

**Diastereoselective Synthesis of Cyclopentene Spiro-rhodanines Containing Three
Contiguous Stereocenters *via* Phosphine-catalyzed [3+2] Cycloaddition or One-pot
Sequential [3+2]/[3+2] Cycloaddition**

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Supporting Information

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General Comments:

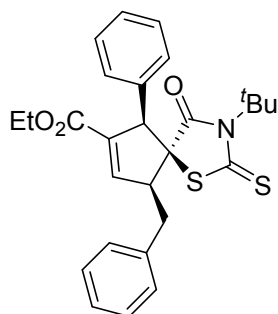
All reactions were performed under N₂ atmosphere in oven-dried glassware with magnetic stirring. Solvents were dried and distilled prior to use according to the standard methods. Unless otherwise indicated, all materials were obtained from commercial sources, and used as purchased without dehydration. Flash column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). Nitrogen gas (99.999%) was purchased from Boc Gas Inc. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded in CDCl₃ at Bruker 400 MHz spectrometers, TMS served as internal standard (δ = 0 ppm) for ¹H NMR and ¹³C NMR. HR-MS were recorded on APEXII and ZAB-HS spectrometer.

General procedure for formal [3+2] cycloaddition reaction for products **3**:

Under a nitrogen atmosphere, to a mixture of 5-arylidene-3-(*tert*-butyl)-2-thioxothiazolidin-4-one **2** (0.1 mmol, 1.0 equiv), and Bu₃P (4.1 mg, 0.02 mmol, 20 mmol%) was added toluene (1 mL) *via* a syringe and allowed to stir for 5 min at room temperature. Ethyl alkynoate **1** (0.15 mmol, 1.5 equiv.) was added and the reaction was allowed to stir for 24 h at room temperature. The reaction was monitored by TLC spectroscopy. After the reaction was completed, the reaction mixture was directly purified by flash column chromatograph (eluted with 20:1 petroleum ether/EtOAc) to afford the product **3**.

Ethyl 9-benzyl-3-(tert-butyl)-4-oxo-6-phenyl-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-

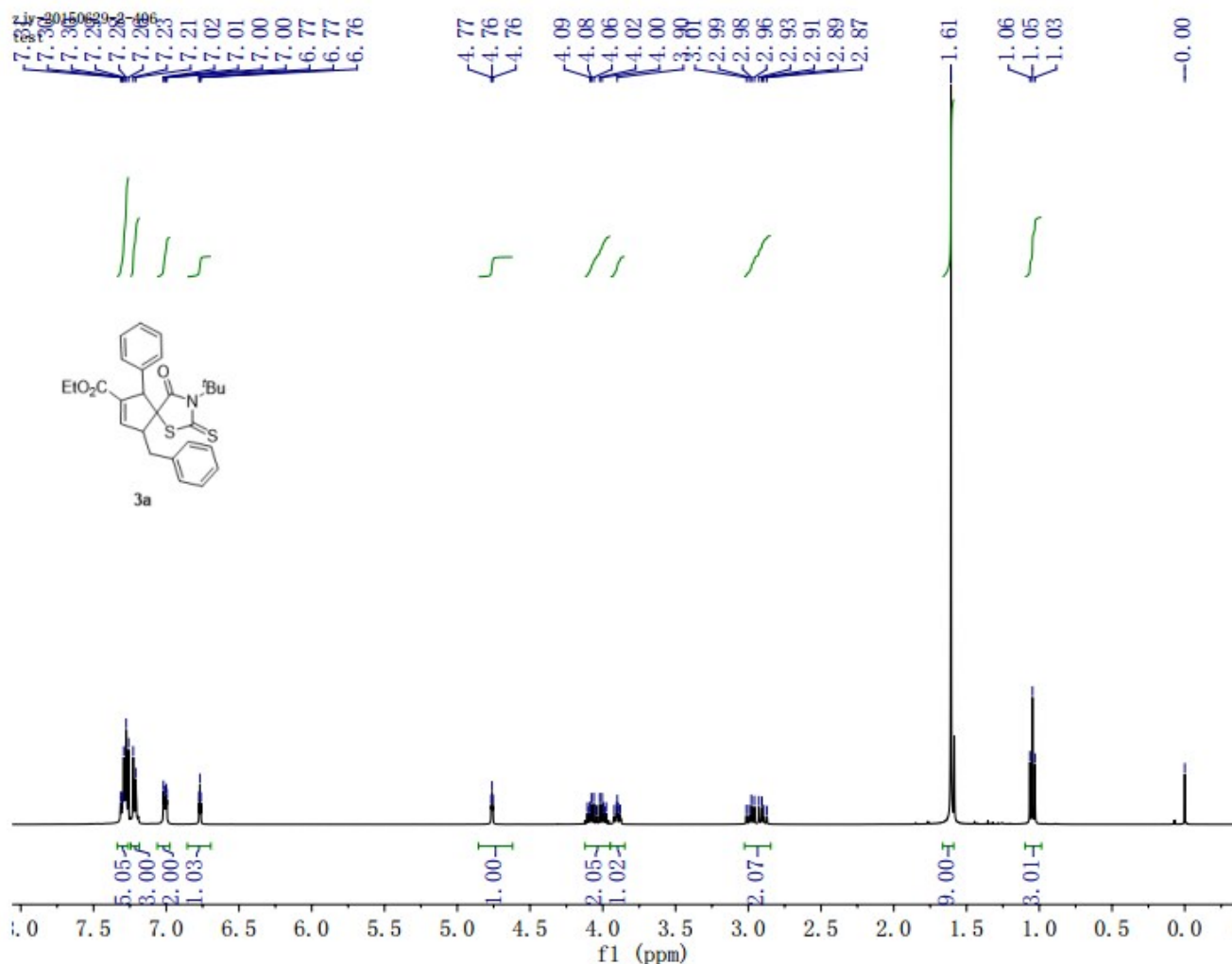
carboxylate (3a):



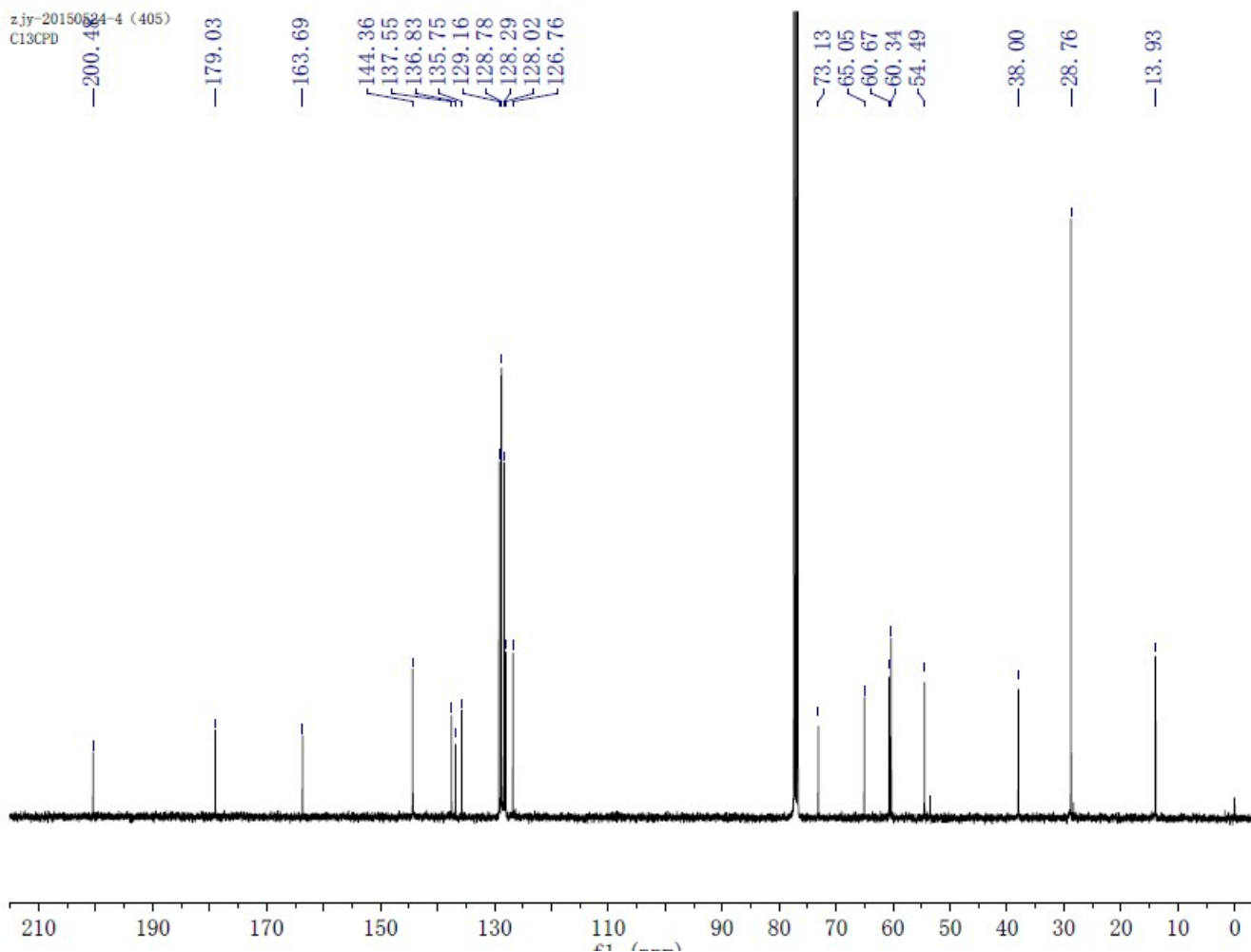
Yellow oil (45.6 mg, 95% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.26 (m, 5H), 7.22 (d, *J* = 6.8 Hz, 3H), 7.01 (dd, *J* = 7.4, 1.9 Hz 2H), 6.77 (t, *J* = 2.3 Hz, 1H), 4.76 (t, *J* = 2.1 Hz, 1H), 4.12-3.95 (m, 2H), 3.95-3.85 (m 1H), 2.99 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.90 (dd, *J* = 13.8, 8.3 Hz, 1H), 1.61 (s, 9H), 1.05 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 200.5, 179.0, 163.7, 144.4, 137.6,

136.8, 135.8, 129.2, 128.8, 128.7, 128.3, 128.0, 126.8, 73.1, 65.1, 60.7, 60.3, 54.5, 38.0, 28.8, 13.9;

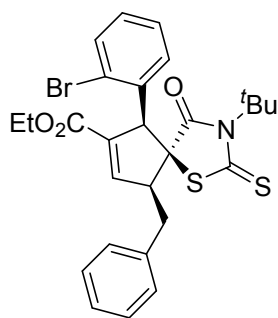
HRMS (ESI): *m/z* calcd for C₂₇H₃₀NO₃S₂ [M+H]⁺ 480.1662, found 480.1664.



zjy-20150824-4 (405)
C13CPD

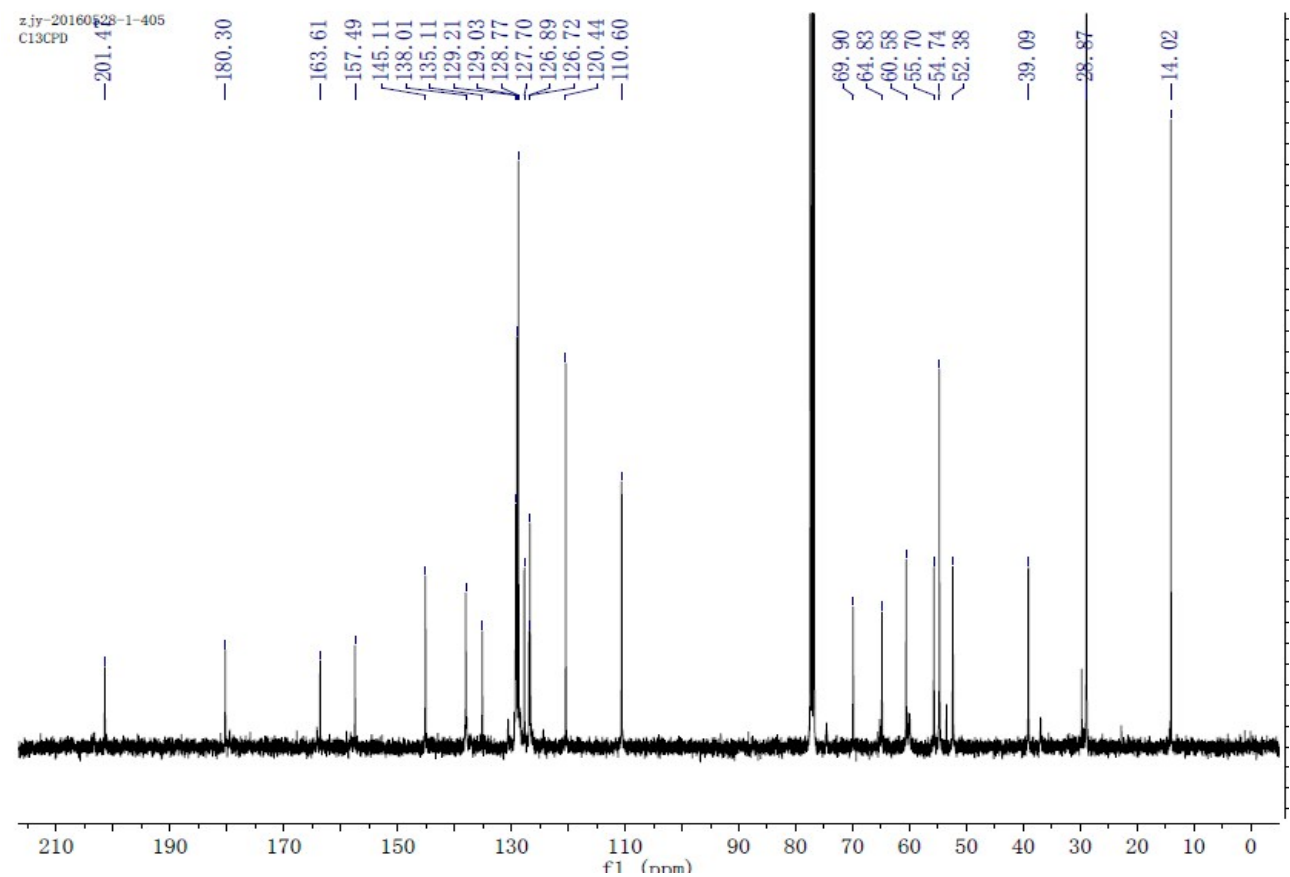
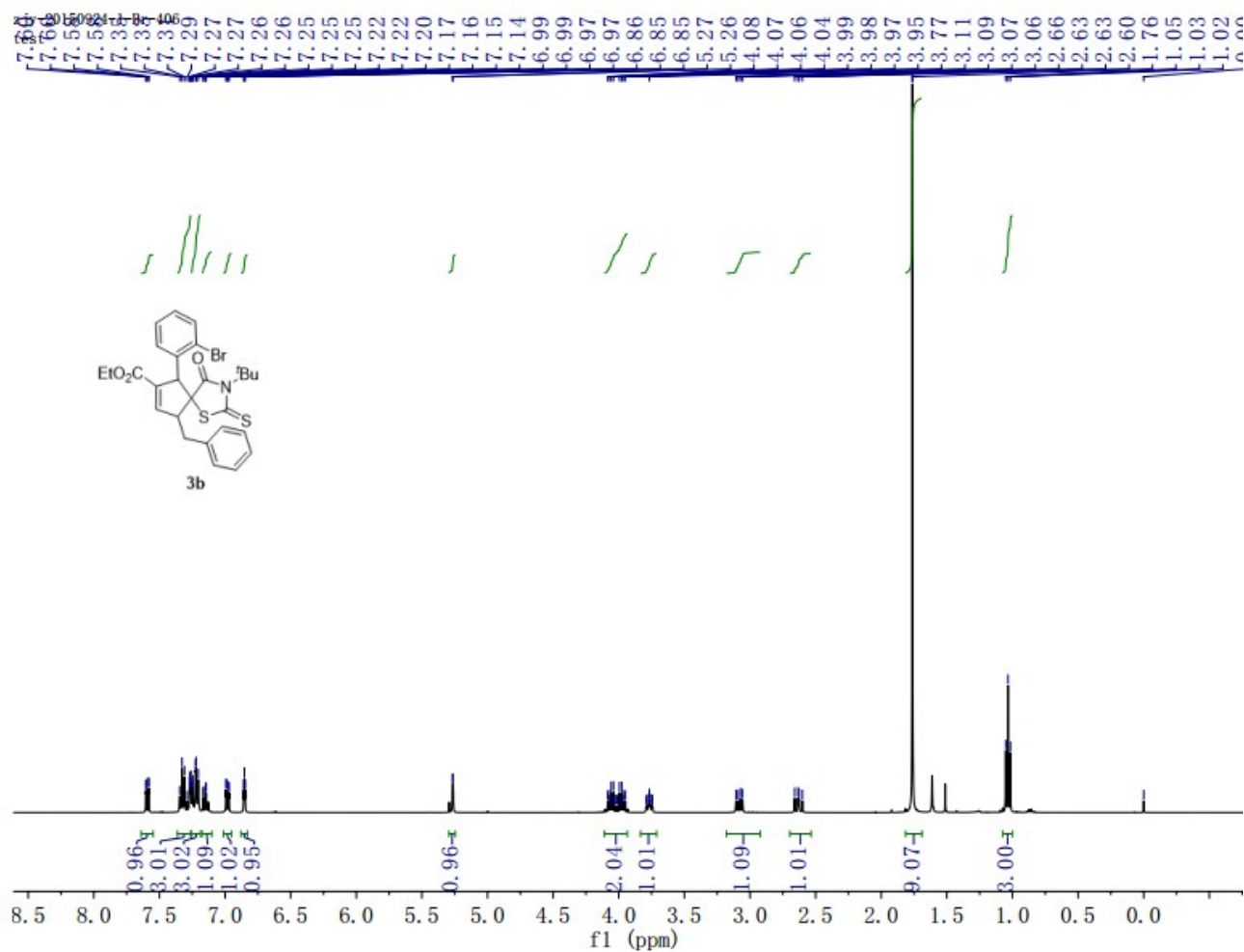


Ethyl 9-benzyl-6-(2-bromophenyl)-3-(tert-butyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3b):

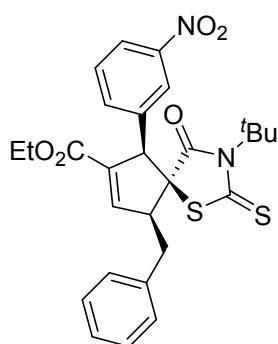


Yellow oil (51.4mg, 92% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.59 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.36-7.26 (m, 3H), 7.26-7.19 (m, 3H), 7.16 (dd, $J = 7.8, 1.6$ Hz, 1H), 6.98 (dd, $J = 7.7, 1.6$ Hz, 1H), 6.85 (t, $J = 2.3$ Hz, 1H), 5.26 (d, $J = 0.9$ Hz, 1H), 4.11-3.93 (m, 2H), 3.83-3.71 (m, 1H), 3.08 (dd, $J = 13.5, 6.8$ Hz, 1H), 2.63 (dd, $J = 13.5, 10.2$ Hz, 1H), 1.76 (s, 9H), 1.03 (t, $J = 7.1$ Hz, 3H); ^{13}C

NMR (101 MHz, CDCl_3): δ 201.0, 180.4, 163.1, 145.2, 138.3, 137.7, 135.4, 133.1, 129.4, 129.0, 128.9, 128.7, 127.6, 126.8, 126.7, 69.5, 65.4, 60.7, 58.4, 56.0, 39.4, 28.8, 13.9; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{29}\text{BrNO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$ 558.0767, found 558.0765.



Ethyl 9-benzyl-3-(tert-butyl)-6-(3-nitrophenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3c):

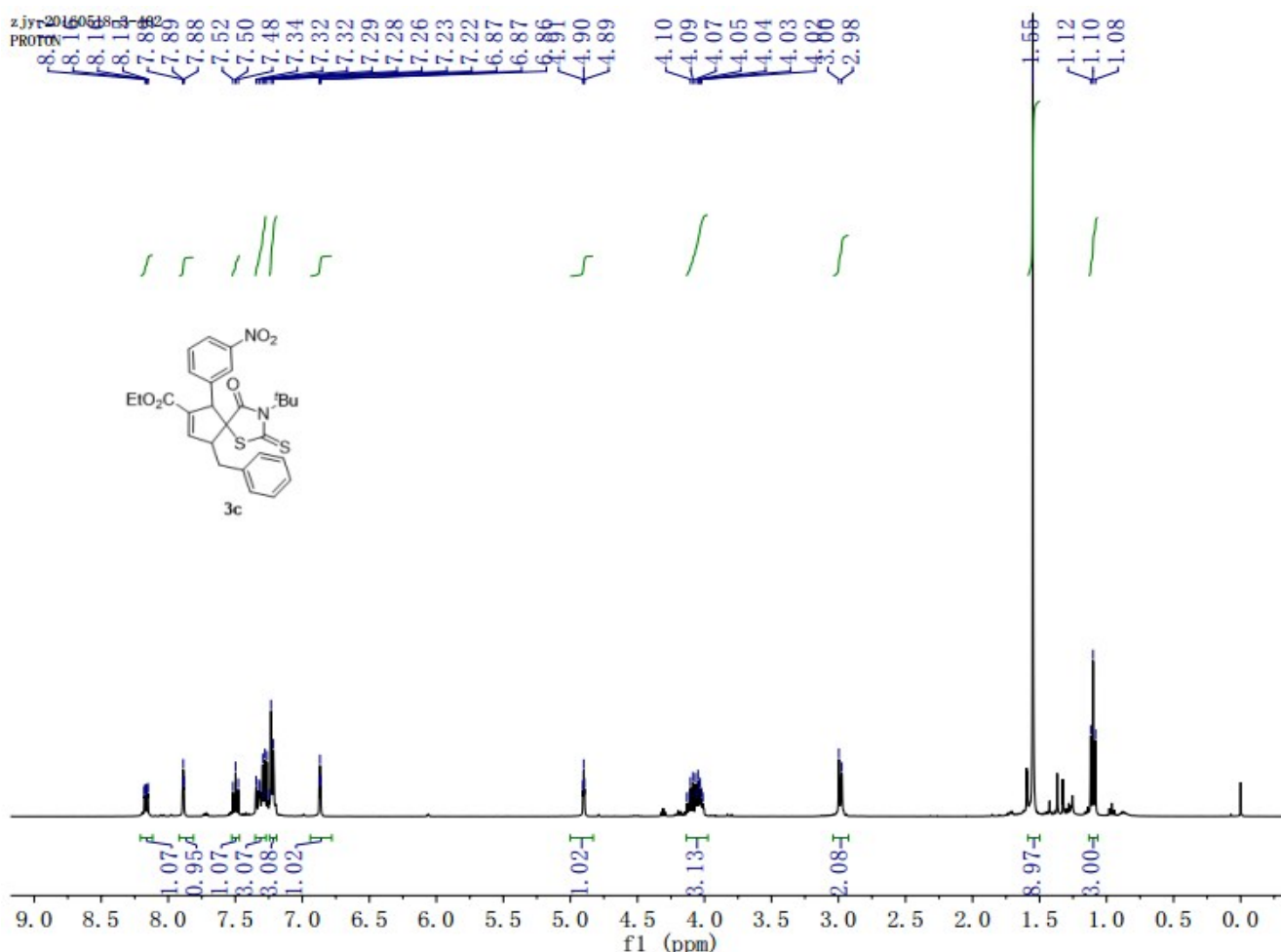


Yellow oil (50.4 mg, 96% yield); ^1H NMR (400 MHz, CDCl_3): δ 8.21-8.12 (m, 1H), 7.89 (t, $J = 1.9$ Hz, 1H), 7.50 (t, $J = 7.9$ Hz, 1H), 7.35-7.27 (m, 3H), 7.22 (d, $J = 7.1$ Hz, 3H), 6.87 (t, $J = 2.3$ Hz, 1H), 4.90 (t, $J = 2.3$ Hz, 1H), 4.08-3.97 (m, 2H), 2.99 (d, $J = 8.6$ Hz, 2H), 1.55 (s, 9H), 1.10 (t, $J = 7.1$ Hz, 3H); ^{13}C

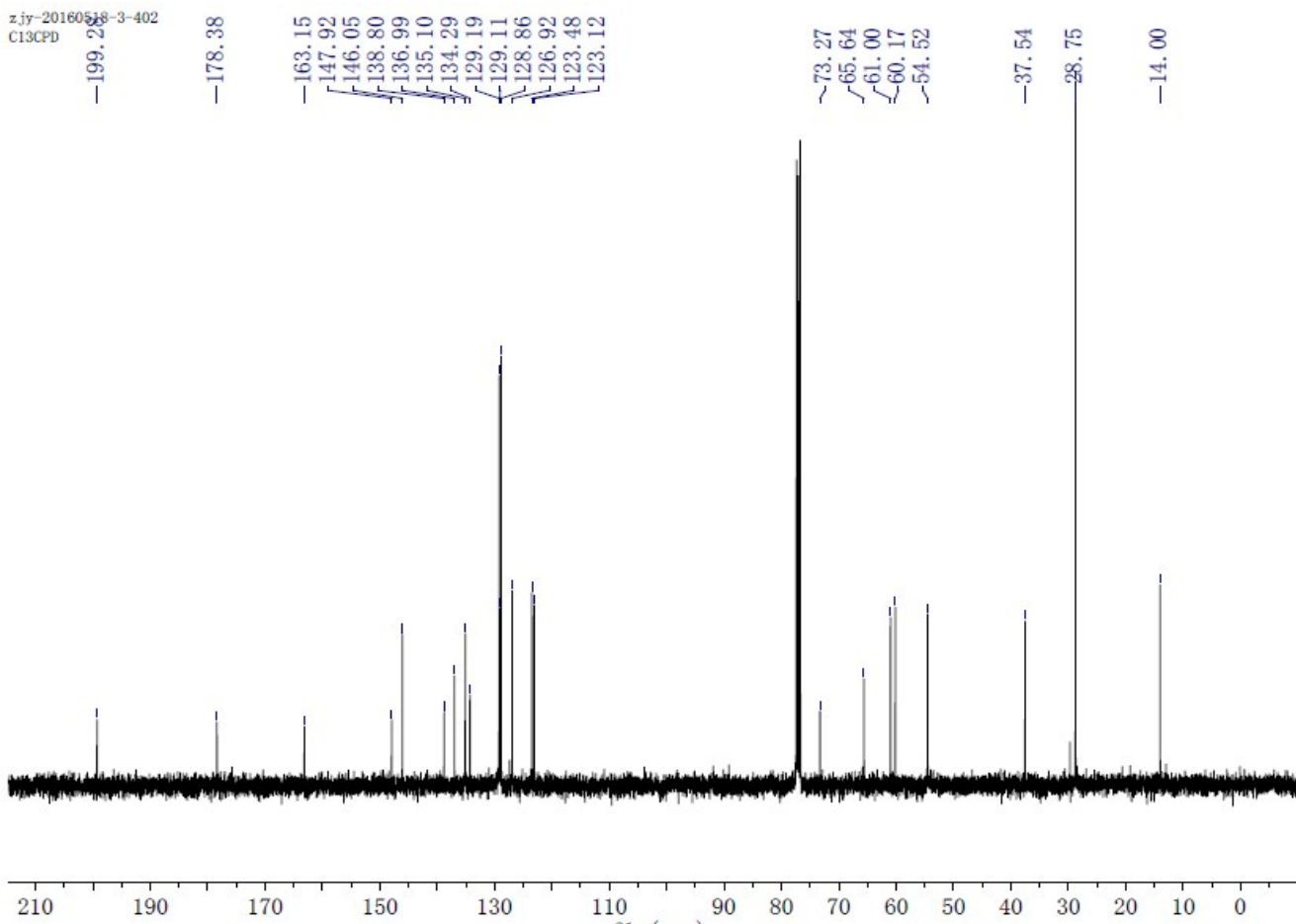
NMR (101 MHz, CDCl_3): δ 199.3, 178.4, 163.2, 147.9, 146.1, 138.8, 137.0,

135.1, 134.3, 129.2, 128.9, 126.9, 123.5, 123.1, 73.3, 65.6, 61.0, 60.2, 54.5, 37.5, 28.8, 14.0; HRMS

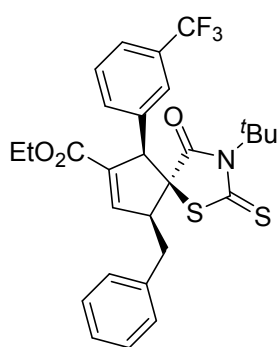
(ESI): m/z calcd for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{O}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 525.1512, found 525.1511.



