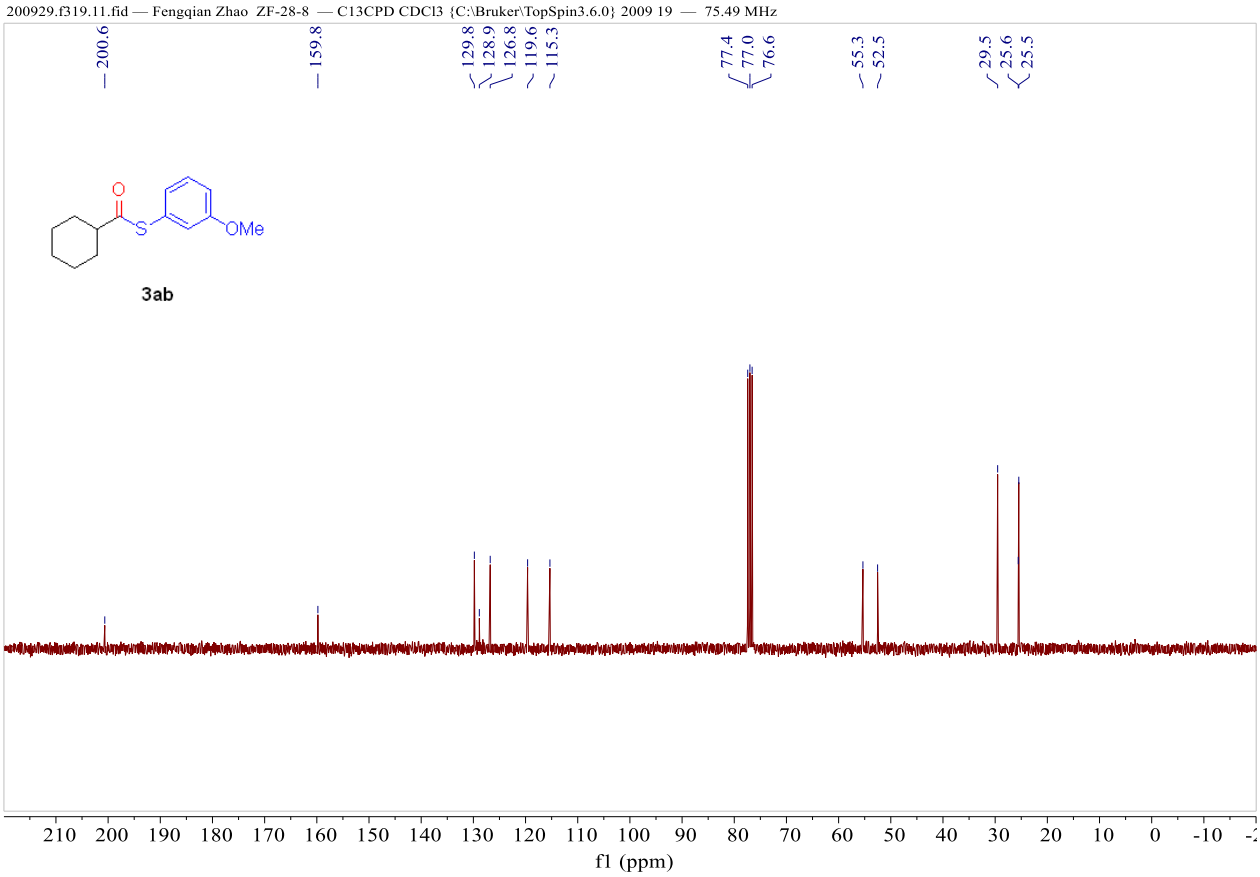
f1 (ppm)

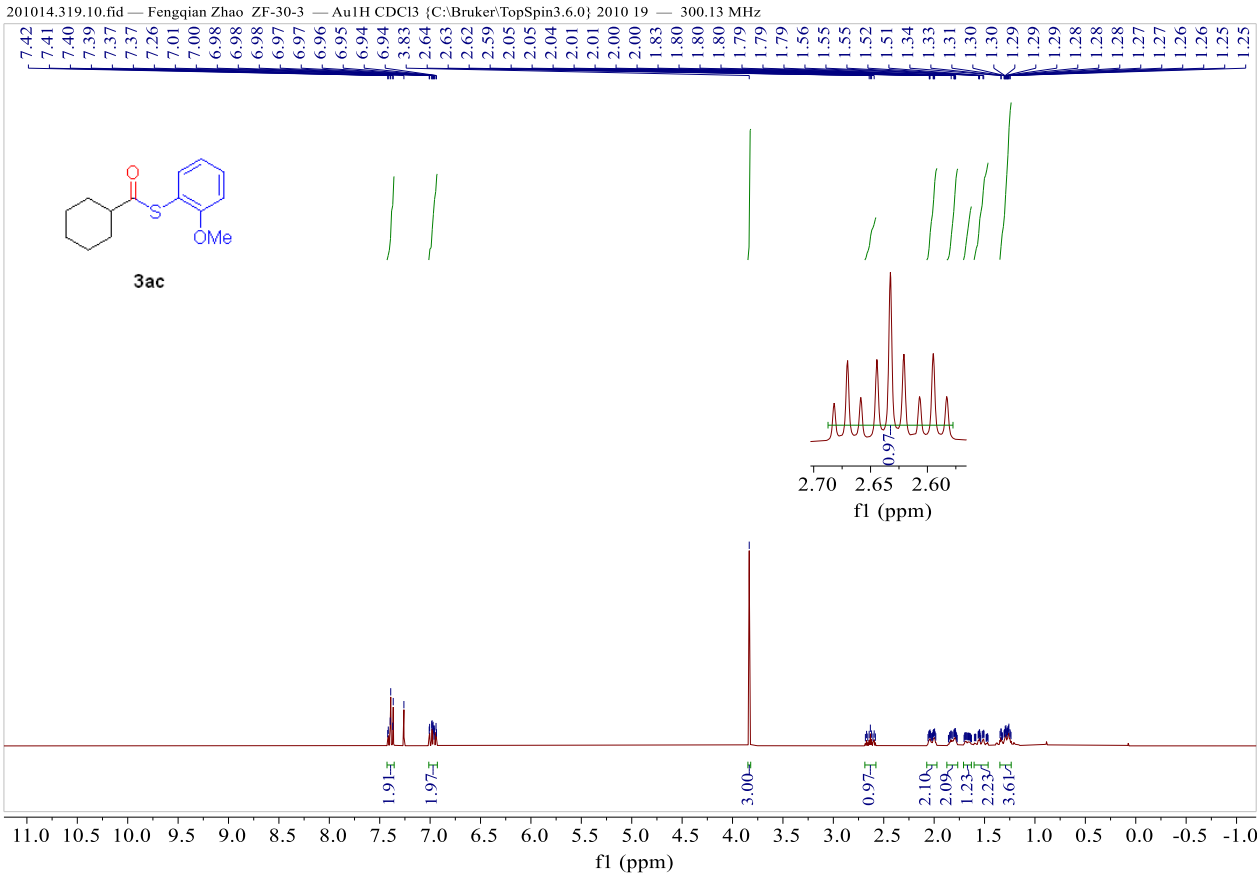

200925.f333.11.fid — Fengqian Zhao ZF-27-10 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 33 — 75.49 MHz
OMe
O
S
3ha
f1 (ppm)

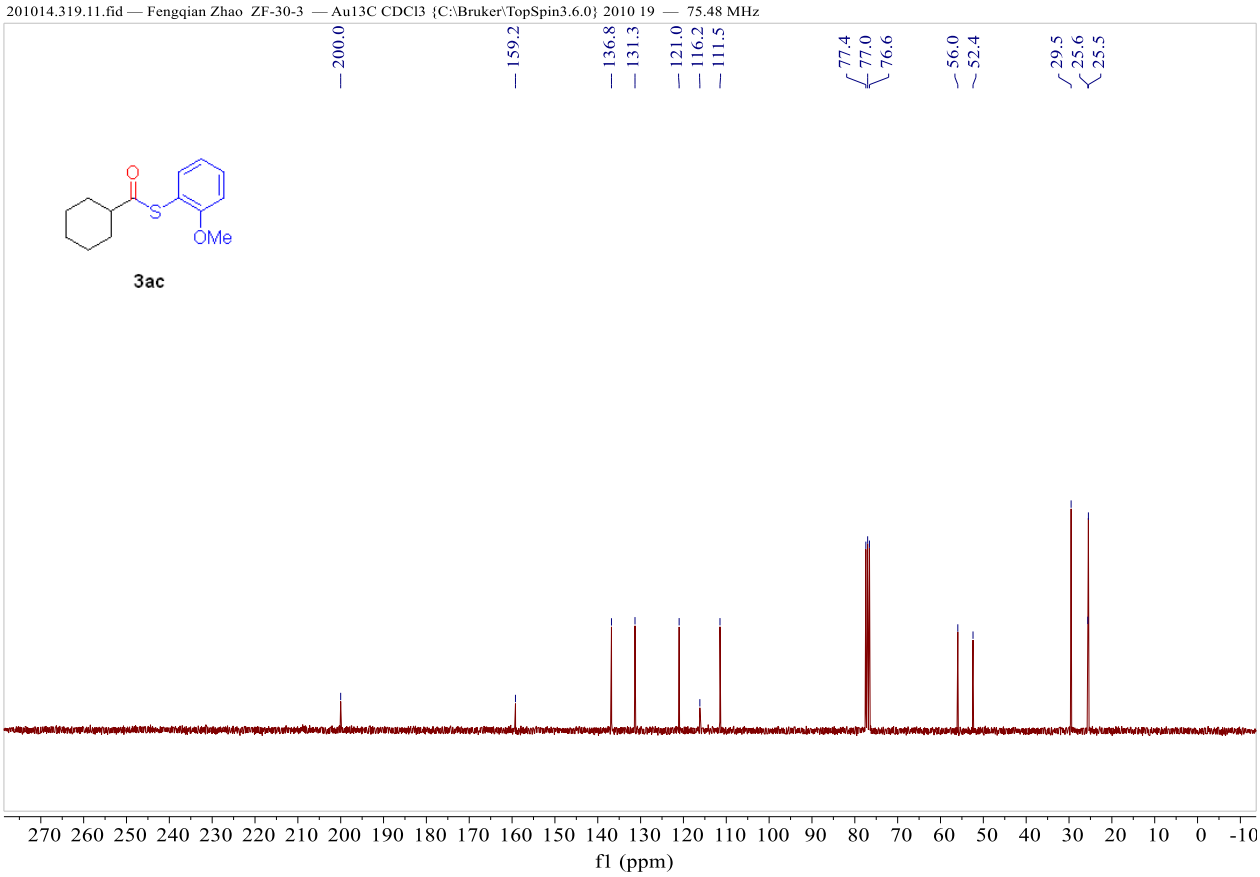

201002.321.10.fid — Fengqian Zhao ZF-28-4 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 21 — 300.13 MHz
7.27 7.26 7.25 7.24 7.23 7.23 7.22 7.13 7.12 7.11 7.09 7.09 7.09 7.08 6.95 6.94 6.93 6.91 6.91 6.91 6.90 6.87 6.86 6.85 6.84 6.83 6.82
3.82 3.80 3.08 3.06 3.04 3.01 3.00 2.97 2.95 2.95 2.93 2.91 2.67 2.65 2.63 2.61 1.23 1.20
OMe
O
S
O
3ia
2.91 2.03 2.02 2.08
7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85
f1 (ppm)
2.90 3.00
3.82 3.78
f1 (ppm)
3.02
1.23 1.20
f1 (ppm)
2.91 2.03 2.02 2.08 2.90 3.00 2.09 1.03 3.02
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 -0.5 -1.0
f1 (ppm)

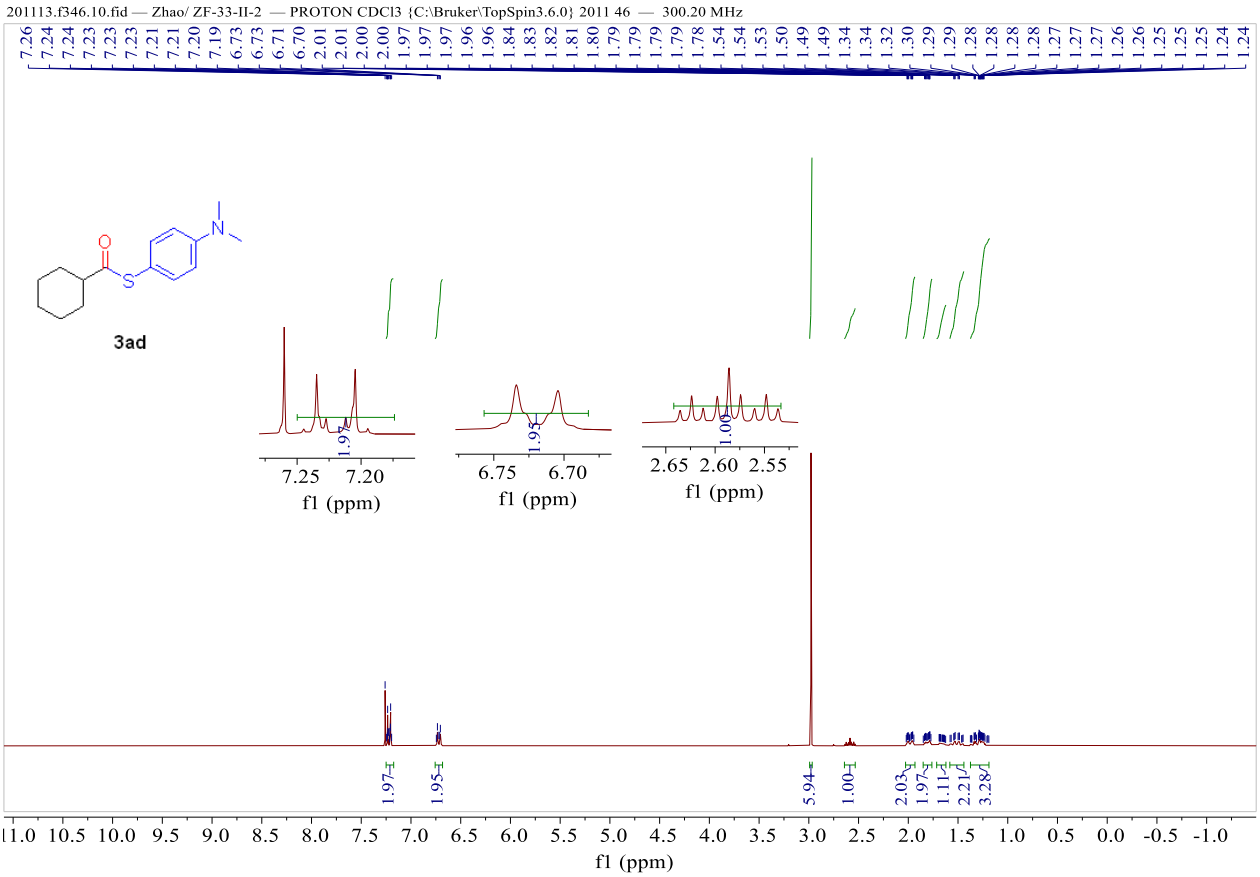

200929.f320.11.fid — Fengqian Zhao ZF-28-4 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 20 — 75.49 MHz
202.1
160.5 158.2
136.1 131.0 130.1
118.5 114.8 113.8
77.4 77.0 76.6
55.3 55.2 50.1
39.1
17.2
OMe
O
S
O
3ia
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

