Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Photoredox-mediated N-centered Radical Addition/Semipinacol Rearrangement for the Convenient Synthesis of β-Amino (Spiro)cyclic Ketones

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Table of Contents

1. General Information

1*H*-Indene-substituted cycloalkanols **1** and alkenylcyclobutanols **4** were synthesized according to the reported procedures.[1] The *N*-protected 1-aminopyridinium salts **2** were prepared according to the known methods.[2]

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods.[3] All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. All of the reactions were carried out using a schlenk borosilicate reaction tube (10 mL) without special photochemical equipment. There is 5.0 cm distance between the reactor and LEDs bulb. ^{1}H NMR spectra were recorded on 400 MHz spectrophotometer. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on Varian Mercury 400 with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). HRMS was recorded on Bruker ultrafleXtreme MALDITOF/TOF mass spectrometer.

References:

[1] a) Sahoo, B.; Li, J.-L.; Glorius, F. *Angew. Chem. Int. Ed*. **2015**, *54*, 11577-11580; b) Romanov, M.; Alexakis, A. *Angew. Chem. Int. Ed*. **2013**, *52*, 9266-9270; c) Romanov, M.; Alexakis, A. *Org. Lett*. **2013**, *15*, 5890-5893; d) Yao, S.; Zhang, K.; Zhou, Q.-Q.; Zhao, Y.; Shi, D.-Q.; Xiao, W.-J. *Chem. Commun*. **2018**, 54, 8096-8099.

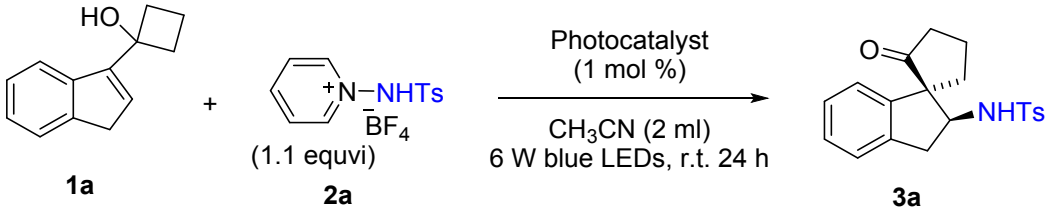
[2] a) Kazuki, M.; Takashi, K.; Akita, M. *Chem. Eur. J.* **2015**, *21*, 11677-11680; b) Li u, W.-D.; Xu, G.-Q.; Hu, X.-Q.; Xu, P.-F. *Org. Lett*. **2017**, 19, 6288-6291.

[3] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals,* 4th ed.; Pergamon Press: Oxford, 1997.

2. Optimization of the Reaction Conditions

2.1 Impact of photocatalysts

Table S1[a]



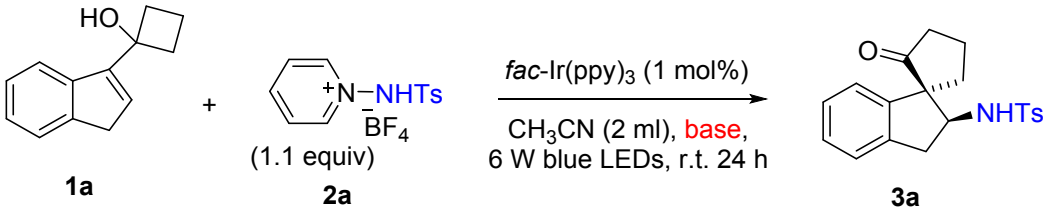
1a **2a** **3a**

entry	Photocatalyst	Yield[b] (%)
1	*fac*-Ir(ppy)$_3$	40
2	Eosin Y	14
3	Ru(bpz)$_3$(PF$_6$)$_2$	23
4	Ir[(ppy)$_2$(dtbpy)$_3$]PF$_6$	30

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.22 mmol), photocatalyst (1 mol%), 2.0 mL of CH_3CN, 6 W blue LEDs, r.t. 24 h. [b]Isolated Yield.

2.2 Impact of bases

Table S2[a]



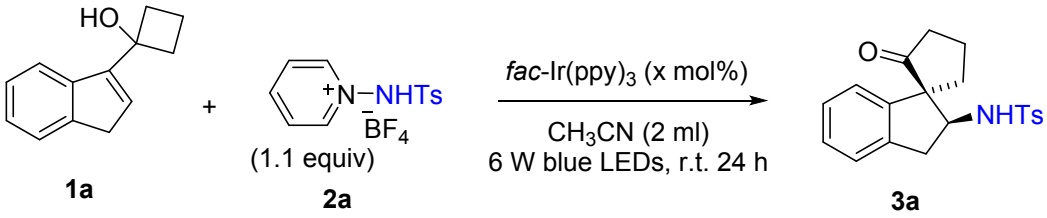
1a **2a** **3a**

entry	Base	Loading of base (equiv)	Yield[b] (%)
1	w/o	0	40
2	$KHCO_3$	1.5	13
3	K_2HPO_4	1.5	20
4	Cs_2CO_3	1.5	18
5	DMAP	1.5	27
6	Pyridine	1.5	23
7	^{i}Pr$_2$NEt	1.5	Messy

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.22 mmol), *fac*-Ir(ppy)$_3$ (1.0 mol%), Base (1.5 equiv), 2.0 mL of CH_3CN, 6 W blue LEDs, r.t. 24 h. [b]Isolated Yield. [i]Pr_2NEt: N,N-Diisopropylethylamine; DMAP: 4-Dimethylaminopyridine. w/o = without

2.3 Impact of loading of photocatalysts

Table S3[a]



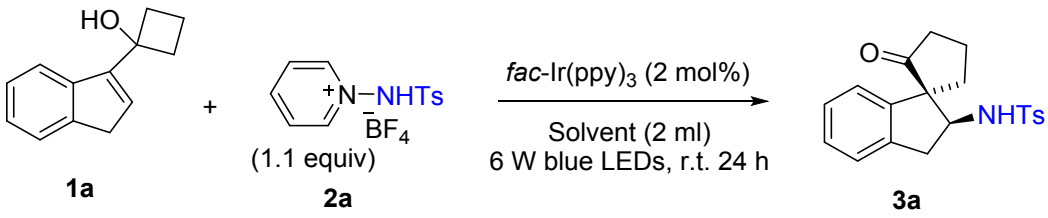
1a **2a** **3a**

Entry	loading of *fac*-Ir(ppy)$_3$ (x mol%)	Yield[b] (%)
1	1	40
2	2	56
3	3	50
4	4	51
5	5	49
6	0	0

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.22 mmol), *fac*-Ir(ppy)$_3$ (x mol%), 2.0 mL of CH_3CN, 6 W blue LEDs, r.t. 24 h. [b]Isolated Yield.