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C13CPD

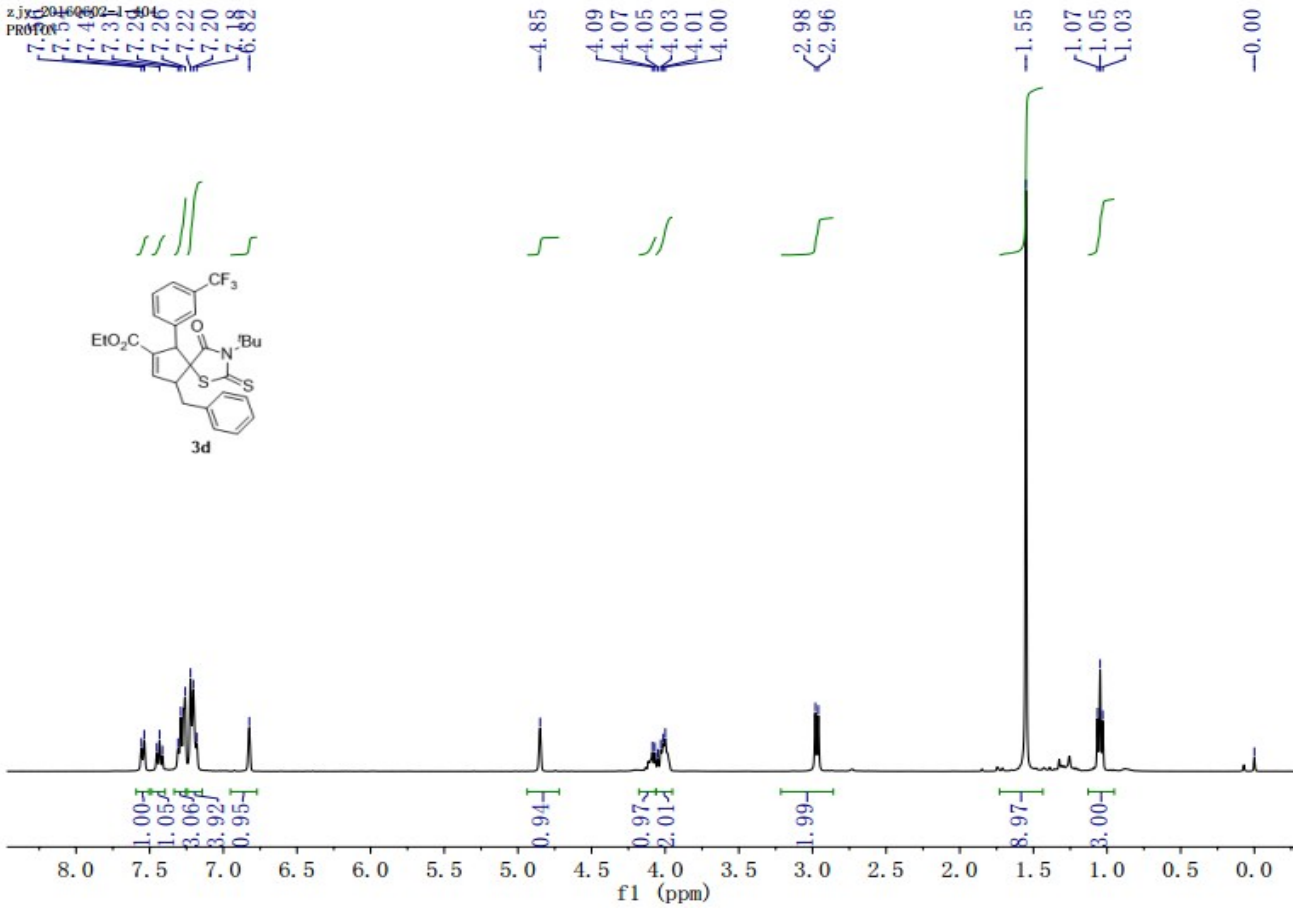


Ethyl 9-benzyl-3-(tert-butyl)-4-oxo-2-thioxo-6-(3-(trifluoromethyl) phenyl)-1-thia-3-azaspiro [4.4]-non-7-ene-7-carboxylate (3d):

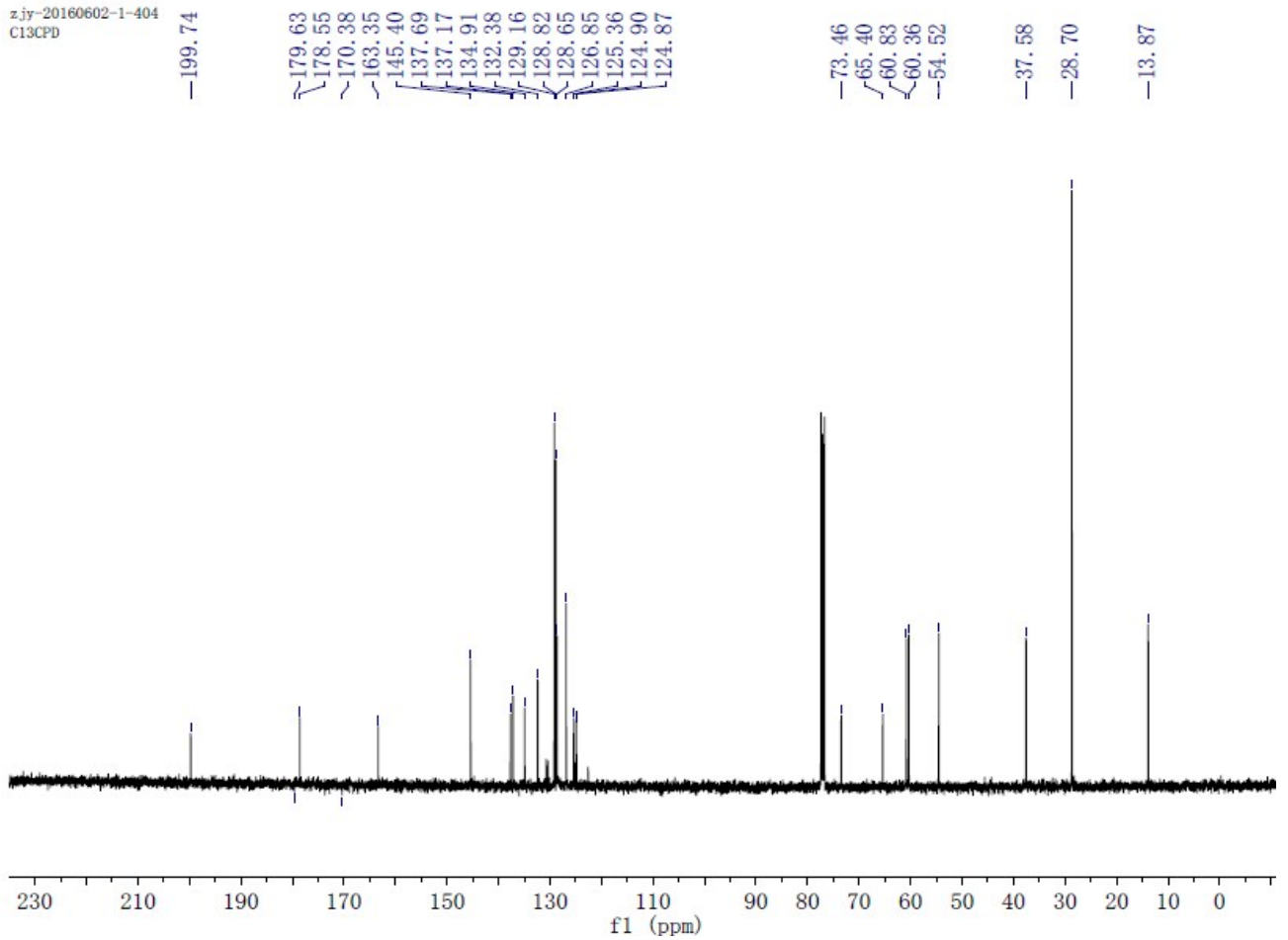


Yellow oil (53.7 mg, 98% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.55 (d, $J = 7.7$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 1H), 7.33-7.26 (m, 3H), 7.24-7.14 (m, 4H), 6.82 (s, 1H), 4.85 (s, 1H), 4.08 (d, $J = 7.1$ Hz, 1H), 4.02 (dd, $J = 7.1$ Hz, 6.9 Hz, 2H), 2.97 (d, $J = 8.2$ Hz, 2H), 1.55 (s, 9H), 1.05 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 199.7, 178.6, 163.4, 145.4, 137.7, 137.2, 134.9, 132.4, 129.2, 128.8, 128.7, 126.9, 125.4, 124.9, 124.9, 60.8, 73.5, 65.4, 60.8, 60.4, 54.5, 37.6, 28.7, 13.9; ^{19}F NMR (376 MHz, CDCl_3): δ -62.59; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{29}\text{F}_3\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 548.1535, found 548.1535.

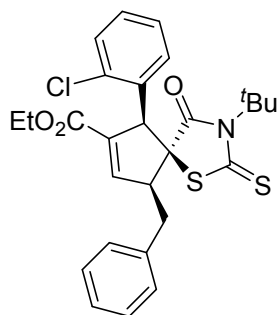
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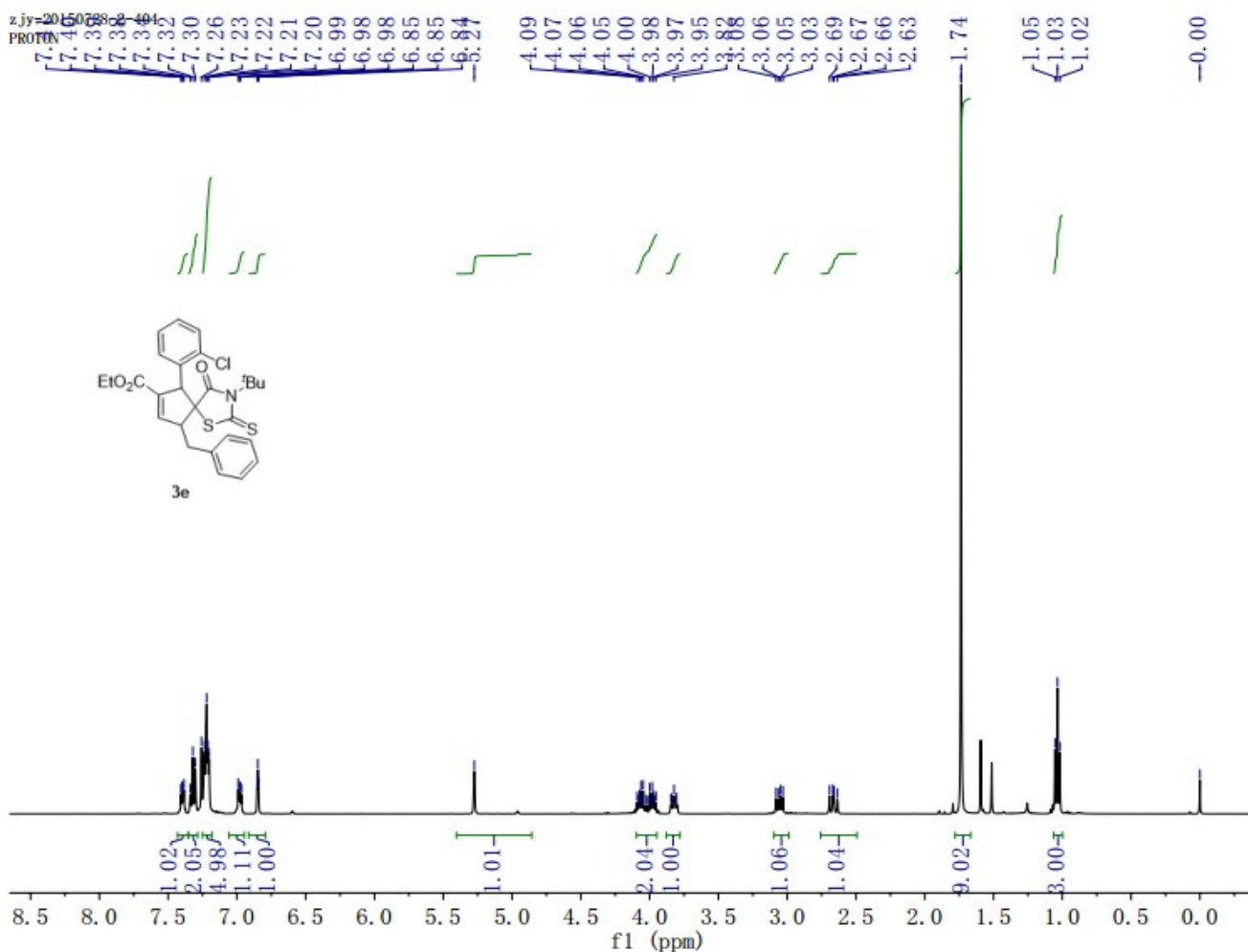
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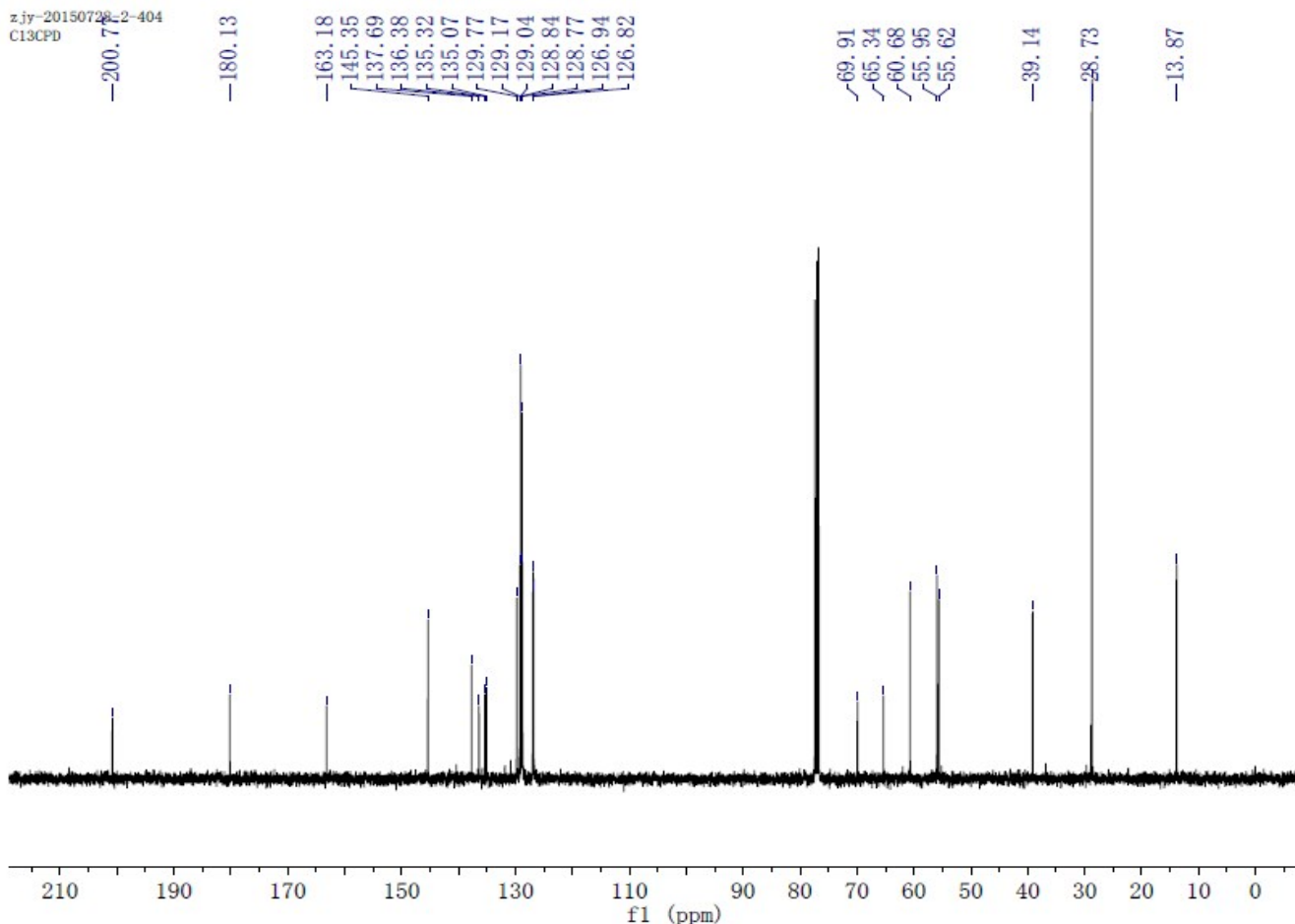
Ethyl 9-benzyl-3-(tert-butyl)-6-(2-chlorophenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3e):



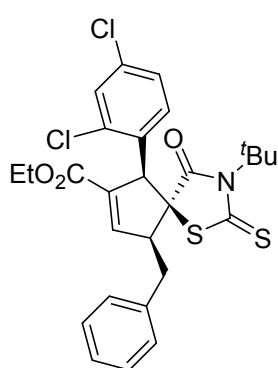
Yellow oil (48.8 mg, 95% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.40 (dd, $J = 5.7, 3.6$ Hz, 1H), 7.32 (t, $J = 7.3$ Hz, 2H), 7.22 (dd, $J = 8.3, 4.7$ Hz, 5H), 6.98 (dd, $J = 5.8, 3.5$ Hz, 1H), 6.85 (t, $J = 2.1$ Hz, 1H), 5.27 (s, 1H), 4.12-4.02 (m, 2H), 3.83 (dd, $J = 12.1, 4.6$ Hz, 1H), 3.06 (dd, $J = 13.5, 7.1$ Hz, 1H), 2.66 (dd, $J = 13.5, 9.9$ Hz, 1H), 1.74 (s, 9H), 1.03 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 200.8, 180.1, 163.2, 145.4, 137.7, 136.4, 135.3, 135.2, 129.8, 129.2, 129.0, 128.8, 128.8, 126.9, 126.8, 69.9, 65.3, 60.7, 56.0, 55.6, 39.1, 28.7, 13.9; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{29}\text{ClNO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 514.1272, found 514.1268.



zjy-20150728-2-404
C13CPD



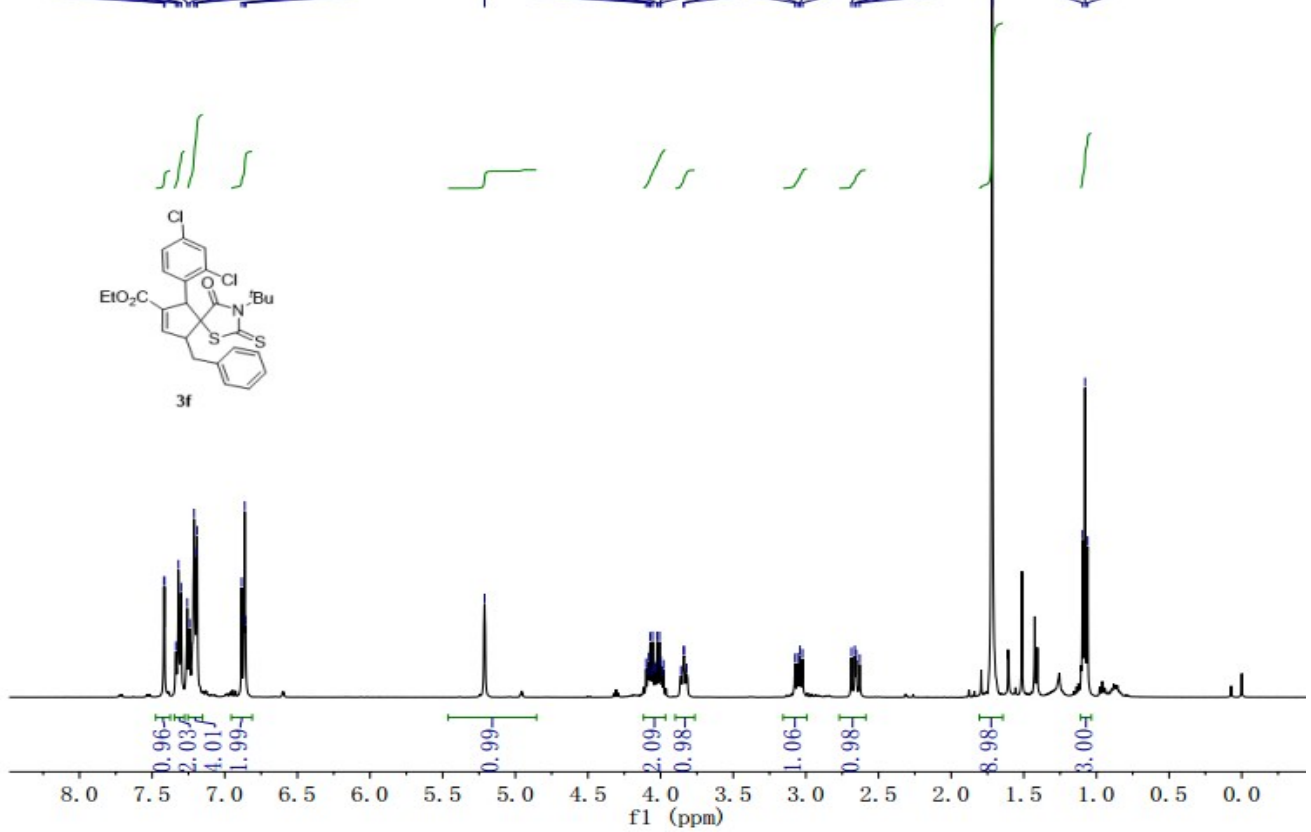
Ethyl 9-benzyl-3-(tert-butyl)-6-(2,4-dichlorophenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3f):



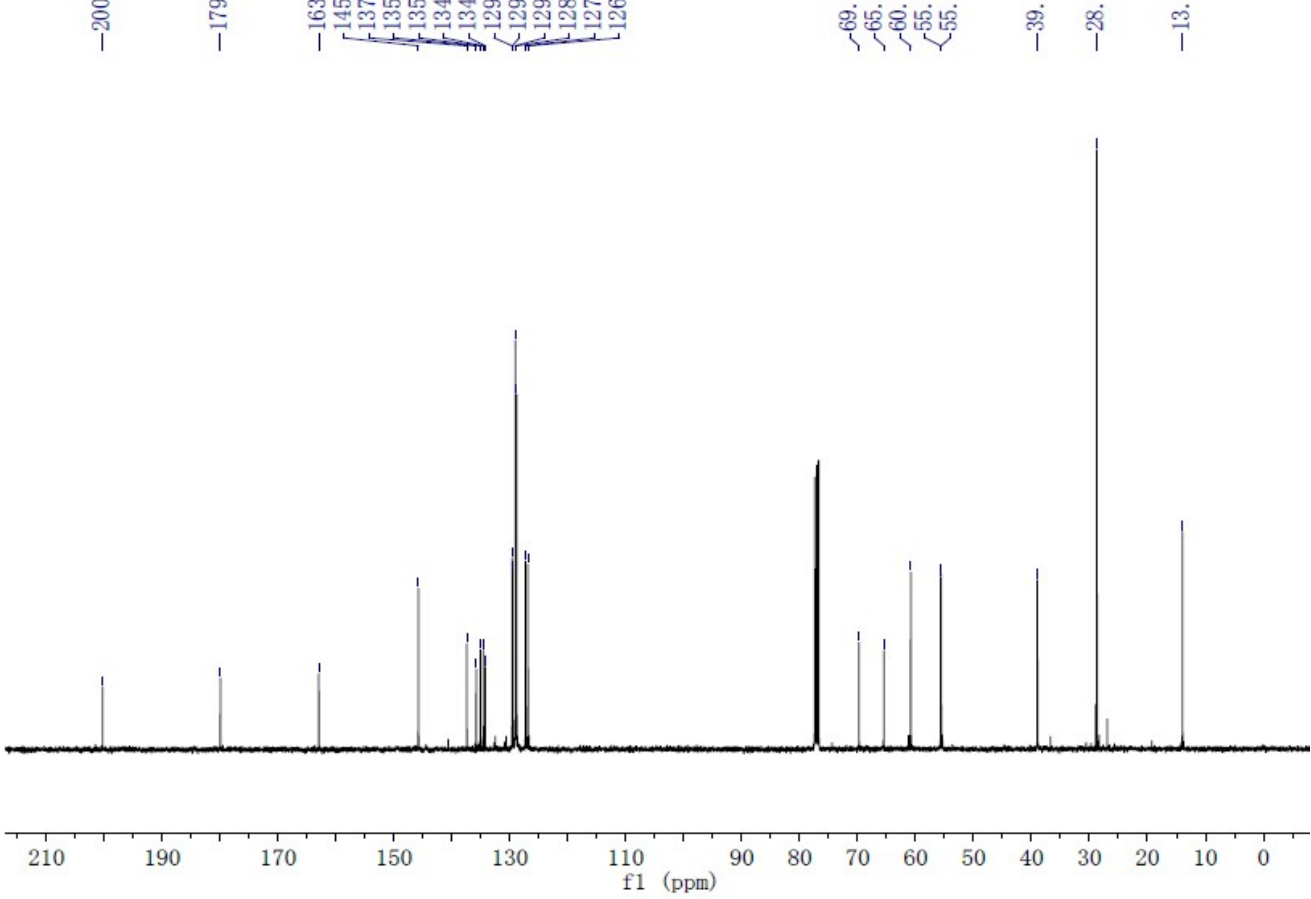
Yellow oil (54.3mg, 99% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, J = 2.1 Hz, 1H), 7.32 (t, J = 7.3 Hz, 2H), 7.21 (dd, J = 13.5, 7.1 Hz, 4H), 6.87 (t, J = 5.5 Hz, 2H), 5.21 (s, 1H), 4.12-3.97 (m, 2H), 3.84 (dd, J = 8.2, 7.3 Hz, 1H), 3.05 (dd, J = 13.6, 7.2 Hz, 1H), 2.66 (dd, J = 13.5, 9.6 Hz, 1H), 1.72 (s, 9H), 1.08 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 200.3, 180.0, 163.0, 145.8, 137.5, 135.8, 135.1, 134.6, 134.3, 129.6, 129.6, 129.1, 128.9, 127.3,

126.9, 69.8, 65.5, 60.9, 55.7, 55.6, 39.0, 28.7, 14.0. HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{28}\text{Cl}_2\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 548.0882, found 548.0873.

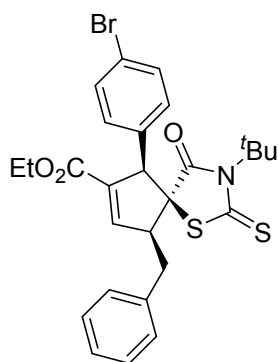
zjy-20160517-3-402
 PROTIN



zjy-20160517-3-402
 C13CPD

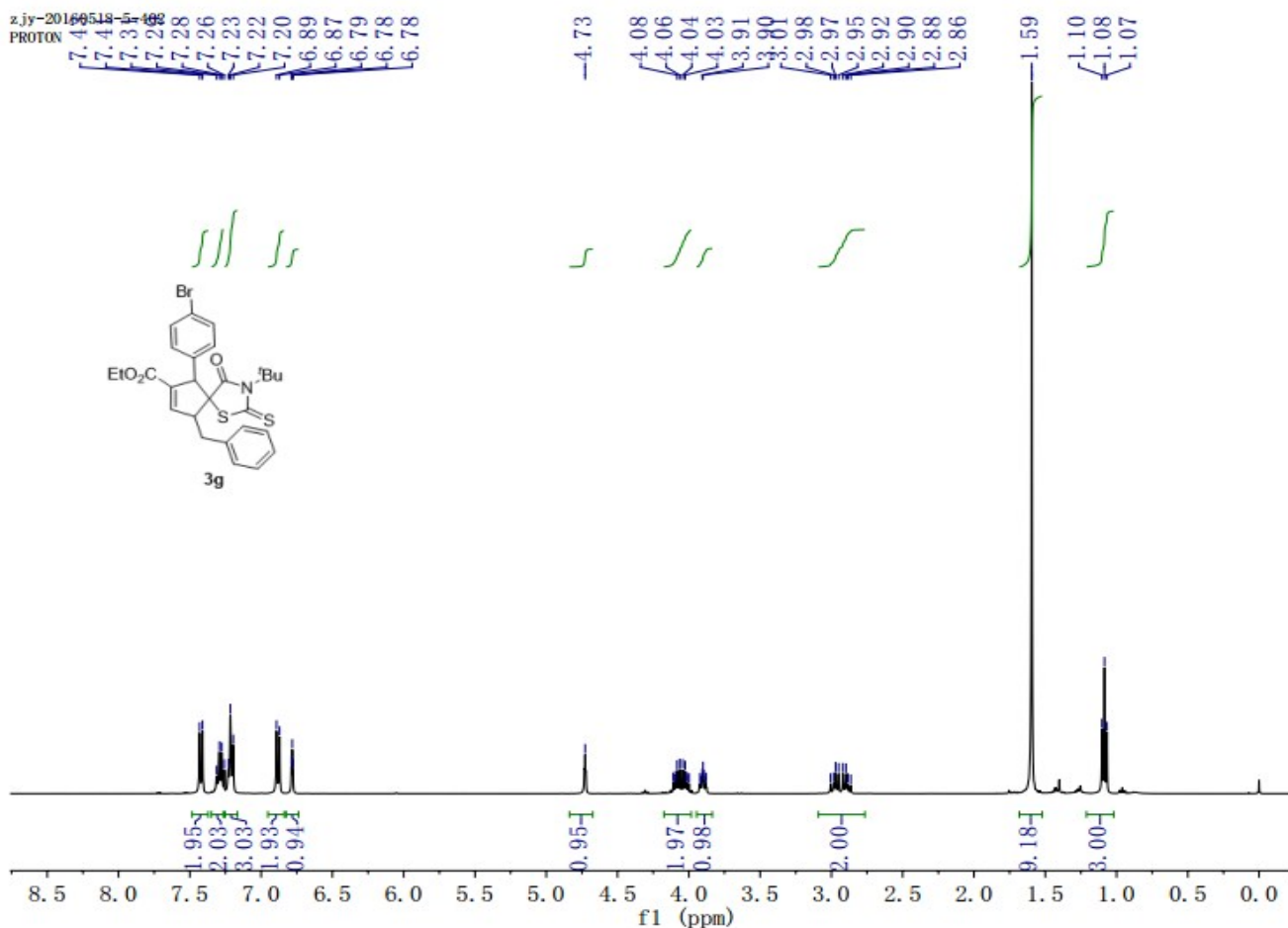


Ethyl 9-benzyl-6-(4-bromophenyl)-3-(tert-butyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3g):

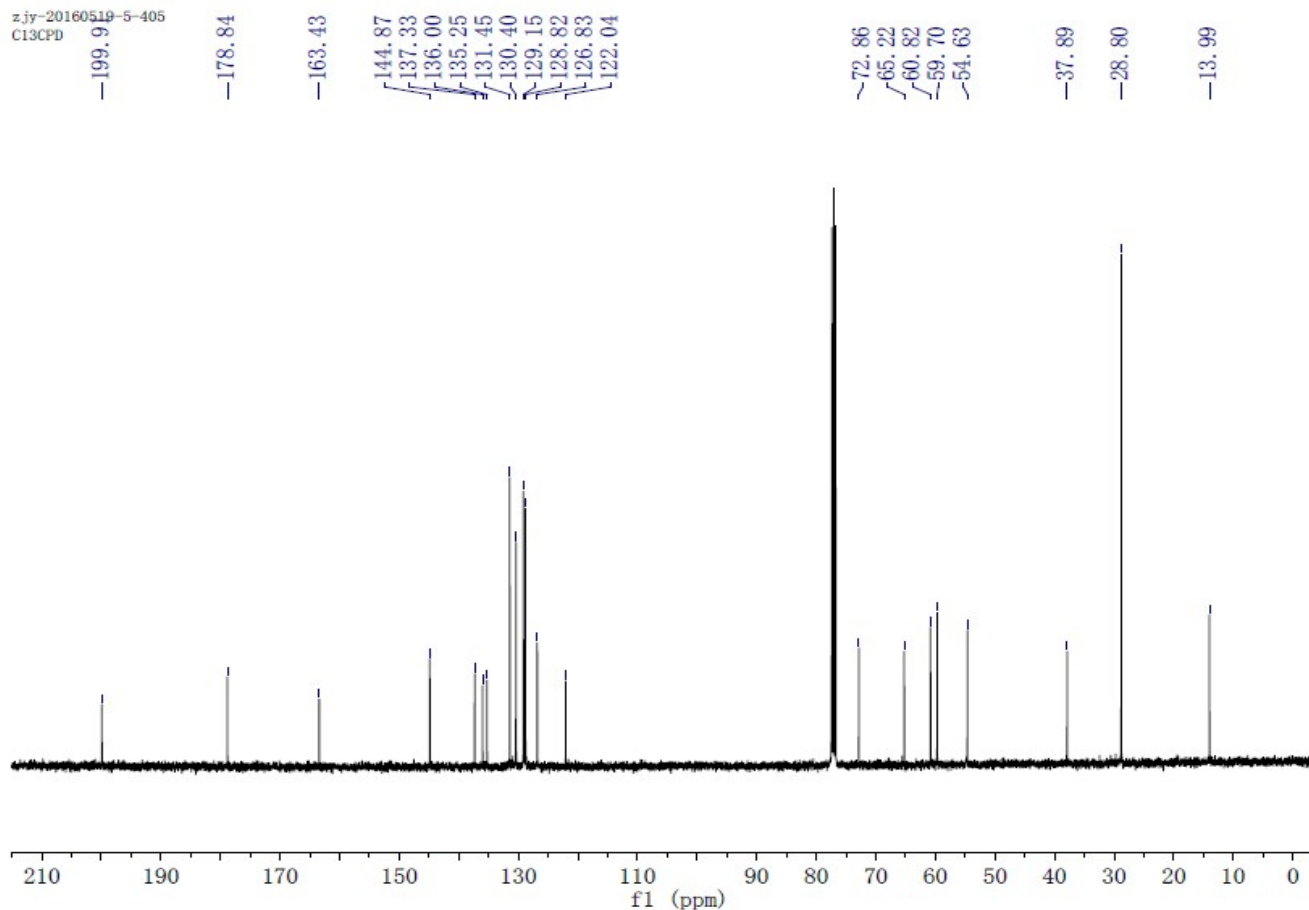


Yellow oil (53.6 mg, 96% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, $J = 8.4$ Hz, 2H), 7.35-7.27 (m, 2H), 7.21 (t, $J = 6.7$ Hz, 3H), 6.88 (d, $J = 8.4$ Hz, 2H), 6.78 (t, $J = 2.3$ Hz, 1H), 4.73 (s, 1H), 4.10-4.05 (m, 2H), 3.92-3.87 (ddd, $J = 21.3, 12.2, 5.1$ Hz, 1H), 3.00-2.86 (ddd, $J = 21.3, 4.9$ Hz, 2H), 1.59 (s, 9H), 1.08 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 199.9, 178.8, 163.4, 144.9, 137.3, 136.0, 135.3, 131.5, 130.4, 129.2, 128.8, 126.8, 122.0, 72.9, 65.2,

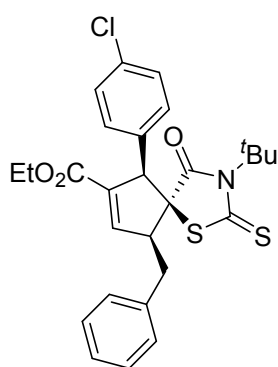
60.8, 59.7, 54.6, 37.9, 28.8, 14.0; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{29}\text{BrNO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 558.0767, found 558.0757.



zjy-20160519-5-405
C13CPD



Ethyl 9-benzyl-3-(tert-butyl)-6-(4-chlorophenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3h):



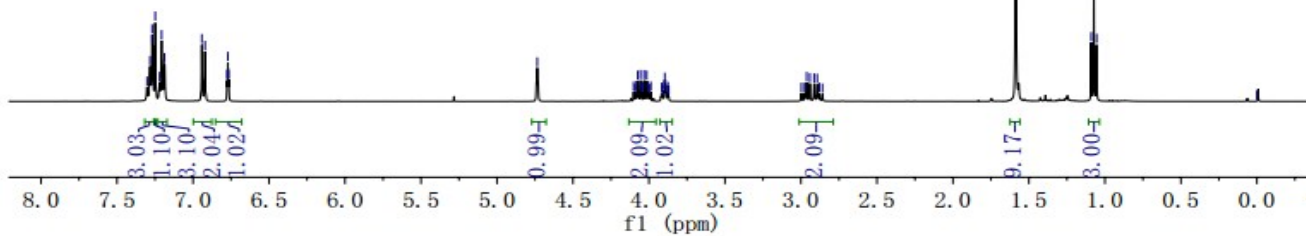
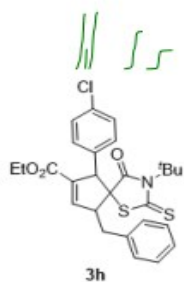
Yellow oil (48.8 mg, 95% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.28 (dd, J = 10.2, 4.7 Hz, 3H), 7.25 (s, 1H), 7.20 (t, J = 6.4 Hz, 3H), 6.93 (d, J = 8.4 Hz, 2H), 6.77 (t, J = 2.3 Hz, 1H), 4.73 (t, J = 2.1 Hz, 1H), 4.13-3.95 (m, 2H), 3.90 (tt, J = 13.8, 2.0 Hz, 1H), 2.99-2.85 (ddd, J = 33.1, 13.8, 8.3 Hz, 2H), 1.58 (d, J = 7.6 Hz, 9H), 1.07 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 199.9, 178.9, 163.4, 144.8, 137.4, 135.5, 135.3, 133.9, 130.1, 129.1, 128.8, 128.5, 126.8, 73.0, 65.2, 60.8, 59.7, 54.6, 37.9, 28.8, 14.0; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{29}\text{ClNO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 514.1272, found 514.1266.