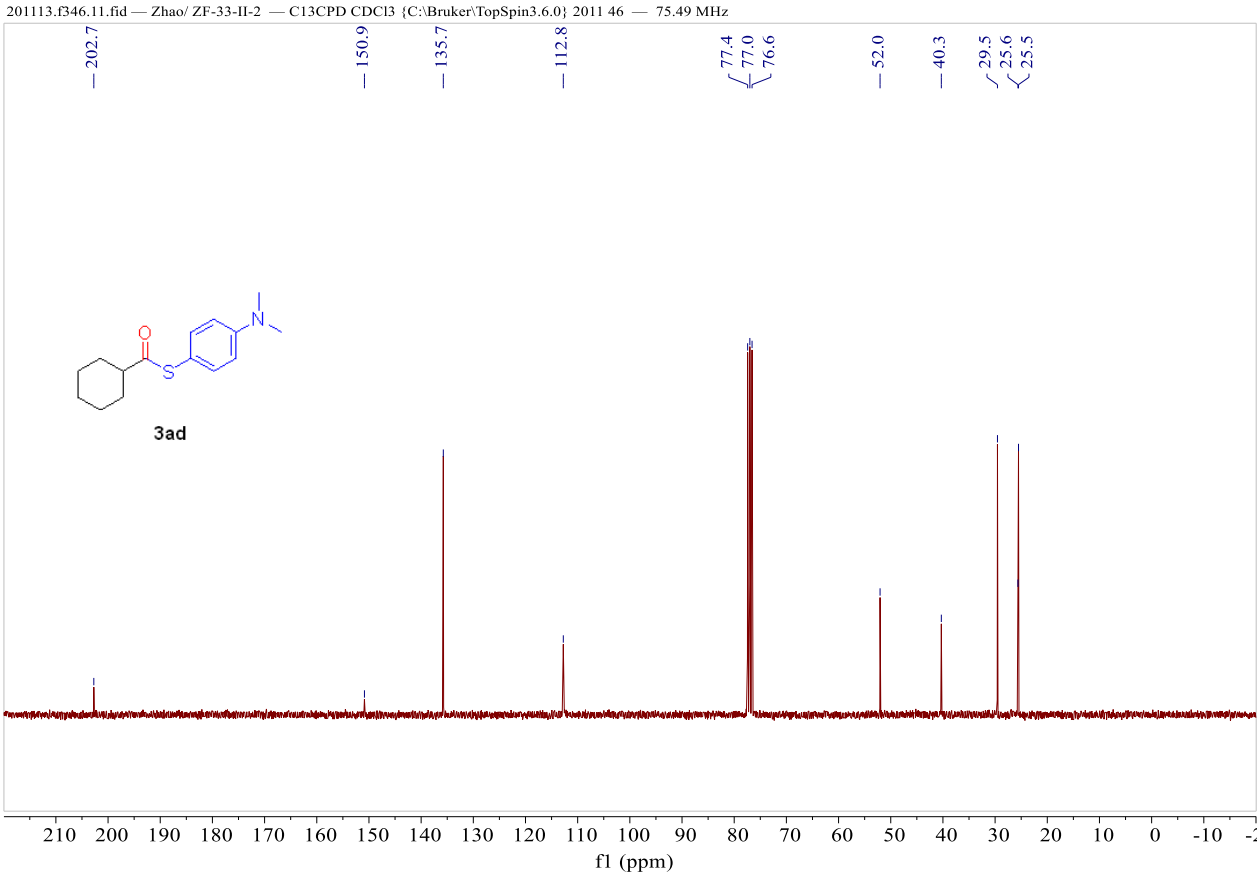

200929.f319.10.fid — Fengqian Zhao ZF-28-8 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 19 — 300.20 MHz
3ab
f1 (ppm)

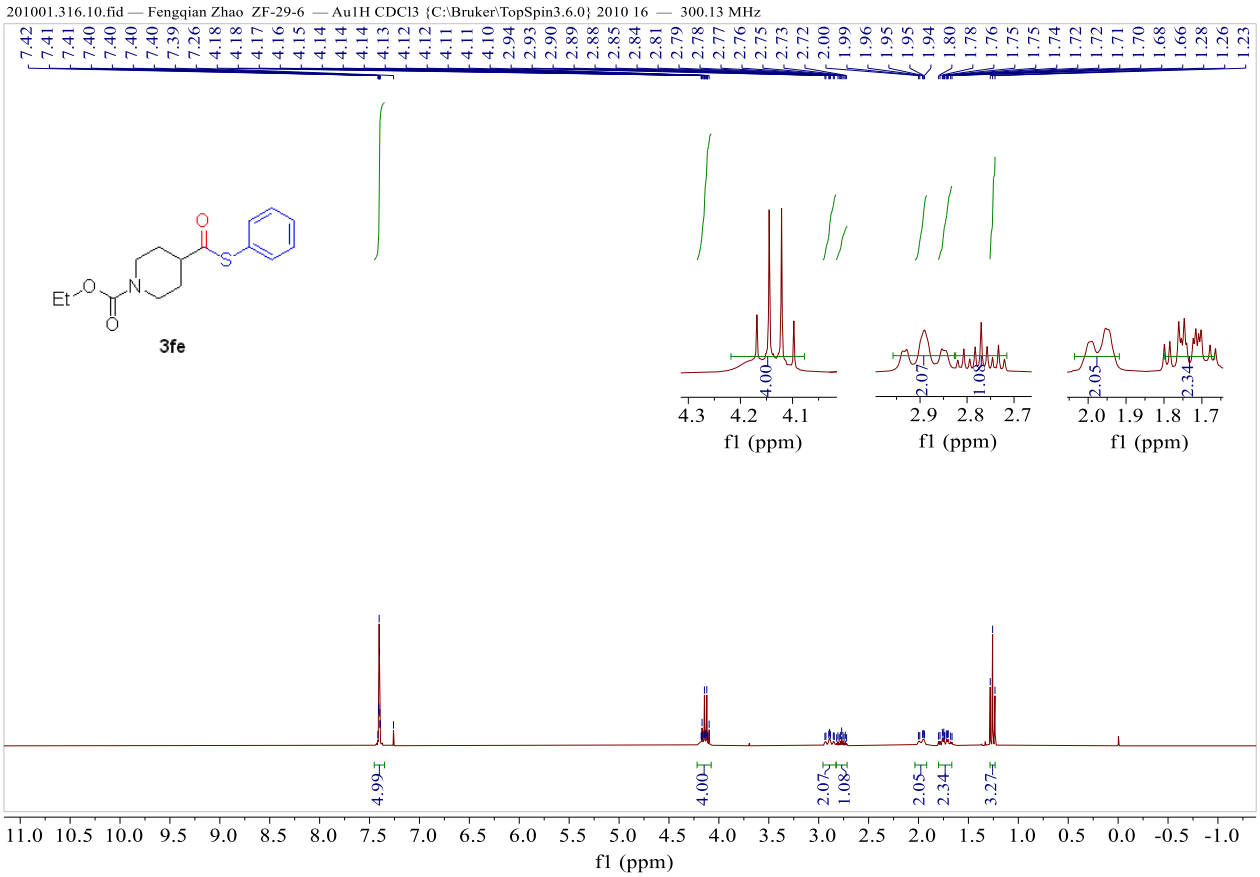

200929.f319.11.fid — Fengqian Zhao ZF-28-8 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2009 19 — 75.49 MHz
3ab
f1 (ppm)

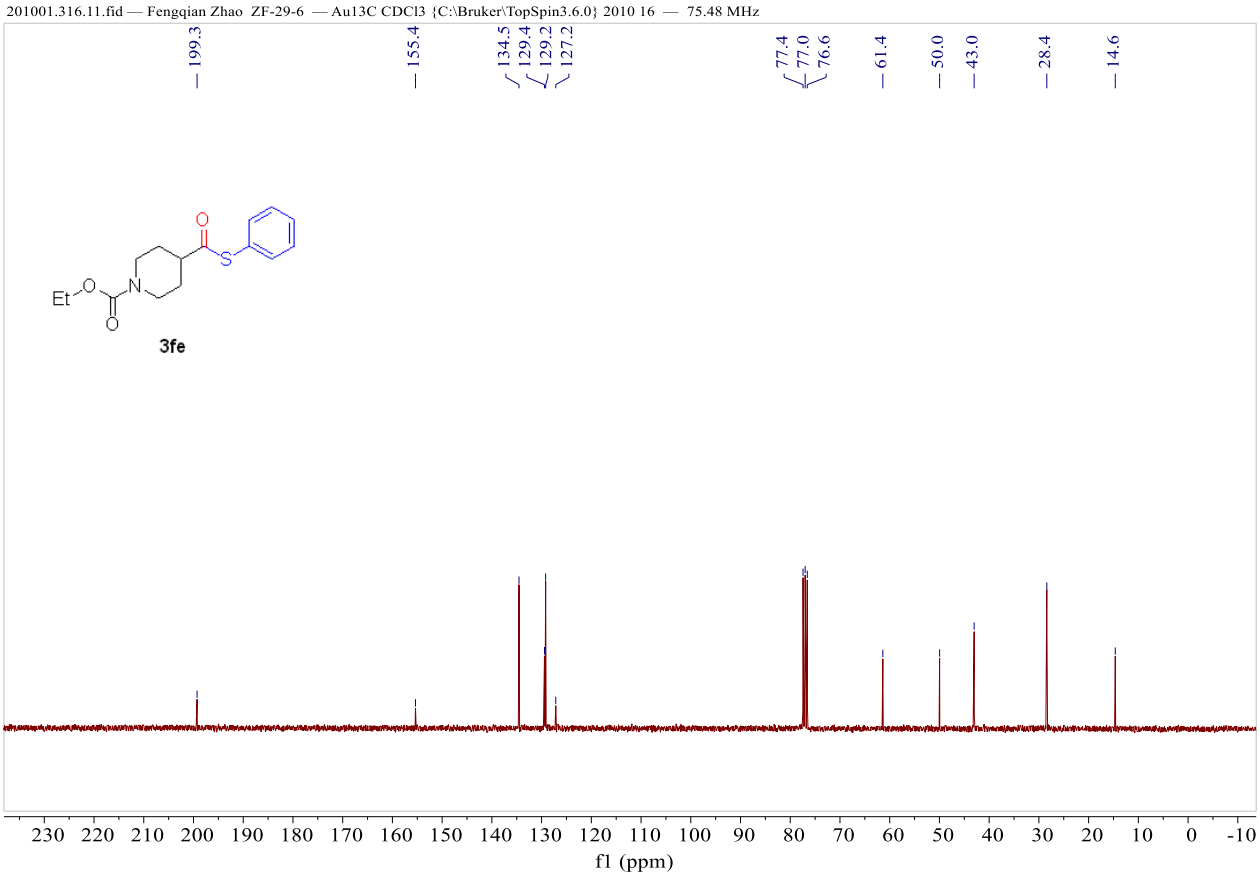

201014.319.10.fid — Fengqian Zhao ZF-30-3 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 19 — 300.13 MHz
3ac
f1 (ppm)

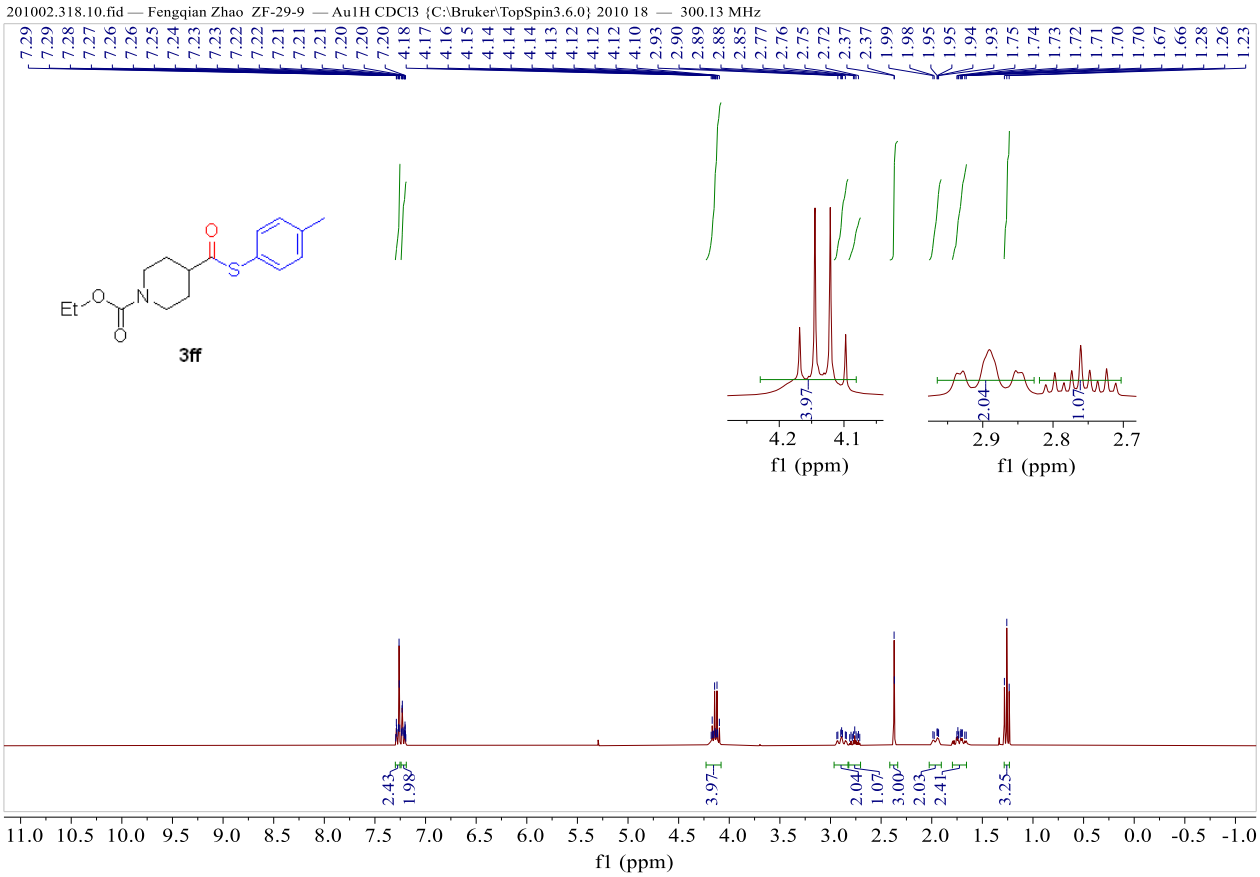

201014.319.11.fid — Fengqian Zhao ZF-30-3 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 19 — 75.48 MHz
3ac
f1 (ppm)

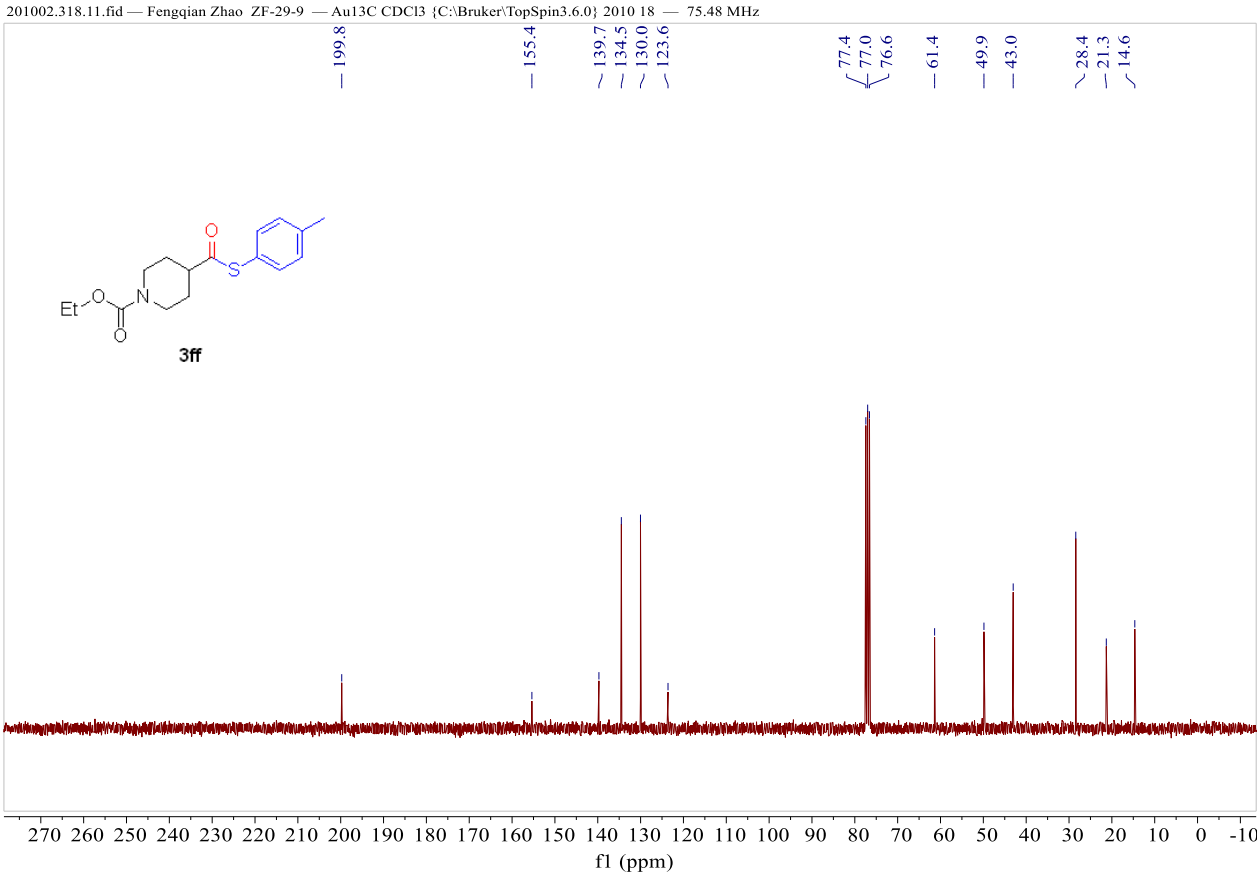

201113.f346.10.fid — Zhao/ ZF-33-II-2 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 46 — 300.20 MHz
3ad
f1 (ppm)