2.4 Impact of solvents

Table S4[a]



1a **2a** **3a**

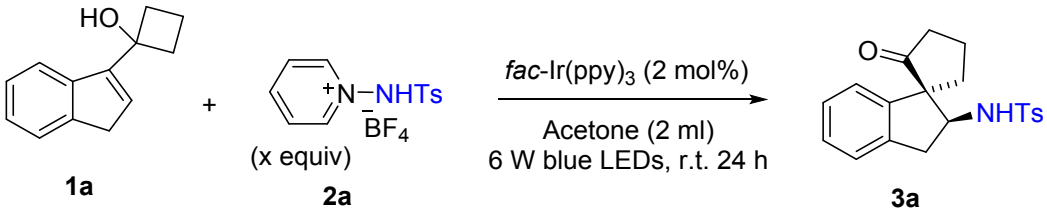
Entry	Solvent	Yield[b] (%)
1	CH_3CN	56

2	DMSO	30
3	Acetone	70
4	DCE	52
5	DCM	50
6	DMF	0

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.22 mmol), *fac*-Ir(ppy)$_3$ (2 mol%), 2.0 mL of Solvent, 6 W blue LEDs, r.t. 24 h. [b]Isolated Yield.

2.5 Impact of the amount of reactant 2a

Table S5[a]



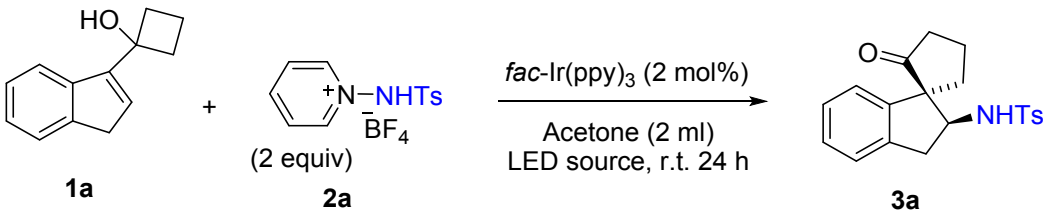
1a **2a** **3a**

Entry	The equiv of **2a**	Yield[b] (%)
1	1.1	70
2	1.5	75
3	2.0	82

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (X equiv), *fac*-Ir(ppy)$_3$ (2 mol %), 2.0 mL of acetone, 6 W blue LEDs, r.t. 24 h. [b]Isolated Yield.

2.6 Impact of LED light sources

Table S6[a]



1a **2a** **3a**

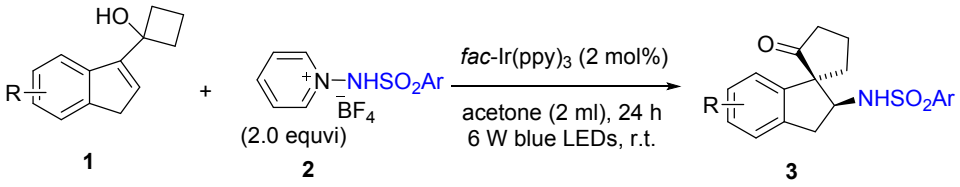
Entry	The visible light	Yield[b] (%)

1	6 W blue LEDs	82
2	3 W blue LEDs	68
3	6 W white LEDs	54
4	w/o	0

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), *fac*-Ir(ppy)$_3$ (2 mol%), 2.0 mL of acetone, LED light source, r.t. 24 h. [b]Isolated Yield. w/o = without

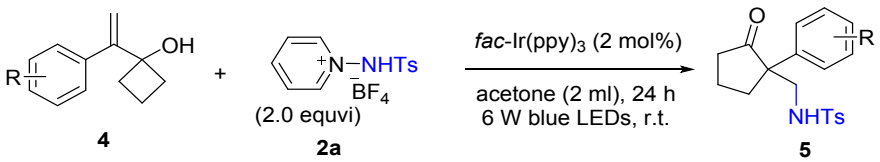
3. General Procedure and Spectral Data of the Products

3.1 General procedure for the synthesis of 3a-q.



Procedure: To a dried Schlenk tube was treated with **1** (0.2 mmol), **2** (0.4 mmol), and *fac*-Ir(ppy)$_3$ (2.6 mg, 0.004 mmol). Then, anhydrous acetone (2 mL) was added. The resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred under the irradiation of 6 W blue LEDs (450-460 nm) at ambient temperature and monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give the desired product **3**.

3.2 General procedure for the synthesis of 5a-g.

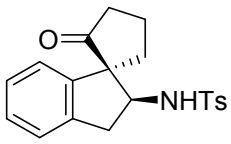


Procedure: To a dried Schlenk tube was treated with **4** (0.2 mmol), **2a** (0.4 mmol), and *fac*-Ir(ppy)$_3$ (2.6 mg, 0.004 mmol). Then, anhydrous acetone (2 mL) was added. The resulting mixture solution degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred under the irradiation of 6 W blue LEDs (450-460 nm) at ambient temperature and monitored by TLC analysis.

The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 15:1) to give the desired product **5**.