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PR030

7.30
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7.22
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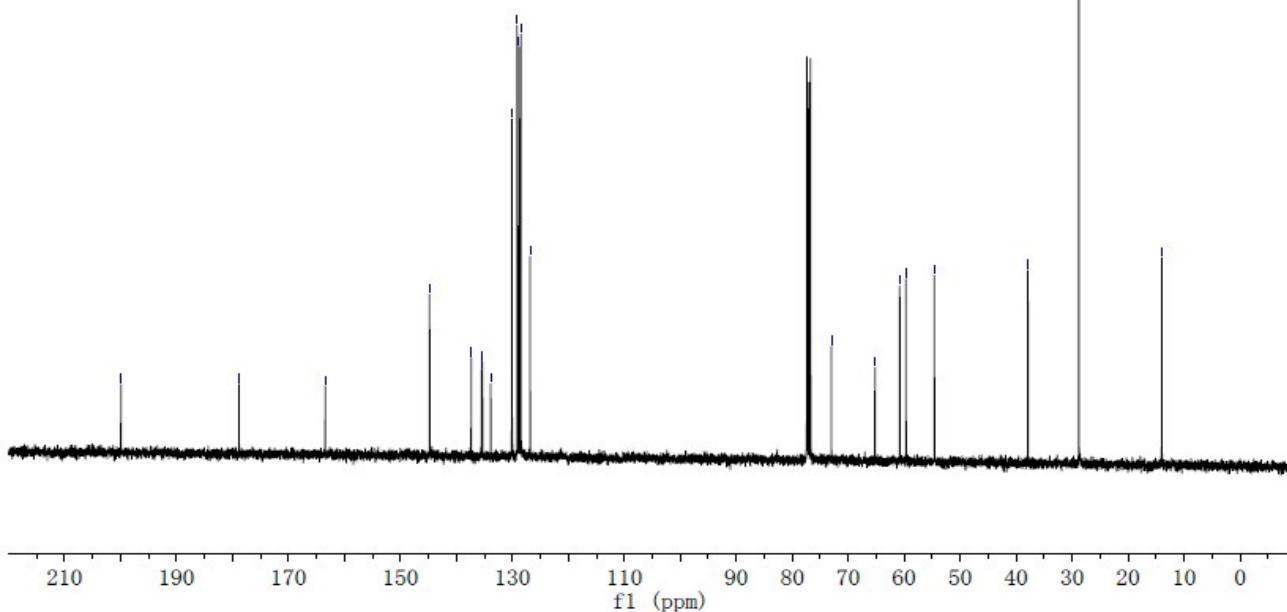
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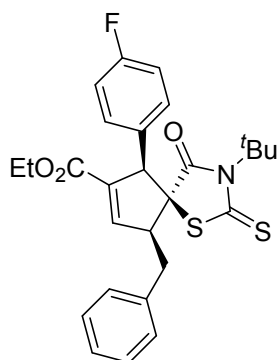
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C13CPD

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129.14
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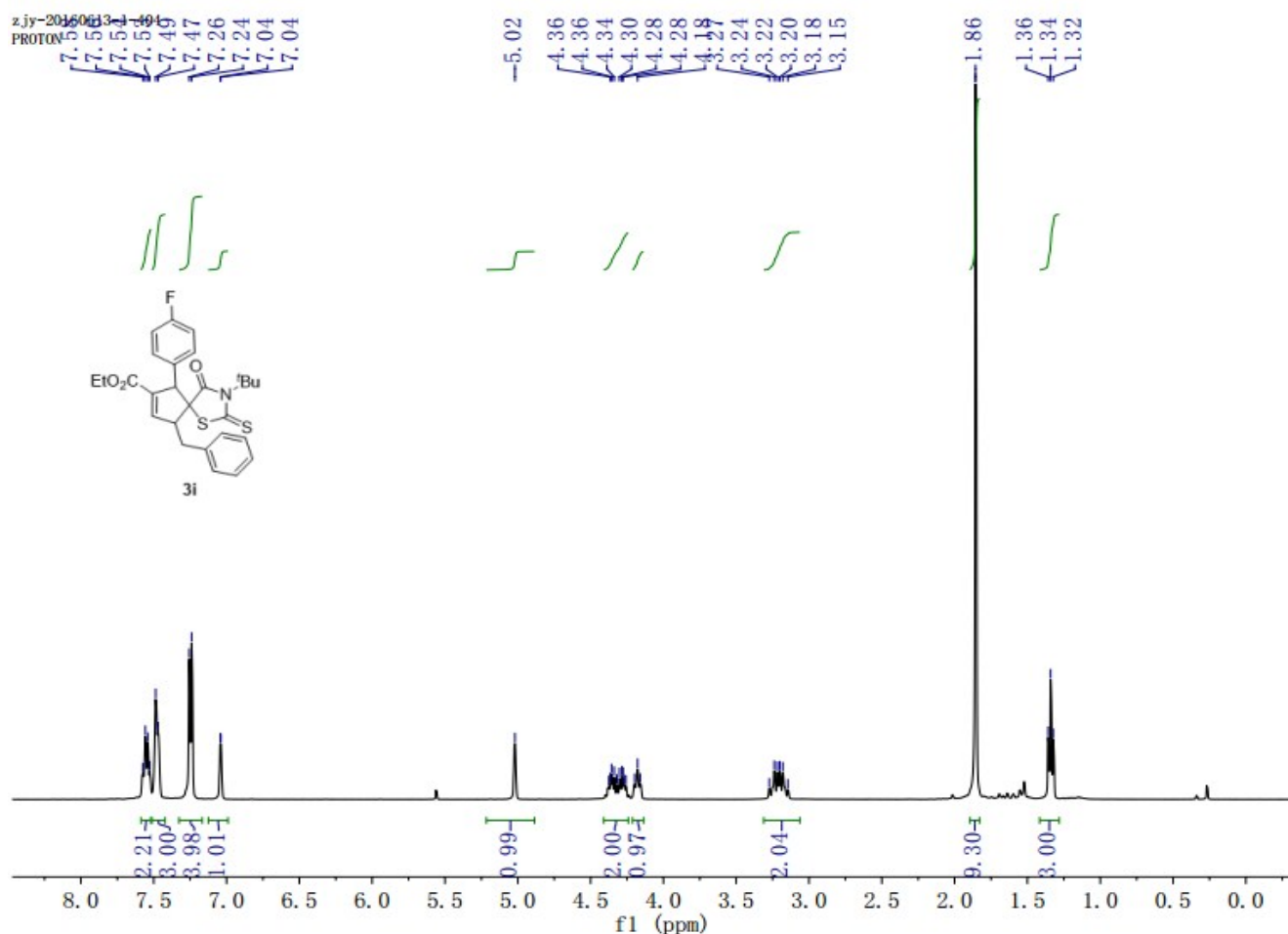


Ethyl 9-benzyl-3-(tert-butyl)-6-(4-fluorophenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3i):

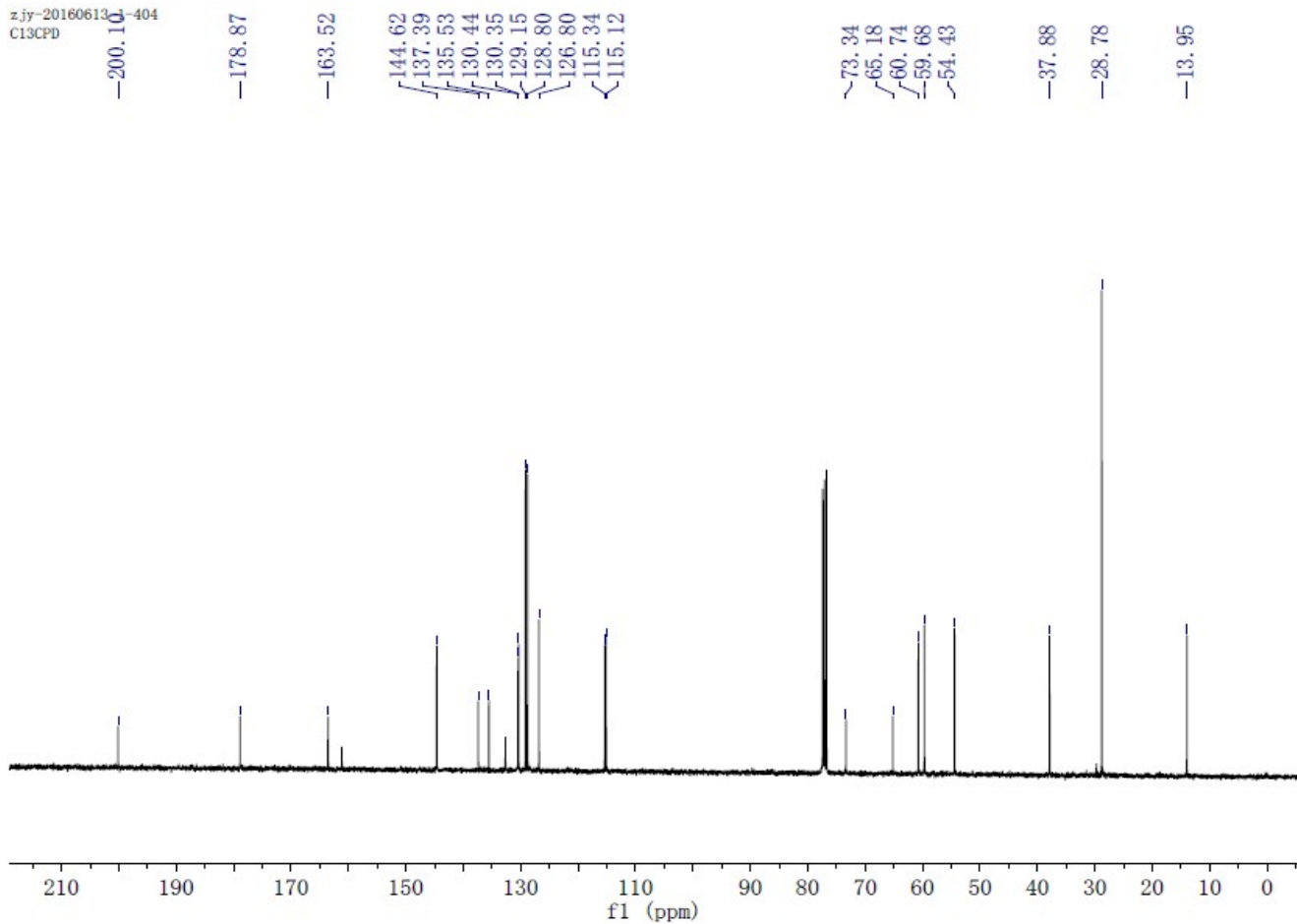


Yellow oil (46.3 mg, 93% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.55 (dd, $J = 12.8, 6.1$ Hz, 2H), 7.48 (d, $J = 6.8$ Hz, 3H), 7.25 (d, $J = 6.6$ Hz, 4H), 7.04 (d, $J = 1.4$ Hz, 1H), 5.02 (s, 1H), 4.41-4.24 (m, 2H), 4.18 (t, $J = 7.7$ Hz, 1H), 3.31-3.06 (m, 2H), 1.86 (s, 9H), 1.34 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 200.1, 178.9, 163.5, 144.6, 137.4, 135.5, 130.4, 130.4, 129.2, 128.8, 126.8, 115.3, 115.1, 73.3, 65.2, 60.7, 59.7, 54.4, 37.9, 28.8, 14.0; ^{19}F NMR (376

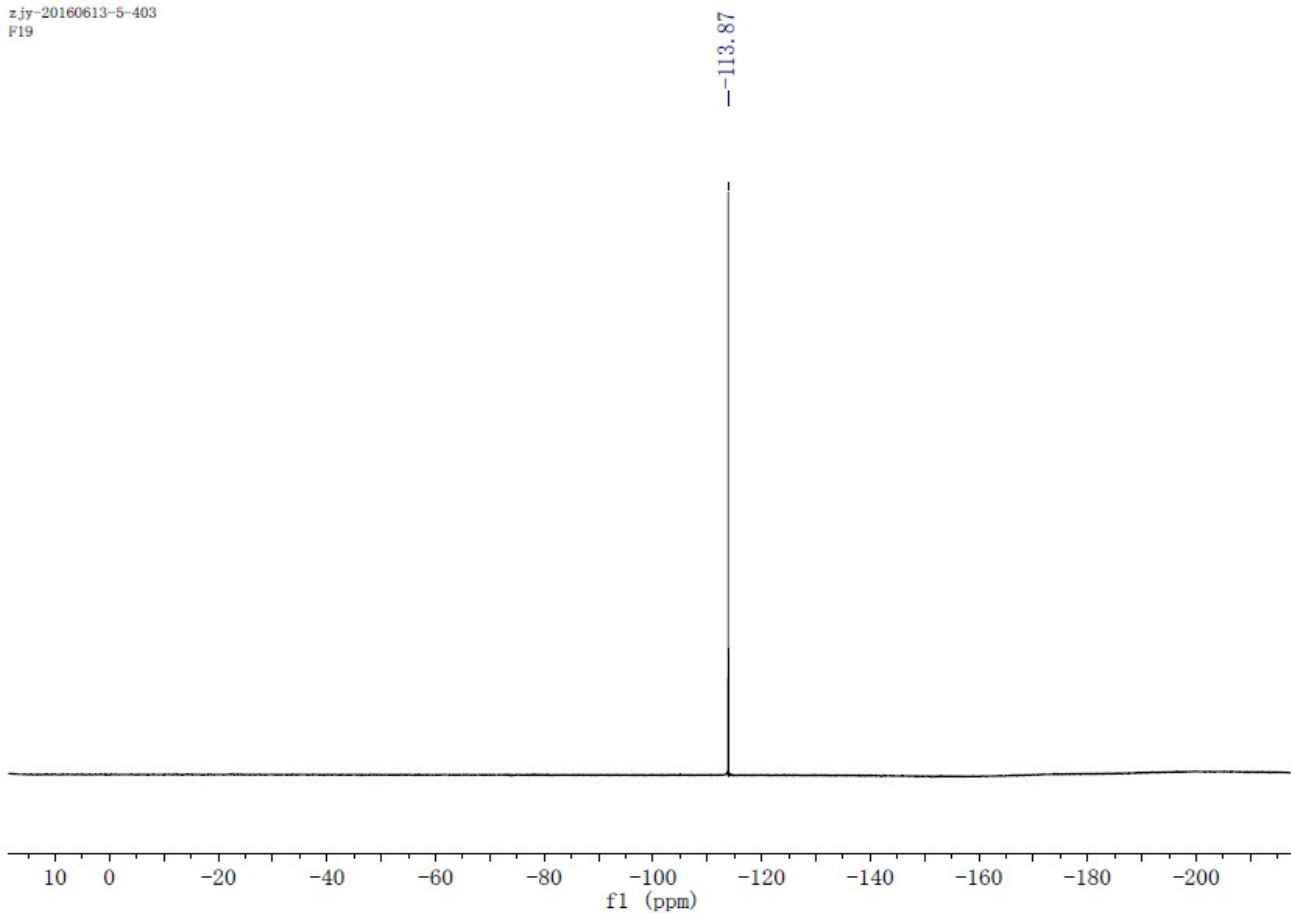
MHz, CDCl_3): δ -113.87; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{29}\text{FNO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 498.1567, found 498.1565.



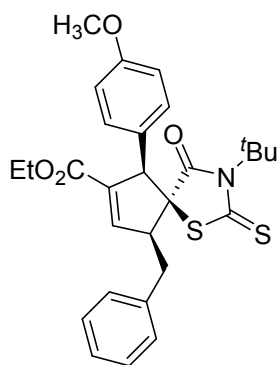
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C13CPD



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F19

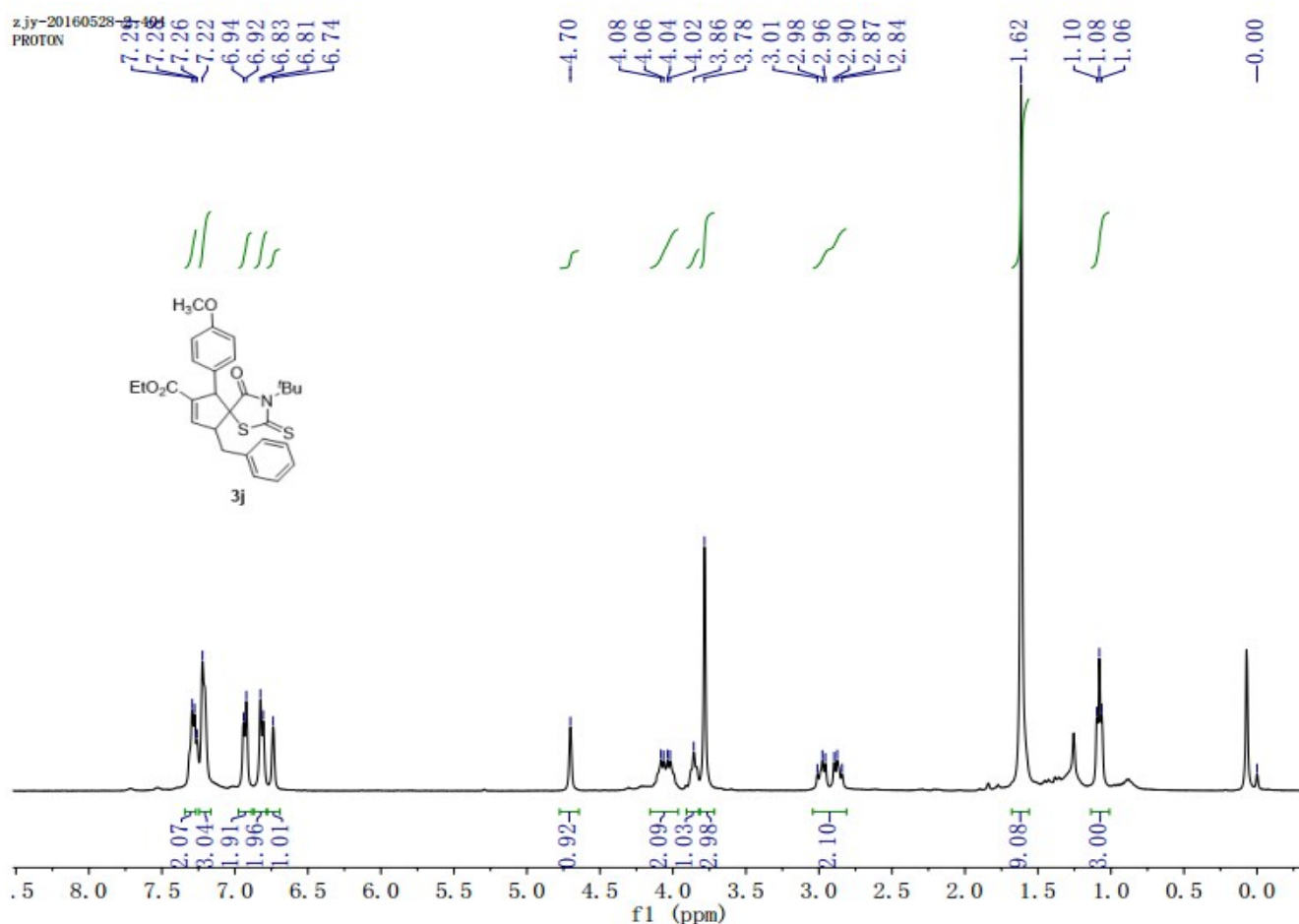


Ethyl 9-benzyl-3-(tert-butyl)-6-(4-methoxyphenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3j):

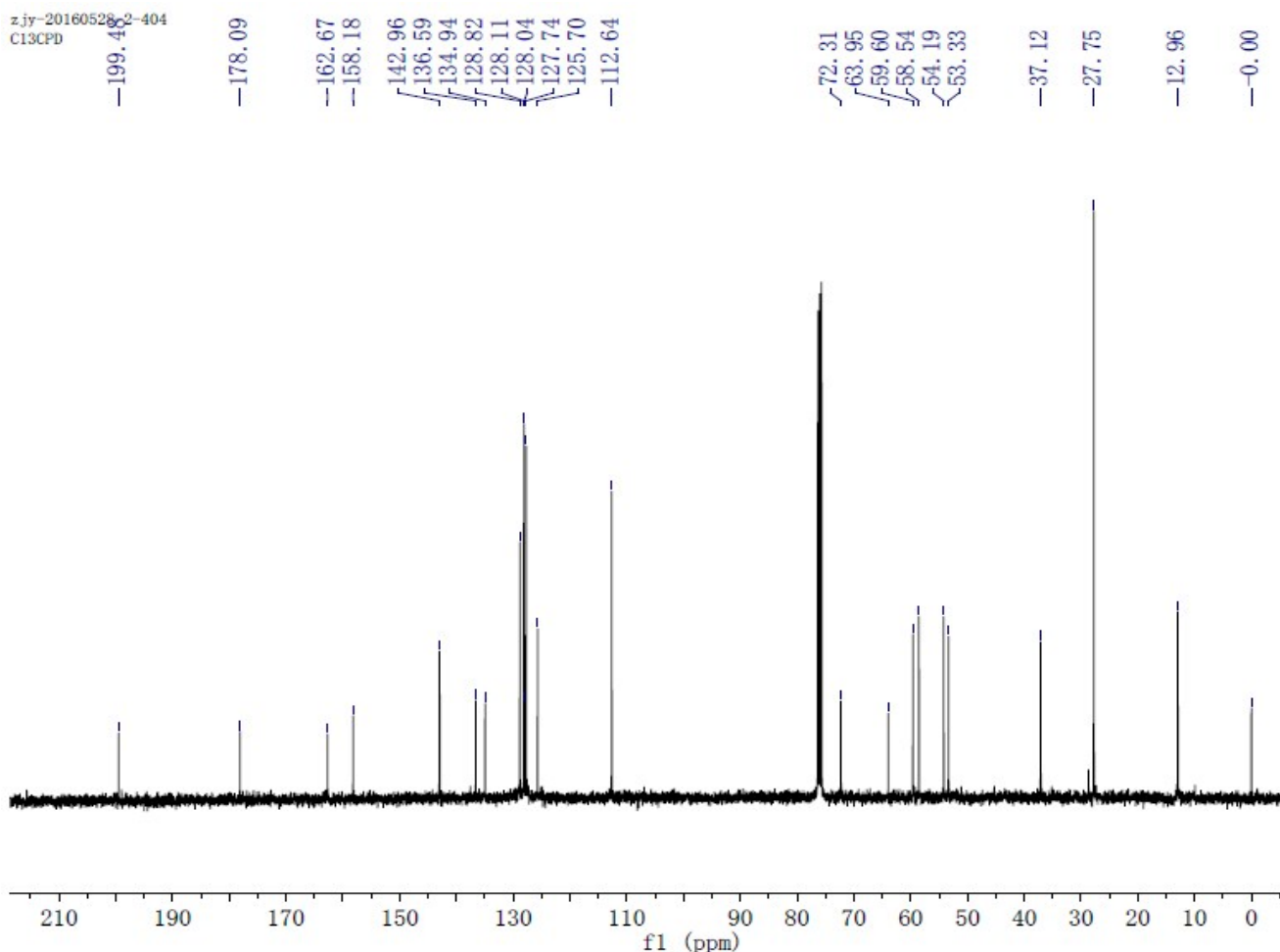


Yellow oil (40.3 mg, 79% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.28 (d, *J* = 6.6 Hz, 2H), 7.22 (s, 3H), 6.93 (d, *J* = 7.3 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.74 (s, 1H), 4.70 (s, 1H), 4.12-3.99 (m, 2H), 3.86 (s, 1H), 3.78 (s, 3H), 2.93 (dt, *J* = 13.4 Hz, 2H), 1.62 (s, 9H), 1.08 (t, *J* = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 199.5, 178.1, 162.7, 158.2, 143.0, 136.6, 134.9, 128.8, 128.1, 128.0, 127.7, 125.7, 112.6, 72.3, 64.0, 59.6, 58.5, 54.2, 53.3, 37.1, 27.8, 13.0; HRMS

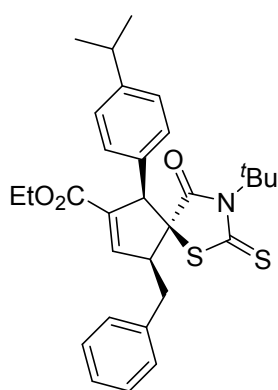
(ESI): *m/z* calcd for C₂₈H₃₂NO₄S₂ [M+H]⁺: 510.1767, found 510.1760.



zjy-20160528-2-404
C13CPD



Ethyl 9-benzyl-3-(tert-butyl)-6-(4-isopropylphenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3k):



Yellow oil (45.4 mg, 87% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.30 (t, $J = 7.2$ Hz, 2H), 7.22 (d, $J = 7.2$ Hz, 3H), 7.13 (d, $J = 7.5$ Hz, 2H), 6.93 (d, $J = 7.5$ Hz, 2H), 6.75 (s, 1H), 4.71 (s, 1H), 4.16-3.94 (m, 2H), 3.84 (t, $J = 8.0$ Hz, 1H), 2.99 (dd, $J = 8.0$ Hz, 1H), 2.93-2.79 (m, 2H), 1.62 (s, 9H), 1.22 (s, 3H), 1.20 (s, 3H), 1.05 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 200.6, 179.0, 163.7, 148.6, 144.0, 137.7, 136.0, 134.1, 129.1, 128.7, 128.7, 126.7, 126.3, 73.1,

64.9, 60.6, 59.8, 54.4, 38.2, 33.7, 28.7, 23.9, 13.9; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{36}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 522.2131, found 522.2130.

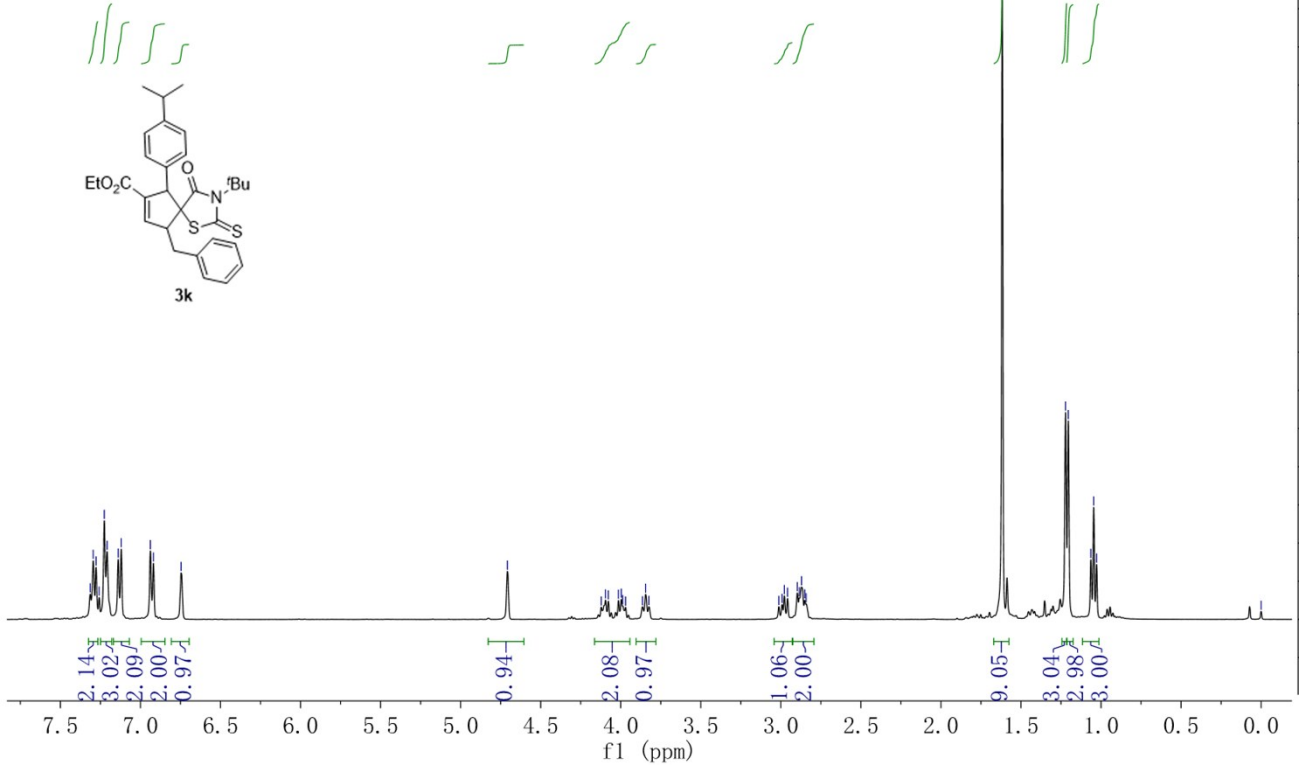
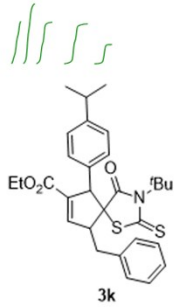
zjy-2015-919-4-402

7.28
7.26
7.23
7.21
7.14
7.12
6.94
6.75

4.71
4.10
4.08
4.01
4.00
3.99
3.86
3.84
3.82
3.81
2.99
2.98
2.96
2.90
2.88
2.87
2.85
2.84