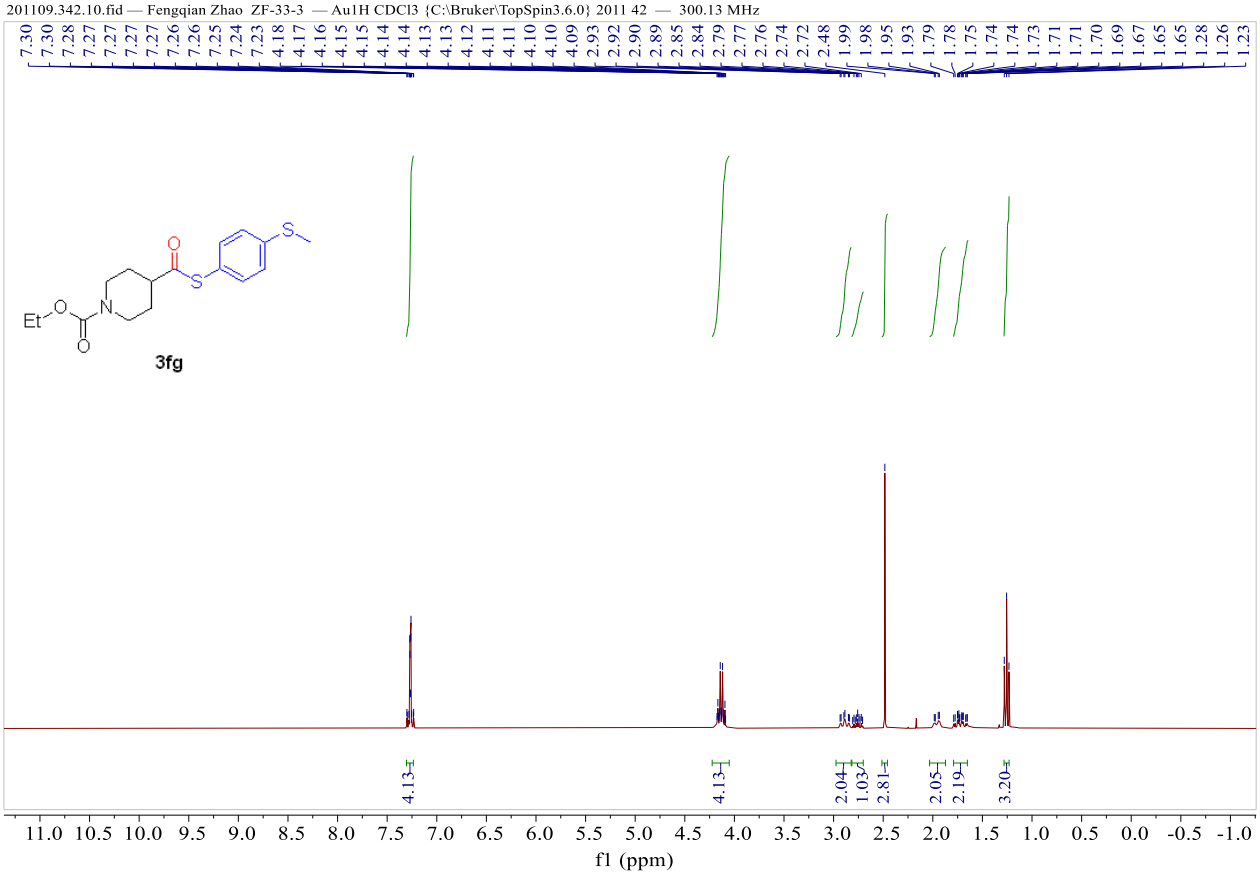

201113.f346.11.fid — Zhao/ ZF-33-II-2 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 46 — 75.49 MHz
3ad
f1 (ppm)

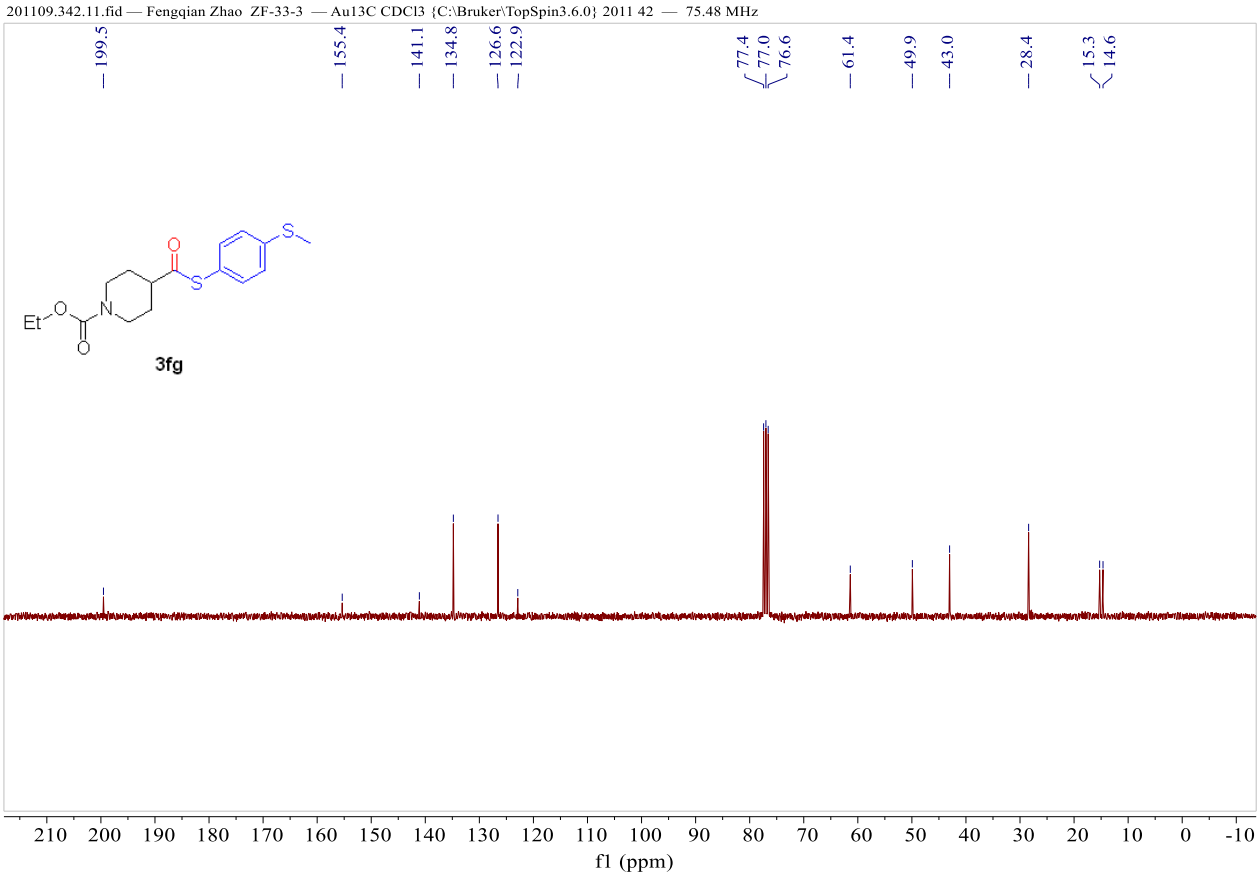

201001.316.10.fid — Fengqian Zhao ZF-29-6 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 16 — 300.13 MHz
3fe
f1 (ppm)

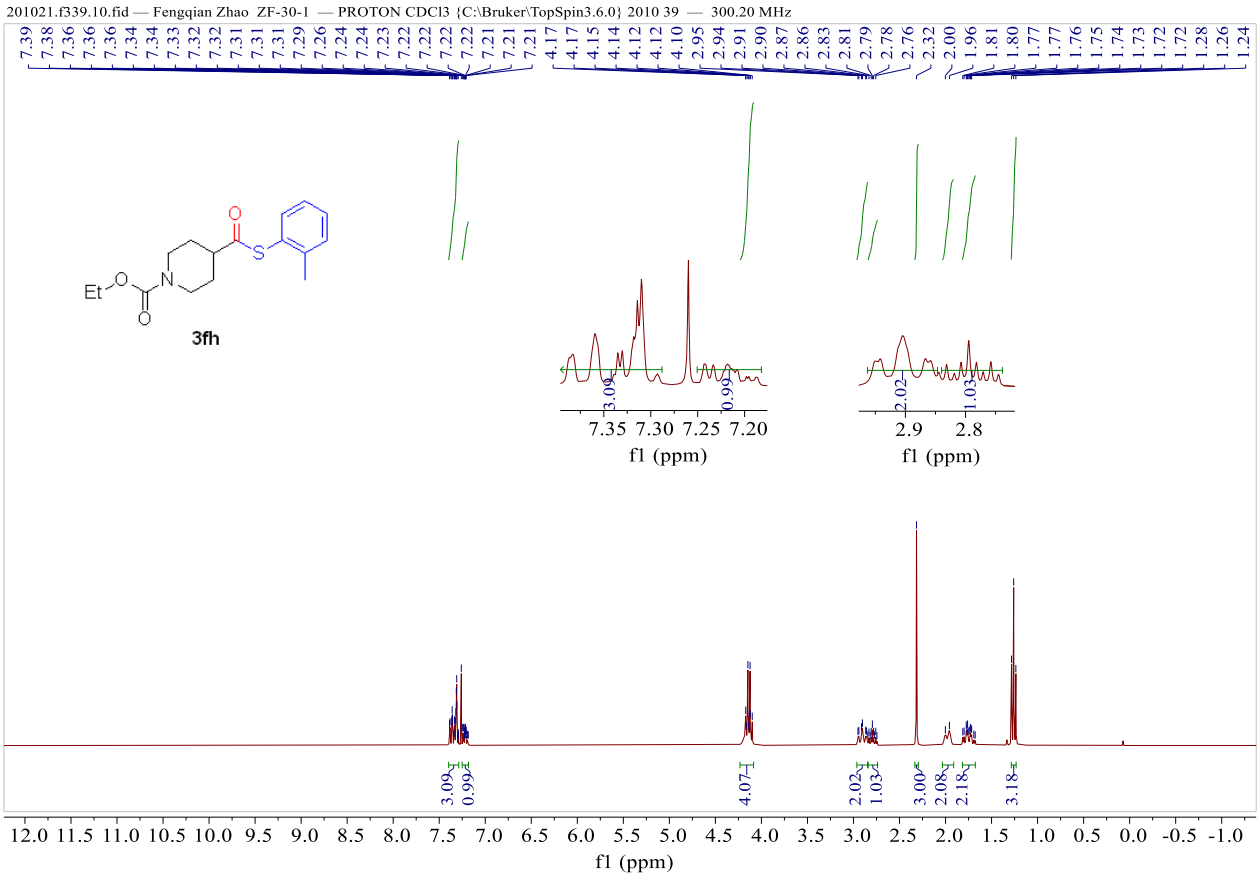

201001.316.11.fid — Fengqian Zhao ZF-29-6 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 16 — 75.48 MHz
3fe
f1 (ppm)

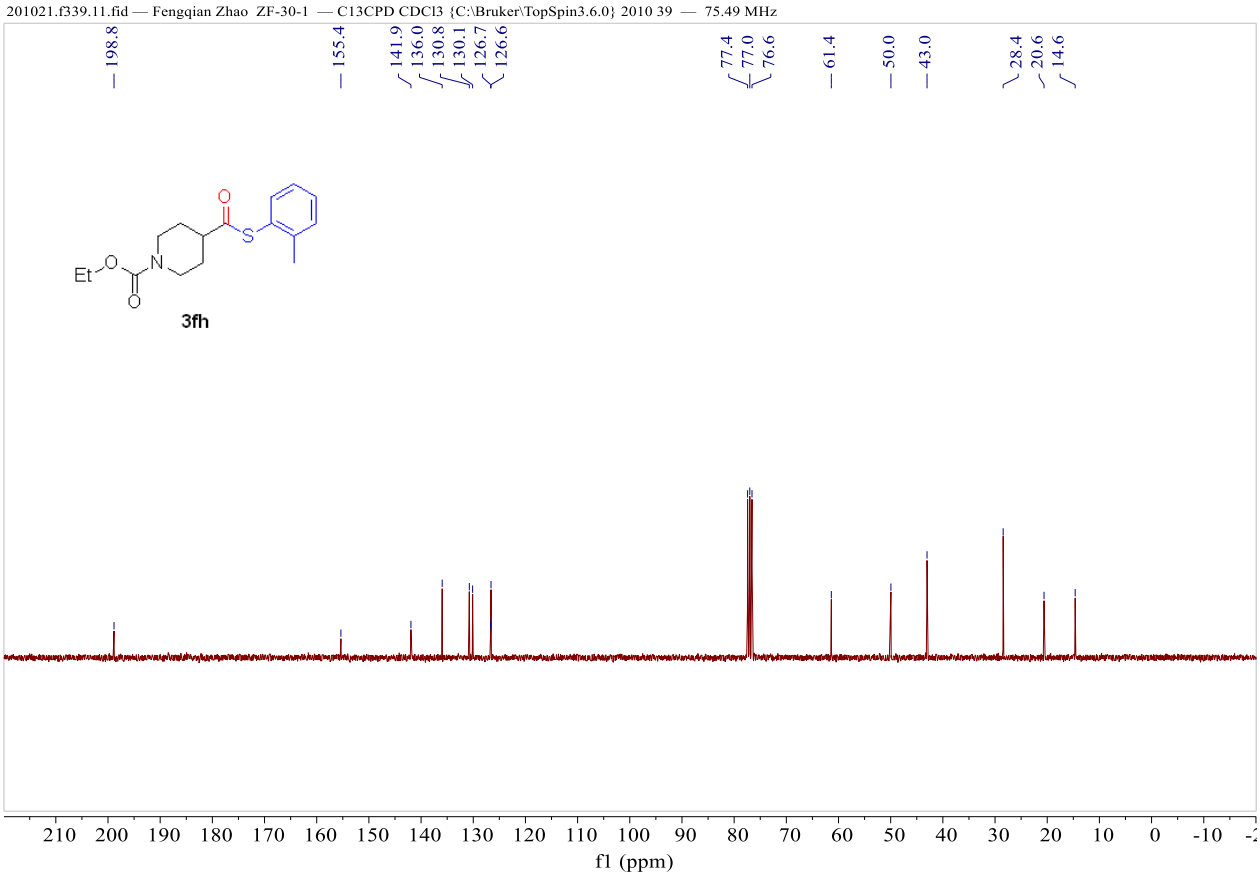

201002.318.10.fid — Fengqian Zhao ZF-29-9 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 18 — 300.13 MHz
3ff
f1 (ppm)

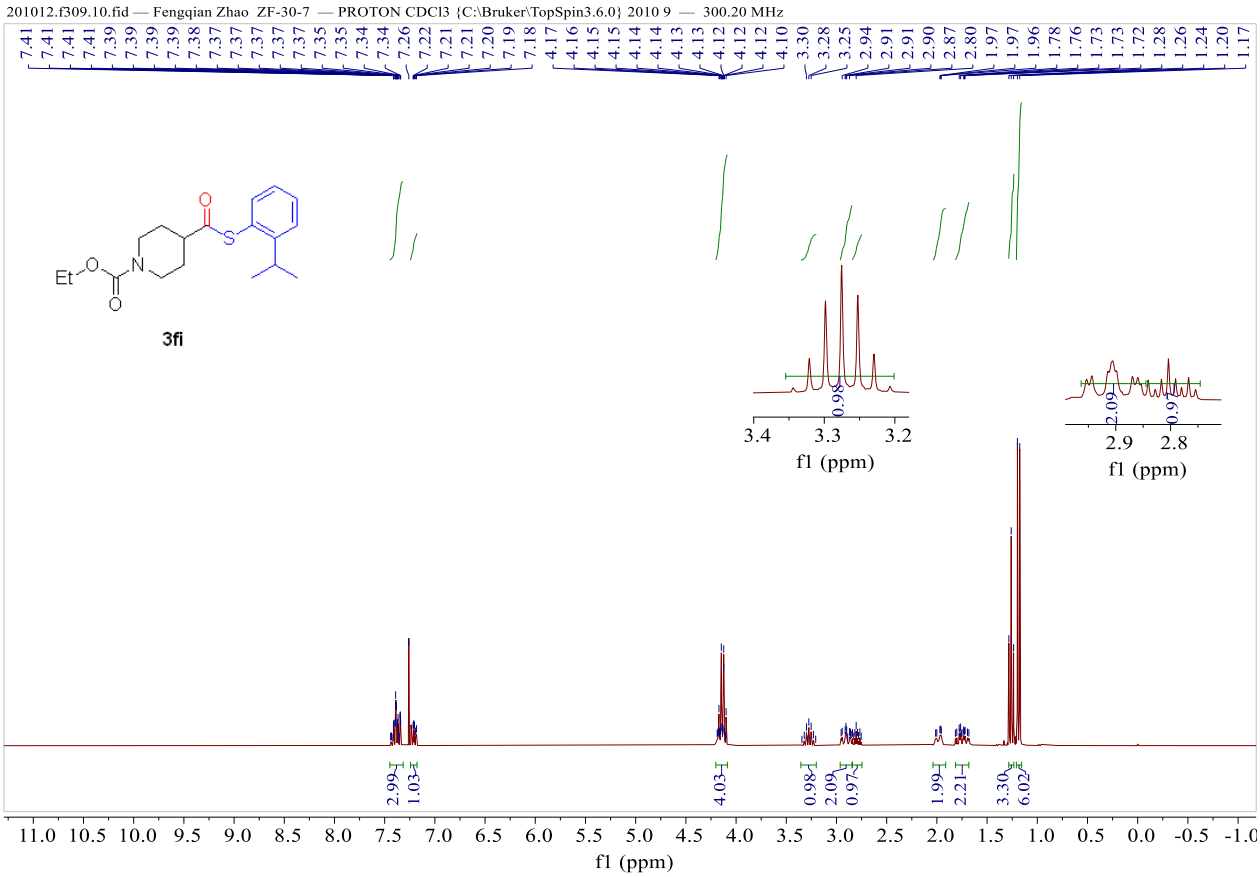

201002.318.11.fid — Fengqian Zhao ZF-29-9 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 18 — 75.48 MHz
3ff
f1 (ppm)