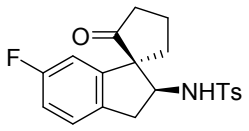
3.3 Spectral data of products 3 and 5

4-methyl-*N*-(2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)benzenesulfonamide (3a)



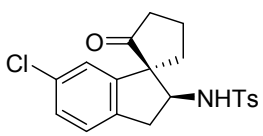
d.r. = 75/25, 58.3 mg, 82% yield; white solid. **M.P.**: 172-174 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.70-7.75 (m, 2H), 7.28-7.31 (m, 2H), 7.13-7.16 (m, 2H), 7.06-7.10 (m, 2H), 5.20-5.23 (d, J = 12.0 Hz, 0.75 H), 5.08-5.11 (d, J = 12.0 Hz, 0.25 H), 4.11-4.16 (dd, J = 8, 12.0 Hz, 0.25 H), 4.01-4.08 (dd, J = 8, 16.0 Hz, 0.75 H), 3.07-3.13 (dd, J = 8.0, 16.0 Hz, 0.25 H), 2.94-3.00 (dd, J = 8.0, 16.0 Hz, 0.75 H), 2.60-2.63 (m, 1H), 2.39-2.49 (m, 5H), 2.31-2.35 (m, 1H), 2.14-2.19 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.5, 143.6, 143.3, 140.6, 137.7, 129.8, 129.7, 127.9, 127.5, 127.3, 127.0, 124.9, 124.6, 123.1, 122.6, 63.6, 62.1, 59.0, 38.4, 38.1, 37.7, 34.2, 31.2, 21.5, 20.1, 19.1; **IR** (in KBr): 3252, 2956, 1735, 1437, 1094 cm^{-1}; **HRMS** (ESI) for $C_{20}H_{21}NO_3S$ $[M+H]^+$: calcd 356.1315, found: 356.1324.

***N*-(6'-fluoro-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)-4-methylbenzenesulfonamide (3b)**



d.r. = 73/27, 65.7 mg, 88% yield; white solid. **M.P.**: 170-172 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.70-7.77 (m, 2H), 7.28-7.32 (m, 2H), 6.89-7.05 (m, 1H), 6.87-6.76 (m, 2H), 5.24-5.29 (m, 1H), 4.11-4.15 (m, 0.27 H), 4.04-4.07 (m, 0.73 H), 3.02-3.08 (m, 0.27 H), 2.87-2.98 (m, 0.73 H), 2.52-2.60 (m, 1H), 2.30-2.48 (m, 5H), 2.29-2.35 (m, 1H), 2.12-2.19 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.5, 218.9, 162.3 (d, J = 218 Hz), 145.0, 143.8, 142.9 (d, J = 8 Hz), 138.9, 137.6, 136.6, 136.0, 129.8 (d, J = 5 Hz), 127.1 (d, J = 20 Hz), 126.0, 125.7, 123.8 (d, J = 10 Hz), 114.7 (J = 20 Hz), 112.2 (d, J = 20 Hz), 110.1(d, J = 21 Hz), 62.9, 62.3, 38.3, 38.2, 38.0, 37.6, 37.0, 34.2, 34.1, 21.5, 20.0, 19.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -113.99, -114.55; **IR** (in KBr): 2956, 1738, 1602, 1433, 1164 cm^{-1}; **HRMS** (ESI) for $C_{20}H_{20}FNO_3S$ $[M+H]^+$: calcd 374.1221, found: 374.1237.

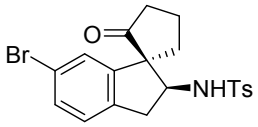
***N*-(6'-chloro-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)-4-methylbenzenesulfonamide (3c)**



d.r. = 72/28, 69.4 mg, 89% yield; white solid. **M.P.**: 138-140 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.70-7.74 (m, 2H), 7.30-

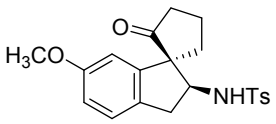
7.32 (m, 2H), 7.11-7.14 (m, 1H), 7.00-7.06 (m, 2H), 5.20 (d, J = 8 Hz, 0.72 H), 5.08 (d, J = 8 Hz, 0.28 H), 4.03-4.15 (m, 1H), 3.05-3.12 (m, 0.28 H), 2.87-2.96 (m, 0.72 H), 2.56-2.63 (m, 1H), 2.38-2.49 (m, 5H), 2.27-2.34 (m, 1H), 2.13-2.19 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.2, 218.8, 145.0, 143.8, 142.5, 141.7, 139.0, 137.6, 133.7, 129.9, 129.8, 128.0, 127.5, 127.2, 127.0, 126.1, 125.2, 123.8, 123.0, 63.6, 63.1, 62.3, 62.1, 38.3, 38.2, 37.5, 37.2, 34.2, 21.6, 20.0, 19.1; **IR** (in KBr): 2958, 1731, 1604, 1436, 1159 cm^{-1}; **HRMS** (ESI) for $C_{20}H_{20}ClNO_3S$ $[M+H]^+$: calcd 390.0925, found: 390.0928.

_N_-(6'-bromo-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)-4-methylbenzenesulfonamide (3d)



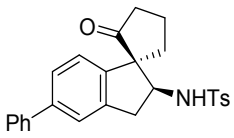
d.r. = 64/36, 64.3 mg, 74% yield; white solid. **M.P.**: 86-88 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.72-7.76 (m, 2H), 7.31-7.34 (m, 2H), 7.21-7.24 (m, 1H), 7.06-7.16 (m, 1H), 6.95-6.98 (m, 1H), 5.13 (d, J = 8 Hz, 0.64 H), 4.86 (d, J = 8 Hz, 0.36 H), 4.02-4.13 (m, 1H), 3.06-3.13 (m, 0.36 H), 2.87-2.97 (m, 0.64 H), 2.56-2.62 (m, 1H), 2.40-2.48 (m, 5H), 2.27-2.34 (m, 1H), 2.12-2.19 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.0, 218.8, 143.9, 142.8, 142.2, 137.5, 130.9, 130.6, 130.4, 129.9, 129.8, 128.2, 127.9, 127.2, 127.0, 126.5, 126.0, 124.6, 124.2, 121.7, 63.2, 62.2, 62.0, 59.1, 38.2, 38.0, 37.5, 37.3, 34.1, 21.6, 20.1, 19.2; **IR** (in KBr): 2956, 1729, 1600, 1439, 1158 cm^{-1}; **HRMS** (ESI) for for $C_{20}H_{20}BrNO_3S$ $[M+H]^+$: calcd 434.0420, found: 434.0438.