1.62
1.22
1.20
1.06
1.05
1.03

0.00

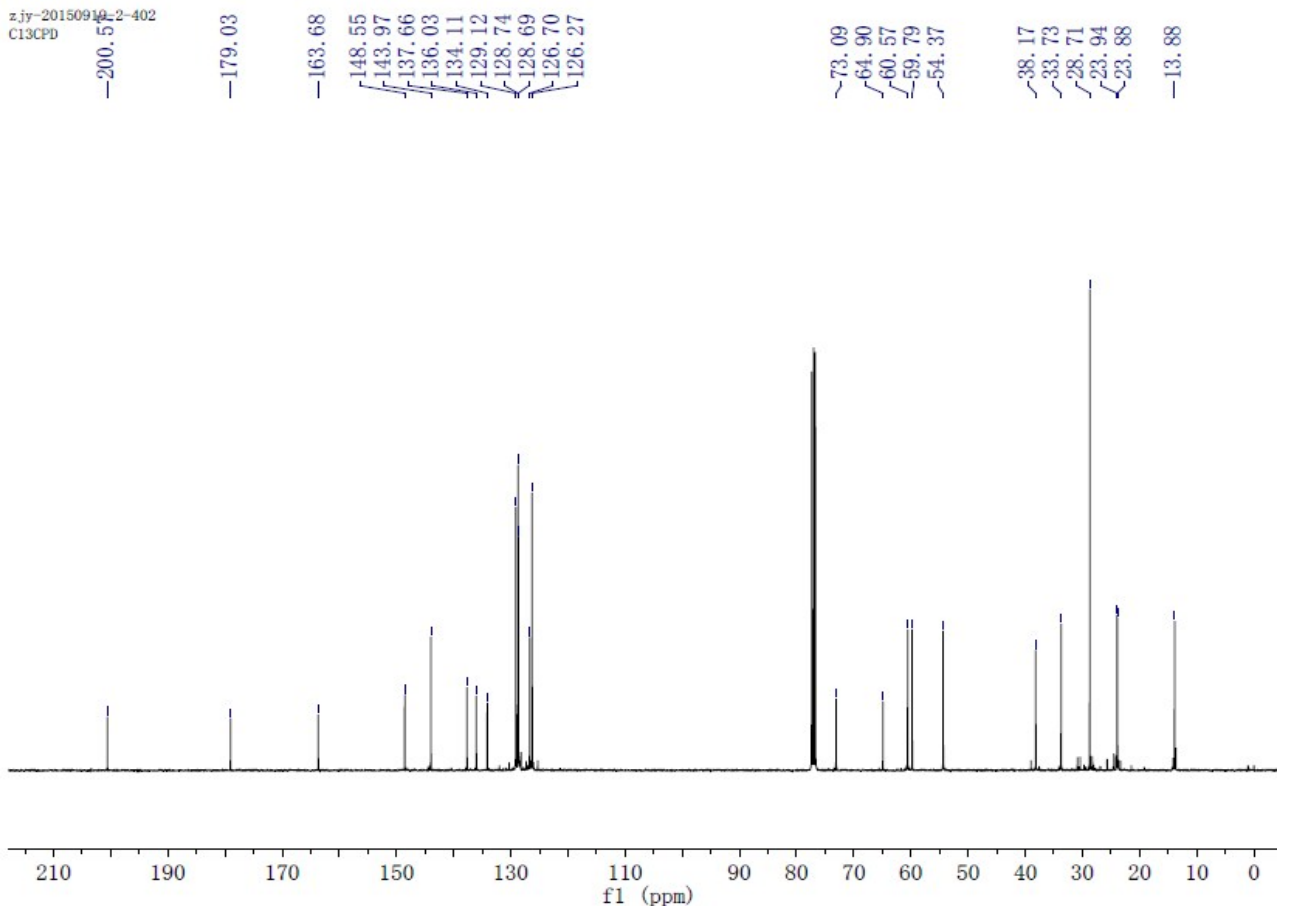


zjy-20150919-2-402
C13CPD

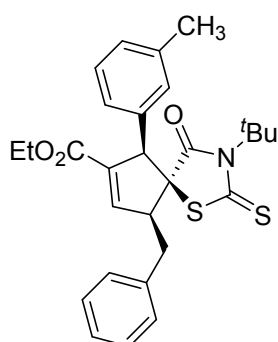
200.51
179.03

163.68
148.55
143.97
137.66
136.03
134.11
129.12
128.74
128.69
126.70
126.27

73.09
64.90
60.57
59.79
54.37
38.17
33.73
28.71
23.94
23.88
13.88

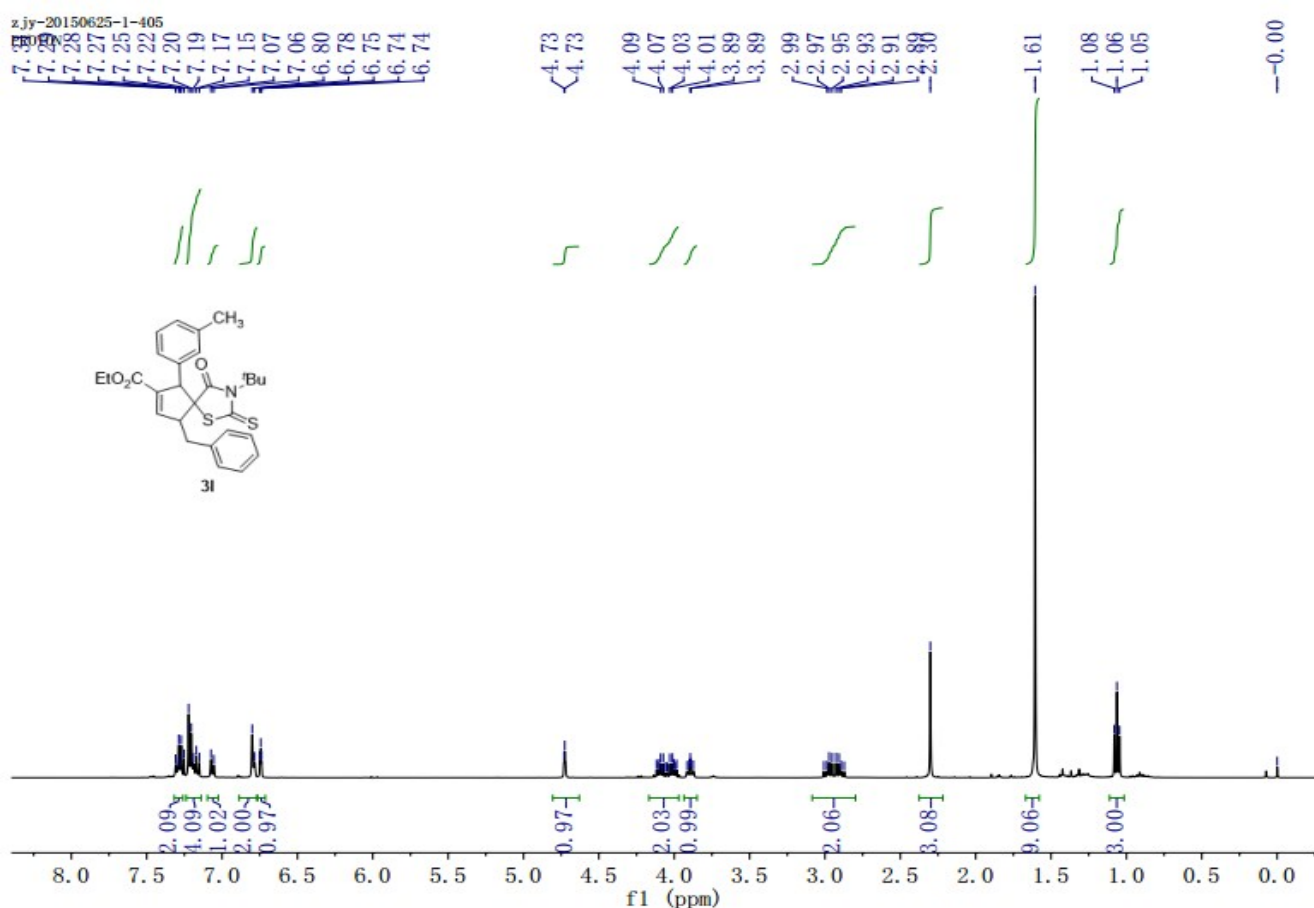


Ethyl 9-benzyl-3-(tert-butyl)-4-oxo-2-thioxo-6-(m-tolyl)-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3I):

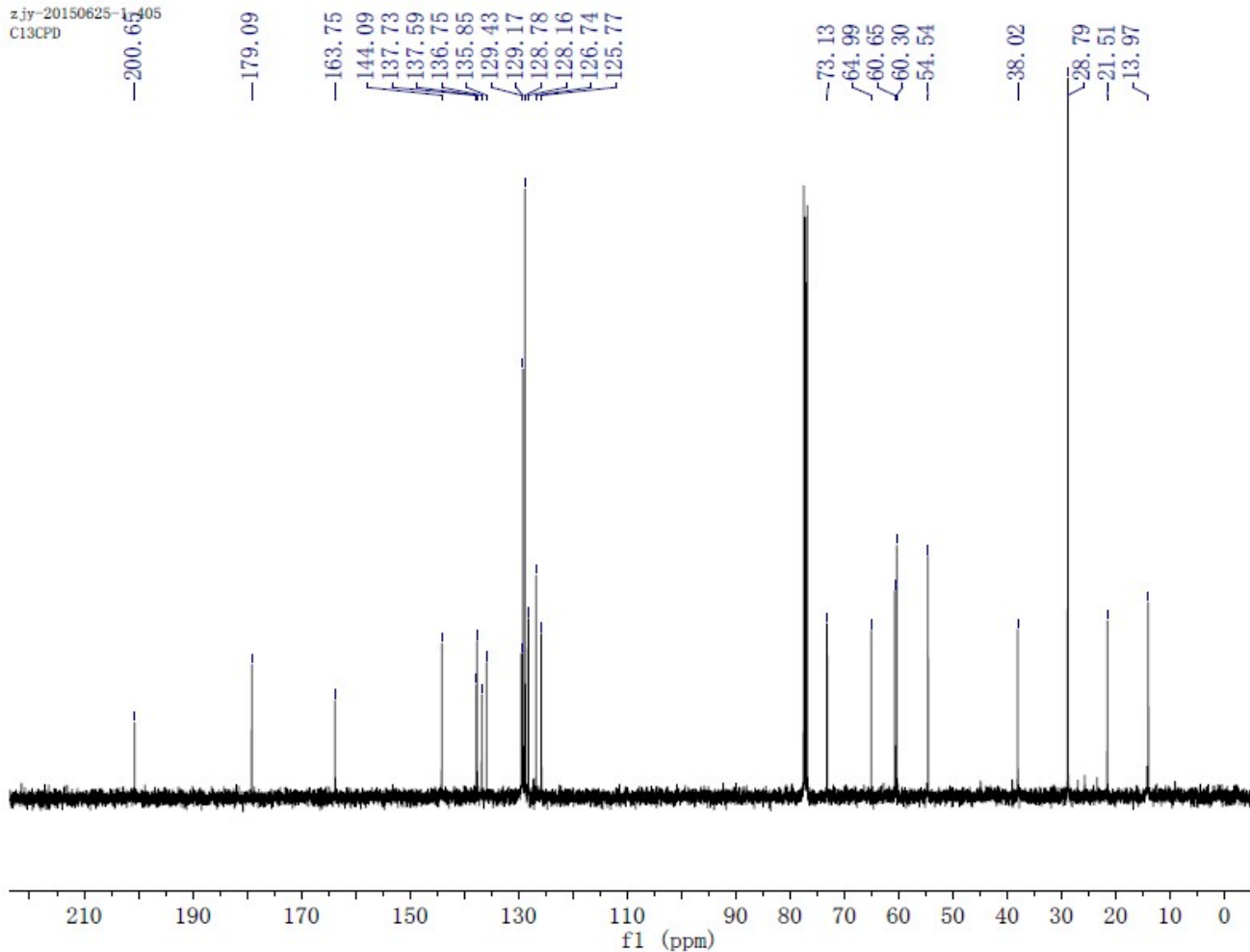


Yellow oil (41.9 mg, 85% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.29 (dd, $J = 9.5, 5.5$ Hz, 2H), 7.24-7.14 (m, 4H), 7.06 (d, $J = 7.5$ Hz, 1H), 6.79 (d, $J = 6.3$ Hz, 2H), 6.74 (t, $J = 2.2$ Hz, 1H), 4.73 (d, $J = 1.9$ Hz, 1H), 4.17-3.97 (m, 2H), 3.94-3.85 (m, 1H), 2.94 (dd, $J = 13.8, 8.3$ Hz, 2H), 2.30 (s, 3H), 1.61 (s, 9H), 1.06 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 200.7, 179.1, 163.8,

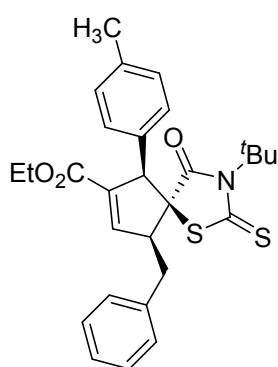
144.1, 137.7, 137.6, 136.8, 135.9, 129.4, 129.2, 128.8, 128.2, 126.7, 125.8, 73.1, 65.0, 60.7, 60.3, 54.5, 38.0, 28.8, 21.5, 14.0; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{32}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 494.1818, found 494.1823.



zjy-20150625-1305
C13CPD



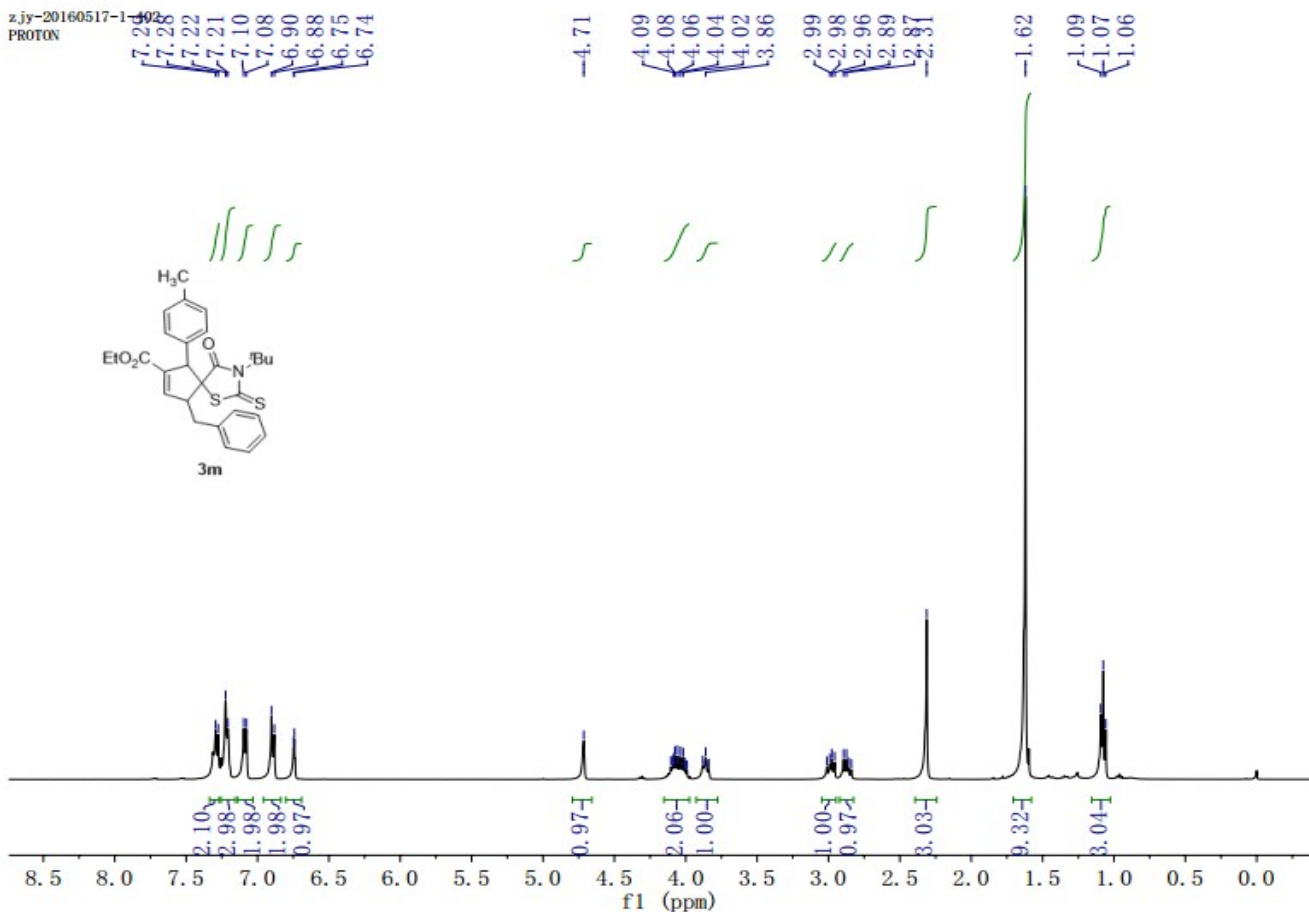
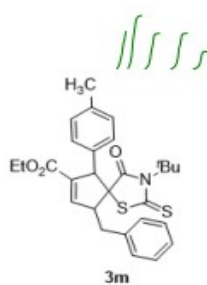
Ethyl 9-benzyl-3-(tert-butyl)-4-oxo-2-thioxo-6-(p-tolyl)-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3m):



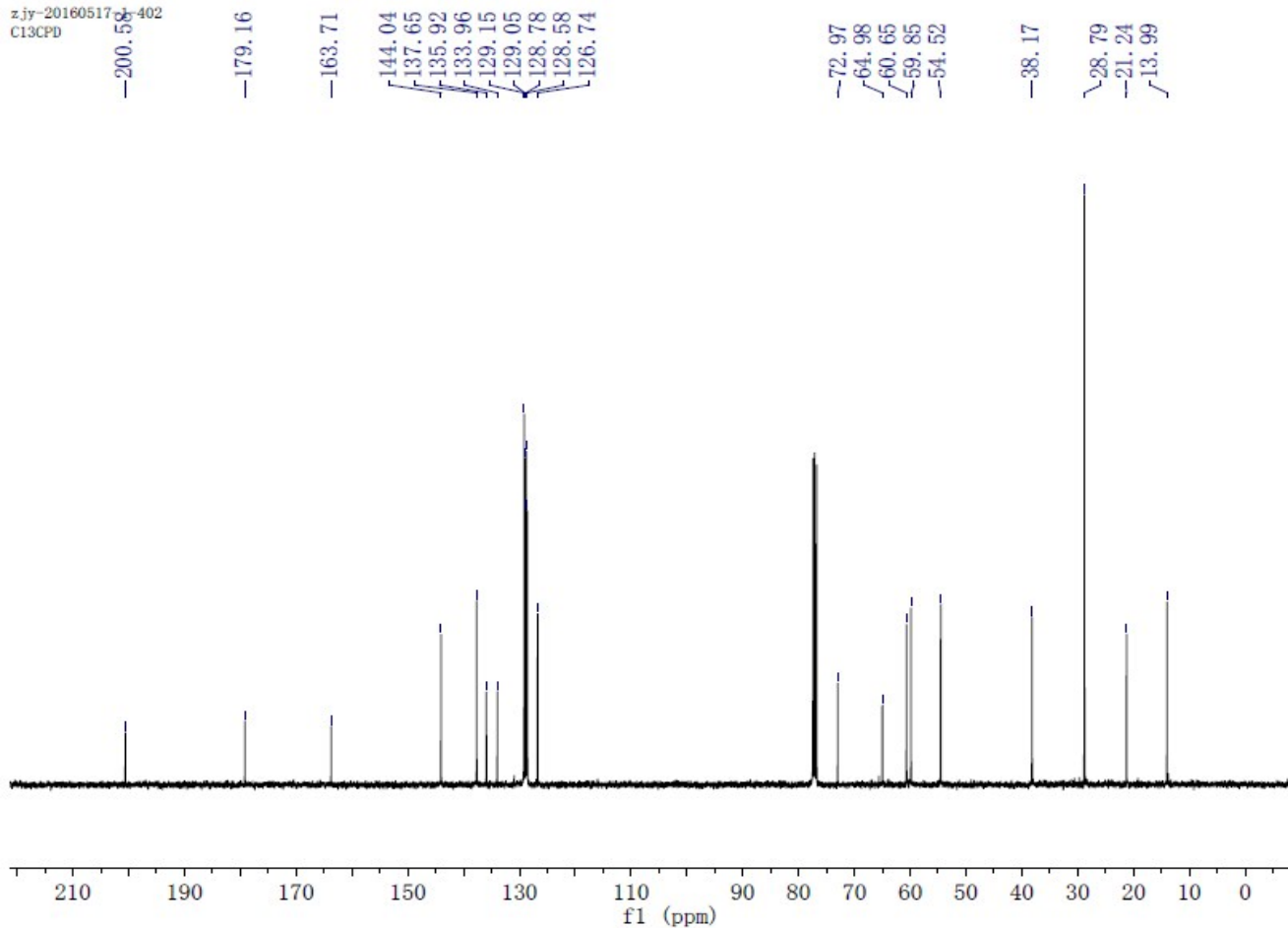
Yellow oil (42.9 mg, 87% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.28 (d, $J = 7.1$ Hz, 2H), 7.22 (d, $J = 6.1$ Hz, 3H), 7.09 (d, $J = 7.7$ Hz, 2H), 6.89 (d, $J = 7.9$ Hz, 2H), 6.74 (d, $J = 2.1$ Hz, 1H), 4.71 (s, 1H), 4.15-3.97 (m, 2H), 3.86 (dd, $J = 11.4, 5.0$ Hz, 1H), 2.98 (dd, $J = 13.6, 8.2$ Hz, 1H), 2.87 (dd, $J = 13.7, 8.5$ Hz, 1H), 2.31 (s, 3H), 1.62 (s, 9H), 1.07 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 200.6, 179.2, 163.7, 144.0, 137.7, 135.9, 134.0, 129.2, 129.1, 128.8,

128.6, 126.7, 73.0, 65.0, 60.7, 59.9, 54.5, 38.2, 28.8, 21.2, 14.0; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{32}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 494.1818, found 494.1820.

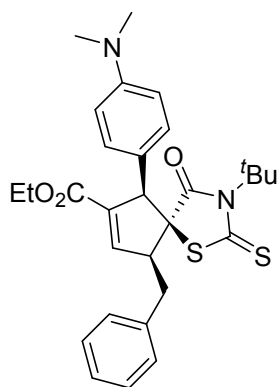
zjy-20160517-1-402
PROTON



zjy-20160517-1-402
C13CPD

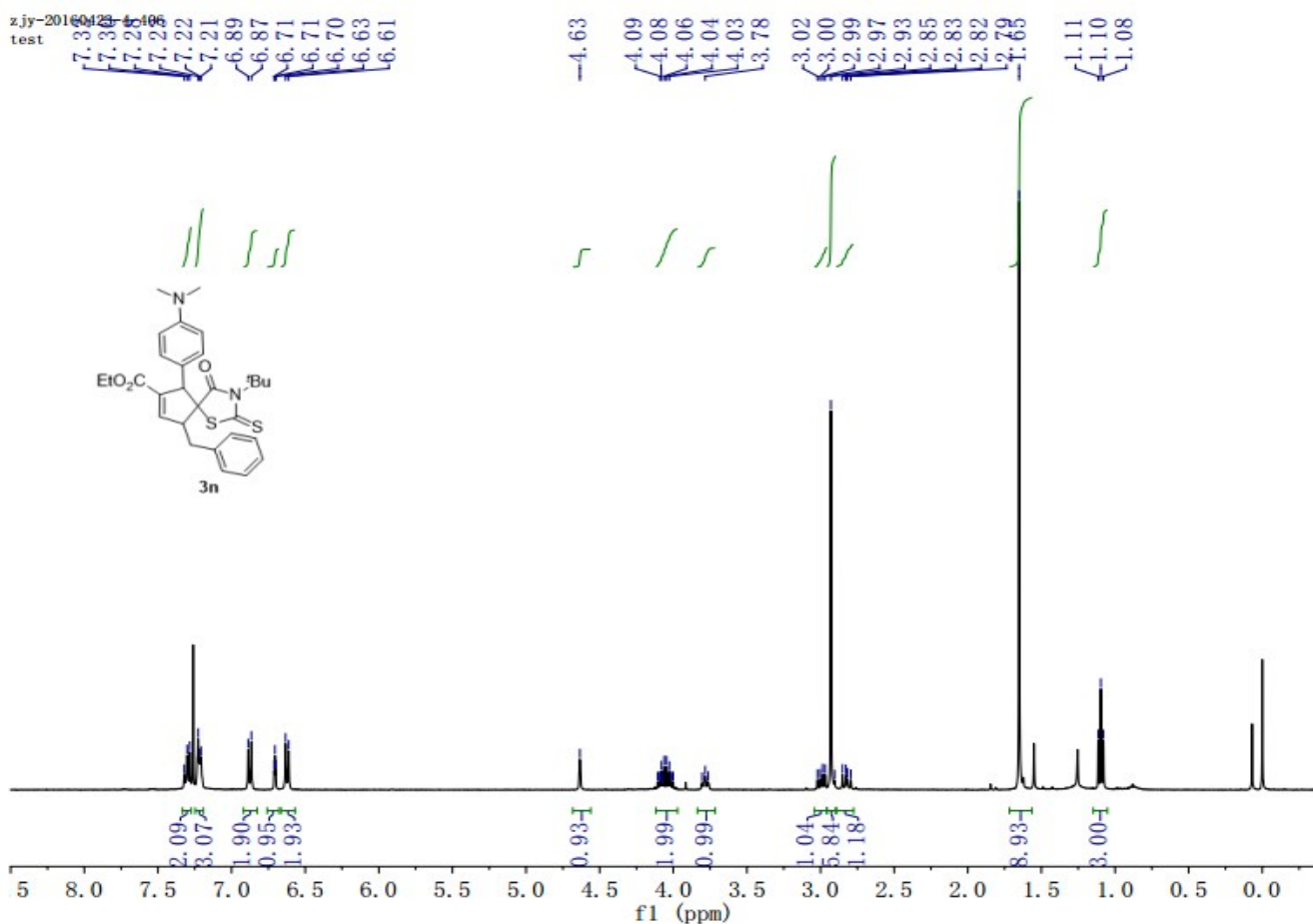


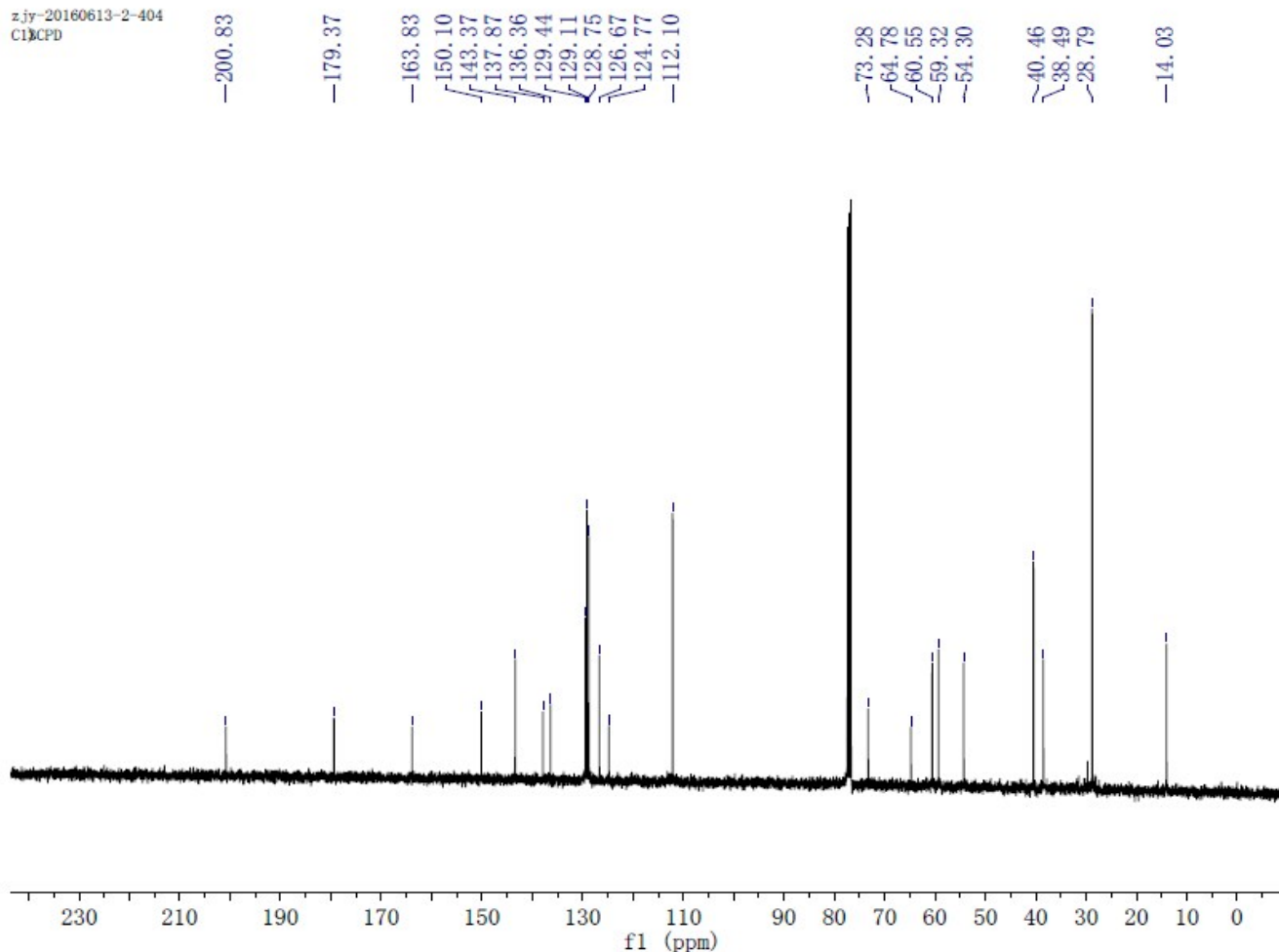
Ethyl 9-benzyl-3-(tert-butyl)-6-(4-(dimethylamino)phenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro-[4.4]-non-7-ene-7-carboxylate (3n):



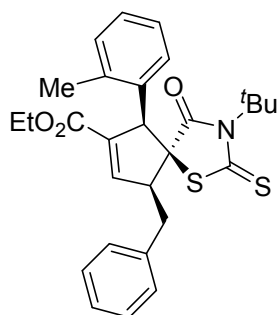
Yellow oil (42.9 mg, 82% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.27 (m, 2H), 7.25-7.19 (m, 3H), 6.88 (d, $J = 8.6$ Hz, 2H), 6.71 (t, $J = 2.2$ Hz, 1H), 6.62 (d, $J = 8.6$ Hz, 2H), 4.63 (s, 1H), 4.12-3.97 (m, 2H), 3.78 (t, $J = 8.3$ Hz, 1H), 2.99 (dd, $J = 13.6, 7.7$ Hz, 1H), 2.92 (d, $J = 10.1$ Hz, 6H), 2.82 (dd, $J = 13.6, 9.0$ Hz, 1H), 1.65 (s, 9H), 1.10 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 200.8, 179.4, 157.0, 150.1, 143.4, 137.9, 136.4, 129.4, 129.1, 128.8,

126.7, 124.8, 112.1, 73.3, 64.8, 60.6, 59.3, 54.3, 40.5, 38.5, 28.8, 14.0; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{35}\text{N}_2\text{O}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 523.2084, found 523.2090.