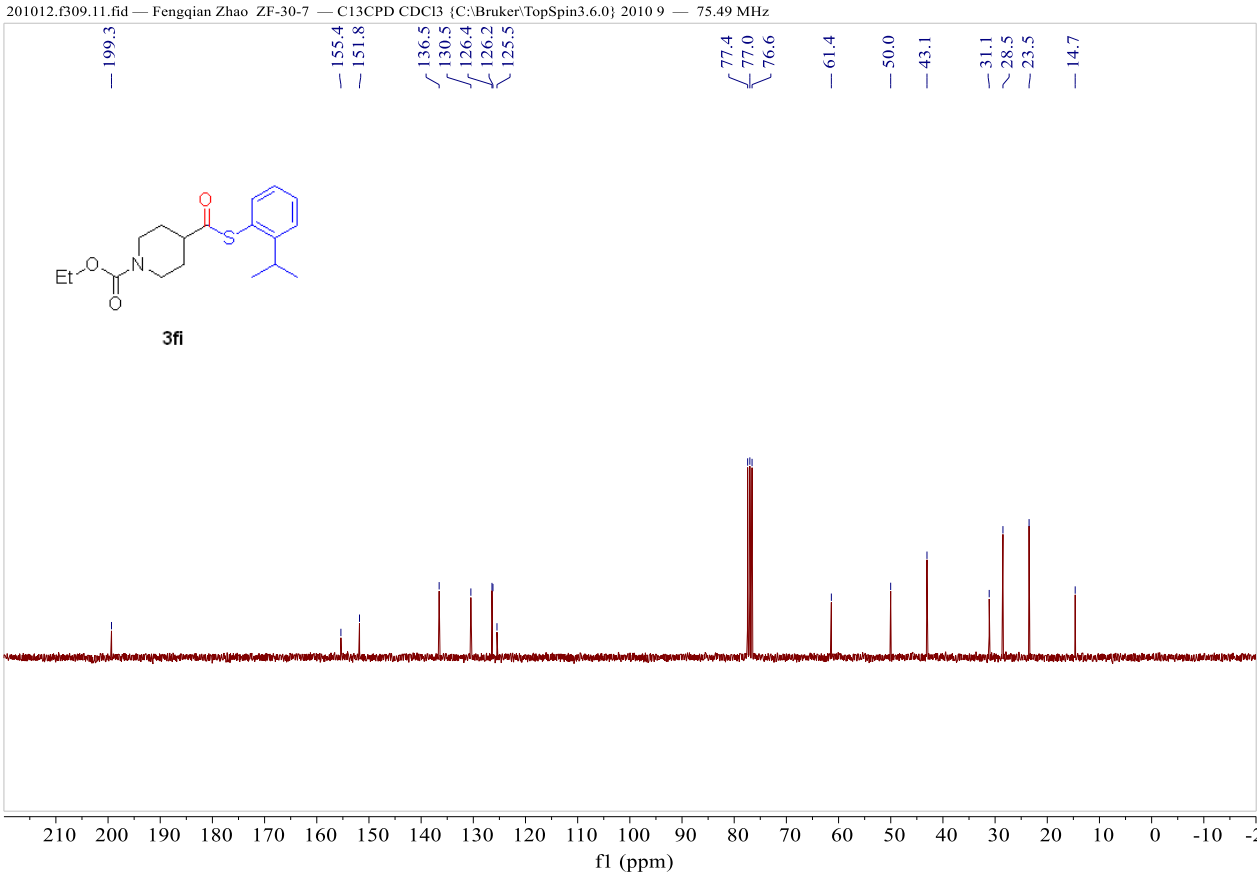

201109.342.10.fid — Fengqian Zhao ZF-33-3 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 42 — 300.13 MHz
7.30 7.30 7.28 7.27 7.27 7.27 7.27 7.26 7.26 7.25 7.24 7.23 4.18 4.17 4.16 4.15 4.15 4.14 4.14 4.13 4.13 4.12 4.11 4.11 4.10 4.10 4.09 2.93 2.92 2.90 2.89 2.85 2.84 2.79 2.77 2.76 2.74 2.72 2.48 1.99 1.98 1.95 1.93 1.79 1.78 1.75 1.74 1.74 1.73 1.71 1.71 1.70 1.69 1.67 1.65 1.65 1.28 1.26 1.23
Et
O
N
O
O
S
O
S
3fg
4.13
4.13
2.04
1.03
2.81
2.05
2.19
3.20
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 -0.5 -1.0
f1 (ppm)

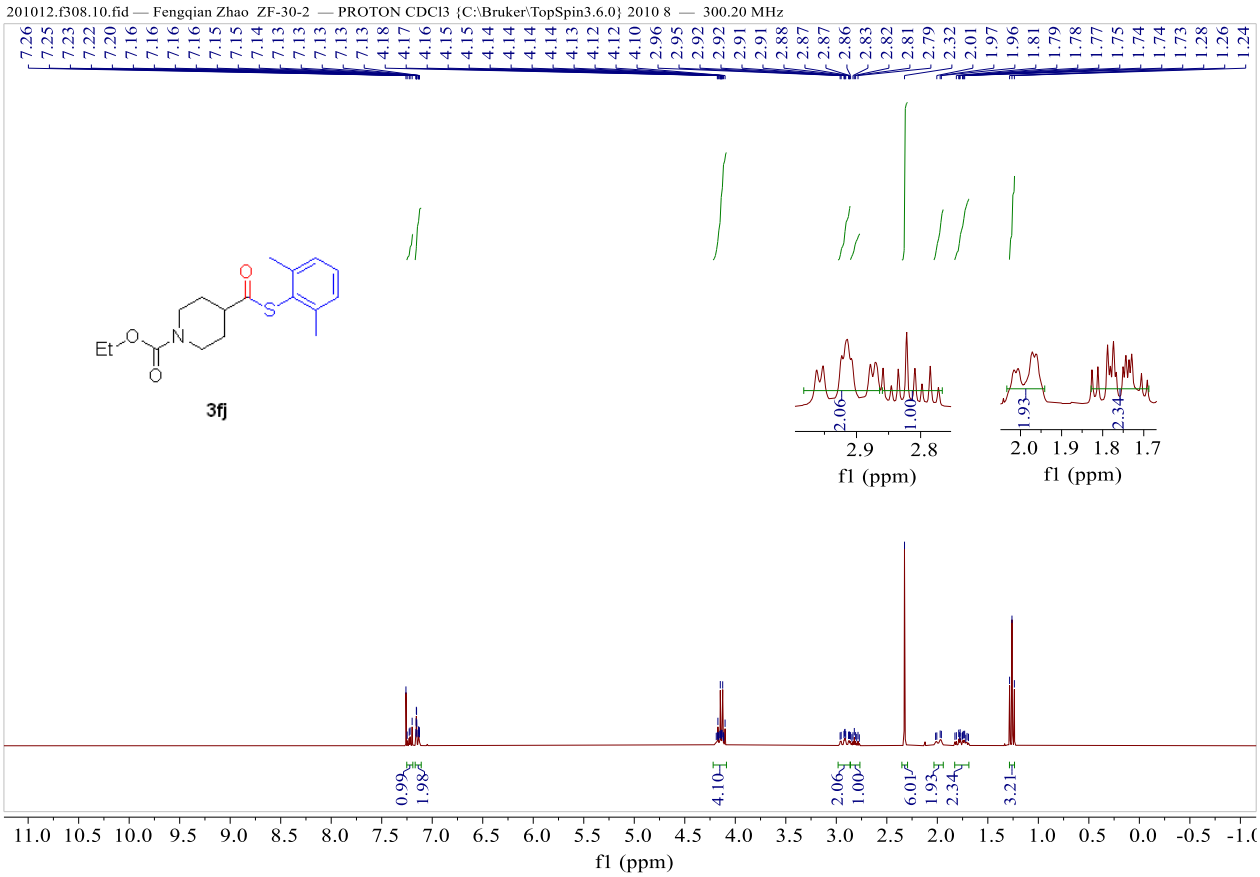

201109.342.11.fid — Fengqian Zhao ZF-33-3 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 42 — 75.48 MHz
199.5
155.4
141.1
134.8
126.6
122.9
77.4
77.0
76.6
61.4
49.9
43.0
28.4
15.3
14.6
Et
O
N
O
O
S
O
S
3fg
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

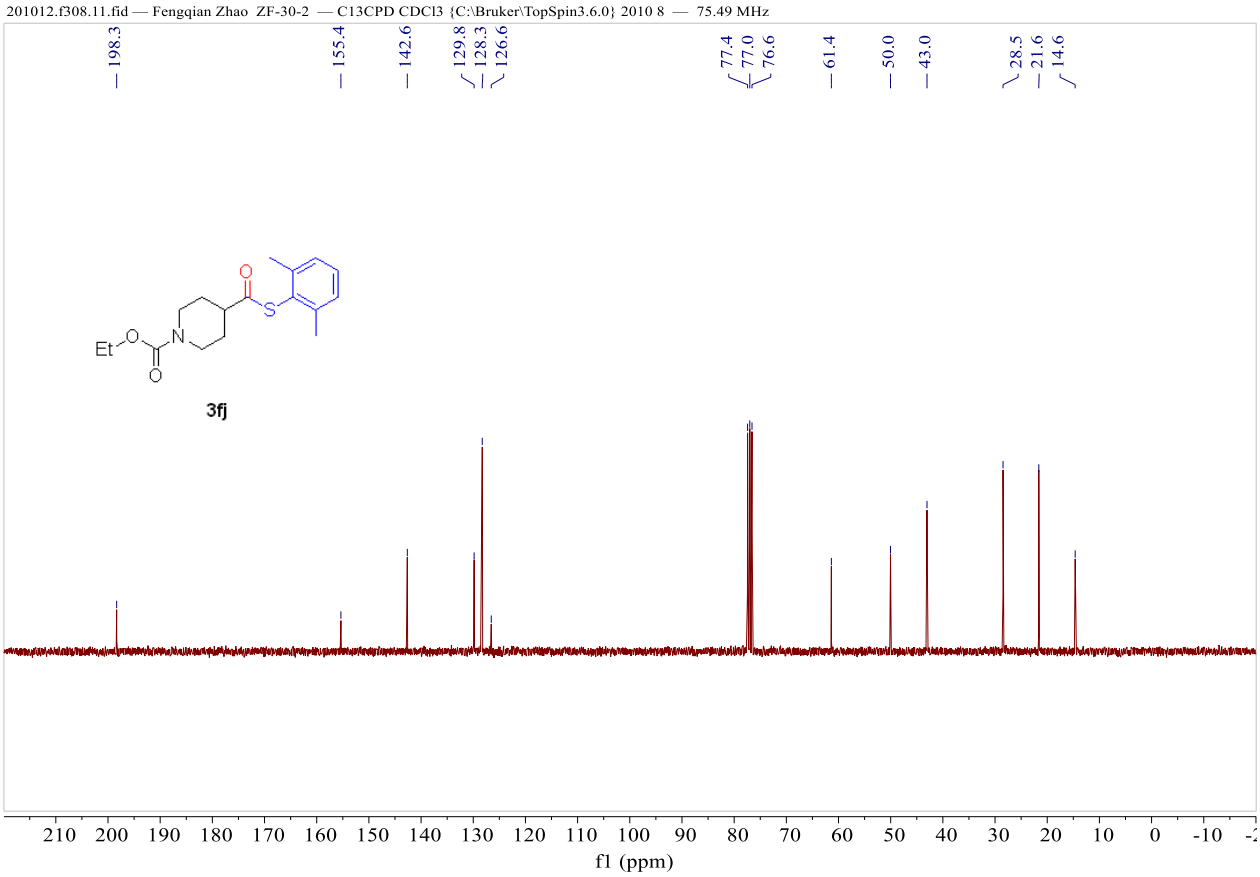

201021.f339.10.fid — Fengqian Zhao ZF-30-1 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 39 — 300.20 MHz
3fh
f1 (ppm)

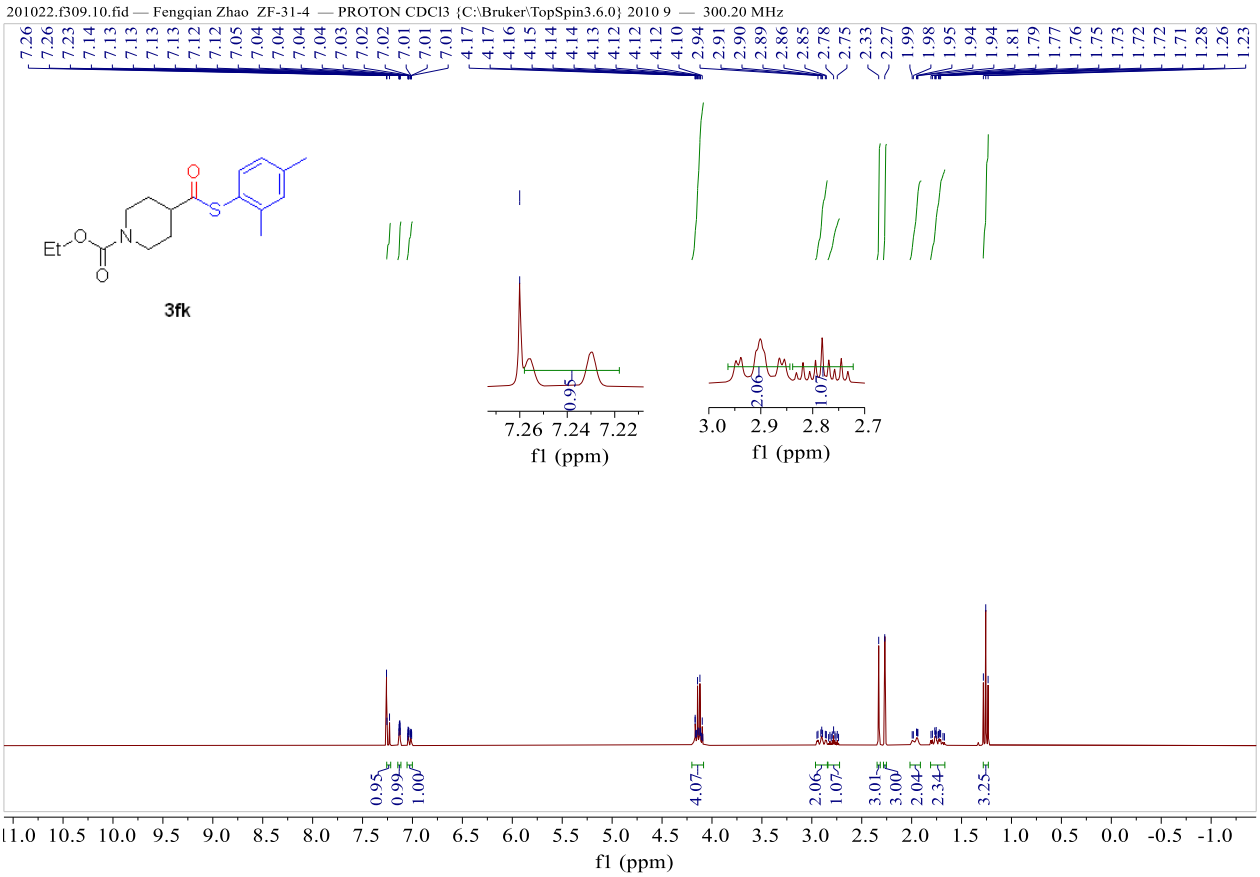

201021.f339.11.fid — Fengqian Zhao ZF-30-1 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 39 — 75.49 MHz
3fh
f1 (ppm)