_N_-(6'-methoxy-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)-4-ethylbenzenesulfonamide (3e)



d.r. = 54/46, 37.7 mg, 49% yield; white solid. **M.P.**: 84-86 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.76 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.97-6.99 (m, 1H), 6.62-6.71 (m, 2H), 5.06 (t, J = 7.8 Hz, 1H), 3.76-4.04 (m, 1H), 3.75 (s, 1.35 H), 3.73 (s, 1.65 H), 2.87-2.90 (m, 1H), 2.54-2.65 (m, 1H), 2.40-2.46 (m, 5H), 2.21-2.32 (m, 2H), 2.14-2.18 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.9, 219.3, 159.7, 159.3, 143.7, 142.0, 137.8, 137.8, 135.4, 132.4, 129.9, 127.1, 125.6, 123.5, 113.3, 113.0, 110.4, 109.0, 63.9, 63.0, 62.4, 62.0, 55.5, 55.4, 38.3, 38.1, 38.0, 37.2, 34.2, 21.6, 20.0; **IR** (in KBr): 2952, 1726, 1609, 1441, 1156, 812 cm^{-1}; **HRMS** (ESI) for $C_{21}H_{23}NO_4S$ $[M+H]^+$: calcd 386.1421, found: 386.1428.

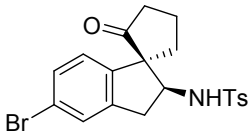
4-methyl-_N_-(2-oxo-5'-phenyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)benzenesulfonamide (3f)



d.r. = 84/16, 81.1 mg, 94% yield; white solid. **M.P.**: 120-122 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.70-7.76 (m, 2H), 7.45-

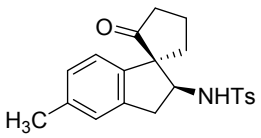
7.49 (m, 2H), 7.38-7.42 (m, 3H), 7.28-7.33 (m, 4H), 7.16 (d, J = 7.9 Hz, 1H), 5.08-5.27 (m, 1H), 4.17-4.21 (m, 0.16 H), 4.06-4.15 (m, 0.84 H), 3.15 (dd, J = 8, 16 Hz, 0.16 H), 3.01 (dd, J = 8, 24 Hz, 0.84 H), 2.66-2.70 (m, 1H), 2.42-2.52 (m, 5H), 2.34-2.38 (m, 1H), 2.16-2.23 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.6, 143.6, 142.3, 141.2, 140.7, 137.7, 129.8, 128.7, 127.3, 127.0, 126.6, 126.4, 123.7, 123.4, 122.9, 64.1, 63.5, 62.2, 60.4, 59.2, 38.2, 38.1, 37.8, 34.2, 22.6, 21.5, 20.1, 19.2; **IR** (in KBr): 2961, 1733, 1604, 1435, 1097 cm^{-1}; **HRMS** (ESI): for $C_{26}H_{25}NO_3S$ $[M+H]^+$: calcd 432.1628, found: 432.1637.

_N_-(5'-bromo-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)-4-methylbenzenesulfonamide (3g)



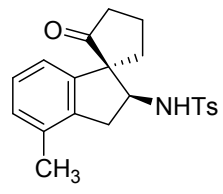
d.r. = 89/11, 44.2 mg, 51% yield; white solid. **M.P.**: 90-92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J = 7.6 Hz, 2H), 7.28-7.32 (m, 3H), 7.21 (s, 1H), 6.96 (d, J = 8.2 Hz, 1H), 5.21-5.24 (m, 1H), 4.00-4.07 (m, 1H), 3.06-3.15 (m, 0.11 H), 2.87-2.97 (m, 0.89 H), 2.55-2.61 (m, 1H), 2.41-2.47 (m, 5H), 2.29-2.34 (m, 1H), 2.13-2.17 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.0, 143.8, 142.9, 142.2, 137.6, 130.4, 129.9, 128.1, 127.0, 126.5, 125.9, 124.2, 121.7, 63.2, 62.1, 38.2, 37.4, 34.1, 21.6, 20.1; **IR** (in KBr): 2958, 1726, 1635, 1385, 1186, 814 cm^{-1}; **HRMS** (ESI) for $C_{20}H_{20}BrNO_3S$ $[M+H]^+$: calcd 434.0420, found: 434.0425.

4-methyl-_N_-(5'-methyl-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)benzenesulfonamide (3h)



d.r. = 85/15, 53.9 mg, 73% yield; white solid. **M.P.**: 130-132 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, *J* = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.96-6.98 (m, 2H), 6.90-6.92 (m, 1H), 5.06 (dd, J = 8, 12 Hz, 1H), 4.17-4.19 (m, 0.15 H), 3.99-4.15 (m, 0.85 H), 3.04-3.10 (m, 0.15 H), 2.89-2.95 (m, 0.85 H), 2.56-2.63 (m, 1H), 2.41-2.45 (m, 5H), 2.26-2.31 (m, 4H), 2.13-2.19 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.7, 219.6, 143.6, 143.3, 140.6, 140.4, 137.8, 137.7, 137.4, 137.1, 129.8, 128.7, 128.1, 127.3, 127.0, 125.7, 124.7, 123.3, 122.4, 63.6, 63.3, 62.2, 62.1, 38.2, 38.1, 37.8, 37.5, 34.2, 21.6, 21.4, 21.2, 20.1; **IR** (in KBr): 2952, 1726, 1610, 1441, 1150, 810 cm^{-1}; **HRMS** (ESI) for $C_{21}H_{23}NO_3S$ $[M+H]^+$: calcd 370.1471, found: 370.1473.