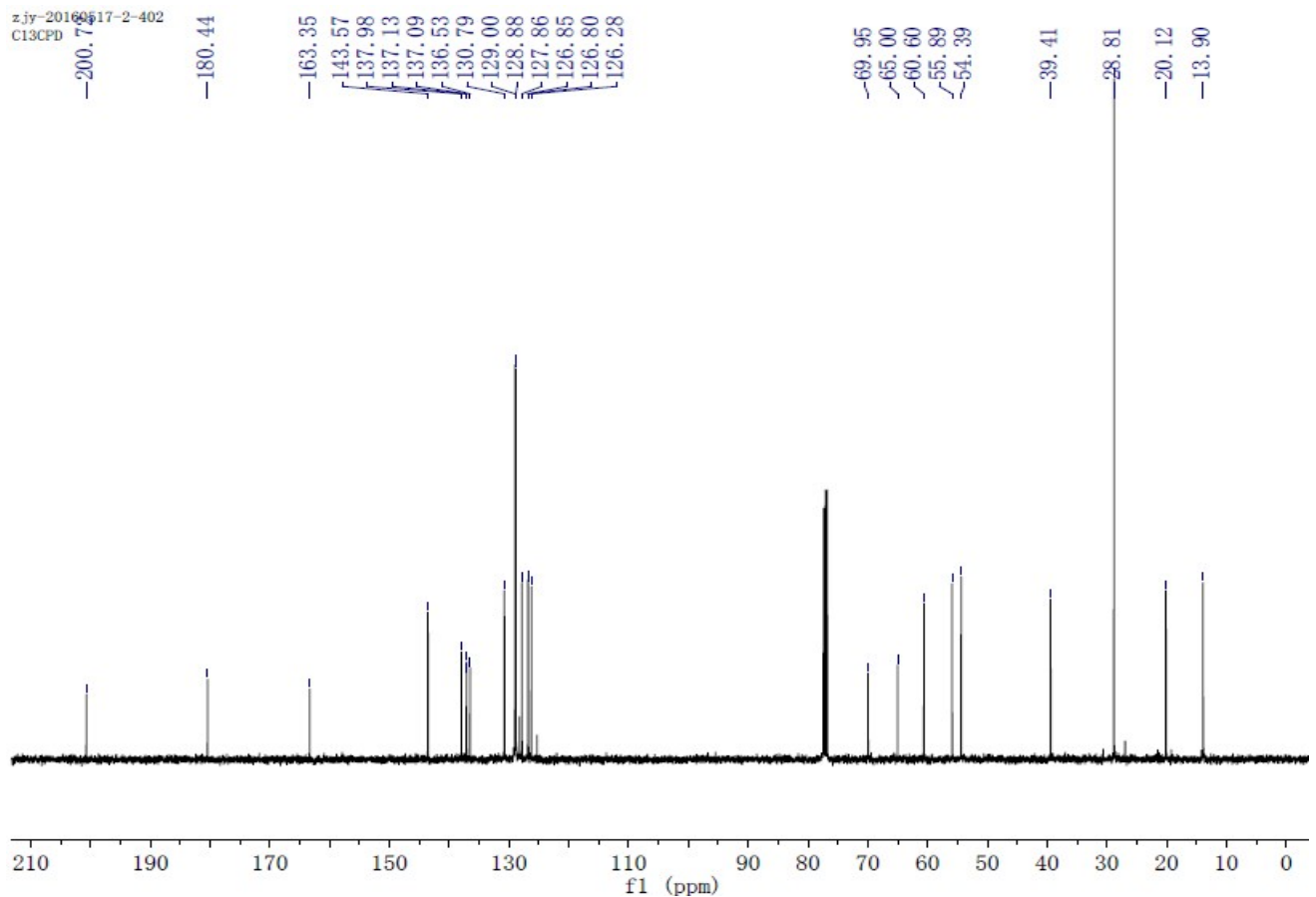
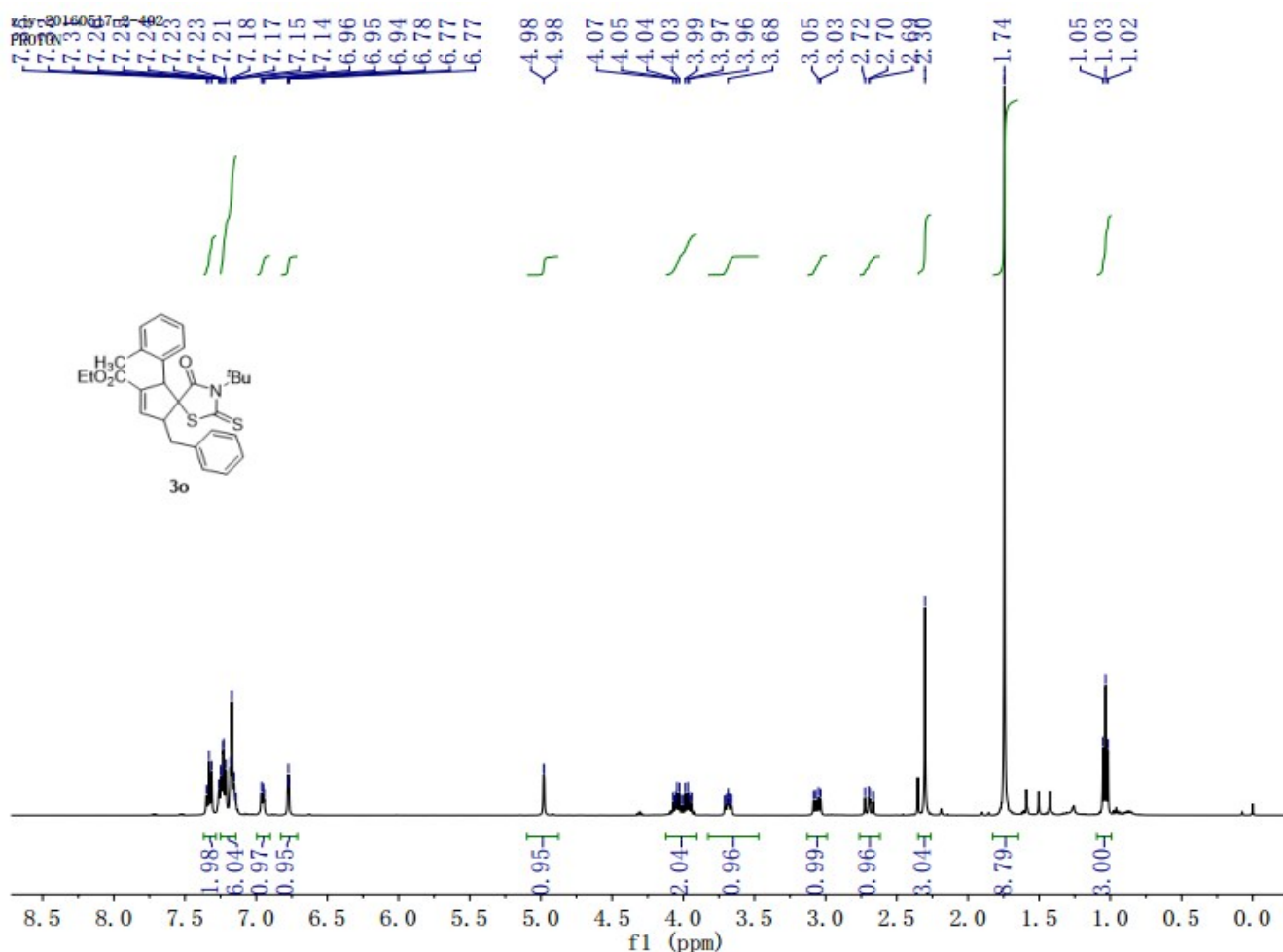




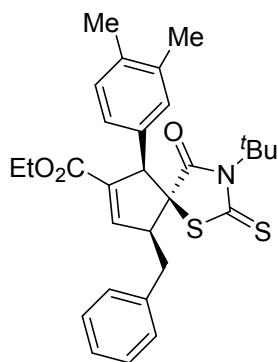
Ethyl 9-benzyl-3-(tert-butyl)-4-oxo-2-thioxo-6-(o-tolyl)-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (30):



Yellow oil (43.9 mg, 89% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.21 (dd, *J* = 8.5, 4.3 Hz, 6H), 6.99-6.90 (m, 1H), 6.83-6.71 (m, 1H), 4.98 (d, *J* = 1.1 Hz, 1H), 4.12-3.91 (m, 2H), 3.83-3.47 (m, 1H), 3.06 (dd, *J* = 13.4, 6.6 Hz, 1H), 2.69 (dd, *J* = 13.4, 10.4 Hz, 1H), 2.30 (s, 3H), 1.74 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 200.7, 180.4, 163.4, 143.6, 138.0, 137.1, 137.1, 136.5, 130.8, 129.0, 128.9, 127.9, 126.9, 126.8, 126.3, 70.0, 65.0, 60.6, 55.9, 54.4, 39.4, 28.8, 20.1, 13.9; HRMS (ESI): *m/z* calcd for C₂₈H₃₂NO₃S₂ [M+H]⁺: 494.1818, found 494.1819.

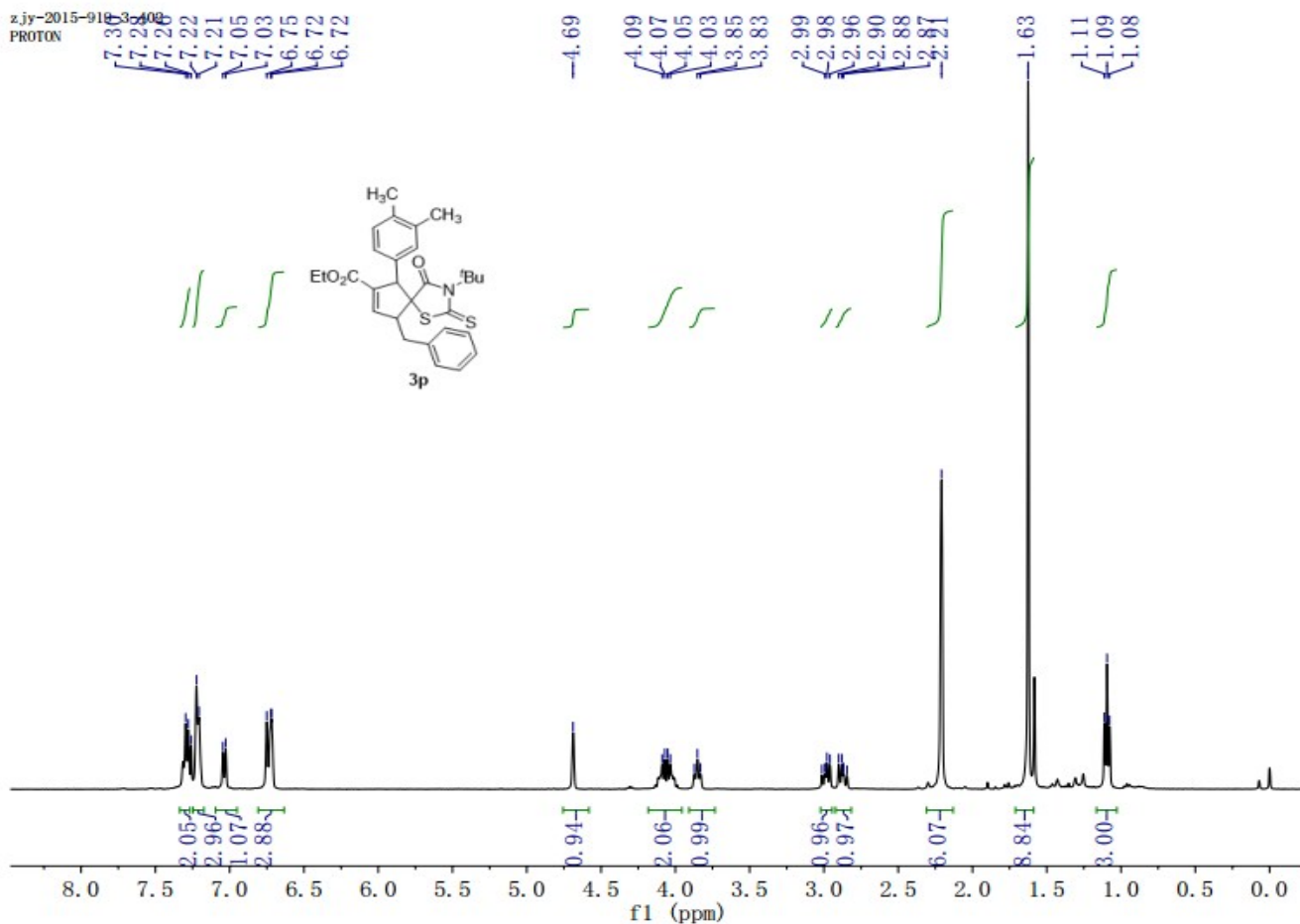


Ethyl 9-benzyl-3-(tert-butyl)-6-(3,4-dimethylphenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3p):

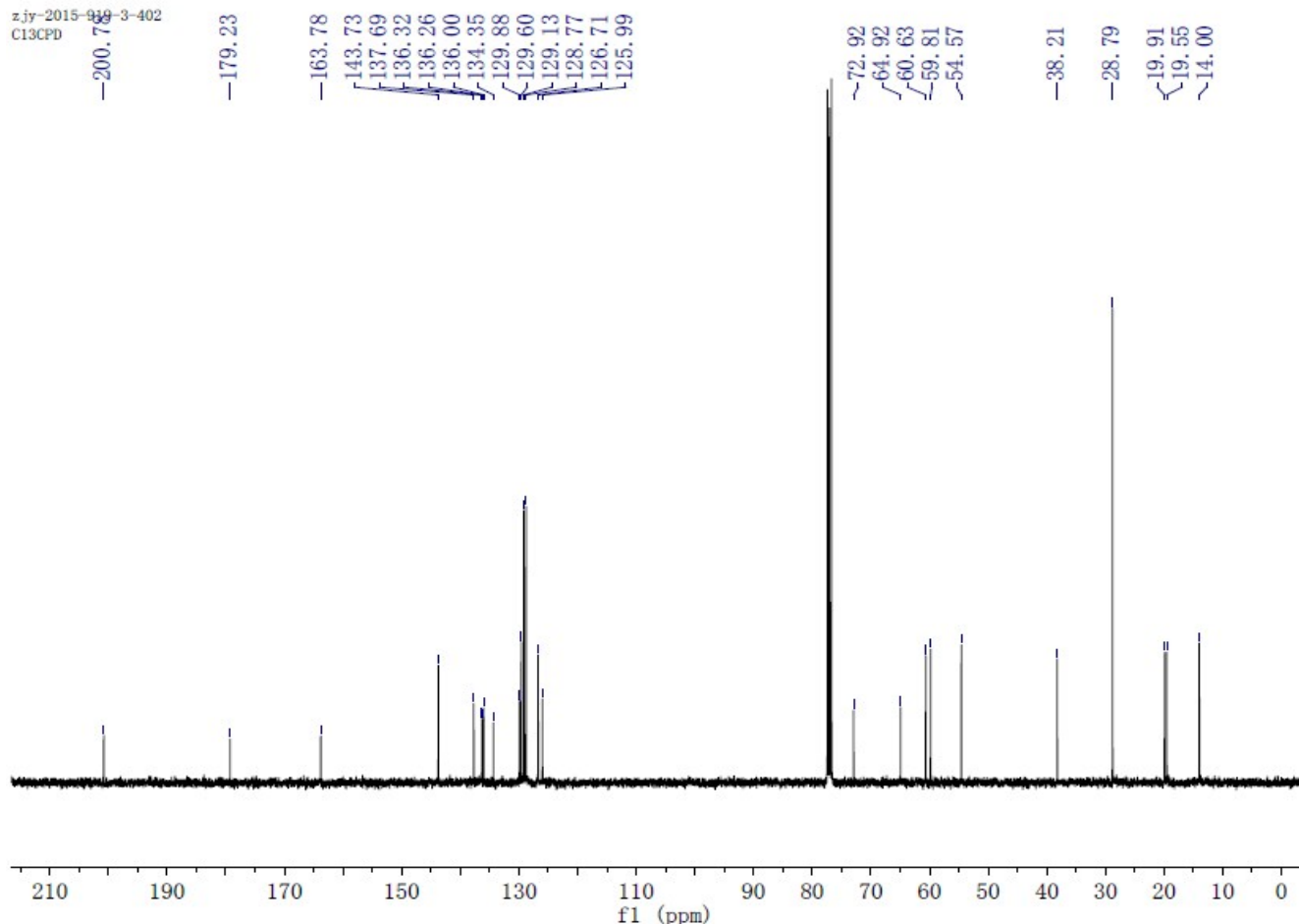


Yellow oil (43.7 mg, 86% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.29 (d, $J = 7.0$ Hz, 2H), 7.22 (d, $J = 6.9$ Hz, 3H), 7.04 (d, $J = 7.6$ Hz, 1H), 6.81-6.63 (m, 3H), 4.69 (s, 1H), 4.00-4.10 (m, 2H), 3.85 (t, $J = 8.1$ Hz, 1H), 2.99 (dd, $J = 13.6$, 8.1 Hz, 1H), 2.87 (dd, $J = 13.6$, 8.7 Hz, 1H), 2.21 (s, 6H), 1.63 (s, 9H), 1.09 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 200.8, 179.2, 163.8, 143.7, 137.7, 136.3, 136.3, 136.0, 134.4, 129.9, 129.6, 129.1, 128.8, 126.7, 126.0, 72.9,

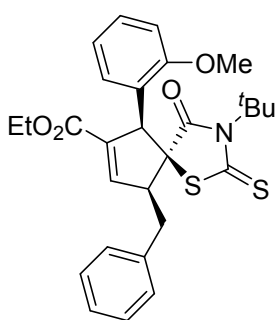
64.9, 60.6, 59.8, 54.6, 38.2, 28.8, 19.9, 19.6, 14.0; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{34}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 508.1975, found 508.1981.



z.jy-2015-03-3-402
C13CPD

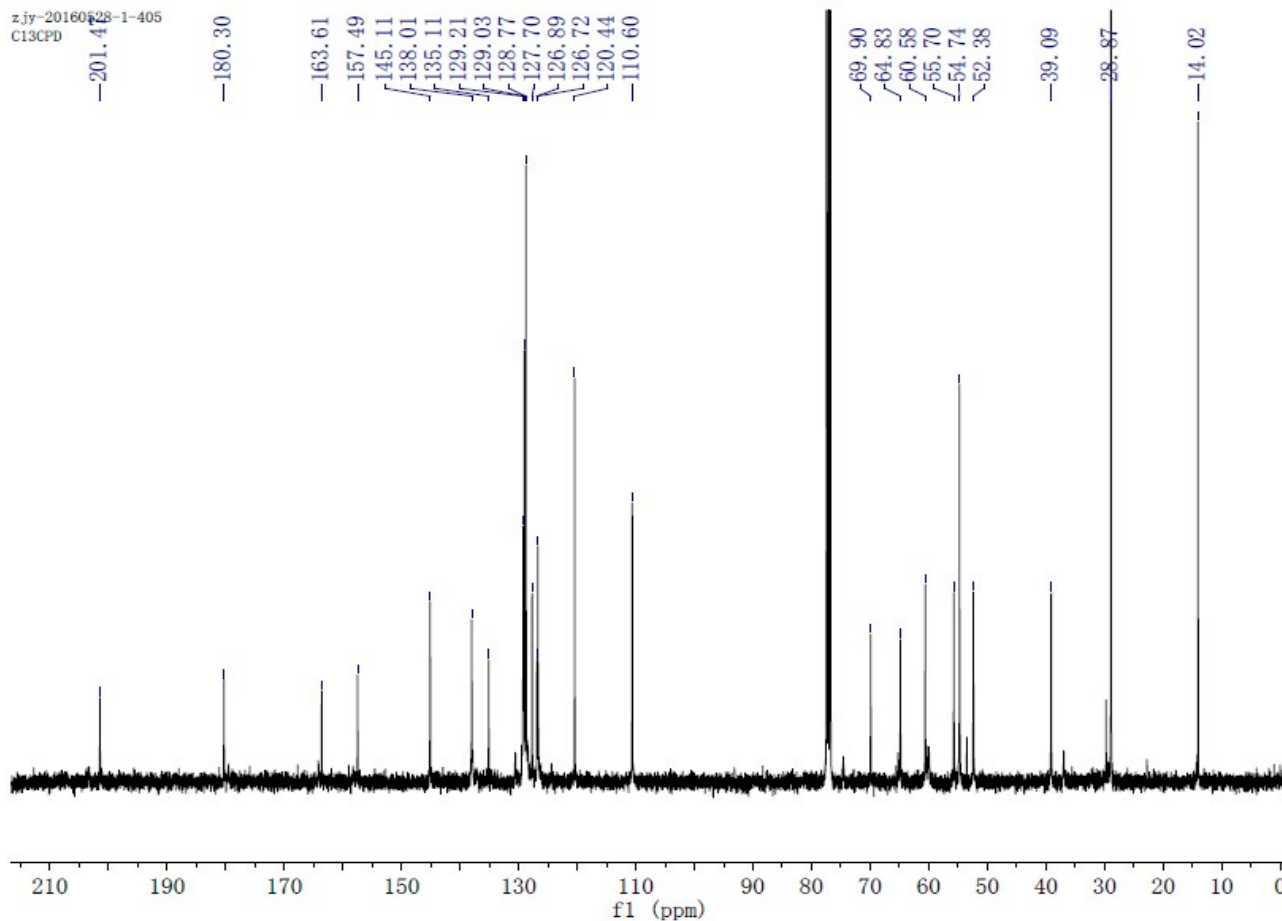
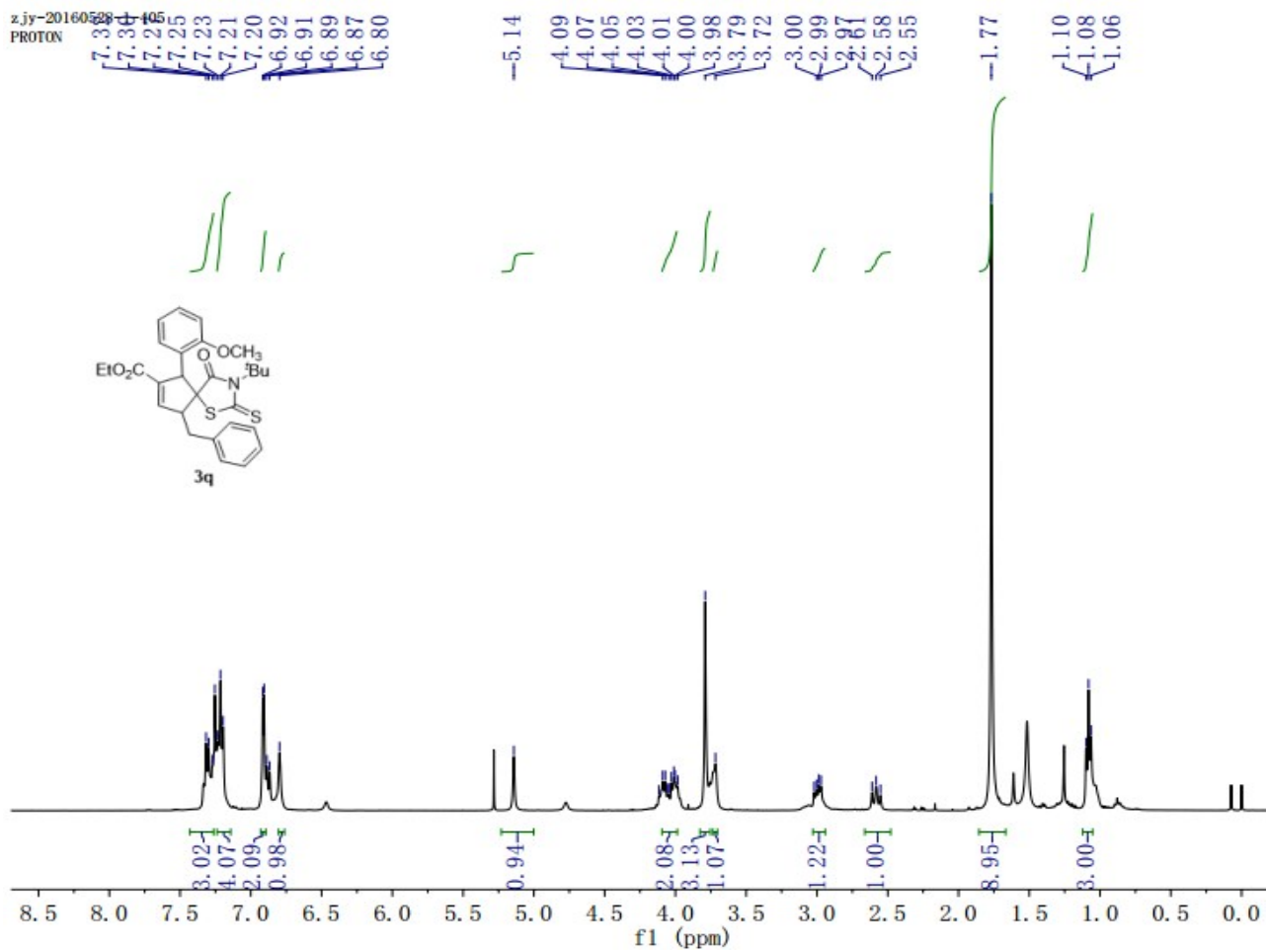


Ethyl 9-benzyl-3-(tert-butyl)-6-(2-methoxyphenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3q):

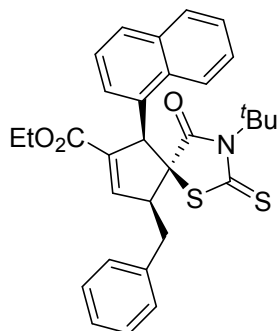


Yellow oil (42.8 mg, 84% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.43-7.26 (m, 3H), 7.21 (t, $J = 7.4$ Hz, 4H), 6.91 (d, $J = 3.8$ Hz, 2H), 6.80 (s, 1H), 5.14 (s, 1H), 4.09-3.99 (m, 2H), 3.79 (s, 3H), 3.72 (s, 1H), 3.00 (dd, $J = 13.1, 6.4$ Hz, 1H), 2.66-2.48 (m, 1H), 1.77 (s, 9H), 1.08 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 201.5, 180.3, 163.6, 157.5, 145.1, 138.0, 135.1, 129.2, 129.0, 128.8,

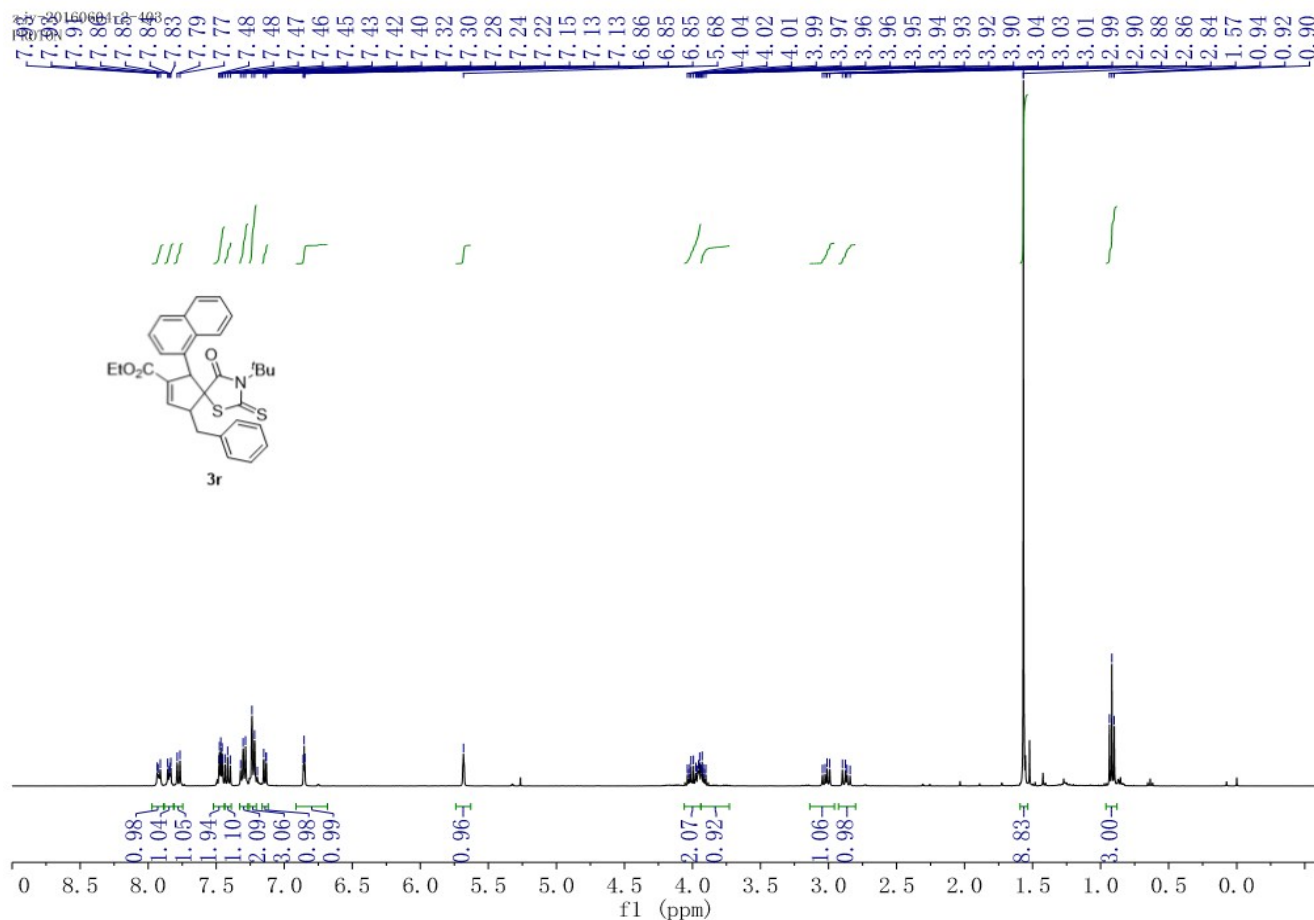
127.7, 126.9, 126.7, 120.4, 110.6, 69.9, 64.8, 60.6, 55.7, 54.7, 52.4, 39.1, 28.9, 14.0; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{32}\text{NO}_4\text{S}_2$ $[\text{M}+\text{H}]^+$: 510.1767, found 510.1771.



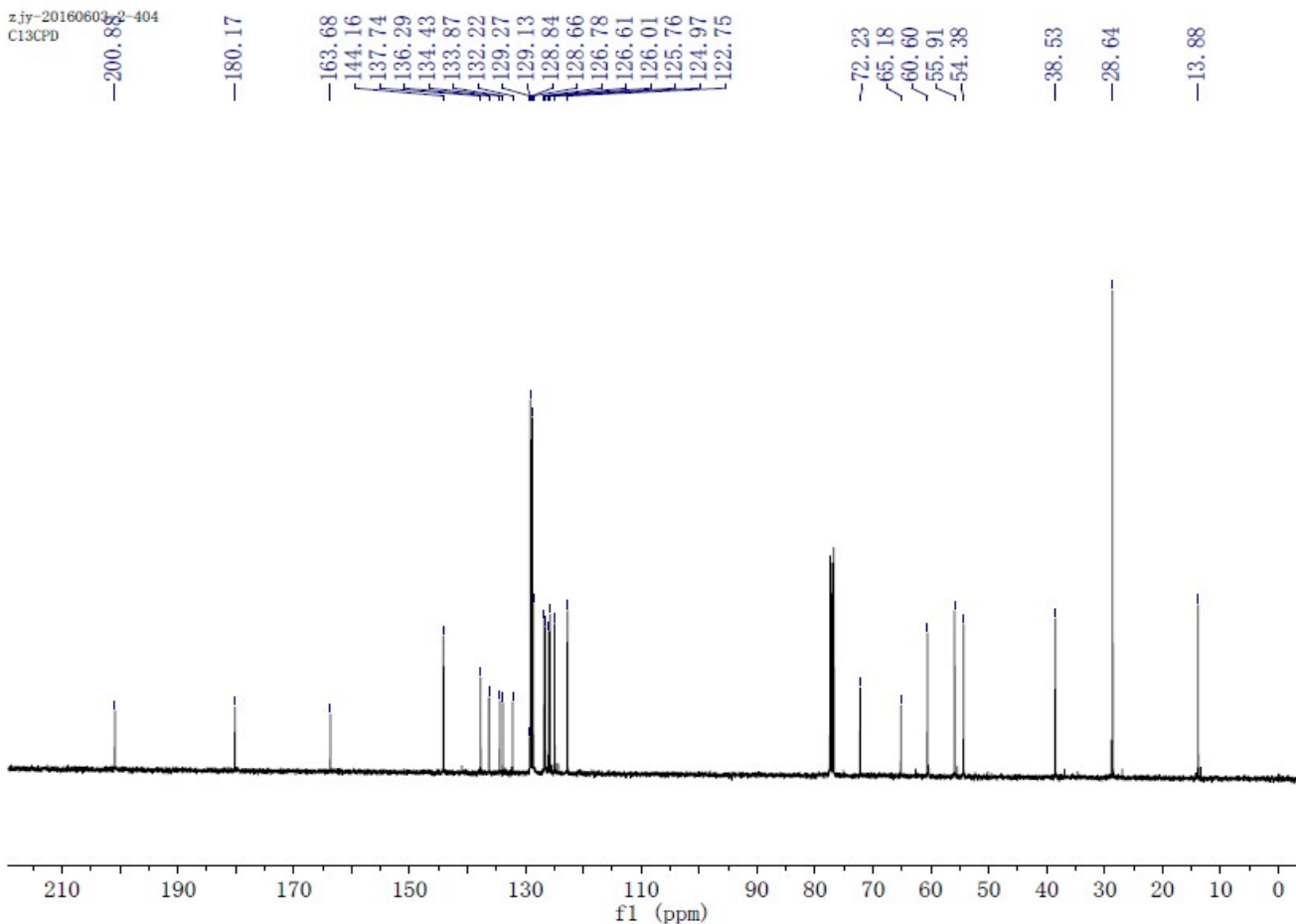
Ethyl 9-benzyl-3-(tert-butyl)-6-(naphthalen-1-yl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3r):



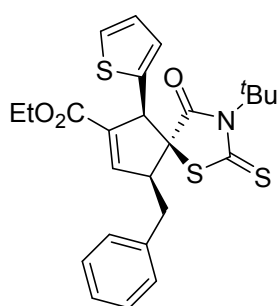
Yellow oil (46.1 mg, 87% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.89 (m, 1H), 7.84 (dd, *J* = 5.9, 3.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.52-7.44 (m, 2H), 7.44-7.39 (m, 1H), 7.33-7.27 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 3H), 7.16-7.12 (m, 1H), 6.85 (t, *J* = 2.3 Hz, 1H), 5.68 (s, 1H), 4.06-3.94 (m, 2H), 3.94-3.73 (m, 1H), 3.02 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.87 (dd, *J* = 13.7, 8.9 Hz, 1H), 1.57 (s, 9H), 0.92 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 200.9, 180.2, 163.7, 144.2, 137.7, 136.3, 134.4, 133.9, 132.2, 129.3, 129.1, 128.8, 128.7, 126.8, 126.6, 126.0, 125.8, 125.0, 122.8, 72.2, 65.2, 60.6, 55.9, 54.4, 38.5, 28.6, 13.9; HRMS (ESI): *m/z* calcd for C₃₁H₃₂NO₃S₂ [M+H]⁺: 530.1818, found 530.1818.