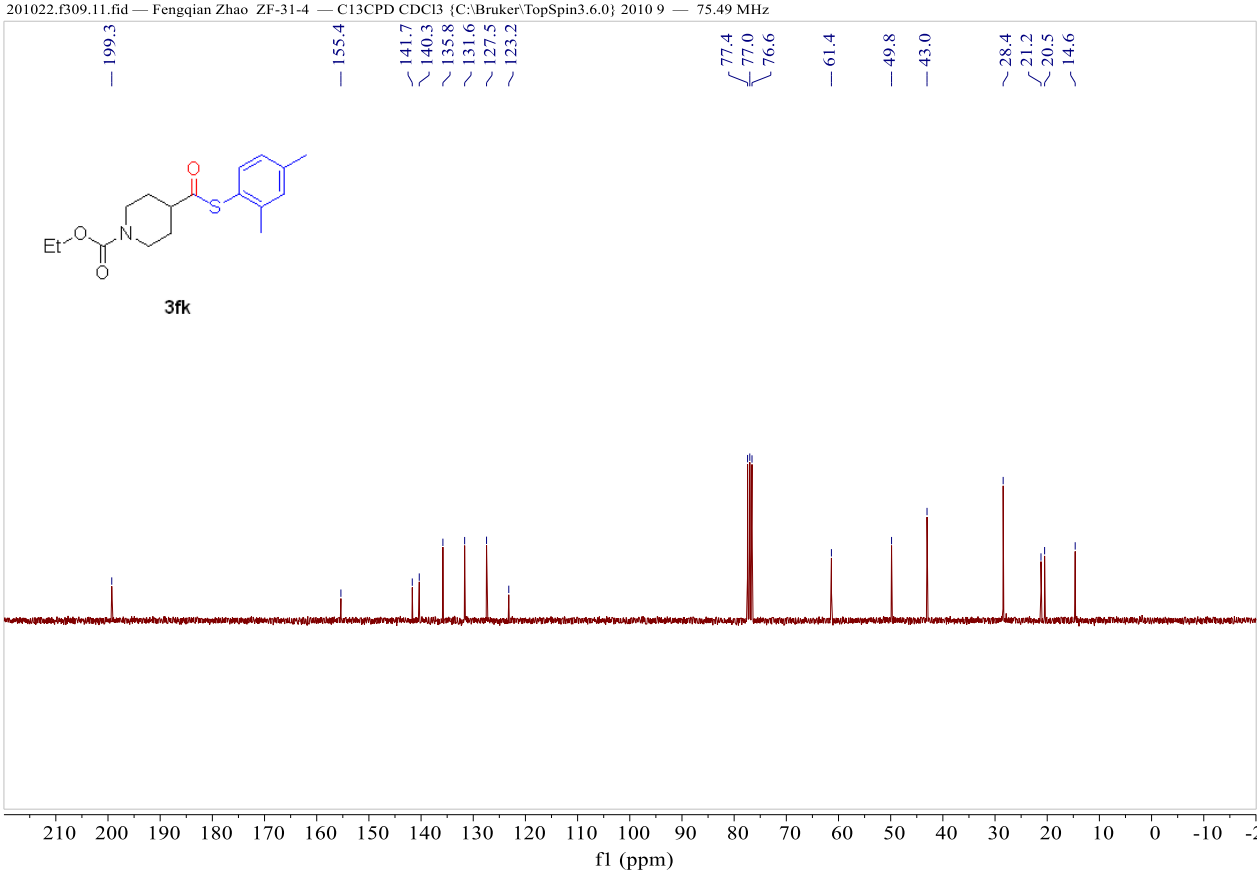

201012.f309.10.fid — Fengqian Zhao ZF-30-7 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 9 — 300.20 MHz
3fi
f1 (ppm)

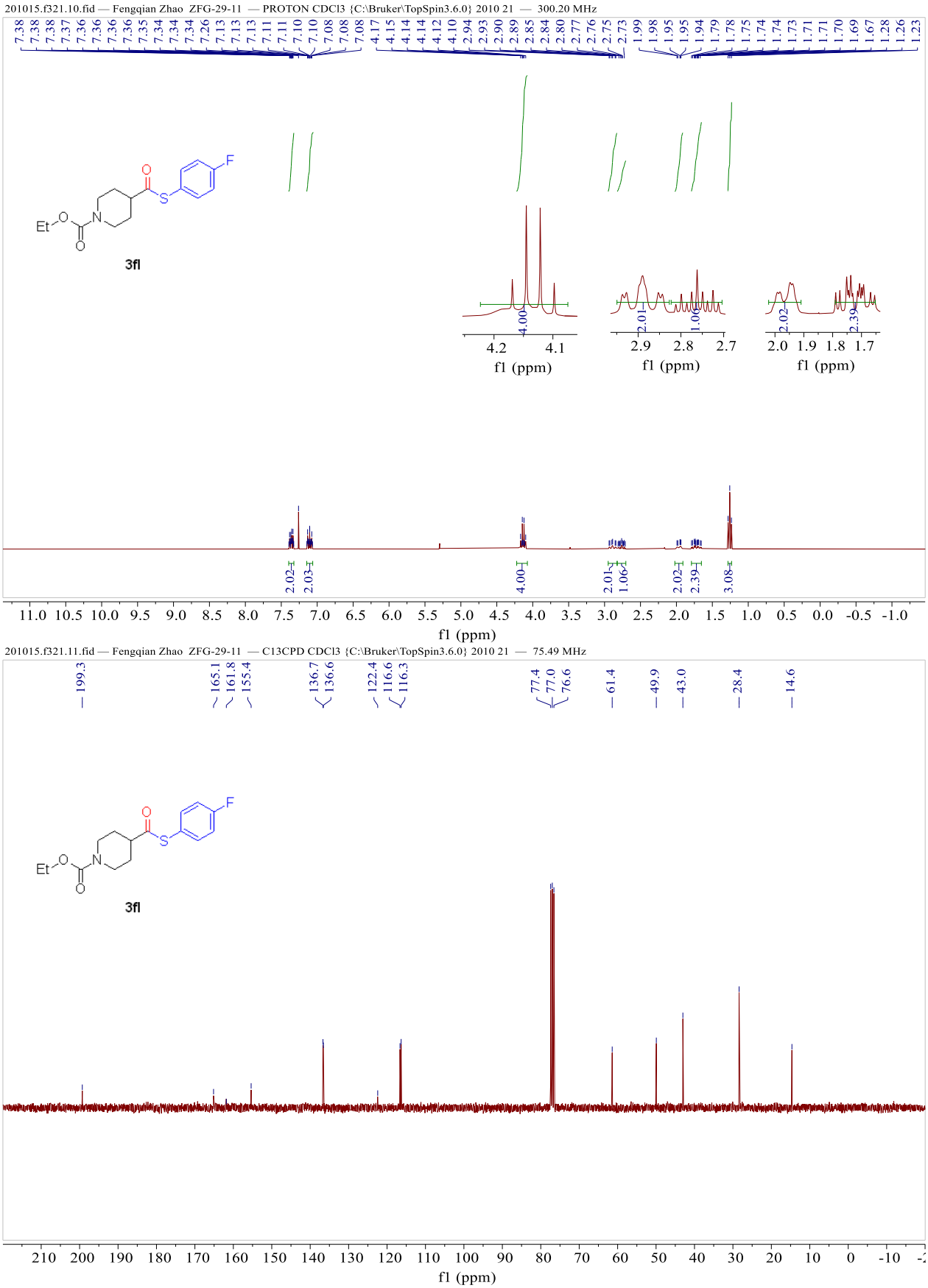

201012.f309.11.fid — Fengqian Zhao ZF-30-7 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 9 — 75.49 MHz
3fi
f1 (ppm)


201012.f308.10.fid — Fengqian Zhao ZF-30-2 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 8 — 300.20 MHz
3fj
f1 (ppm)

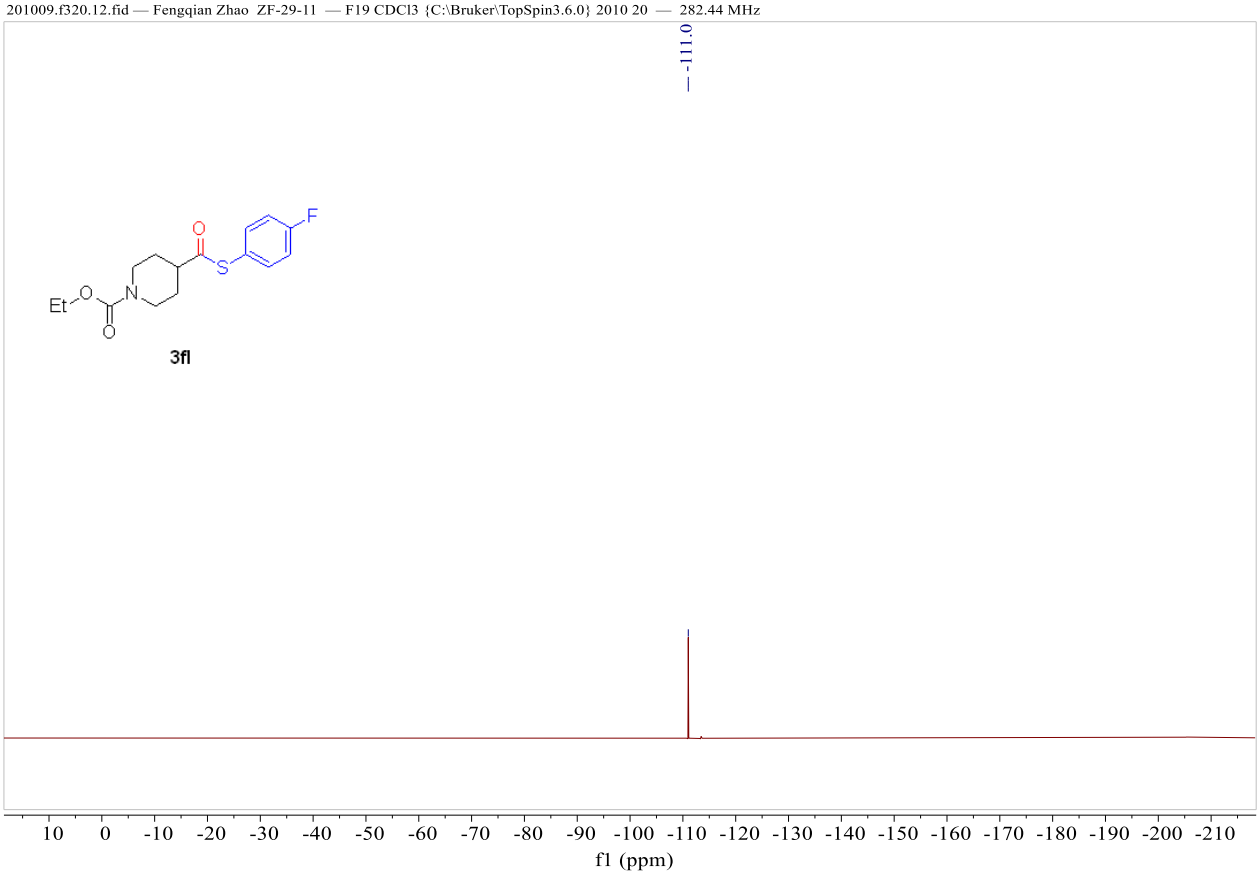

201012.f308.11.fid — Fengqian Zhao ZF-30-2 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 8 — 75.49 MHz
3fj
f1 (ppm)


201022.f309.10.fid — Fengqian Zhao ZF-31-4 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 9 — 300.20 MHz
3fk
f1 (ppm)


201022.f309.11.fid — Fengqian Zhao ZF-31-4 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 9 — 75.49 MHz
3fk
f1 (ppm)

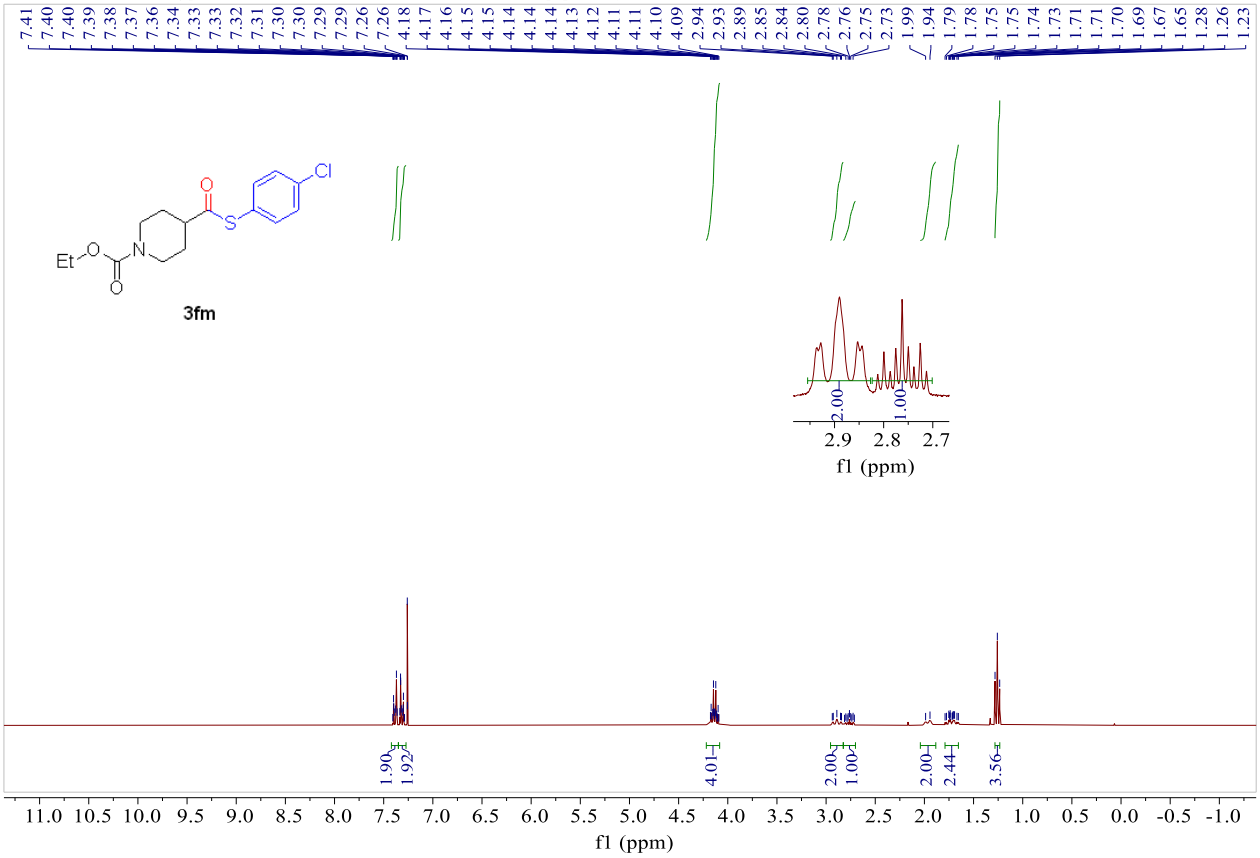

201015.f321.10.fid — Fengqian Zhao ZFG-29-11 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 21 — 300.20 MHz
3fl
f1 (ppm)
201015.f321.11.fid — Fengqian Zhao ZFG-29-11 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 21 — 75.49 MHz
3fl
f1 (ppm)

201009.f320.12.fid — Fengqian Zhao ZF-29-11 — F19 CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 20 — 282.44 MHz