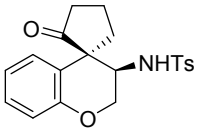
4-methyl-_N_-(4'-methyl-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)benzenesulfonamide (3i)



d.r. = 74/26, 62.8 mg, 85% yield; white solid. **M.P.**: 140-142 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.74-7.78 (m, 2H), 7.31-7.34 (m, 2H), 7.04-7.09 (m, 1H), 6.92-6.99 (m, 2H), 5.15 (d, J = 12 Hz, 0.74 H), 4.90 (d, J = 8 Hz, 0.26 H), 4.11-4.17 (m, 0.26 H), 4.01-

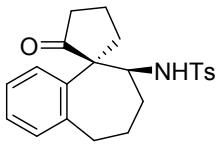
4.06 (m, 0.74 H), 3.07 (dd, J = 8, 16 Hz, 0.26 H), 2.86 (dd, J = 8, 16 Hz, 0.74 H), 2.82-3.11 (m, 1H), 2.58-2.70 (m, 1H), 2.36-2.46 (m, 5H), 2.23-2.29 (m, 1H), 2.10-2.16 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.6, 144.8, 143.7, 143.6, 143.1, 139.4, 137.9, 137.8, 136.7, 134.4, 134.0 129.8, 128.8, 128.6, 127.7, 127.5, 127.3, 127.1, 120.4, 119.9, 64.3, 63.9, 61.7, 58.7, 38.1, 38.0, 37.2, 36.6, 34.3, 31.3, 21.5, 20.0, 19.2, 19.0; **IR** (in KBr): 2940, 1724, 1436, 1163 cm^{-1}; **HRMS** (ESI) for $C_{21}H_{23}NO_3S$ $[M+H]^+$: calcd 370.1471, found: 370.1476.

4-methyl-*N*-(2'-oxospiro[chromane-4,1'-cyclopentan]-3-yl)benzenesulfonamide (3j)



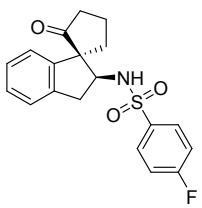
d.r. = 45/55, 23.1 mg, 31% yield; white solid. **M.P.**: 164-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.73 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 7.8 Hz, 1H), 6.92-6.77 (m, 3H), 5.10 (d, *J* = 6.8 Hz, 1H), 4.25 (d, J = 8 Hz, 0.45 H), 4.24 (d, J = 8 Hz, 0.55 H), 3.87 (d, J = 8 Hz, 0.55 H), 3.85 (d, J = 8 Hz, 0.45 H), 3.56-3.59 (m, 1H), 2.44 (s, 3H), 2.26-2.36 (m, 3H), 2.04-2.06 (m, 1H), 1.90-1.94 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.0, 153.9, 143.8, 137.2, 129.8, 128.7, 127.3, 122.8, 121.7, 117.2, 65.2, 52.6, 50.9, 40.4, 38.8, 21.6, 18.5; **IR** (in KBr): 2967, 1734, 1633, 1340, 1108, 878 cm^{-1}; **HRMS** (ESI) for $C_{20}H_{21}NO_4S$ $[M+H]^+$: calcd 372.1264, found: 372.1254.

4-methyl-*N*-(2'-oxo-6,7,8,9-tetrahydrospiro[benzo[7]annulene-5,1'-cyclopentan]-6-yl)benzenesulfonamide (3k)



d.r. = 45/55, 27.6 mg, 36% yield; white solid. **M.P.**: 128-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.68-7.75 (m, 2H), 7.27-7.29 (m, 2H), 6.75-7.16 (m, 4H), 5.08 (br, 1H), 4.30 (d, J = 8 Hz, 0.55 H), 3.94-3.99 (m, 0.45 H), 3.12-3.15 (m, 1H), 2.66-2.83 (m, 1H), 2.35-2.45 (m, 6H), 2.19-2.24 (m, 1H), 1.93-1.97 (m, 2H), 1.80-1.83 (m, 1H), 1.62-1.69 (m, 2H), 1.51-1.54 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 221.8, 143.4, 143.2, 142.3, 138.1, 136.2, 136.1, 132.3, 131.7, 129.5, 129.4, 128.9, 128.7, 127.9, 127.8, 127.7, 127.0, 126.3, 126.2, 63.1, 60.5, 55.7, 54.5, 38.6, 37.6, 36.8, 36.2, 35.3, 33.1, 30.7, 21.6, 21.3, 18.5; **IR** (in KBr): 2934, 1728, 1633, 1441, 1156 cm^{-1}; **HRMS** (ESI) for $C_{22}H_{25}NO_3S$ $[M+H]^+$: calcd 384.1628, found: 384.1627.

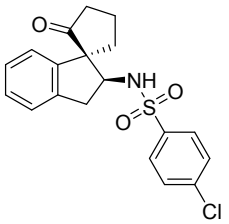
4-fluoro-*N*-(2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)benzene sulfonamide (3l)



d.r. = 73/27, 66.1 mg, 92% yield; white solid. **M.P.**: 178-180 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.87-7.91 (m, 2H), 7.15-7.22 (m, 4H), 6.90-7.12 (m, 2H), 5.44 (d, J = 12 Hz, 0.73 H), 5.28 (d, J = 12 Hz, 0.27 H), 4.06-4.15 (m, 0.27 H), 4.02-4.04 (m, 0.73

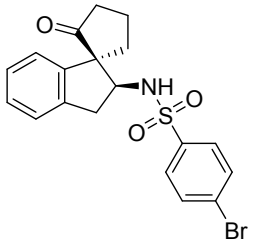
H), 3.11 (dd, J = 8, 16 Hz, 0.27 H), 2.99 (dd, J = 8, 12 Hz, 0.73 H), 2.63-2.67 (m, 1H), 2.42-2.47 (m, 2H), 2.31-2.36 (m, 1H), 2.15-2.20 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.6, 165.1 (d, J = 254 Hz), 145.0, 143.2, 140.4, 138.8, 136.8, 130.0 (d, J = 9 Hz), 129.8 (d, J = 9 Hz), 128.9 (d, J = 20 Hz), 127.5 (d, J = 10 Hz), 125.0, 124.6, 123.1, 122.7, 116.5 (d, J = 5 Hz), 116.3 (d, J = 6 Hz), 64.1, 63.6, 62.1, 59.0, 38.3, 38.2, 38.1, 37.7, 34.2, 31.1, 20.1, 19.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -111.68, -112.14; **IR** (in KBr): 3265, 2958, 1734, 1593, 1335, 1097 cm^{-1}; **HRMS** (ESI) for $C_{19}H_{18}FNO_3S$ $[M+H]^+$: calcd 360.1064, found: 360.1071.