zjy-20160603-2-404
C13CPD



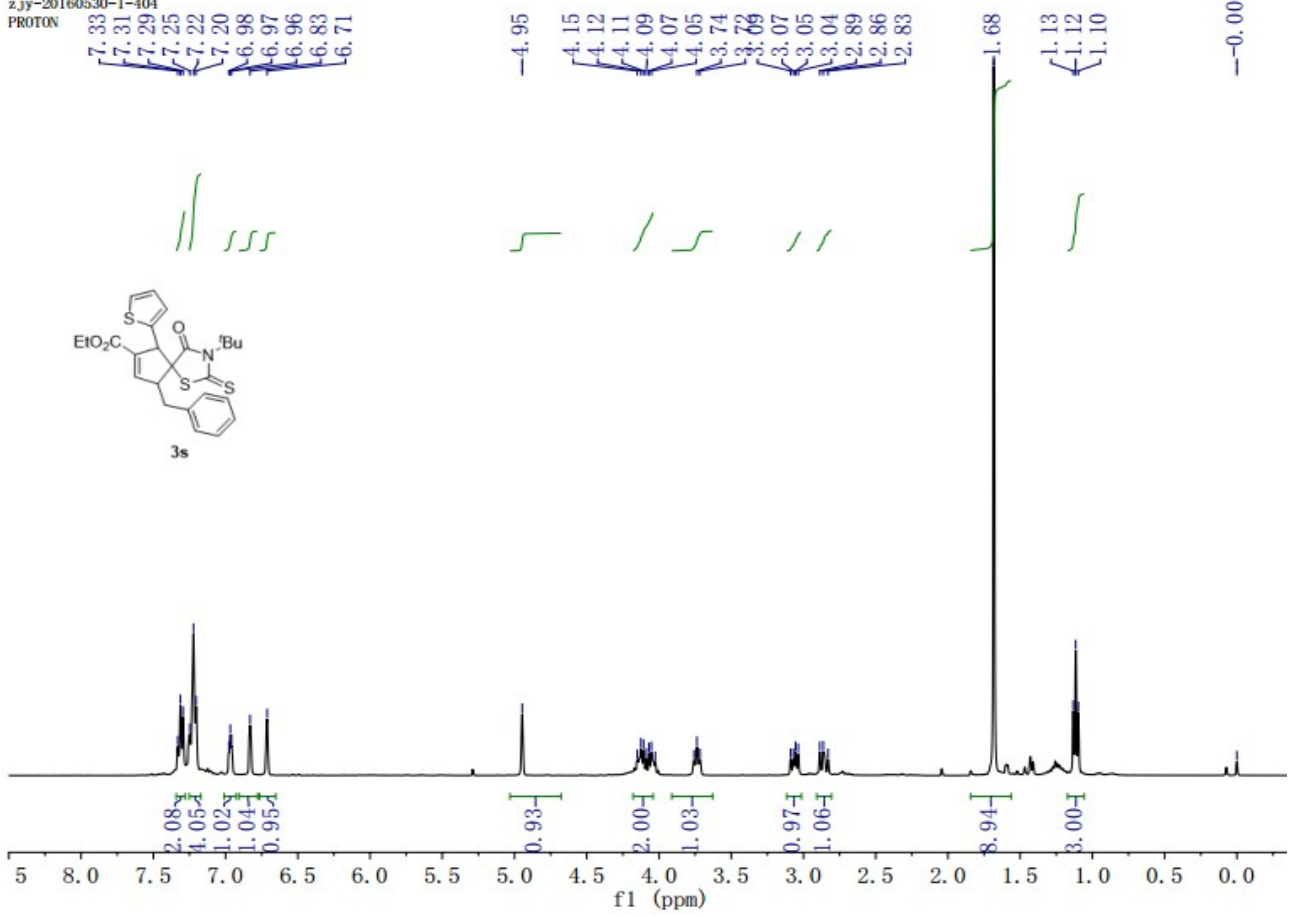
Ethyl 9-benzyl-3-(tert-butyl)-4-oxo-6-(thiophen-2-yl)-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3s):



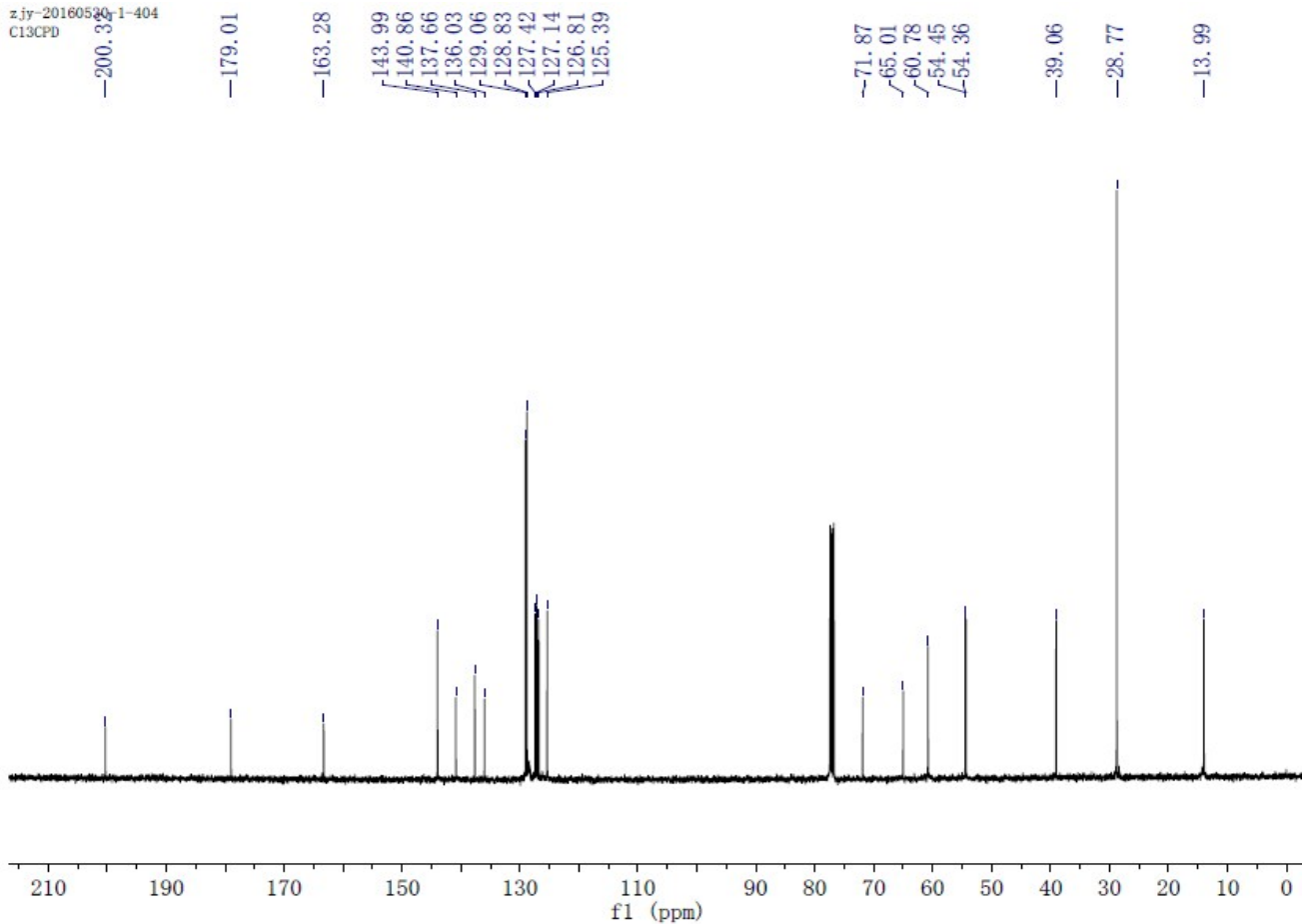
Yellow oil (48.1 mg, 99% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.31 (t, $J = 7.2$ Hz, 2H), 7.22 (t, $J = 8.6$ Hz, 4H), 6.97 (t, $J = 3.5$ Hz, 1H), 6.83 (s, 1H), 6.71 (s, 1H), 4.95 (s, 1H), 4.18-4.04 (m, 2H), 3.74 (t, $J = 8.3$ Hz, 1H), 3.06 (dd, $J = 13.4, 7.5$ Hz, 1H), 2.91-2.81 (m, 1H), 1.68 (s, 9H), 1.12 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 200.3, 179.0, 163.3, 144.0, 140.9, 137.7, 136.0,

129.1, 128.8, 127.4, 127.1, 126.8, 125.4, 71.9, 65.0, 60.8, 54.5, 54.4, 39.1, 28.8, 14.0; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{28}\text{NO}_3\text{S}_3$ $[\text{M}+\text{H}]^+$: 486.1226, found 486.1224.

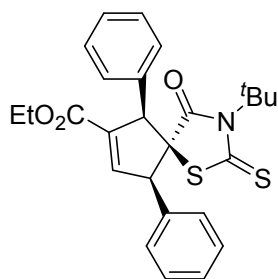
zjy-20160530-1-404
PROTON



zjy-20160530-1-404
C13CPD

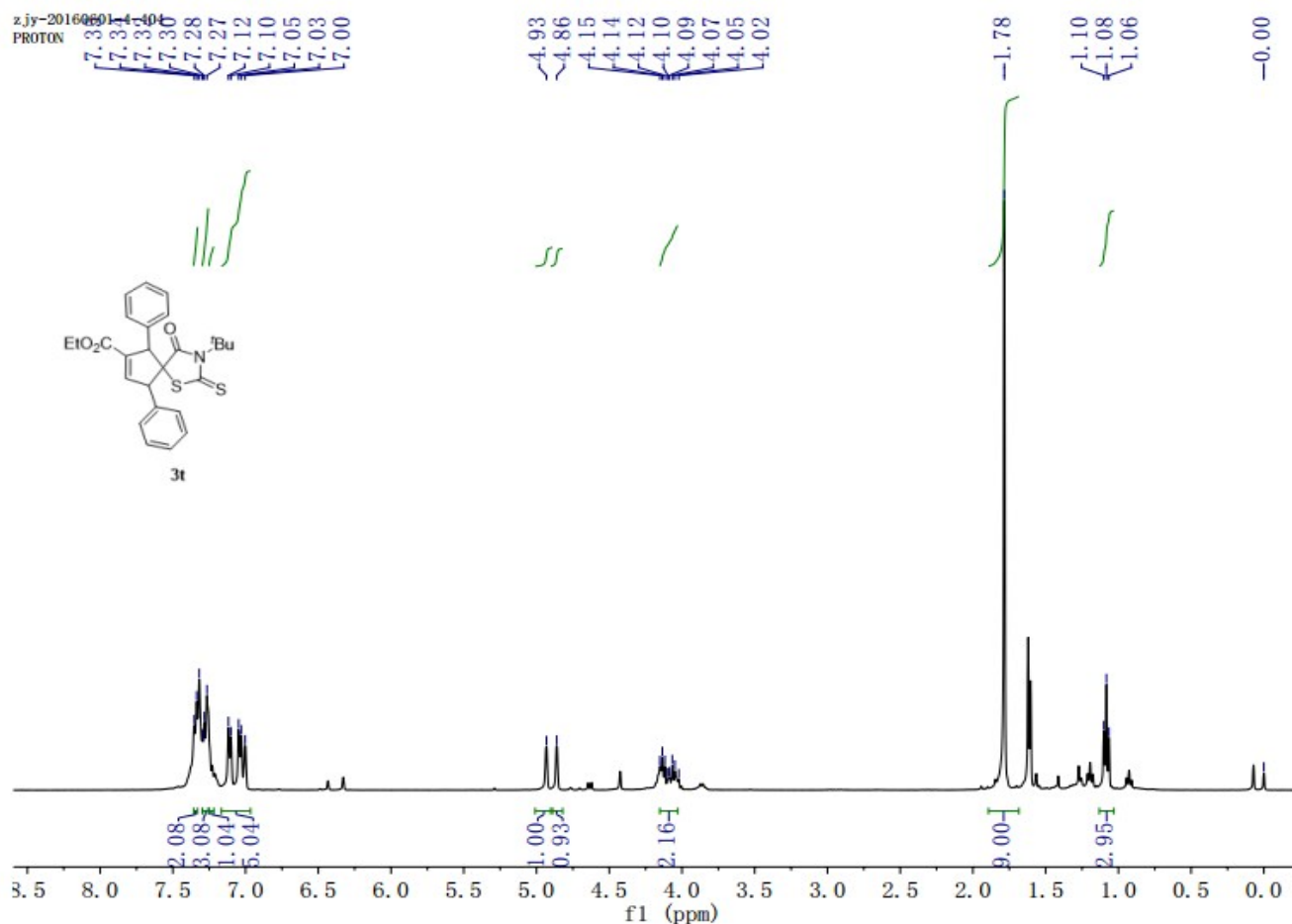


Ethyl 3-(tert-butyl)-4-oxo-6,9-diphenyl-2-thioxo-1-thia-3-azaspiro [4.4]non-7-ene-7-carboxylate (3t):

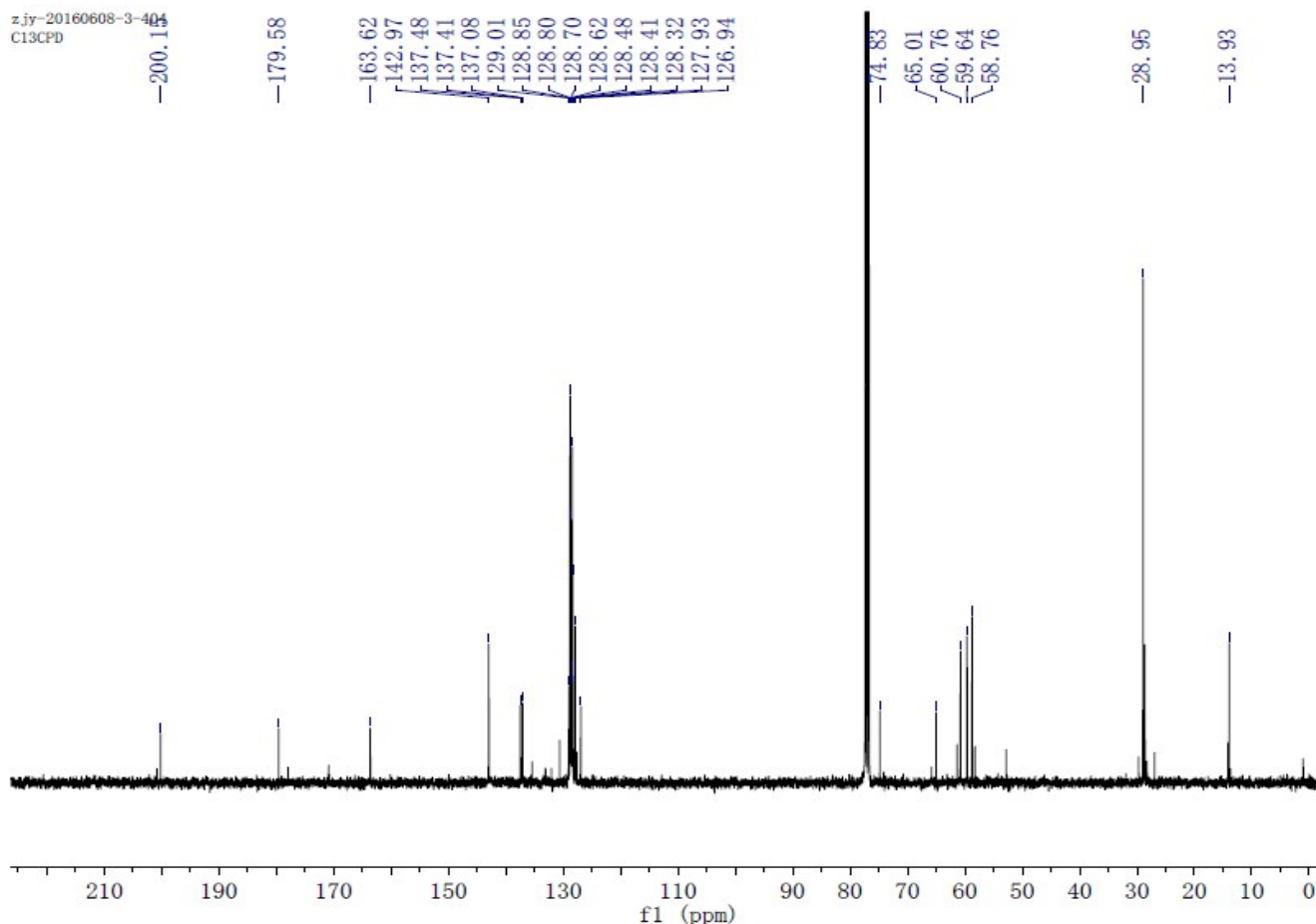


Yellow oil (42.4 mg, 91% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.34 (d, $J=7.0$ Hz, 2H), 7.27 (d, $J=7.0$ Hz, 3H), 7.23 (s, 1H), 7.17-6.97 (m, 5H), 4.93 (s, 1H), 4.86 (s, 1H), 4.15-4.03 (m, 2H), 1.78 (s, 9H), 1.08 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 200.2, 179.6, 163.6, 143.0, 137.5, 137.4, 137.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 126.9, 74.8, 65.0, 60.8,

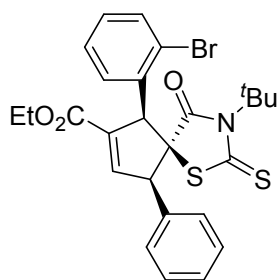
59.6, 58.8, 29.0, 13.9; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 466.1505, found 466.1502.



zjy-20160608-3-404
C13CPD

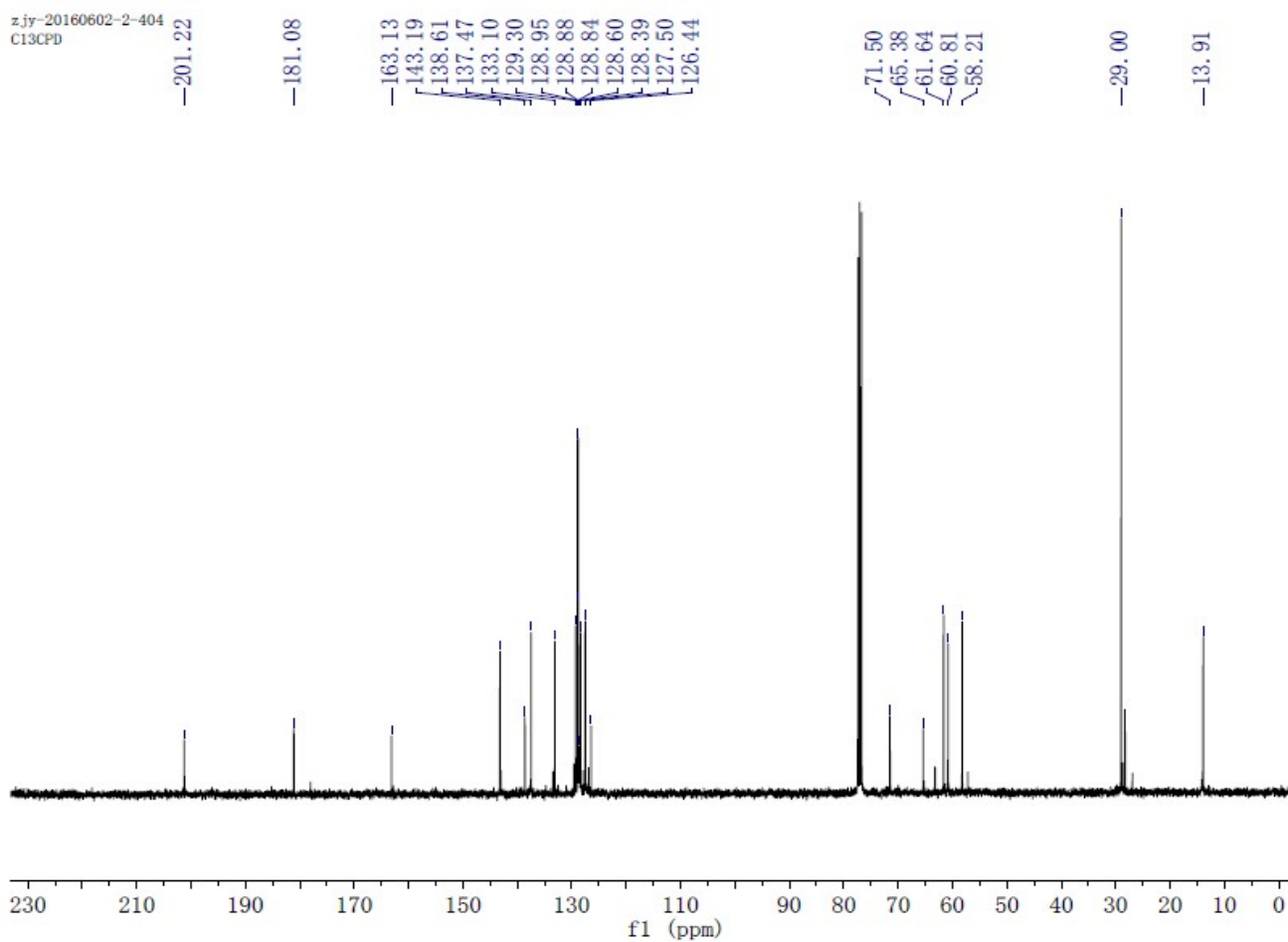
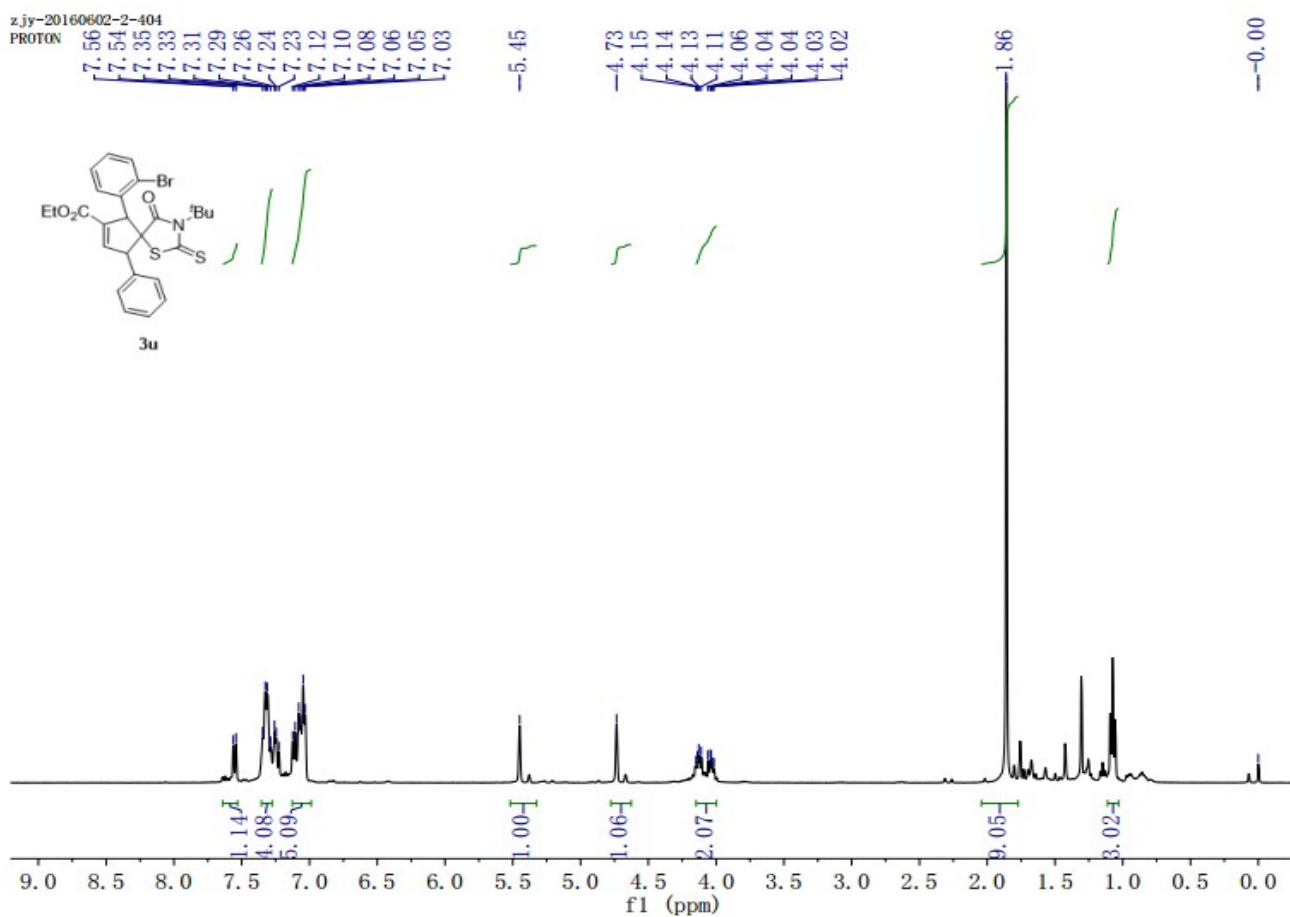


Ethyl 6-(2-bromophenyl)-3-(tert-butyl)-4-oxo-9-phenyl-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3u):

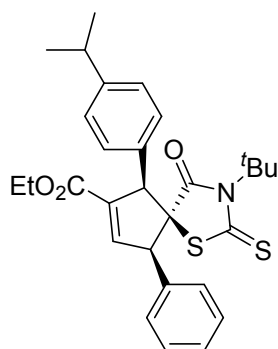


Yellow oil (50.6 mg, 93% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.55 (d, $J = 7.9$ Hz, 1H), 7.32 (dd, $J = 14.5, 8.6$ Hz, 4H), 7.13-6.99 (m, 5H), 5.45 (s, 1H), 4.73 (s, 1H), 4.17-4.00 (m, 2H), 1.86 (s, 9H), 1.07 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 201.2, 181.1, 163.1, 143.2, 138.6, 137.5, 133.1, 129.3, 129.0, 128.9, 128.8, 128.6, 128.4, 127.5, 126.4, 71.5, 65.4, 61.6, 60.8, 58.2,

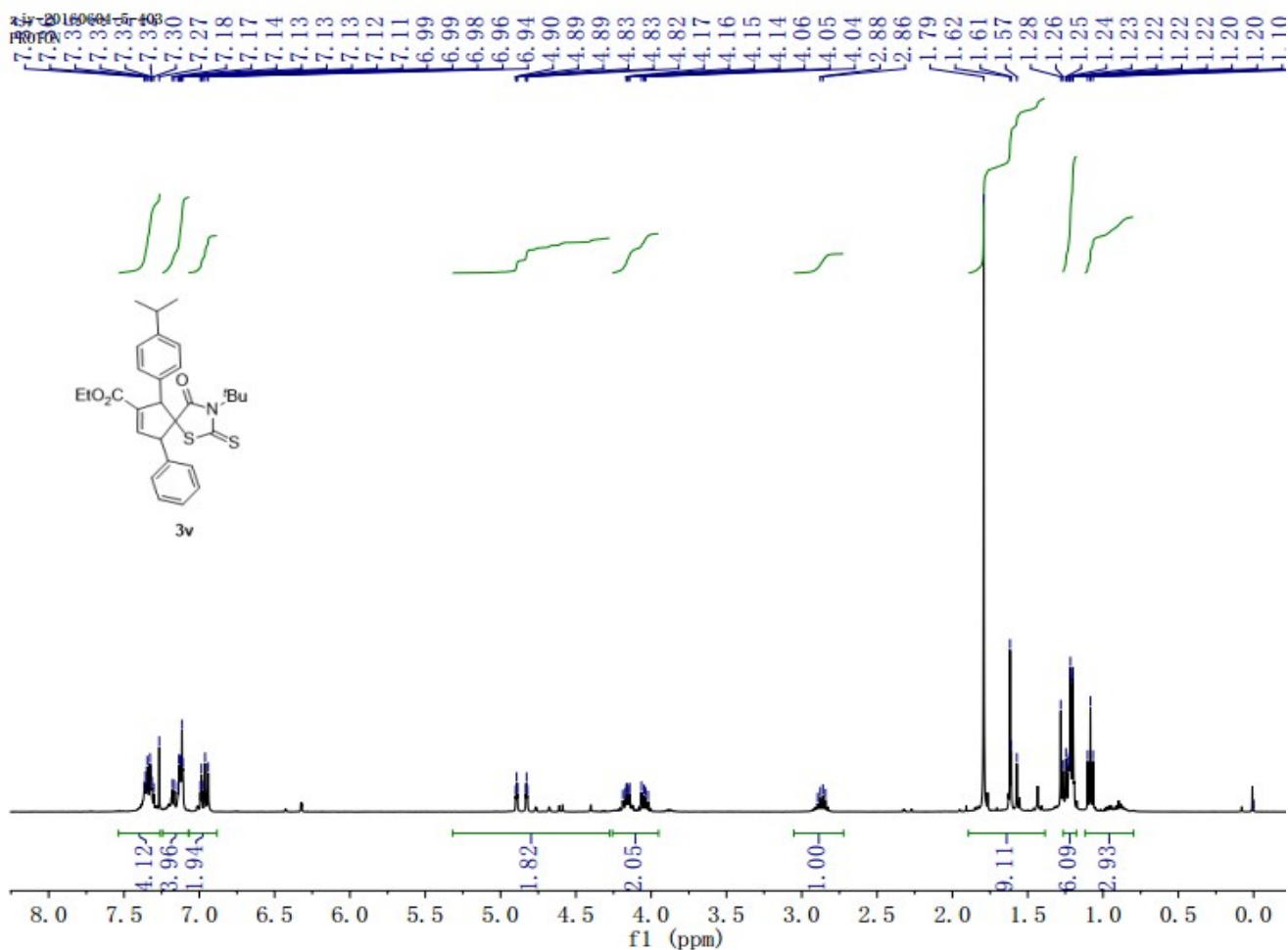
29.0, 13.9; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{27}\text{BrNO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 544.0610, found 544.0646.

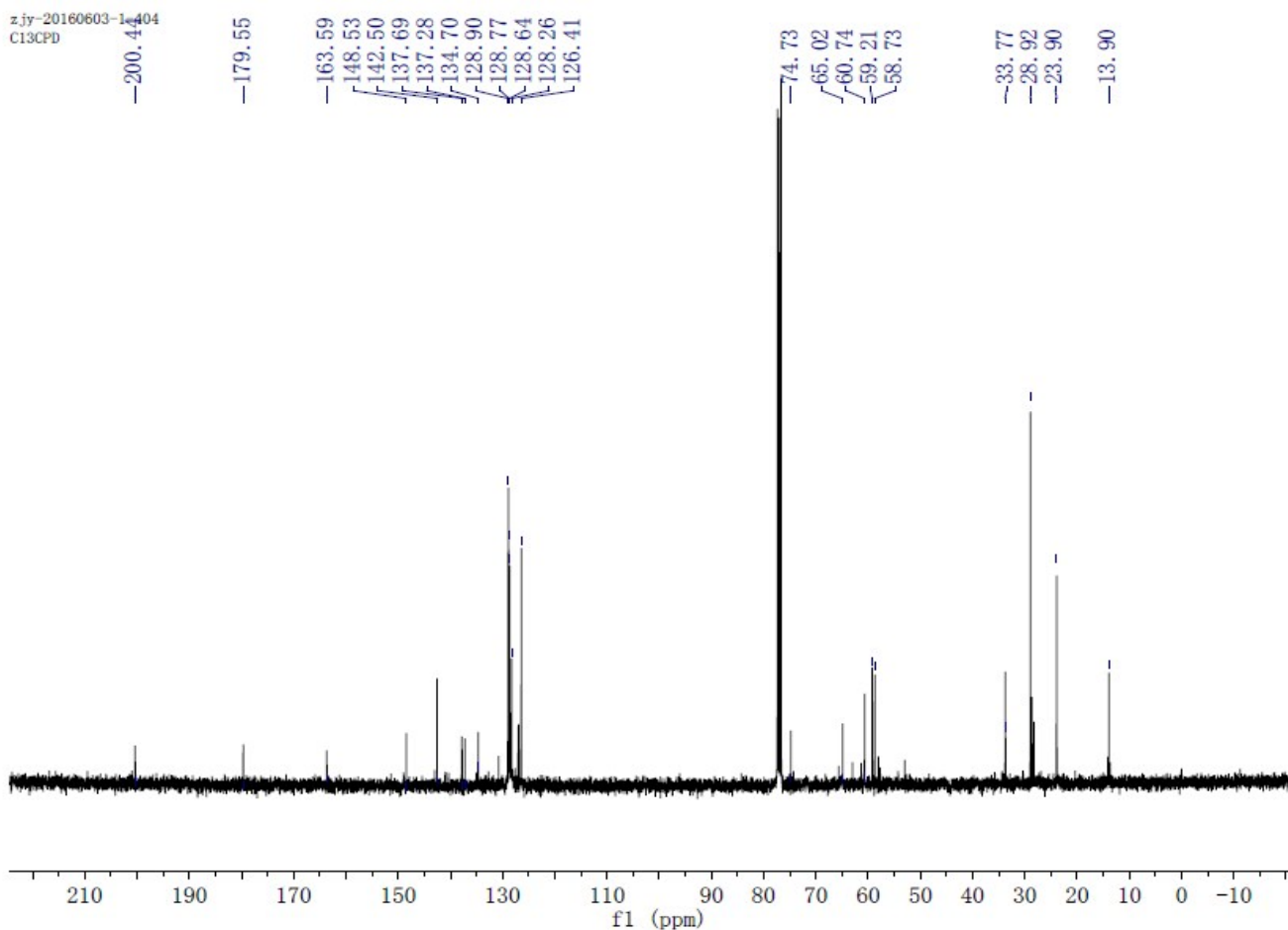


Ethyl 3-(tert-butyl)-6-(4-isopropylphenyl)-4-oxo-9-phenyl-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (3v):



Yellow oil (41.1 mg, 81% yield); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.33 (ddd, $J = 15.1, 14.1, 9.1$ Hz, 4H), 7.14 (ddd, $J = 15.0, 8.0, 3.3$ Hz, 4H), 7.07-6.88 (m, 2H), 4.89 (t, $J = 2.2$ Hz, 1H), 4.83 (t, $J = 2.1$ Hz, 1H), 4.26-3.95 (m, 2H), 2.87 (dd, $J = 14.0, 7.0$ Hz, 1H), 1.89-1.39 (m, 9H), 1.22 (ddd, $J = 7.6, 7.0, 1.1$ Hz, 6H), 1.08 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 200.4, 179.6, 163.6, 148.5, 142.5, 137.7, 137.3, 134.7, 128.9, 128.8, 128.6, 128.3, 127.6, 127.0, 126.4, 74.7, 65.0, 60.7, 59.2, 58.7, 33.8, 28.9, 23.9, 13.9; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{34}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 508.1975, found 508.1982.