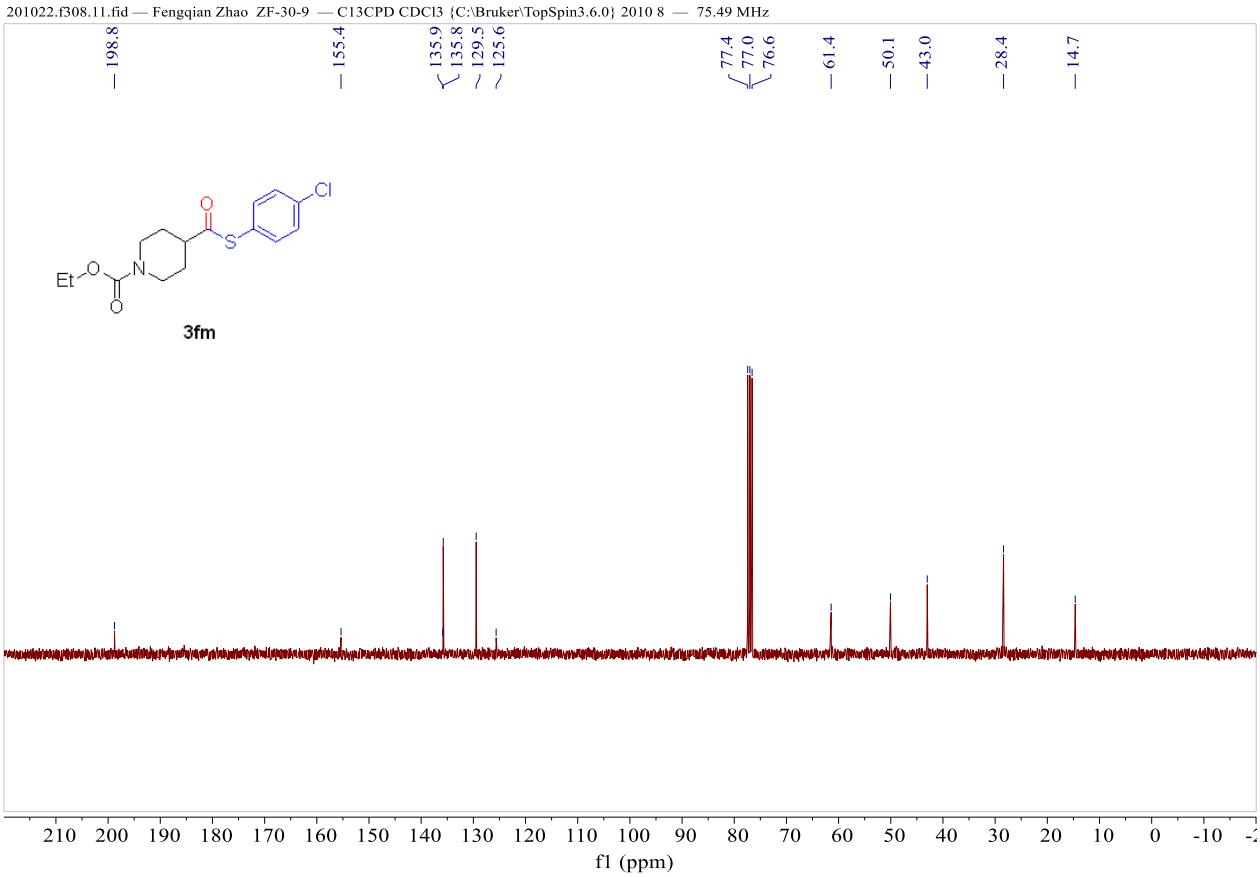


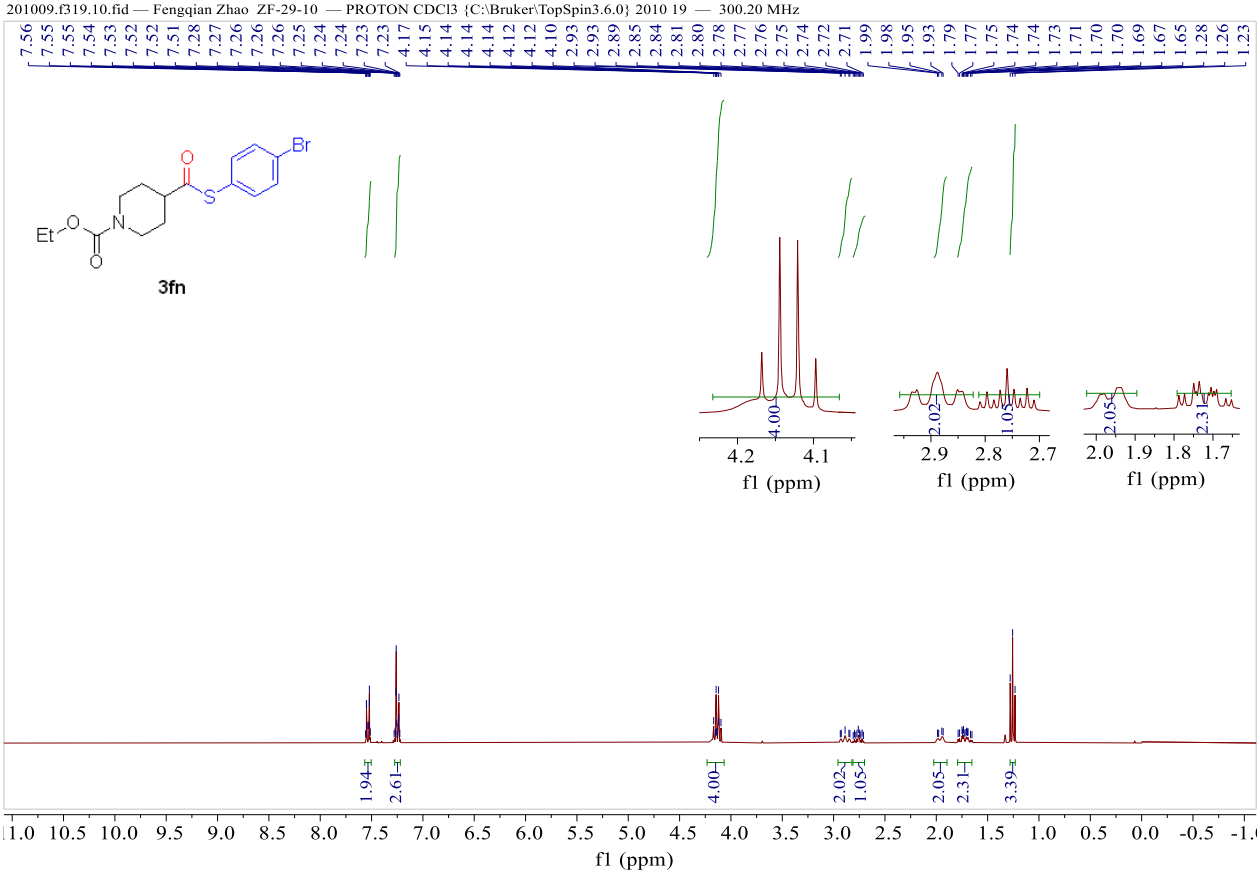
3fl

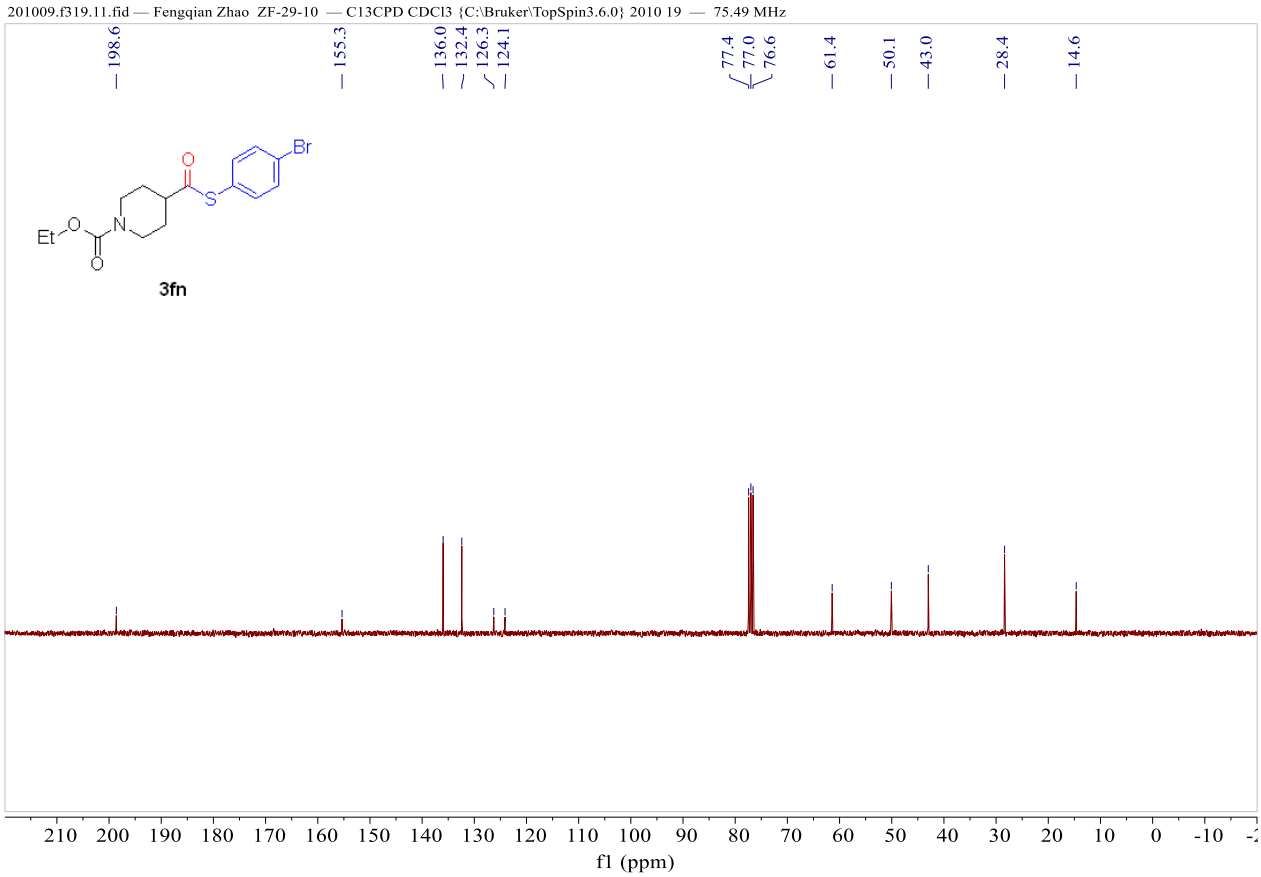
201022.f308.10.fid — Fengqian Zhao ZF-30-9 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 8 — 300.20 MHz

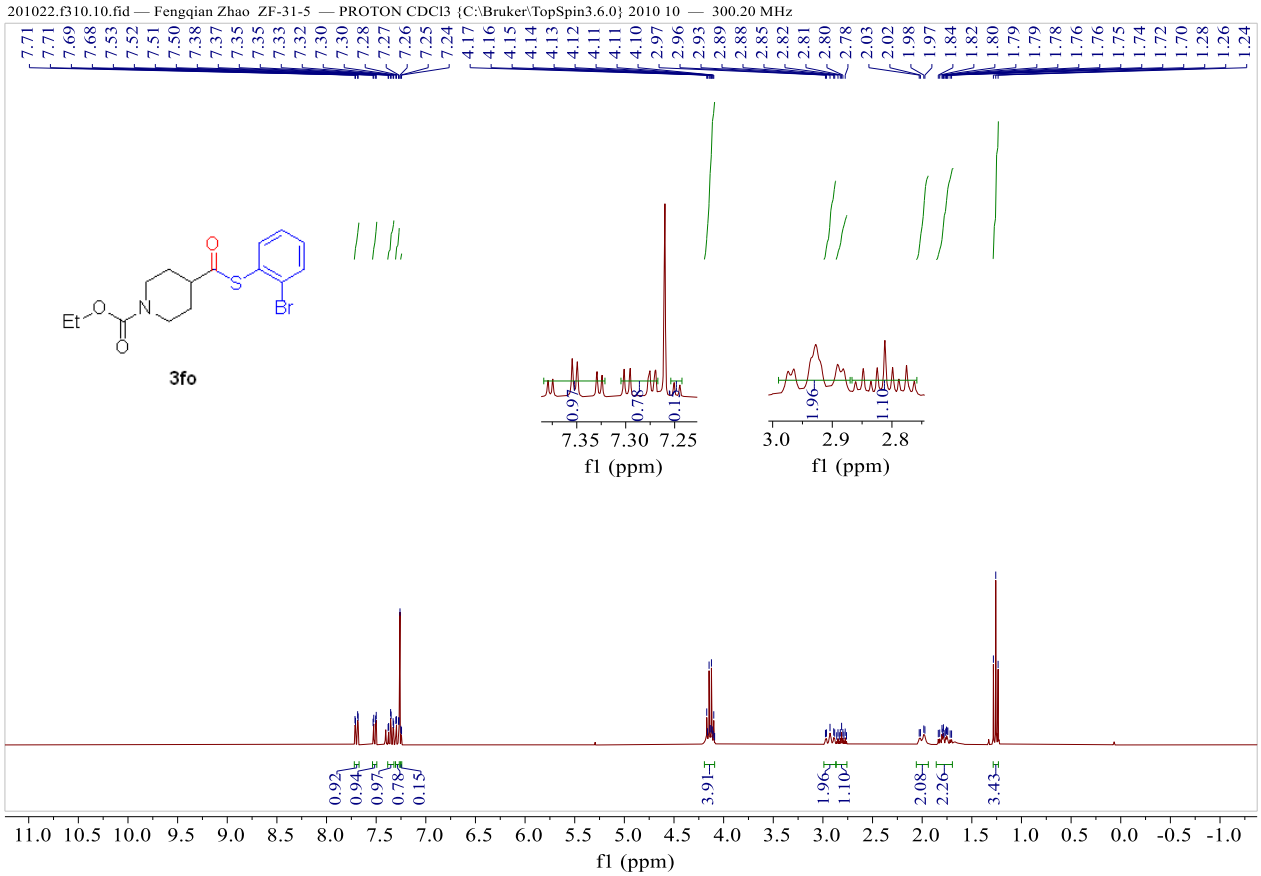


3fm

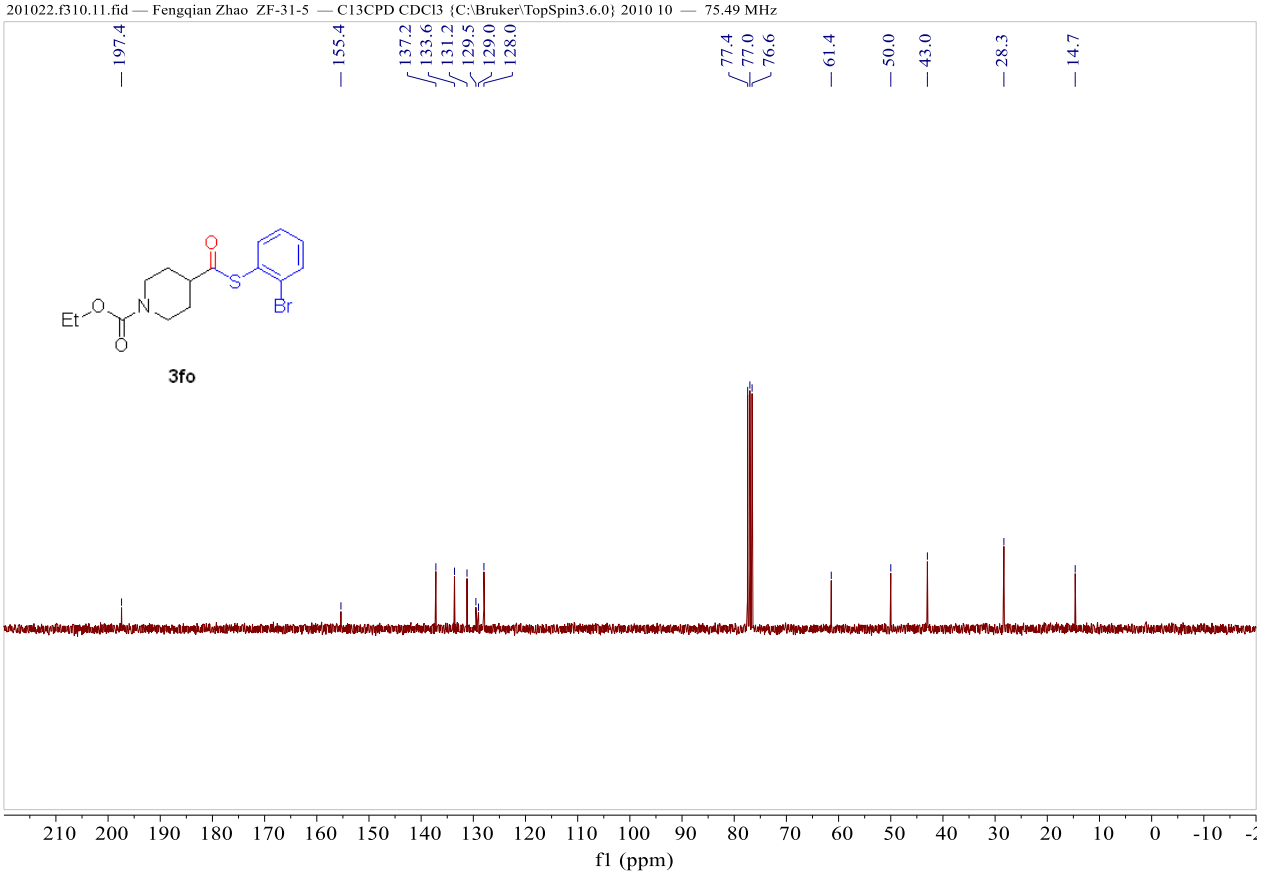

201022.f308.11.fid — Fengqian Zhao ZF-30-9 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 8 — 75.49 MHz
198.8
155.4
135.9
135.8
129.5
125.6
77.4
77.0
76.6
61.4
50.1
43.0
28.4
14.7
Cl
O
S
Et
O
N
O
3fm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


201009.f319.10.fid — Fengqian Zhao ZF-29-10 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 19 — 300.20 MHz
Br
O
S
Et
O
N
O
3fn
4.00
2.02
1.05
2.05
2.31
4.2 4.1
2.9 2.8 2.7
2.0 1.9 1.8 1.7
f1 (ppm)
1.94
2.61
4.00
2.02
1.05
2.05
2.31
3.39
f1 (ppm)

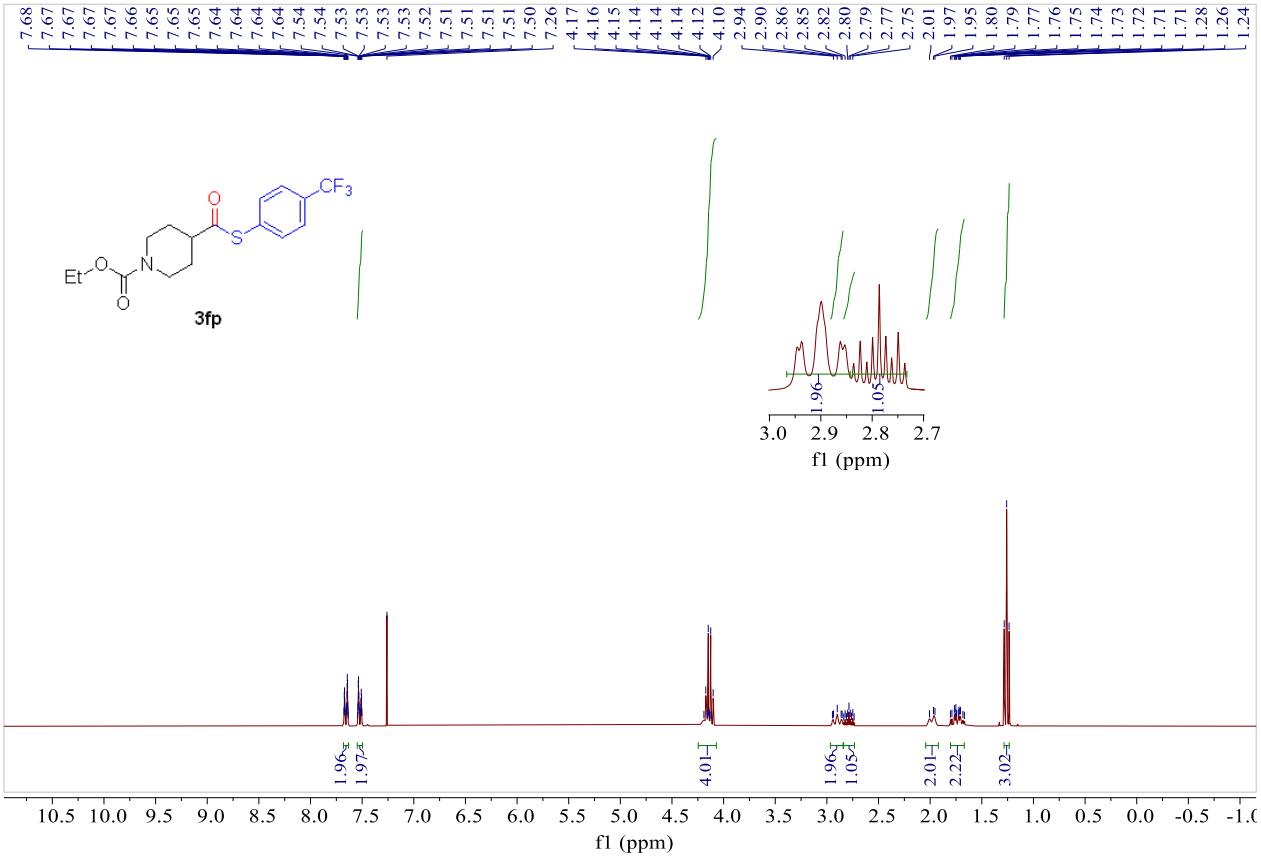

201009.f319.11.fid — Fengqian Zhao ZF-29-10 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 19 — 75.49 MHz
198.6
155.3
136.0
132.4
126.3
124.1
77.4
77.0
76.6
61.4
50.1
43.0
28.4
14.6
Br
O
S
N
Et
O
O
3fn
f1 (ppm)