4-chloro-*N*-(2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)benzene sulfonamide (3m)



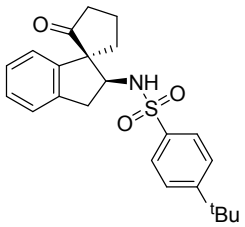
d.r. = 65/35, 48.1 mg, 64% yield; white solid. **M.P.**: 140-142 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.81-7.88 (m, 2H), 7.48-7.51 (m, 2H), 7.16-7.18 (m, 2H), 7.10-7.12 (m, 2H), 5.38 (d, J = 12 Hz, 0.65 H), 5.16 (d, J = 12 Hz, 0.35 H), 4.07-4.16 (m, 0.35 H), 4.03-4.05 (m, 0.65 H), 3.15 (dd, J = 8, 16 Hz, 0.35 H), 2.99 (dd, J = 12, 16 Hz, 0.65 H), 2.55-2.70 (m, 1H), 2.42-2.49 (m, 2H), 2.31-2.36 (m, 1H), 2.12-2.22 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.6, 219.5, 144.8, 143.1, 140.3, 139.4, 139.3, 138.8, 138.2, 129.5, 128.7, 128.5, 128.0, 127.8, 127.6, 127.5, 125.0, 124.6, 123.1, 122.7, 64.1, 63.7, 62.0, 59.0, 38.4, 38.2, 38.0, 37.7, 34.2, 31.1, 20.1, 19.1; **IR** (in KBr): 2961, 1730, 1635, 1435, 1097 cm^{-1}; **HRMS** (ESI) for $C_{19}H_{18}ClNO_3S$ $[M+H]^+$: calcd 376.0769, found: 376.0765.

4-bromo-*N*-(2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)benzene sulfonamide (3n)



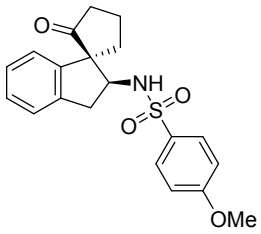
d.r. = 69/31, 65.6 mg, 78% yield; white solid. **M.P.**: 186-188 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.71-7.75 (m, 2H), 7.64-7.67 (m, 2H), 7.15-7.18 (m, 2H), 7.10-7.12 (m, 2H), 5.46 (d, J = 12 Hz, 0.69 H), 5.25 (d, J = 12 Hz, 0.31 H), 4.13-4.17 (m, 0.31 H), 4.03-4.09 (m, 0.69 H), 3.14 (dd, J = 8, 16 Hz, 0.31 H), 2.99 (dd, J = 12, 16 Hz, 0.69 H), 2.64-2.67 (m, 1H), 2.41-2.49 (m, 2H), 2.31-2.36 (m, 1H), 2.06-2.20 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.6, 219.5, 144.9, 143.1, 140.3, 139.8, 138.8, 138.7, 132.5, 132.4, 128.8, 128.5, 128.0, 127.8, 127.7, 127.6, 127.5, 125.0, 124.6, 123.1, 122.7, 64.1, 63.7, 62.0, 59.0, 38.3, 38.2, 38.1, 37.7, 34.2, 31.1, 20.1, 19.1; **IR** (in KBr): 2959, 1733, 1636, 1434, 1161 cm^{-1}; **HRMS** (ESI) for $C_{19}H_{18}BrNO_3S$ $[M+H]^+$: calcd 420.0264, found: 420.0273.

4-(tert-butyl)-*N*-(2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)benzene sulfonamide (3o)



d.r. = 68/32, 71.5 mg, 90% yield; white solid. **M.P.**: 147-149 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.77-7.81 (m, 2H), 7.51-7.56 (m, 2H), 7.11-7.17 (m, 2H), 7.08-7.10 (m, 2H), 5.12 (d, J = 12 Hz, 0.68 H), 4.86 (d, J = 12 Hz, 0.32 H), 4.10-4.17 (m, 0.32 H), 4.03-4.07 (m, 0.68 H), 3.15 (dd, J = 8, 16 Hz, 0.32 H), 2.99 (dd, J = 8, 12 Hz, 0.68 H), 2.60-2.71 (m, 1H), 2.40-2.45 (m, 2H), 2.27-2.32 (m, 1H), 2.10-2.13 (m, 2H), 1.35 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.5, 156.7, 143.4, 140.6, 137.6, 136.1, 128.1, 127.9, 127.7, 127.5, 127.4, 127.3, 127.2, 126.9, 126.3, 126.2, 125.0, 124.6, 123.2, 122.7, 64.2, 63.7, 62.0, 59.0, 58.5, 38.6, 38.2, 38.0, 35.2, 34.3, 31.1, 31.0, 20.1, 19.2; **IR** (in KBr): 3261, 2960, 1737, 1443, 1159 cm^{-1}; **HRMS** (ESI) for $C_{23}H_{27}NO_3S$ $[M+H]^+$: calcd 398.1784, found: 398.1788.