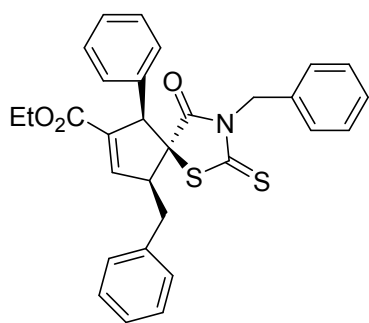




General procedure for one-pot sequential [3+2]/[3+2] cycloaddition for products **7**:

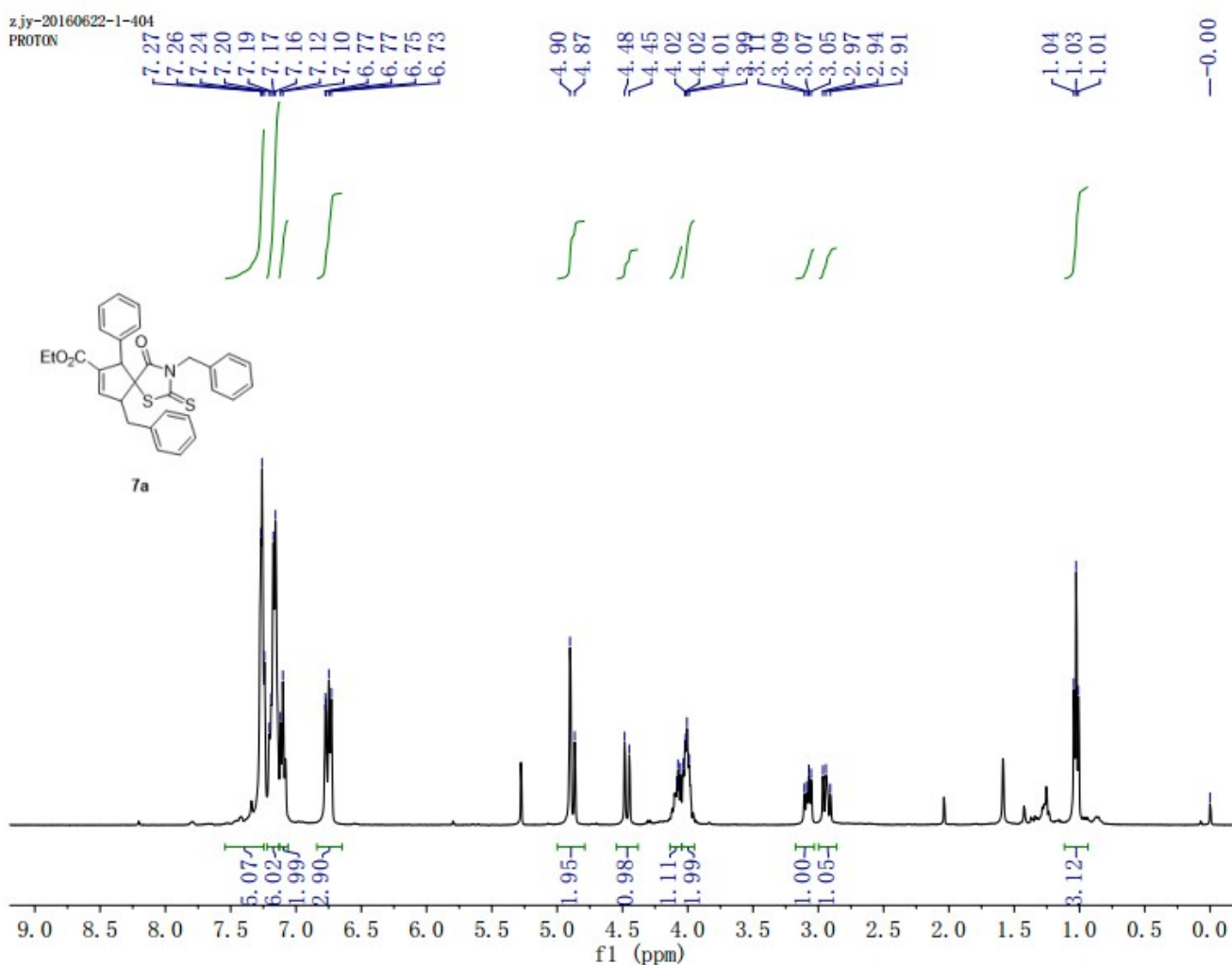
A mixture of amine **5** (0.22 mmol, 2.2 equiv.) and carbon disulfide **6** (0.11 mmol, 1.1 equiv.) in dry toluene (1.0 mL) was stirred at room temperature for about 3 h. PBU_3 (4.1 mg, 0.02 mmol, 20 mmol%) and phenylethylpropiolate **4** (0.1 mmol, 1 equiv.) were added to the mixture under N_2 . After stirring for 6 h at room temperature, ethyl 5-phenylpent-2-ynoate **1a** (30.3 mg, 0.15 mmol, 1.5 equiv.) was added slowly and the mixture was stirred 15 hours at room temperature. The reaction was monitored by TLC spectroscopy. After the reaction was completed, the reaction mixture was directly purified by flash column chromatograph (eluted with 20:1 petroleum ether/EtOAc) to afford the product **7**.

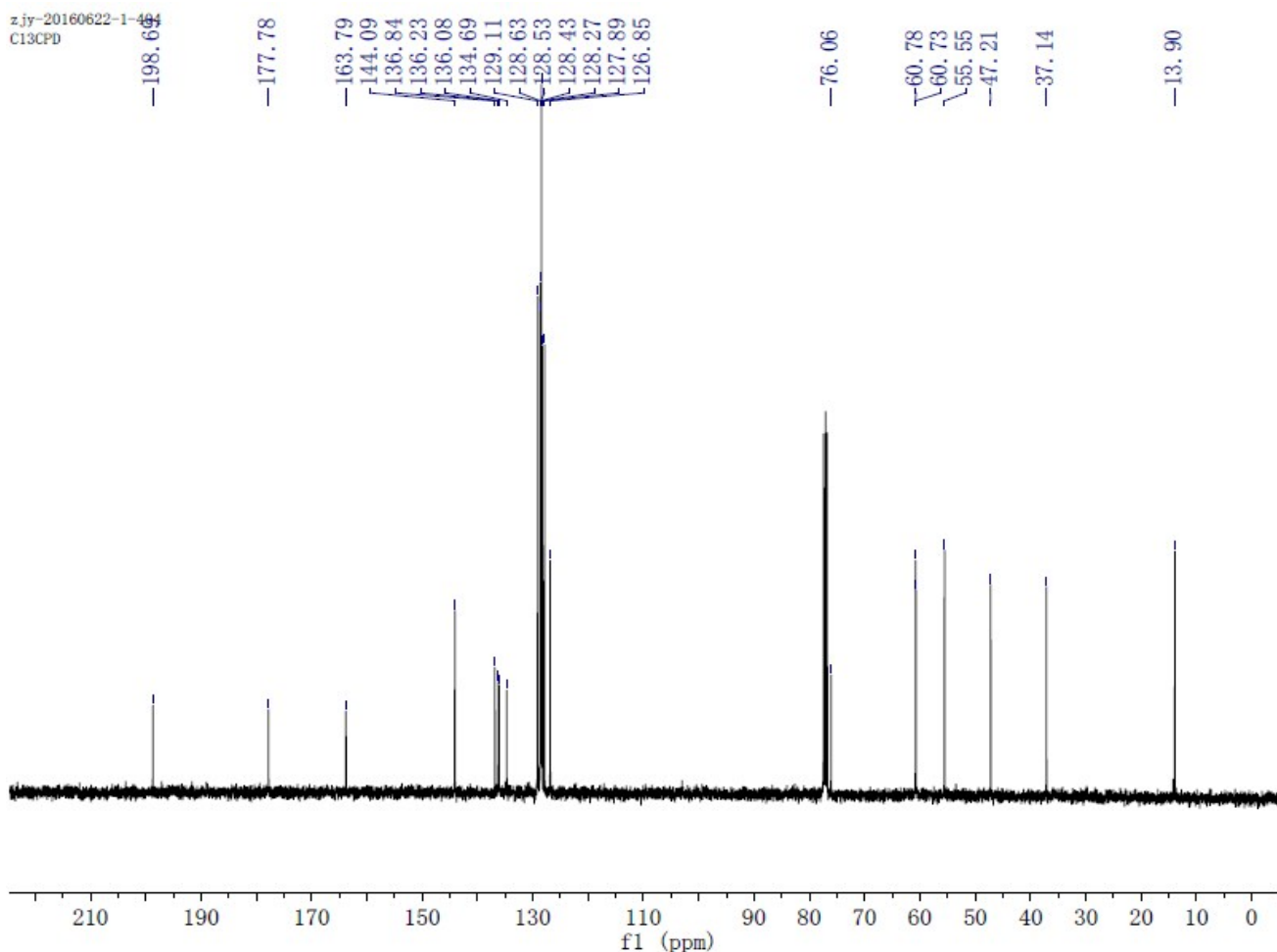
Ethyl 3,9-dibenzyl-4-oxo-6-phenyl-2-thioxo-1-thia-3-azaspiro[4.4] non-7-ene-7-carboxylate (7a):



Yellow oil (43.6 mg, 85% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.26 (d, $J = 3.2$ Hz, 5H), 7.18 (dd, $J = 12.7, 6.4$ Hz, 6H), 7.11 (d, $J = 7.3$ Hz, 2H), 6.76 (dd, $J = 13.7, 4.5$ Hz, 3H), 4.88 (d, $J = 14.6$ Hz, 2H), 4.47 (d, $J = 14.3$ Hz, 1H), 4.14-4.05 (m, 1H), 4.04-3.95 (m, 2H), 3.08 (dd, $J = 13.8, 7.2$ Hz, 1H), 2.99-2.86 (m, 1H), 1.03 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101

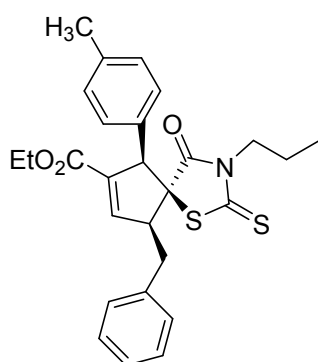
MHz, CDCl_3): δ 198.7, 177.8, 163.8, 144.1, 136.8, 136.2, 136.1, 134.7, 129.1, 128.6, 128.5, 128.4, 128.3, 127.9, 126.9, 76.1, 60.8, 60.7, 55.6, 47.2, 37.1, 13.9; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{28}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 514.1505, found 514.1514.





Ethyl 9-benzyl-4-oxo-3-propyl-2-thioxo-6-(p-tolyl)-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate

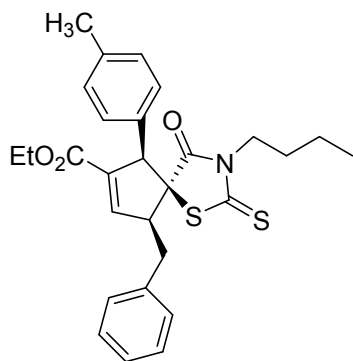
(7b):



Yellow oil (37.9 mg, 79% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.23 (d, J = 7.0 Hz, 2H), 7.17 (d, J = 7.5 Hz, 3H), 7.03 (d, J = 7.8 Hz, 2H), 6.81 (d, J = 7.9 Hz, 2H), 6.76 (d, J = 2.1 Hz, 1H), 4.95 (d, J = 41.2 Hz, 1H), 4.17-4.02 (m, 2H), 4.01-3.94 (m, 1H), 3.57 (ddd, J = 13.1, 9.1, 6.1 Hz, 1H), 3.45-3.30 (m, 1H), 3.05 (dd, J = 13.9, 7.4 Hz, 1H), 2.95 (dd, J = 13.9, 9.5 Hz, 1H), 2.28 (s, 3H), 1.44-1.32 (m, 2H), 1.08 (t, J = 7.1 Hz, 3H), 0.79 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 199.2, 178.1, 163.8, 144.0, 137.6, 137.0, 136.4, 133.3, 129.0, 129.0, 128.6, 128.3, 126.8, 76.0, 60.7, 60.6, 55.5, 45.9, 37.3, 21.2, 20.2, 14.0, 11.1; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{30}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 480.1662, found 480.1665.

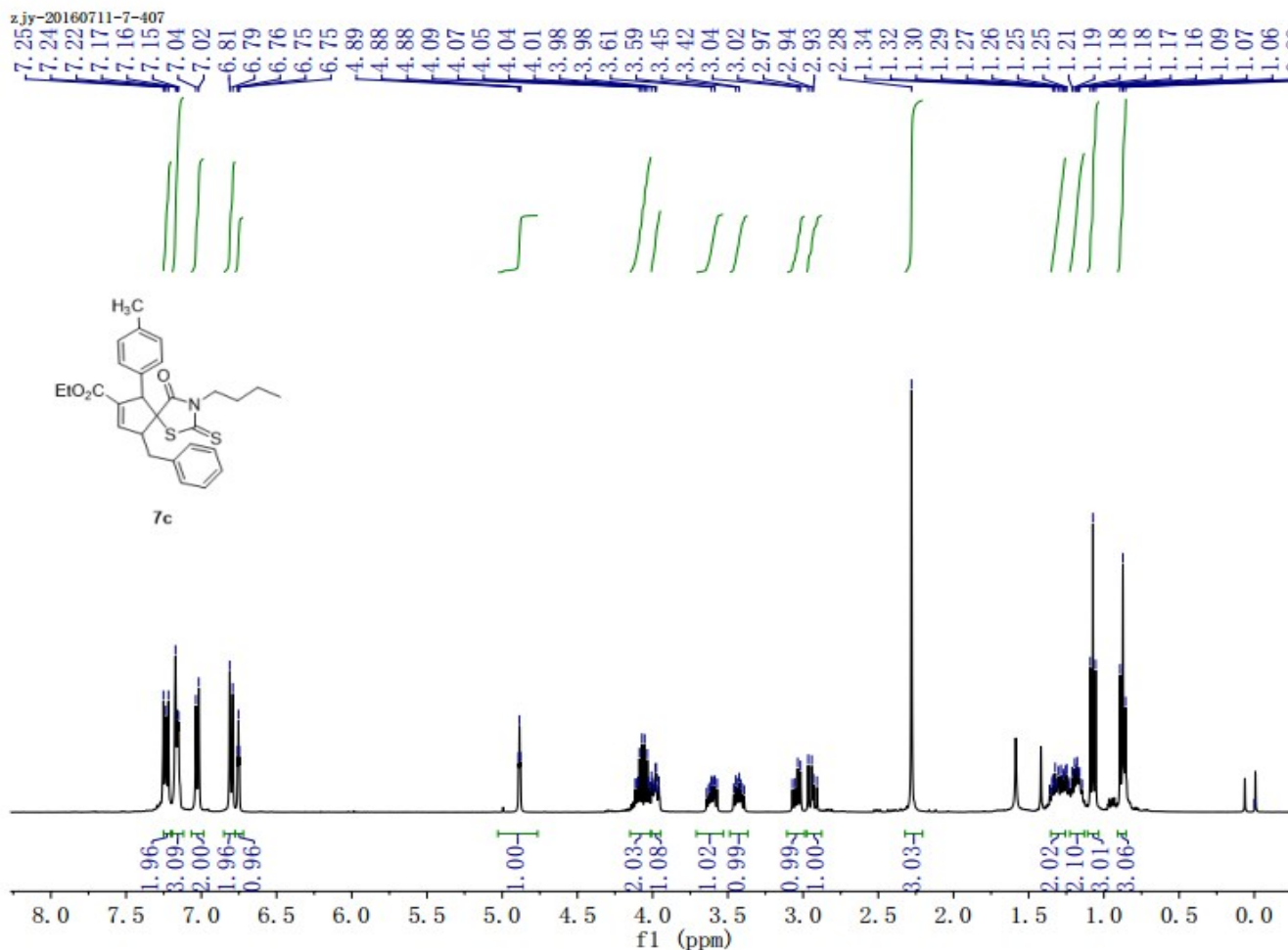
Ethyl 9-benzyl-3-butyl-4-oxo-2-thioxo-6-(p-tolyl)-1-thia-3-azaspiro [4.4]non-7-ene-7-carboxylate

(7c):

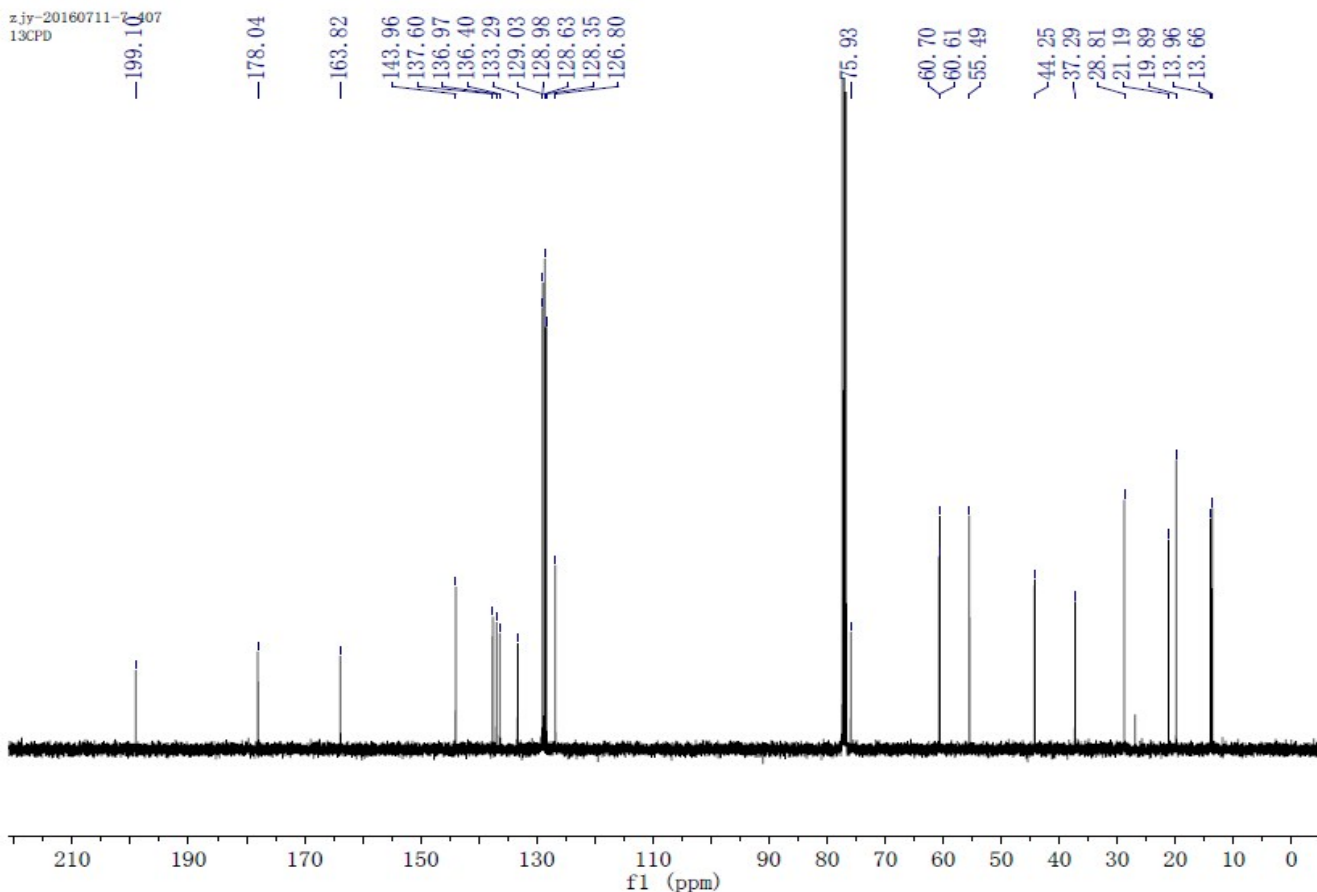


Yellow oil (37.5 mg, 76% yield); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.23 (d, $J = 7.0$ Hz, 2H), 7.19-7.12 (m, 3H), 7.03 (d, $J = 7.9$ Hz, 2H), 6.80 (d, $J = 8.0$ Hz, 2H), 6.75 (t, $J = 2.3$ Hz, 1H), 4.88 (t, $J = 2.4$ Hz, 1H), 4.15-4.01 (m, 2H), 3.98 (ddd, $J = 9.5, 6.3, 2.6$ Hz, 1H), 3.61 (ddd, $J = 13.2, 9.0, 5.9$ Hz, 1H), 3.49-3.37 (m, 1H), 3.04 (dd, $J = 13.9, 7.4$ Hz, 1H), 2.94 (dd, $J = 13.9, 9.5$ Hz, 1H), 2.28 (s, 3H), 1.35-1.26 (m, 2H), 1.23-1.13 (m, 2H),

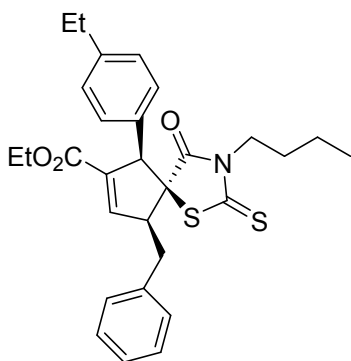
1.07 (t, $J = 7.1$ Hz, 3H), 0.87 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 199.1, 178.0, 163.8, 144.0, 137.6, 137.0, 136.4, 133.3, 129.0, 129.0, 128.6, 128.4, 126.8, 75.9, 60.7, 60.6, 55.5, 44.3, 37.3, 28.8, 21.2, 19.9, 14.0, 13.7; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{32}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 494.1818, found 494.1823.



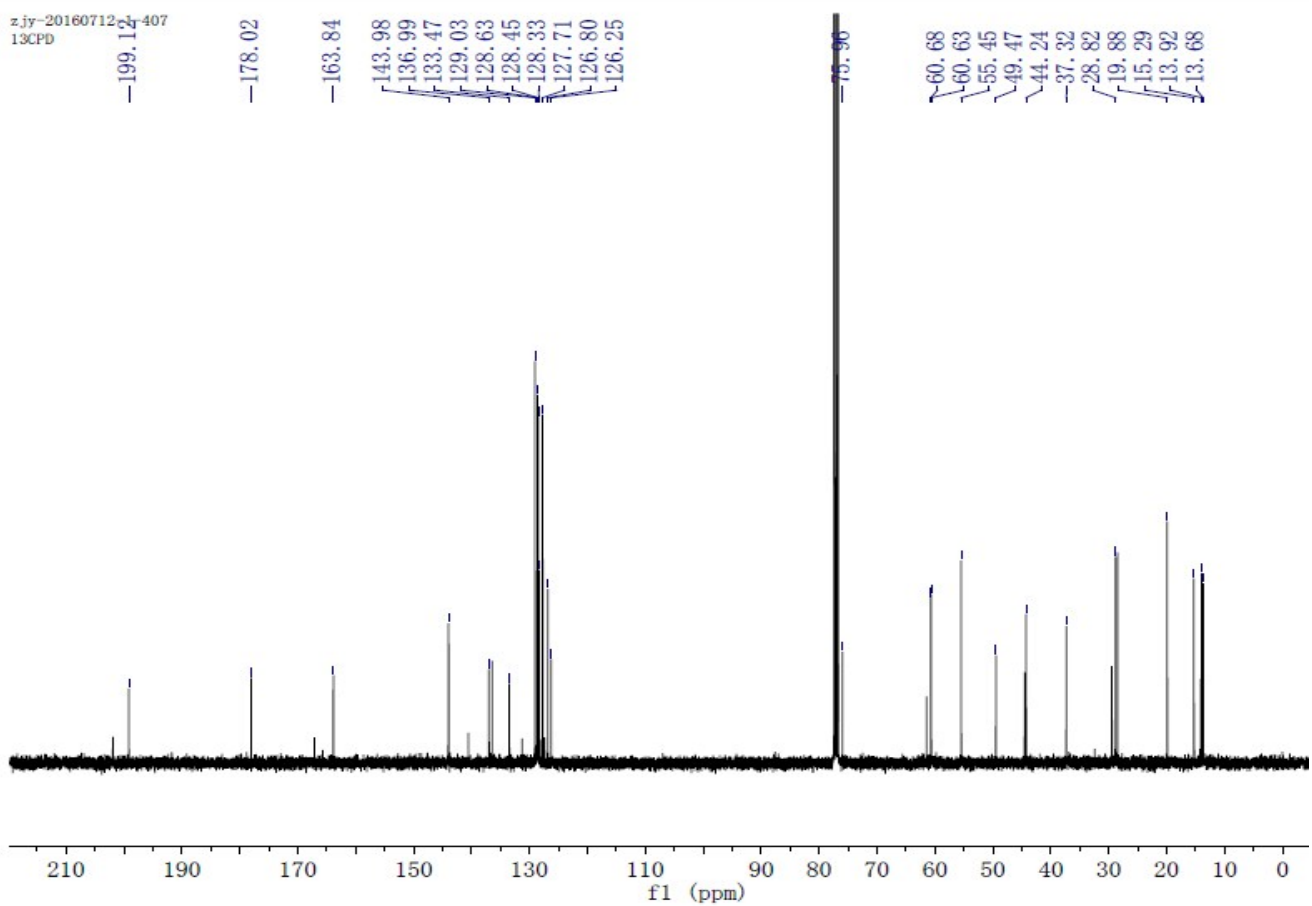
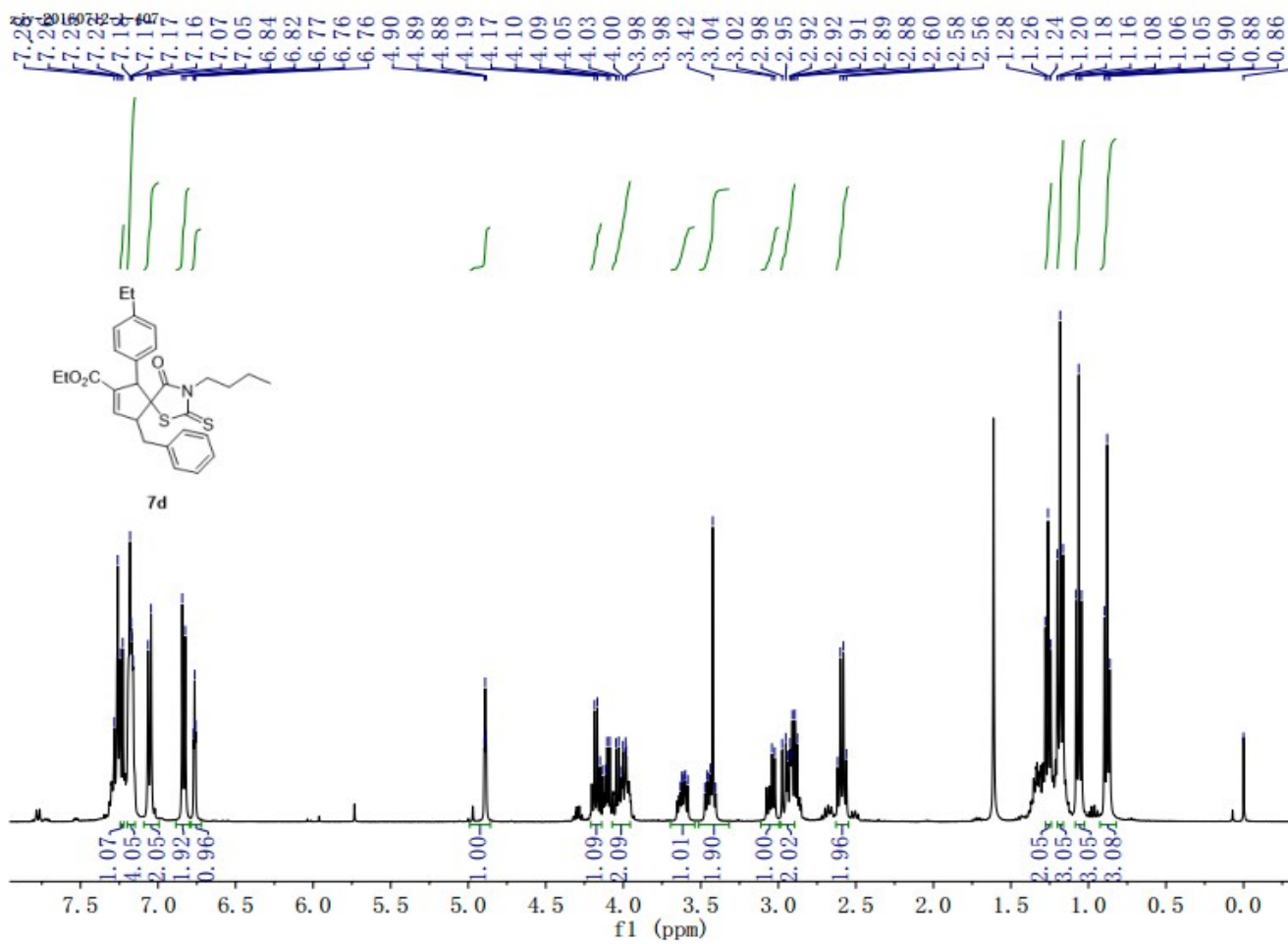
zjy-20160711-7_407
13CPD



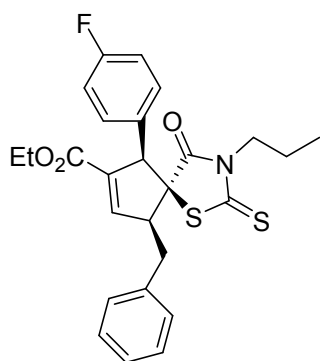
Ethyl 9-benzyl-3-butyl-6-(4-ethylphenyl)-4-oxo-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (7d):



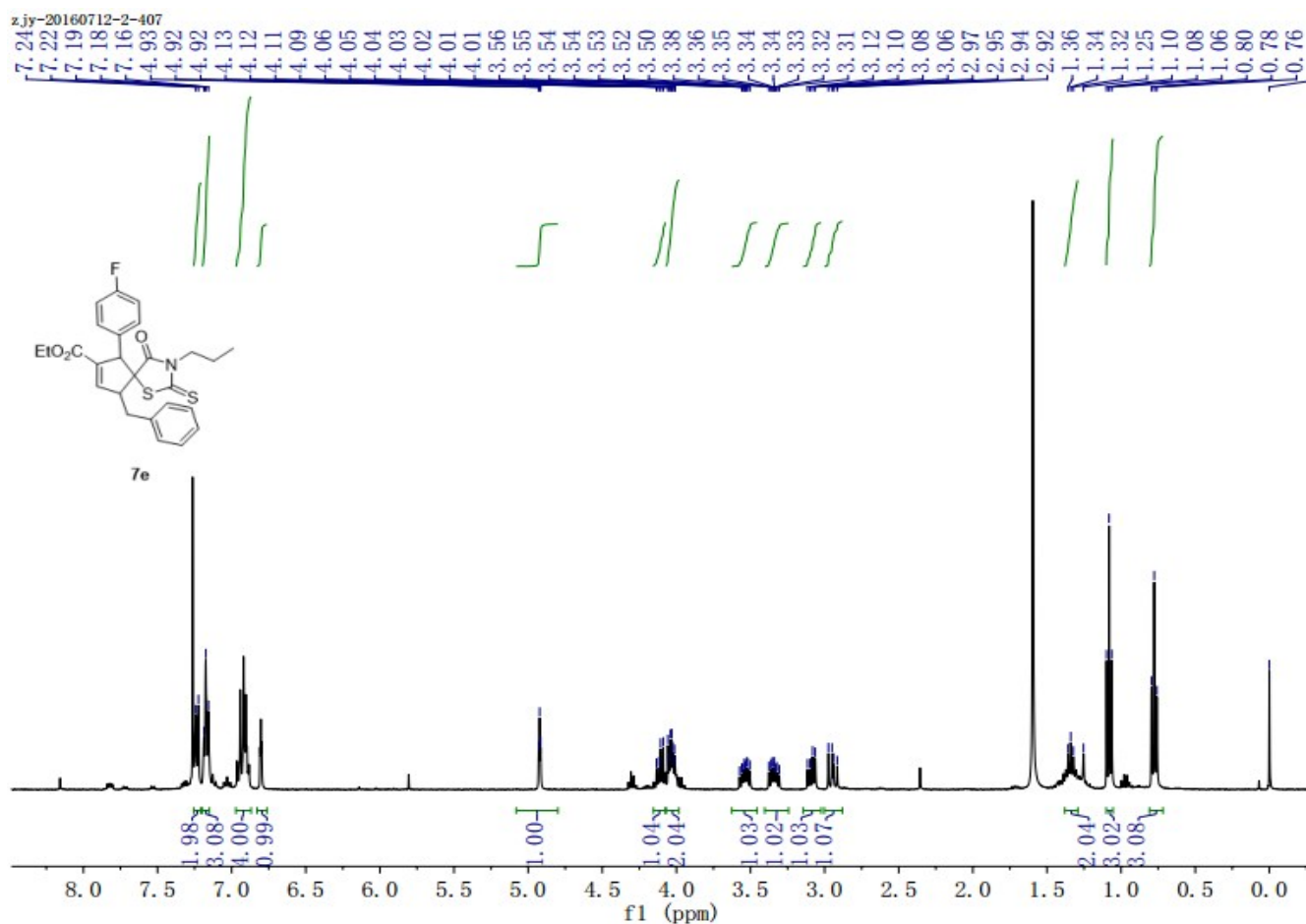
Yellow oil (37.5 mg, 74% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.23 (s, 1H), 7.17 (dd, $J = 5.0, 2.5$ Hz, 4H), 7.04 (t, $J = 8.9$ Hz, 2H), 6.83 (d, $J = 8.0$ Hz, 2H), 6.76 (t, $J = 2.3$ Hz, 1H), 4.91 (dd, $J = 18.3, 16.0$ Hz, 1H), 4.18 (dd, $J = 14.3, 7.2$ Hz, 1H), 4.07-3.96 (m, 2H), 3.62 (ddd, $J = 13.1, 8.9, 6.0$ Hz, 1H), 3.51-3.32 (m, 2H), 3.05 (dd, $J = 13.9, 7.4$ Hz, 1H), 2.99-2.89 (m, 2H), 2.59 (q, $J = 7.6$ Hz, 2H), 1.25 (d, $J = 7.1$ Hz, 2H), 1.17 (d, $J = 7.6$ Hz, 3H), 1.06 (t, $J = 7.1$ Hz, 3H), 0.92-0.82 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 199.1, 178.0, 163.8, 144.0, 137.0, 133.5, 129.0, 128.6, 128.5, 128.3, 127.7, 126.8, 126.3, 76.0, 60.7, 60.6, 55.5, 49.5, 44.2, 37.3, 28.8, 19.9, 15.3, 13.9, 13.7; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{34}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 508.1975, found 508.1976.