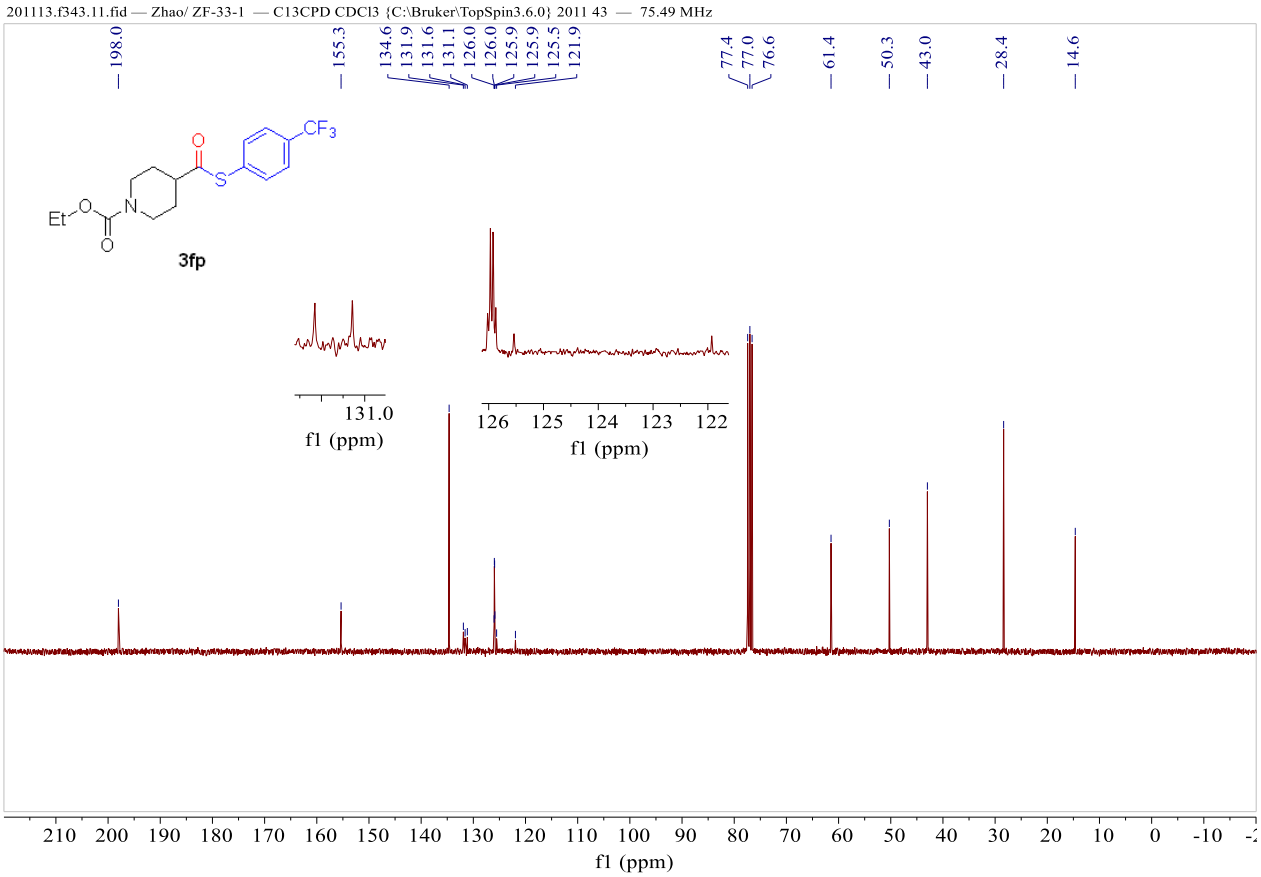

201022.f310.10.fid — Fengqian Zhao ZF-31-5 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 10 — 300.20 MHz
7.71
7.71
7.69
7.68
7.53
7.52
7.51
7.50
7.38
7.37
7.35
7.35
7.33
7.32
7.30
7.30
7.28
7.27
7.26
7.25
7.24
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.11
4.10
2.97
2.96
2.93
2.89
2.88
2.85
2.82
2.81
2.80
2.78
2.03
2.02
1.98
1.97
1.84
1.82
1.80
1.79
1.79
1.78
1.76
1.76
1.75
1.74
1.72
1.70
1.28
1.26
1.24
Br
O
S
N
Et
O
O
3fo
0.97
0.78
0.15
1.96
1.10
7.35 7.30 7.25
f1 (ppm)
3.0 2.9 2.8
f1 (ppm)
0.92
0.94
0.97
0.78
0.15
3.91
1.96
1.10
2.08
2.26
3.43
f1 (ppm)

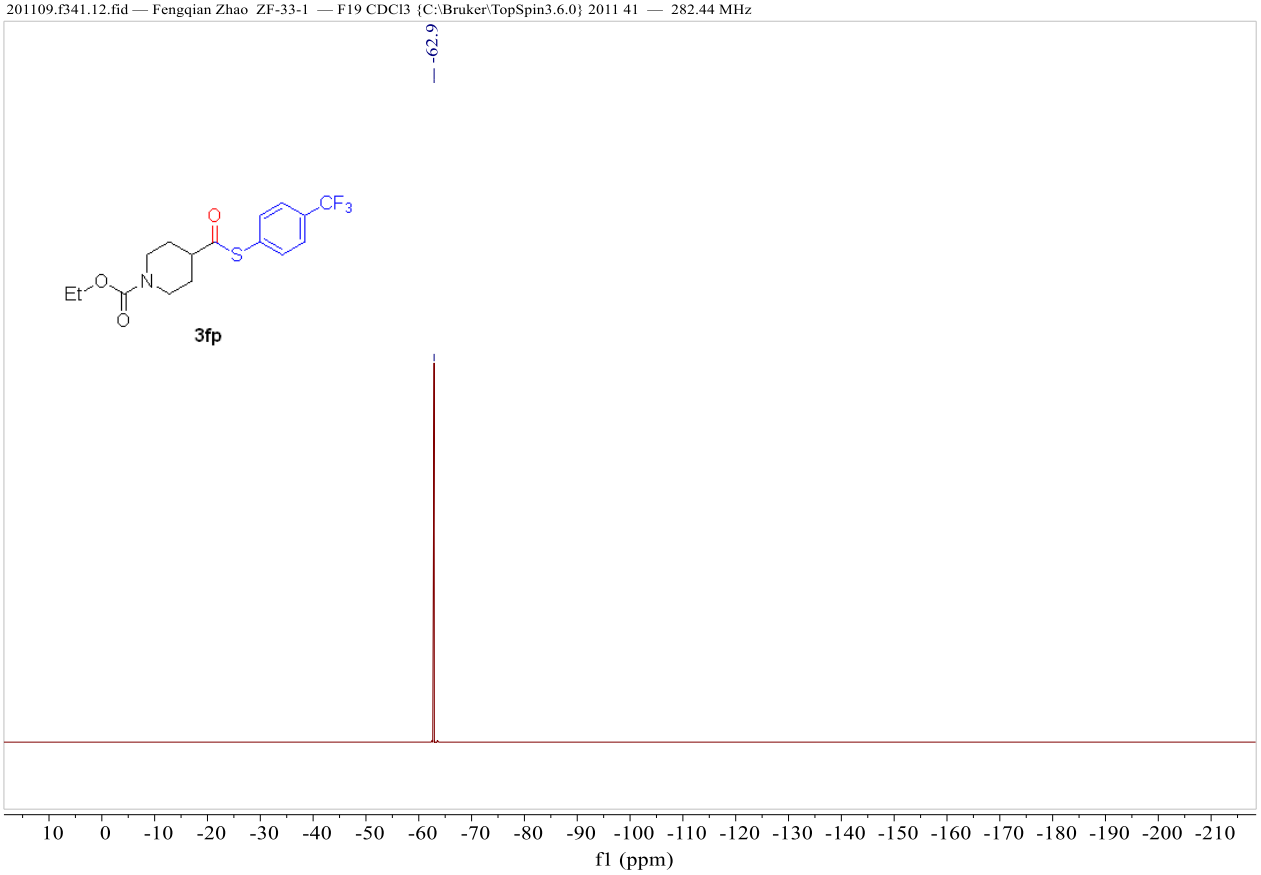
201022.f310.11.fid — Fengqian Zhao ZF-31-5 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 10 — 75.49 MHz

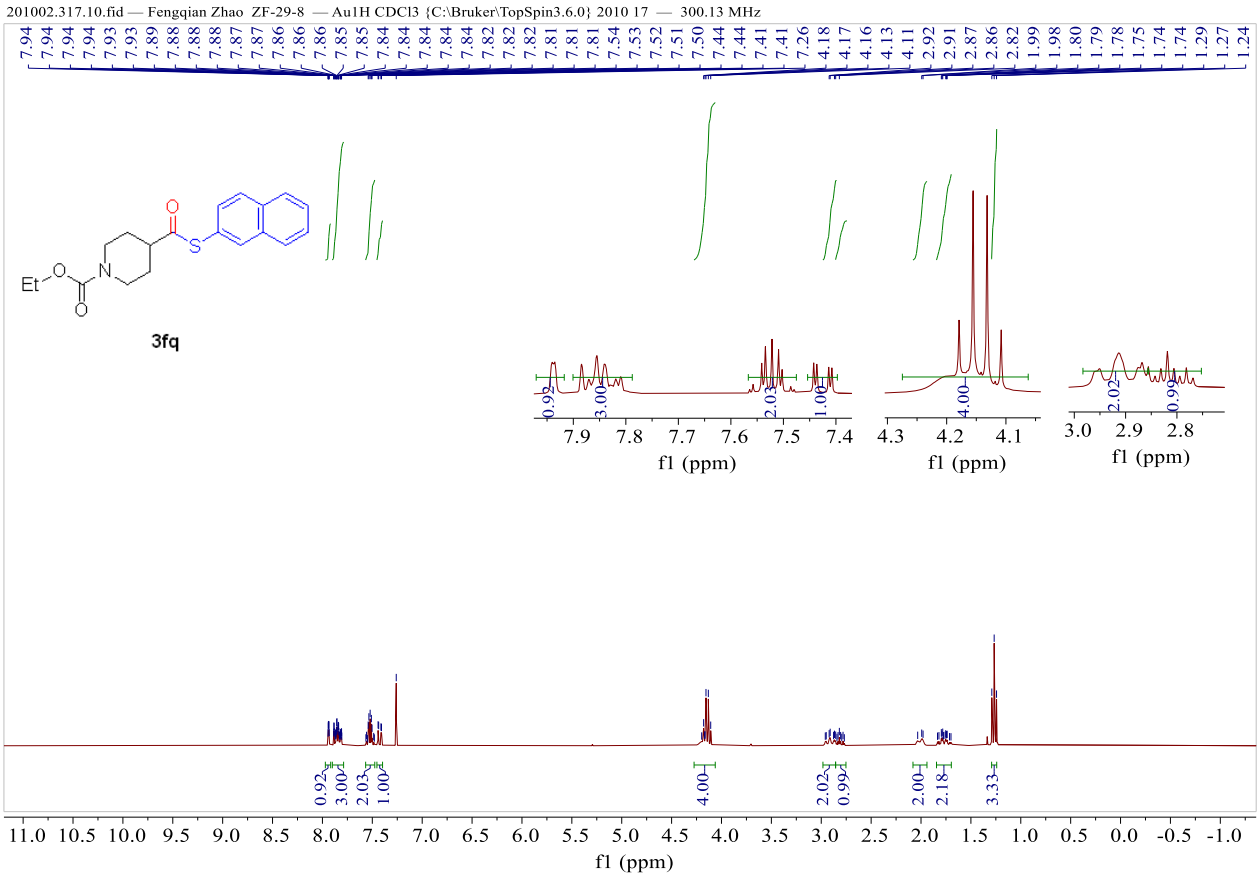


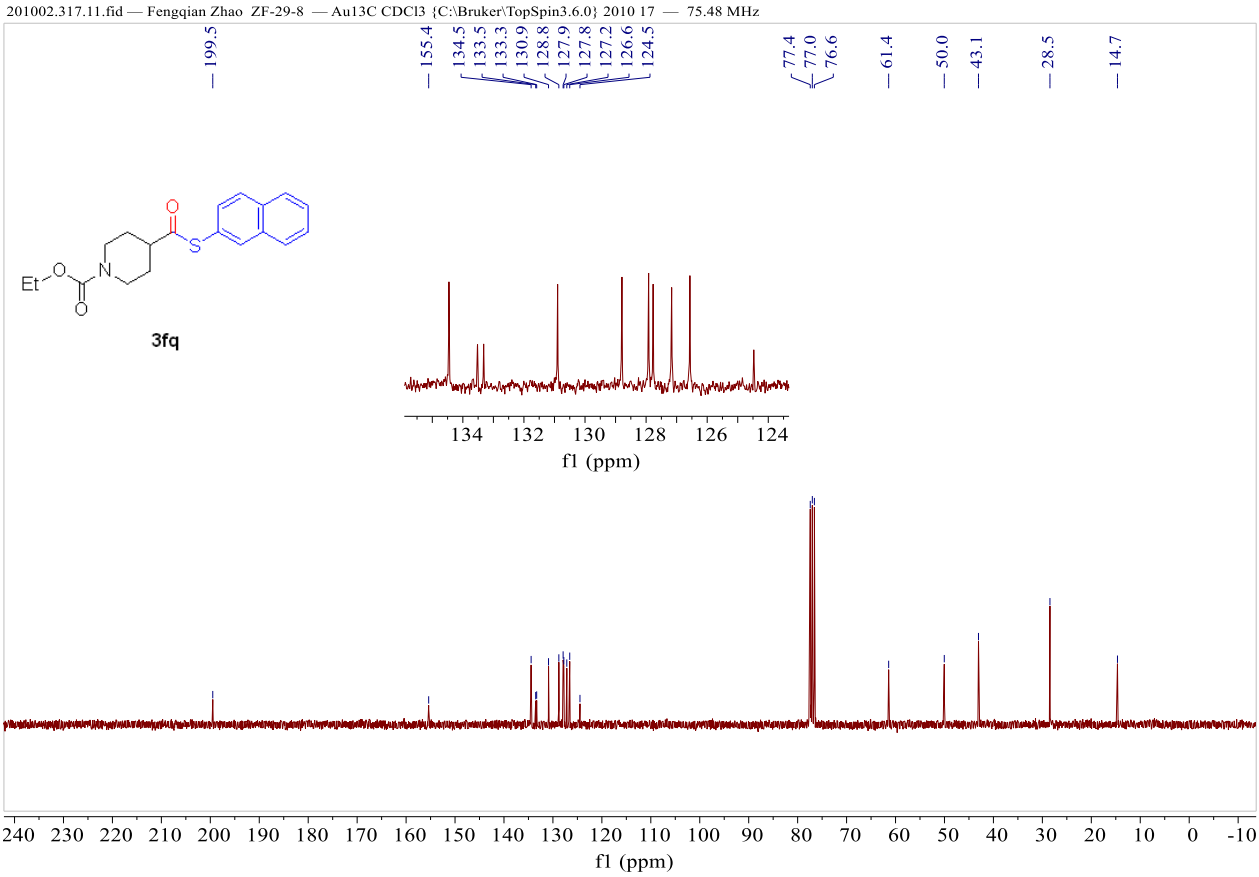
201113.f343.10.fid — Zhao/ ZF-33-1 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 43 — 300.20 MHz