4-methoxy-*N*-(2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden-2'-yl)benzene sulfonamide (3p)

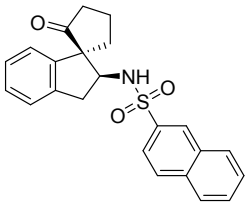


d.r. = 67/33, 49.1 mg, 66% yield; white solid. **M.P.**:170-172 °C. **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.6, 166.3, 163.8, 145.0, 143.2, 140.4, 138.8, 136.8, 130.1, 130.0, 129.8, 129.7, 128.0, 127.8, 127.5, 127.4, 125.0, 124.6, 123.1, 122.7, 116.5, 116.3, 64.1, 63.6, 62.1, 58.9, 38.3, 38.2, 38.1, 37.7, 34.2, 31.1, 20.1, 19.2; **IR** (in KBr): 3249, 2845, 1731, 1592, 1439, 1023 cm^{-1}; **HRMS** (ESI) for $C_{20}H_{21}NO_4S$ $[M+H]^+$: calcd 372.1264, found: 372.1258.

diastereomer (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, J = 8.0 Hz, 2H), 7.13-7.19 (m, 2H), 7.01-7.10 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 5.05 (d, J = 8.0 Hz, 1H), 4.04 (dd, J = 8.0, 16 Hz, 1H), 3.89 (s, 3H), 2.96 (dd, J = 8.0, 16 Hz, 1H), 2.65 (dd, J = 8.0, 16 Hz, 1H), 2.40-2.50 (m, 2H), 2.25-2.37 (m, 2H), 2.13-2.22 (m, 2H);

diastereomer (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.08-7.12 (m, 1H), 6.94-7.03 (m, 3H), 4.74 (d, J = 12.0 Hz, 1H), 4.13 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H), 3.14 (dd, J = 8.0, 16.0 Hz, 1H), 2.53-2.67 (m, 2H), 2.42-2.51 (m, 2H), 2.10-2.21 (m, 2H), 1.99-2.06 (m, 1H);

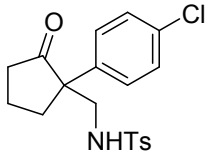
***N*-(2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2'-yl)naphthalene-2-sulfonamide (3q)**



d.r. = 79/21, 71.2 mg, 91% yield; white solid. **M.P.**: 105-107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.45 (s, 1H), 7.91-7.99 (m, 3H), 7.81-7.86 (m, 1H), 7.59-7.67 (m, 2H), 7.09-7.14 (m, 3H), 6.97-7.08 (m, 1H), 5.49 (br, 1H), 4.14-4.25 (m, 0.21 H), 4.09-4.13 (m, 0.79 H), 3.04-3.09 (m, 0.21 H), 2.95-3.01 (m, 0.79 H), 2.56-2.61 (m, 1H), 2.42-2.48 (m, 2H), 2.29-2.35 (m, 1H), 2.13-2.15 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.6, 143.2, 140.5, 139.0, 137.4, 136.5, 134.8, 132.1, 129.6, 129.5, 129.4, 129.2, 128.9, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 124.9, 124.5, 123.1, 122.6, 122.2, 64.2, 63.6, 62.2, 59.1, 38.2, 37.7, 34.2,

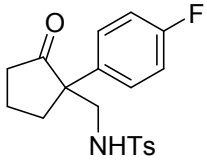
31.2, 20.1, 19.2; **IR** (in KBr): 3240, 2951, 1726, 1437, 1433, 1154 cm^{-1}; **HRMS** (ESI) for $C_{23}H_{21}NO_3S$ $[M+H]^+$: calcd 392.1315, found: 392.1323.

***N*-((1-(4-chlorophenyl)-2-oxocyclopentyl)methyl)-4-methylbenzenesulfonamide (5a)**



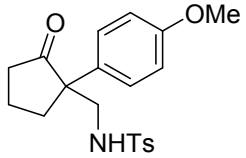
40.1 mg, 53% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.59 (d, J = 8.0 Hz, 2H), 7.19-7.24 (m, 6H), 4.81 (br, 1H), 3.11-3.19 (m, 2H), 2.45-2.48 (m, 1H), 2.41 (s, 3H), 2.25-2.31 (m, 3H), 1.96-2.02 (m, 1H), 1.69-1.75 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 218.9, 143.5, 136.7, 135.4, 133.8, 129.7, 129.1, 128.2, 126.8, 57.2, 49.3, 37.5, 32.1, 21.5, 18.4; **IR** (in KBr): 2960, 1729, 1635, 1450, 1154, 871 cm^{-1}; **HRMS** (ESI) for $C_{19}H_{20}ClNO_3S$ $[M+H]^+$: calcd 378.0925, found: 378.0944.

***N*-((1-(4-fluorophenyl)-2-oxocyclopentyl)methyl)-4-methylbenzenesulfonamide (5b)**



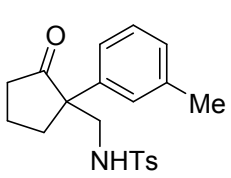
16.6 mg, 23% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.60 (d, J = 8.0 Hz, 2H), 7.23-7.25 (m, 4H), 6.97 (t, J = 8.0 Hz, 2H), 4.88 (t, J = 8.0 Hz, 1H), 3.10-3.24 (m, 2H), 2.47-2.51 (m, 1H), 2.40 (s, 3H), 2.31-2.37 (m, 2H), 2.21-2.28 (m, 1H), 1.86-1.99 (m, 1H), 1.75-1.77 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.0, 162.1 (d, J = 246 Hz), 143.4, 136.7, 132.5 (d, J = 3 Hz), 129.6, 128.5, 126.8, 115.8 (d, J = 21 Hz), 57.0, 49.4, 37.4, 32.1, 21.4, 18.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -115.07; **IR** (in KBr): 2970, 1727, 1448, 1106, 985 cm^{-1}; **HRMS** (ESI) for $C_{19}H_{20}FNO_3S$ $[M+H]^+$: calcd 362.1221, found: 362.1239.