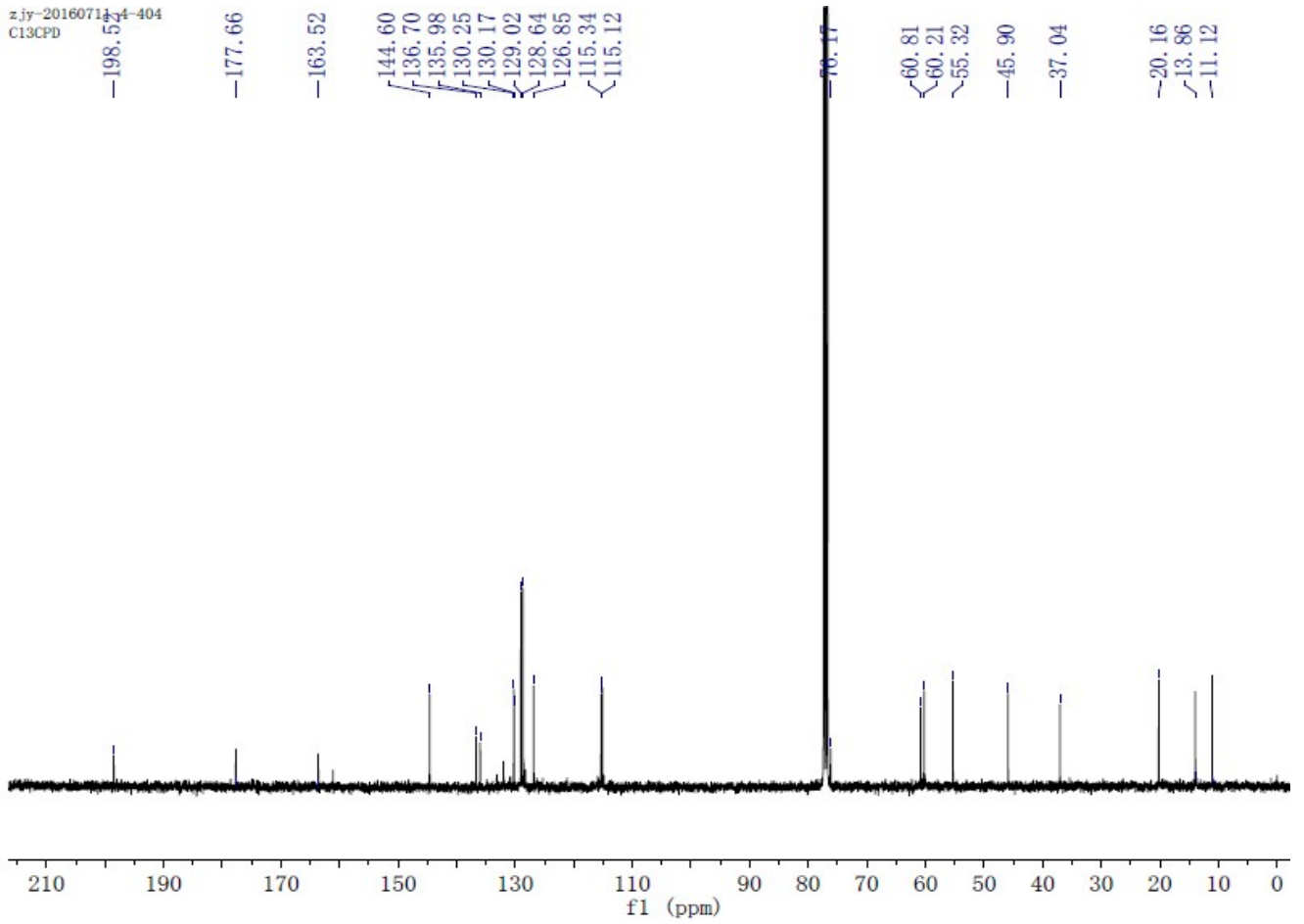
Ethyl 9-benzyl-6-(4-fluorophenyl)-4-oxo-3-propyl-2-thioxo-1-thia-3-azaspiro[4.4]non-7-ene-7-carboxylate (7e):



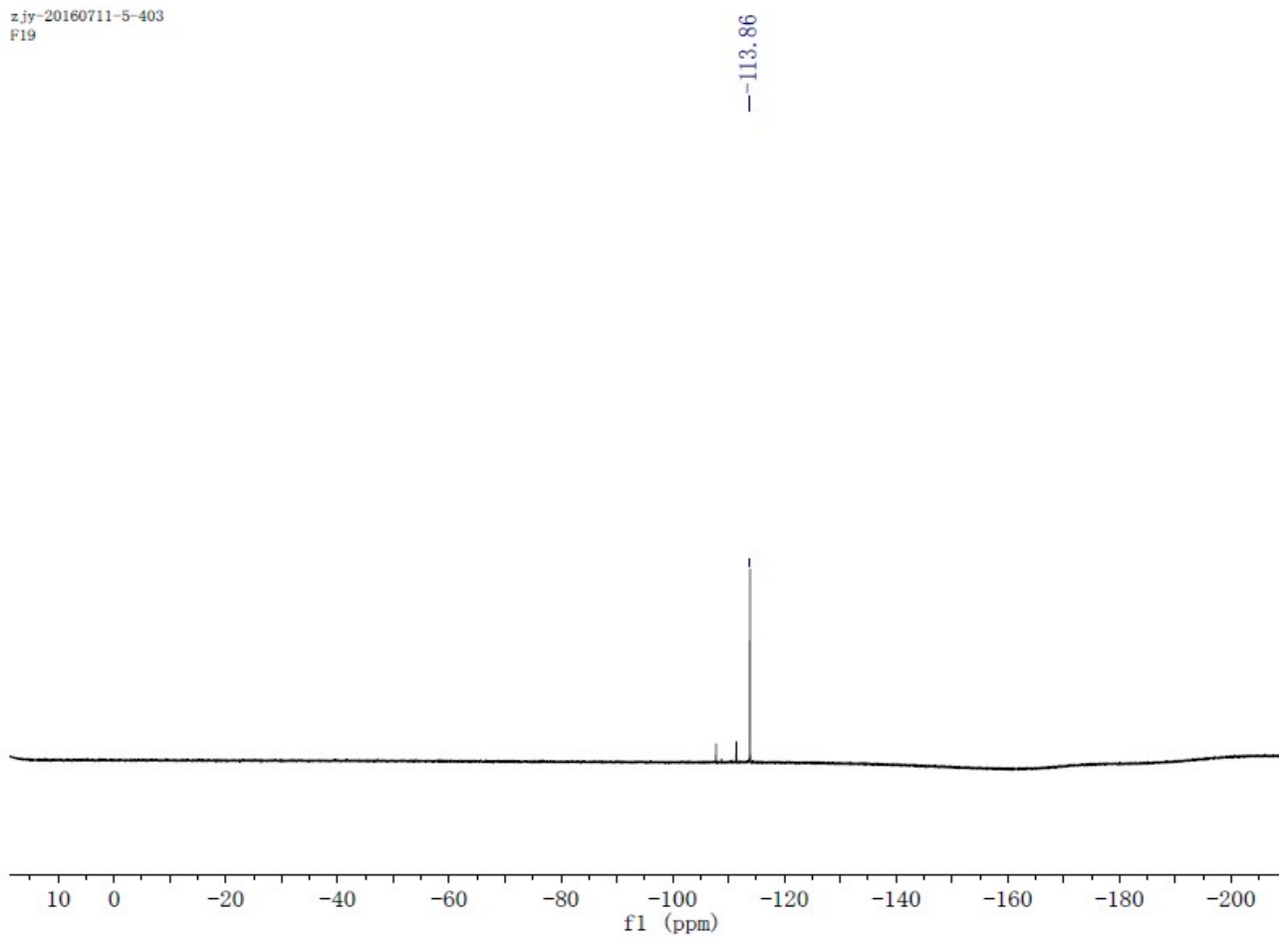
Yellow oil (44.4 mg, 92% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.26 (d, $J = 7.0$ Hz, 2H), 7.19 (t, $J = 6.1$ Hz, 3H), 6.99-6.89 (m, 4H), 6.82 (t, $J = 2.4$ Hz, 1H), 4.94 (t, $J = 2.6$ Hz, 1H), 4.18-4.10 (m, 1H), 4.05 (ddd, $J = 16.8, 9.6, 6.7$ Hz, 2H), 3.56 (ddd, $J = 13.0, 9.2, 6.1$ Hz, 1H), 3.36 (ddd, $J = 13.0, 9.2, 6.0$ Hz, 1H), 3.11 (dd, $J = 14.0, 7.0$ Hz, 1H), 2.97 (dd, $J = 14.0, 9.8$ Hz, 1H), 1.40-1.31 (m, 2H), 1.10 (t, $J = 7.1$ Hz, 3H), 0.80 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 198.5, 177.7, 163.5, 144.6, 136.7, 136.0, 130.3, 130.2, 129.0, 128.6, 126.9, 115.3, 115.1, 76.2, 60.8, 60.2, 55.3, 45.9, 37.0, 20.2, 13.9, 11.1; ^{19}F NMR (376 MHz, CDCl_3) δ -113.86; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{27}\text{FNO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 484.1411, found 484.1408.



zjy-20160711-4-404
C13CPD

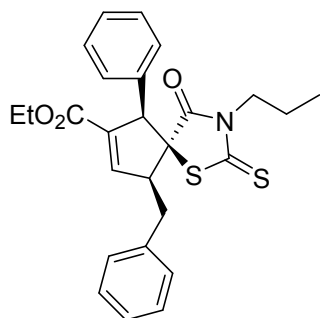


zjy-20160711-5-403
F19

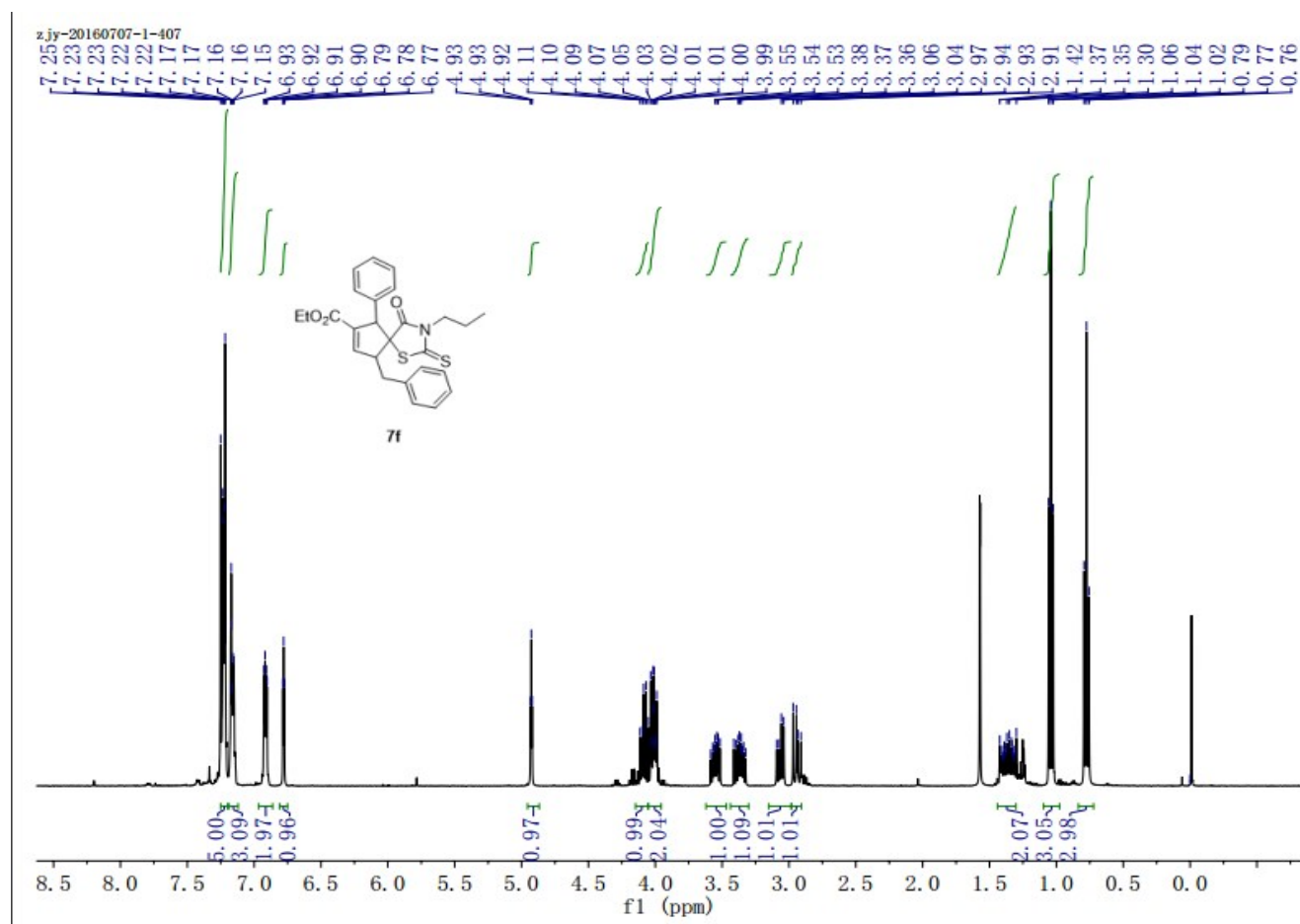


Ethyl 9-benzyl-4-oxo-6-phenyl-3-propyl-2-thioxo-1-thia-3-azaspiro [4.4]non-7-ene-7-carboxylate

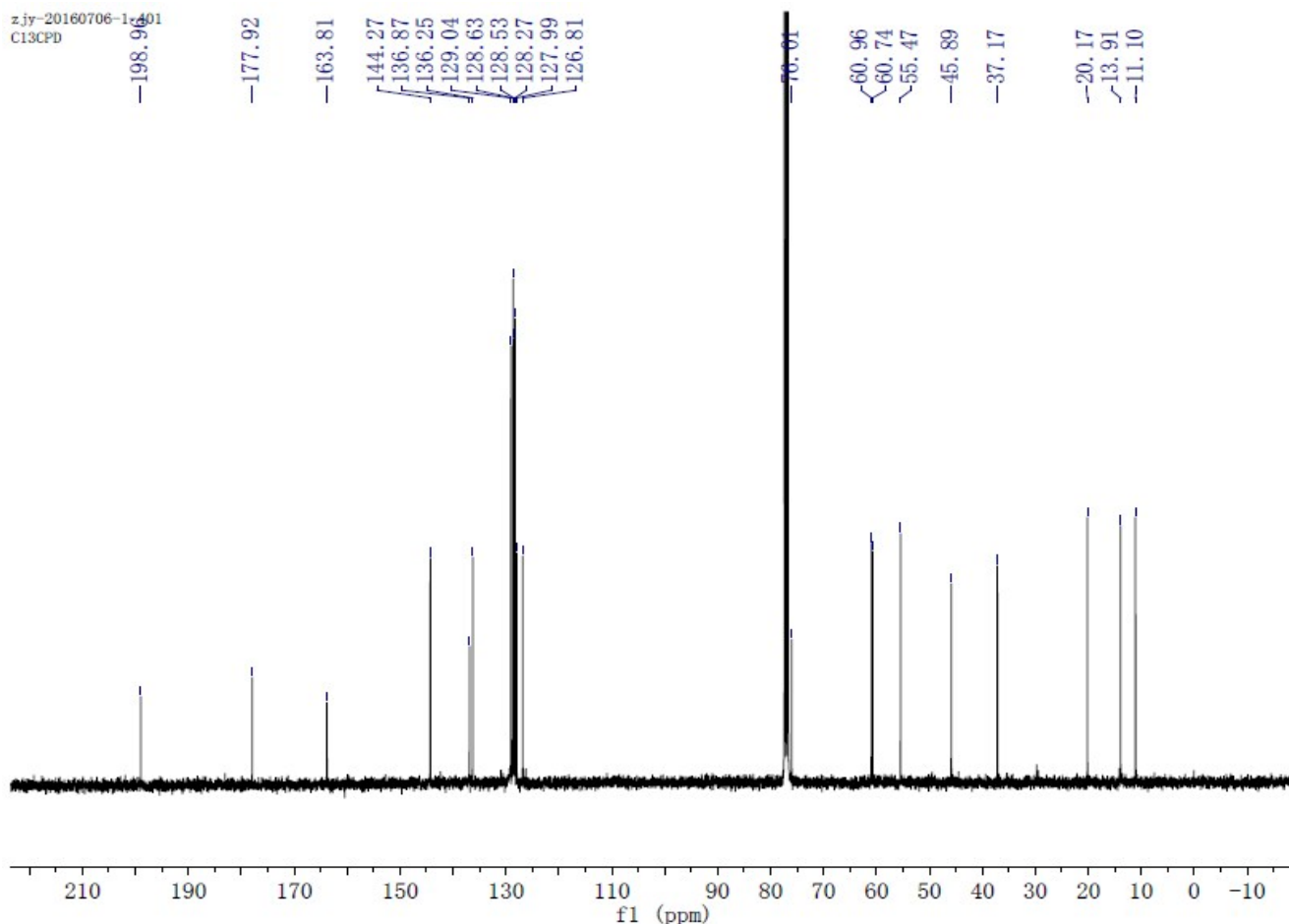
(7f):



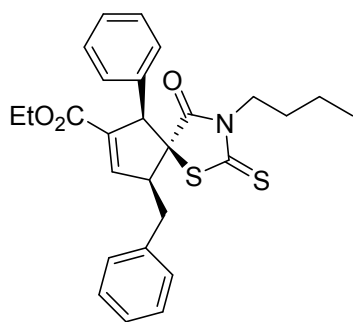
Yellow oil (41.4 mg, 89% yield); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.25-7.20 (m, 5H), 7.19-7.12 (m, 3H), 6.91 (dd, $J = 6.7, 2.8$ Hz, 2H), 6.81-6.75 (m, 1H), 4.93 (t, $J = 2.6$ Hz, 1H), 4.09 (dd, $J = 10.8, 7.1$ Hz, 1H), 4.05-3.96 (m, 2H), 3.55 (ddd, $J = 13.0, 9.2, 6.1$ Hz, 1H), 3.44-3.30 (m, 1H), 3.07 (dd, $J = 14.0, 7.3$ Hz, 1H), 2.94 (dd, $J = 13.9, 9.6$ Hz, 1H), 1.44-1.30 (m, 2H), 1.04 (t, $J = 7.1$ Hz, 3H), 0.77 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 199.0, 177.9, 163.8, 144.3, 136.9, 136.3, 129.0, 128.6, 128.5, 128.3, 128.0, 126.8, 76.0, 61.0, 60.7, 55.5, 45.9, 37.2, 20.2, 13.9, 11.1; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 466.1505, found 466.1514.



zjy-20160706-1-401
C13CPD

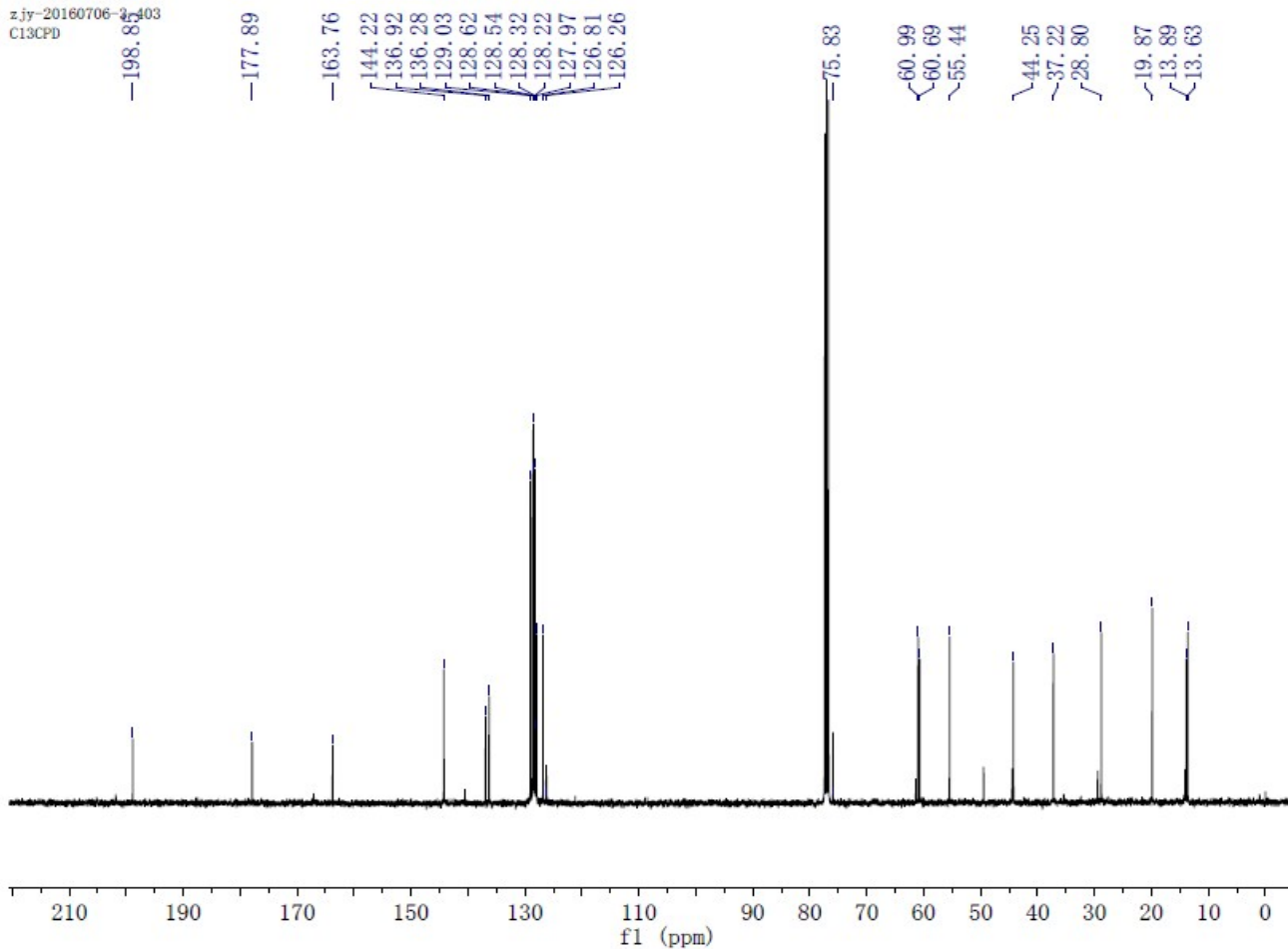
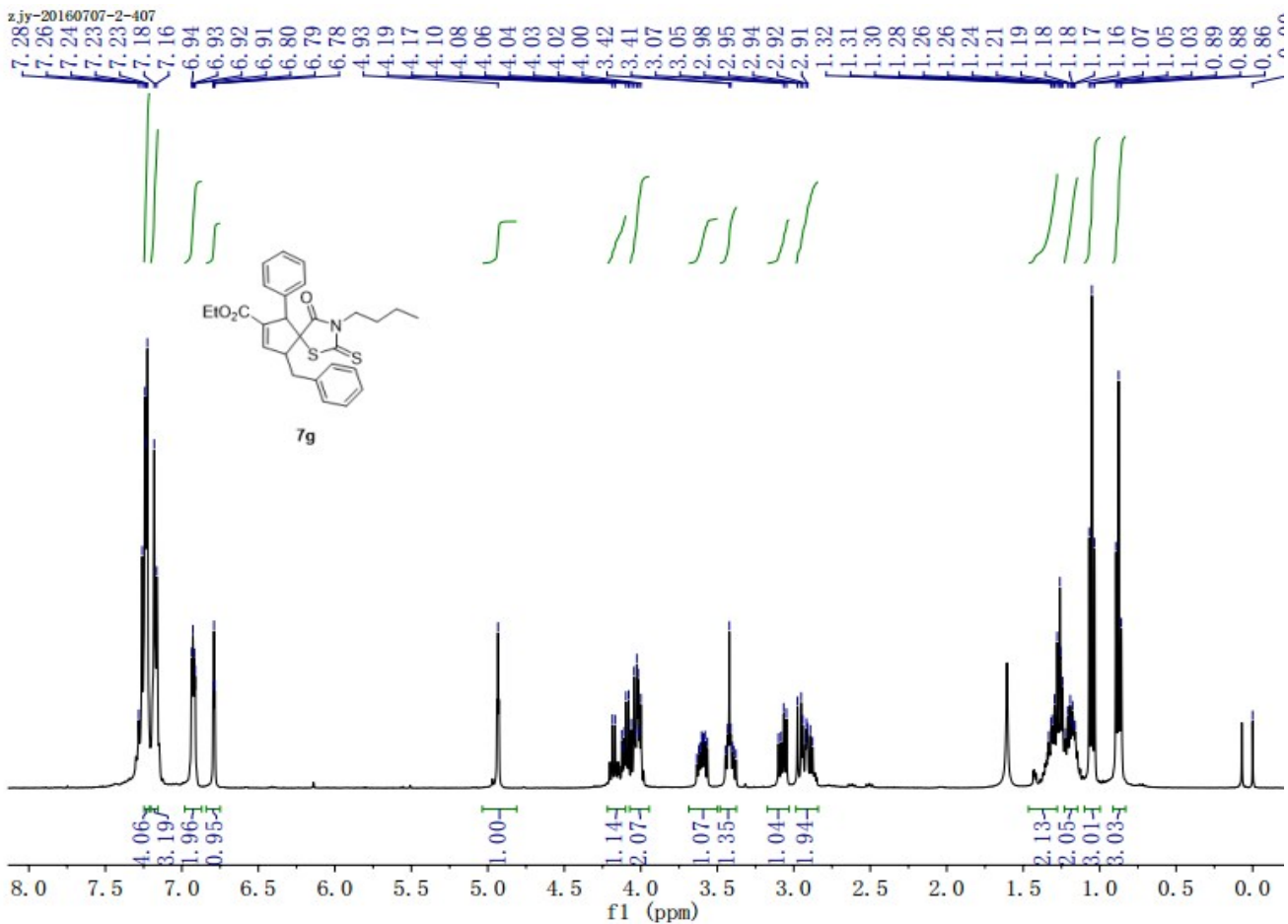


Ethyl 9-benzyl-3-butyl-4-oxo-6-phenyl-2-thioxo-1-thia-3-azaspiro [4.4]non-7-ene-7-carboxylate (7g):



Yellow oil (41.7 mg, 87% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.24 (dd, $J = 8.5, 5.0$ Hz, 5H), 7.17 (d, $J = 6.5$ Hz, 3H), 6.92 (dd, $J = 6.5, 2.8$ Hz, 2H), 6.79 (t, $J = 2.3$ Hz, 1H), 4.93 (s, 1H), 4.22-4.10 (m, 1H), 4.07-3.94 (m, 2H), 3.60 (ddd, $J = 13.3, 9.0, 5.8$ Hz, 1H), 3.48-3.38 (m, 1H), 3.07 (dd, $J = 14.0, 7.2$ Hz, 1H), 2.92 (ddd, $J = 15.9, 13.5, 7.8$ Hz, 2H), 1.47-

1.28 (m, 2H), 1.23-1.14 (m, 2H), 1.05 (t, $J = 7.1$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 198.9, 177.9, 163.8, 144.2, 136.9, 136.3, 129.0, 128.6, 128.5, 128.3, 128.2, 128.0, 126.8, 126.3, 75.8, 61.0, 60.7, 55.4, 44.3, 37.2, 28.8, 19.9, 13.9, 13.6; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{30}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 480.1662, found 480.1667.



X-ray crystallographic data of compound **3I**

Crystallographic data for the structural analysis of compound **3I** has been deposited at the Cambridge Crystallographic Data Centre as No. CCDC 1494917. These data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.

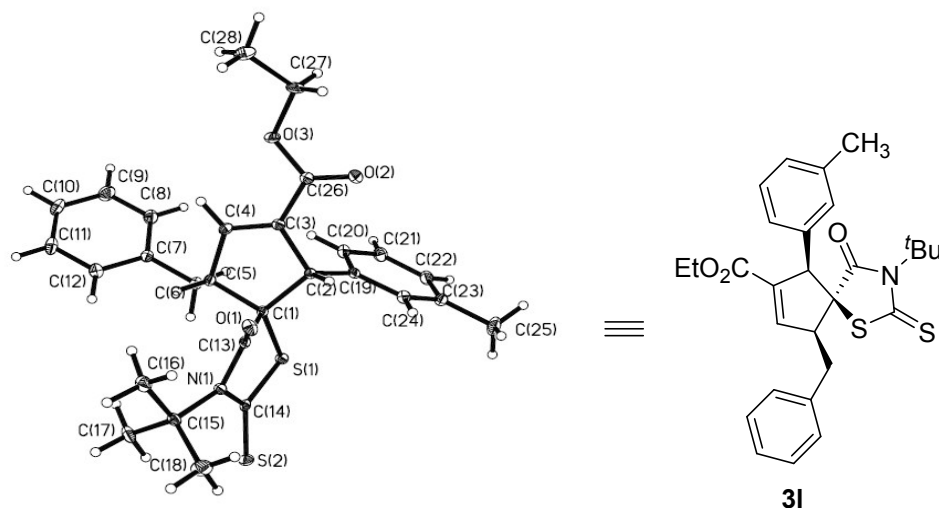


Table 1. Crystal data and structure refinement for shelxl.

Identification code	shelxl	
Empirical formula	C ₂₈ H ₃₁ NO ₃ S ₂	
Formula weight	493.66	
Temperature	113(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 10.588(2) Å	alpha = 76.88(3) deg.
	b = 10.777(2) Å	beta = 77.78(3) deg.
	c = 12.326(3) Å	gamma = 72.35(3) deg.
Volume	1289.7(5) Å ³	
Z	2	
Calculated density	1.271 Mg/m ³	
Absorption coefficient	0.236 mm ⁻¹	

F(000)	524
Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	2.04 to 27.92 deg.
Limiting indices	-13<=h<=13, -14<=k<=14, -15<=l<=16
Reflections collected / unique	13062 / 6028 [R(int) = 0.0359]
Completeness to theta = 27.92	97.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9722 and 0.9543
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6028 / 0 / 312
Goodness-of-fit on F ²	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.1063
R indices (all data)	R1 = 0.0538, wR2 = 0.1132
Largest diff. peak and hole	0.602 and -0.365 e.A ⁻³