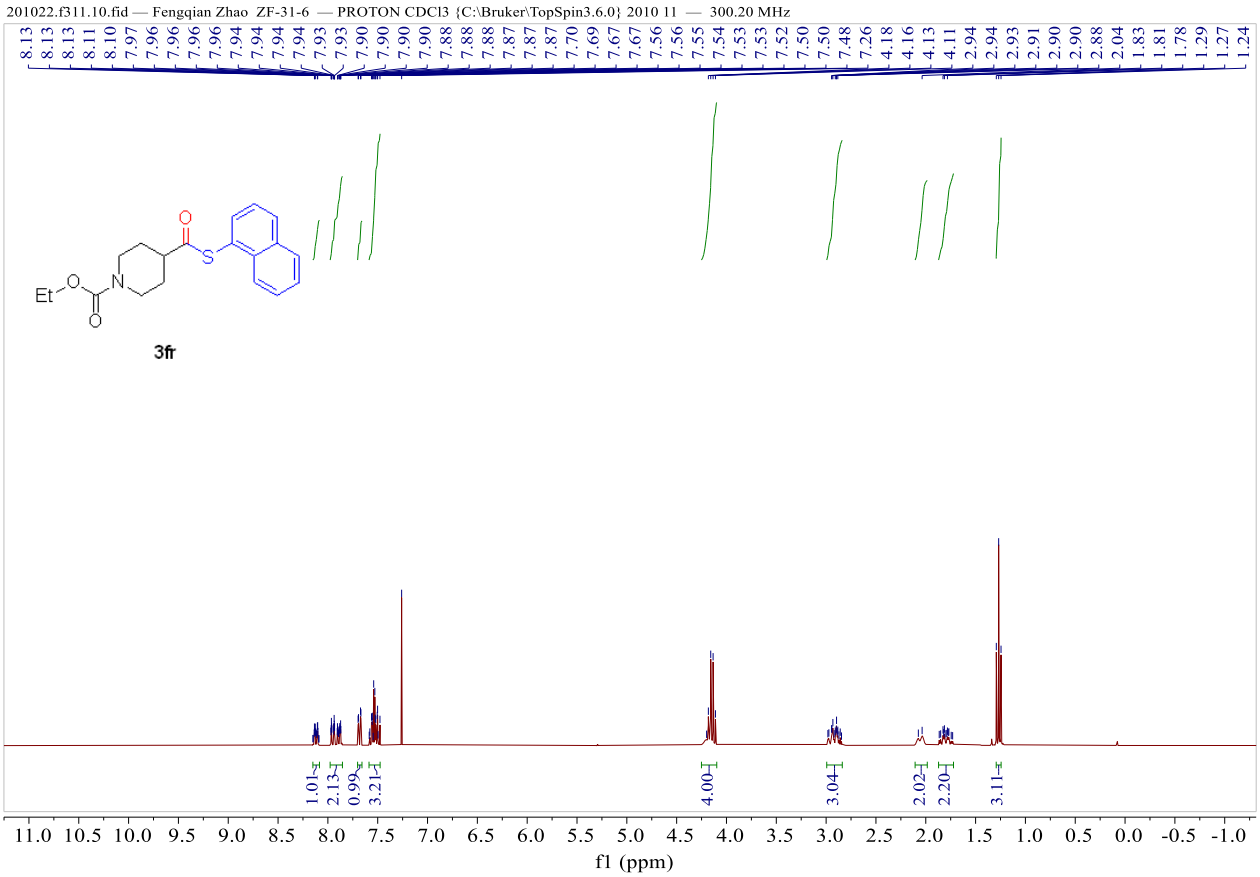


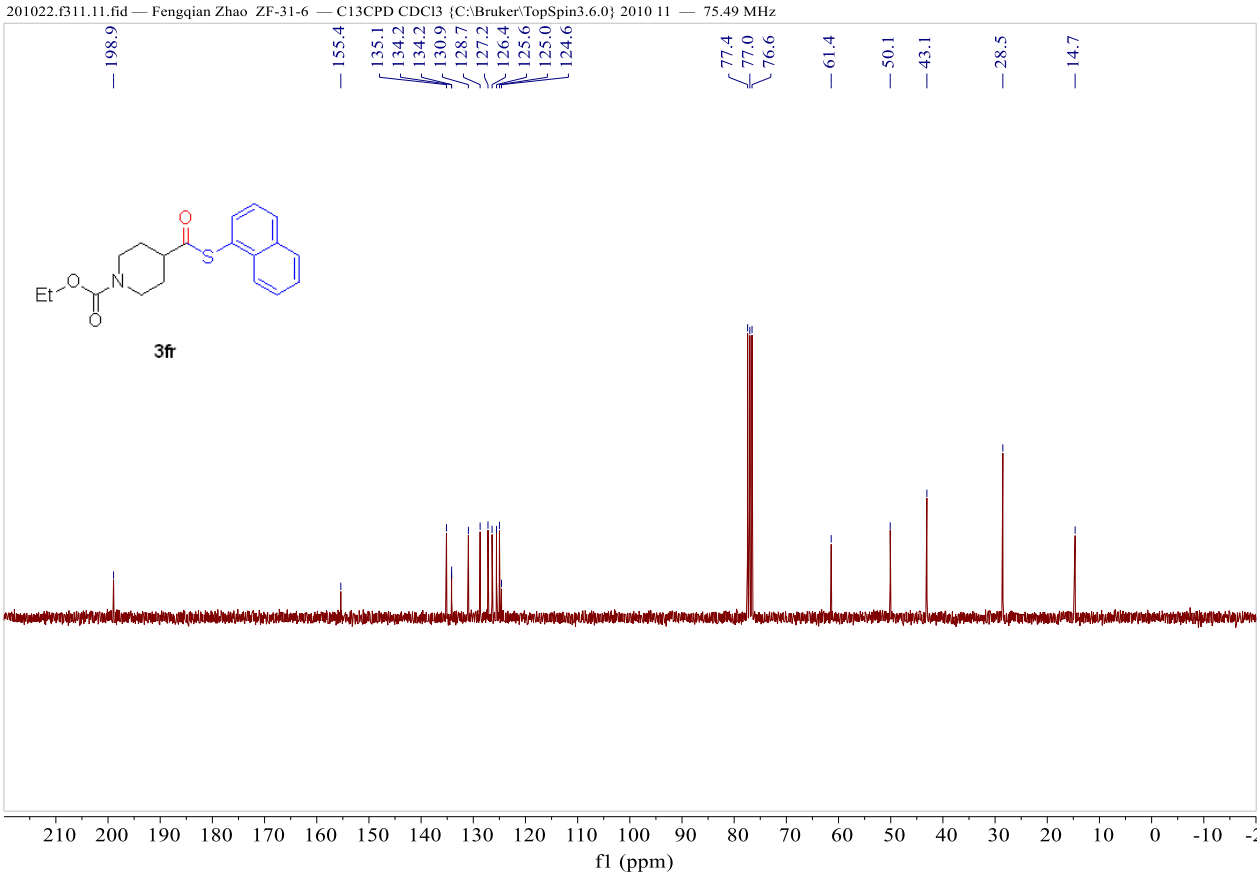

201113.f343.11.fid — Zhao/ ZF-33-1 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 43 — 75.49 MHz
198.0
155.3
134.6
131.9
131.6
131.1
126.0
126.0
125.9
125.9
125.5
121.9
77.4
77.0
76.6
61.4
50.3
43.0
28.4
14.6
CF3
O
S
N
O
Et
O
3fp
131.0
f1 (ppm)
126 125 124 123 122
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

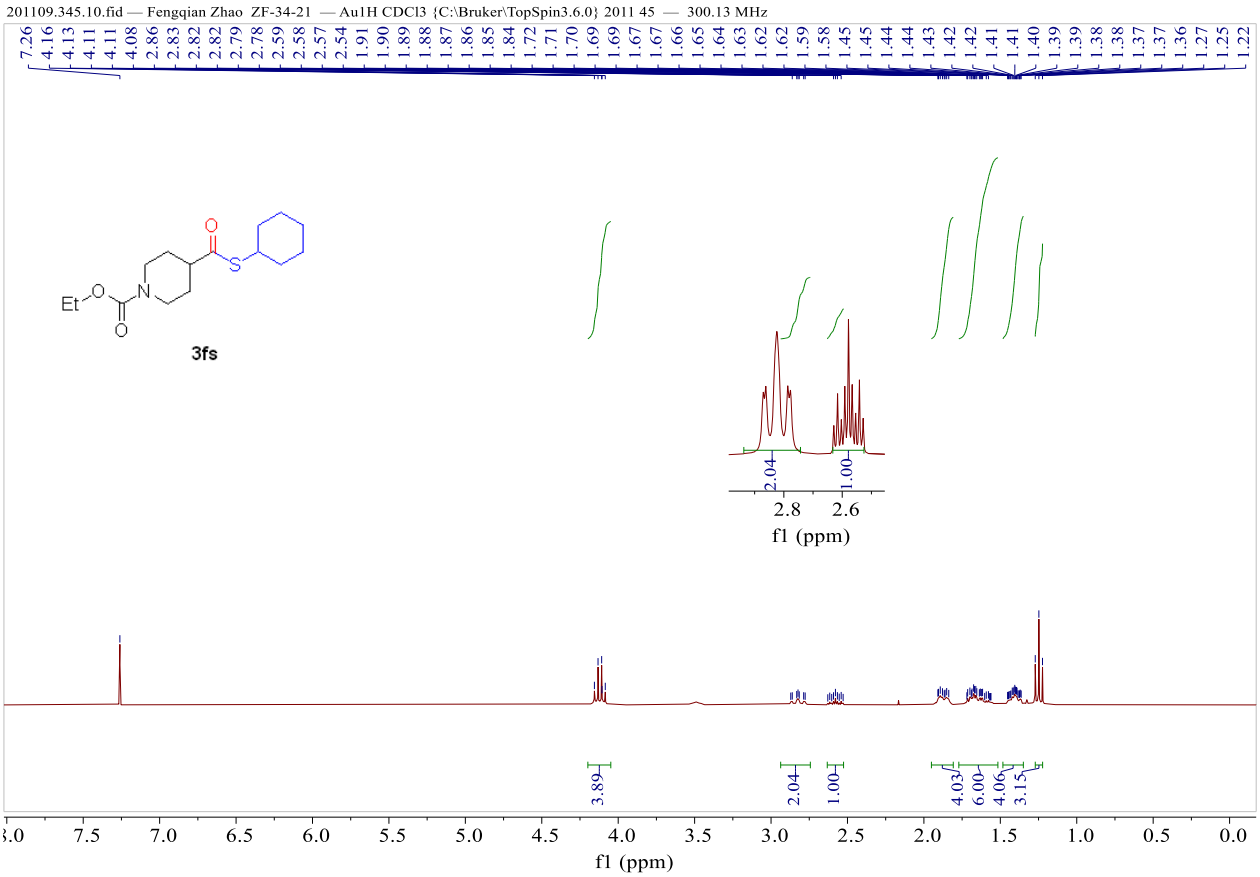

201109.f341.12.fid — Fengqian Zhao ZF-33-1 — F19 CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 41 — 282.44 MHz
-62.9
CF3
O
S
N
O
Et
O
3fp
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

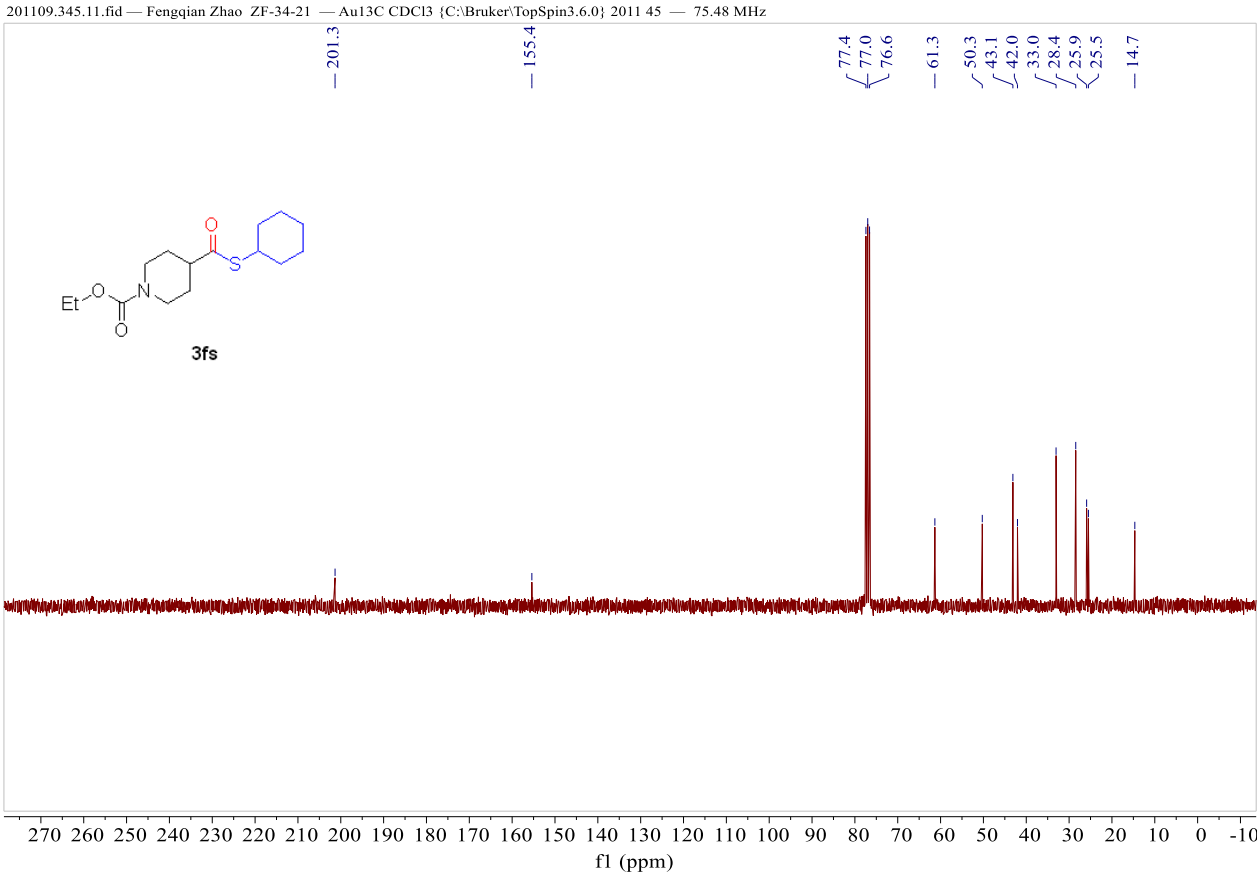

201002.317.10.fid — Fengqian Zhao ZF-29-8 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 17 — 300.13 MHz
3fq
f1 (ppm)


201002.317.11.fid — Fengqian Zhao ZF-29-8 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 17 — 75.48 MHz
3fq
f1 (ppm)


201022.f311.10.fid — Fengqian Zhao ZF-31-6 — PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 11 — 300.20 MHz
8.13 8.13 8.13 8.11 8.10 7.97 7.96 7.96 7.96 7.96 7.94 7.94 7.94 7.94 7.93 7.93 7.90 7.90 7.90 7.90 7.88 7.88 7.88 7.87 7.87 7.87 7.70 7.69 7.67 7.67 7.56 7.56 7.55 7.54 7.53 7.53 7.52 7.50 7.50 7.48 7.26 4.18 4.16 4.13 4.11 2.94 2.94 2.93 2.91 2.90 2.90 2.88 2.04 1.83 1.81 1.78 1.29 1.27 1.24
O
S
N
O
Et
O
3fr
1.01
2.13
0.99
3.21
4.00
3.04
2.02
2.20
3.11
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 -0.5 -1.0
f1 (ppm)


201022.f311.11.fid — Fengqian Zhao ZF-31-6 — C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2010 11 — 75.49 MHz
198.9
155.4
135.1
134.2
134.2
130.9
128.7
127.2
126.4
125.6
125.0
124.6
77.4
77.0
76.6
61.4
50.1
43.1
28.5
14.7
O
S
N
O
Et
O
3fr
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)


201109.345.10.fid — Fengqian Zhao ZF-34-21 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 45 — 300.13 MHz
7.26 4.16 4.13 4.11 4.11 4.08 2.86 2.83 2.82 2.82 2.79 2.78 2.59 2.58 2.57 2.54 1.91 1.90 1.89 1.88 1.87 1.86 1.85 1.84 1.72 1.71 1.70 1.69 1.69 1.67 1.67 1.66 1.65 1.64 1.63 1.62 1.62 1.59 1.58 1.45 1.45 1.44 1.44 1.43 1.42 1.42 1.41 1.41 1.40 1.39 1.39 1.38 1.38 1.37 1.37 1.36 1.27 1.25 1.22
Et
O
N
O
O
S
3fs
2.04
1.00
2.8
2.6
f1 (ppm)
3.89
2.04
1.00
4.03
6.00
4.06
3.15
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)


201109.345.11.fid — Fengqian Zhao ZF-34-21 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 45 — 75.48 MHz
201.3
155.4
77.4
77.0
76.6
61.3
50.3
43.1
42.0
33.0
28.4
25.9
25.5
14.7
Et
O
N
O
O
S
3fs
270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)