***N*-((1-(4-methoxyphenyl)-2-oxocyclopentyl)methyl)-4-methylbenzenesulfonamide (5c)**



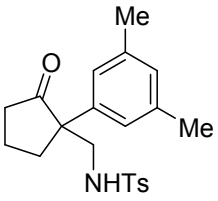
70.8 mg, 95% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.61 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 4.78 (t, J = 8.0 Hz, 1H), 3.77 (s, 3H), 3.09-3.21 (m, 2H), 2.49-2.54 (m, 1H), 2.40 (s, 3H), 2.18-2.36 (m, 2H), 2.16-2.25 (m, 1H), 1.93-1.96 (m, 1H), 1.73-1.77 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.2, 159.0, 143.3, 136.8, 129.6, 128.2, 127.8, 126.8, 114.3, 57.0, 55.2, 49.4, 37.3, 31.8, 21.4, 18.2; **IR** (in KBr): 2964, 1729, 1610, 1334, 1156, 821 cm^{-1}; **HRMS** (ESI) for $C_{20}H_{23}NO_4S$ $[M+H]^+$: calcd 374.1421, found: 374.1435.

4-methyl-*N*-((2-oxo-1-(m-tolyl)cyclopentyl)methyl)benzenesulfonamide (5d)



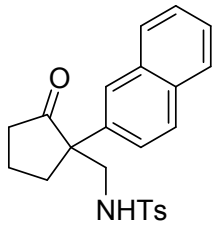
46.5 mg, 65% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.60 (d, J = 8.0 Hz, 2H), 7.18-7.25 (m, 3H), 7.05-7.08 (m, 3H), 4.80 (br, 1H), 3.12-3.23 (m, 2H), 2.52-2.57 (m, 1H), 2.30-2.39 (m, 8H), 2.21-2.25 (m, 1H), 1.93-1.97 (m, 1H), 1.73-1.78 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.3, 143.2, 138.7, 136.7, 136.6, 129.6, 128.8, 128.4, 127.2, 126.8, 123.6, 57.7, 49.3, 37.4, 31.8, 21.5, 21.4, 18.3; **IR** (in KBr): 2815, 1638, 1449, 1105 cm^{-1}; **HRMS** (ESI) for $C_{20}H_{23}NO_3S$ $[M+H]^+$: calcd 358.1471, found: 358.1476.

_N_-((1-(3,5-dimethylphenyl)-2-oxocyclopentyl)methyl)-4-methylbenzene sulfonamide (5e)



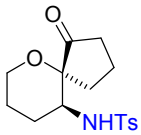
47.6 mg, 64% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.60 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.90 (s, 1H), 6.85 (s, 2H), 4.80 (t, J = 8.0 Hz, 1H), 3.12-3.21 (m, 2H), 2.51-2.56 (m, 1H), 2.39 (s, 3H), 2.30-2.34 (m, 2H), 2.23-2.26 (m, 7H), 1.92-1.96 (m, 1H), 1.74-1.76 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.3, 143.2, 138.5, 136.7, 136.6, 129.6, 129.3, 126.8, 124.3, 57.6, 49.4, 37.3, 31.8, 21.4, 21.3, 18.3; **IR** (in KBr): 2812, 2177, 1638, 1443, 1104, 862 cm^{-1}; **HRMS** (ESI) for $C_{21}H_{25}NO_3S$ $[M+H]^+$: calcd 372.1628, found: 372.1633.

4-methyl-_N_-((1-(naphthalen-2-yl)-2-oxocyclopentyl)methyl)benzenesulfonamide (5f)



58.2 mg, 74% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.73-7.79 (m, 3H), 7.65 (s, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 4.94 (t, J = 8.0 Hz, 1H), 3.24-3.35 (m, 2H), 2.64-2.69 (m, 1H), 2.37-2.42 (m, 1H), 2.35-2.36 (m, 4H), 2.23-2.30 (m, 1H), 1.96-1.98 (m, 1H), 1.76-1.77 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 219.2, 143.2, 136.6, 134.1, 133.1, 132.5, 129.5, 128.9, 128.0, 127.4, 126.7, 126.4, 126.0, 124.0, 57.8, 49.3, 37.5, 32.1, 21.4, 18.4; **IR** (in KBr): 2968, 1726, 1637, 1433, 1154, 812 cm^{-1}; **HRMS** (ESI) for $C_{23}H_{23}NO_3S$ $[M+H]^+$: calcd 394.1471, found: 394.1459..

4-methyl-_N_-(1-oxo-6-oxaspiro[4.5]decan-10-yl)benzenesulfonamide (5g)



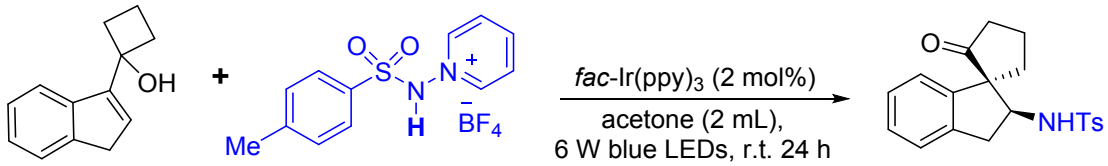
d.r. > 19:1, 37.5 mg, 58% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.73 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.62 (d, J = 8.0 Hz, 1H), 3.60-3.62 (m, 1H), 3.45-3.47 (m, 1H), 3.29-3.32 (m, 1H), 2.43 (s, 3H), 2.33-2.42 (m, 2H), 1.99-2.04 (m, 3H), 1.78-1.81 (m, 2H), 1.30-1.56 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 216.2, 143.6, 137.8, 129.7, 127.0, 63.0, 51.4, 36.8, 33.8, 26.5, 24.3, 21.5, 17.6; **IR** (in KBr):

2960, 1730, 1633, 1437, 1159, 878 cm^{-1}; **HRMS** (ESI) for $C_{16}H_{21}NO_4S$ $[M+H]^+$: calcd 324.1264, found: 324.1282.

4. Mechanism Investigation

4.1 The control experiments

Table S7[a]

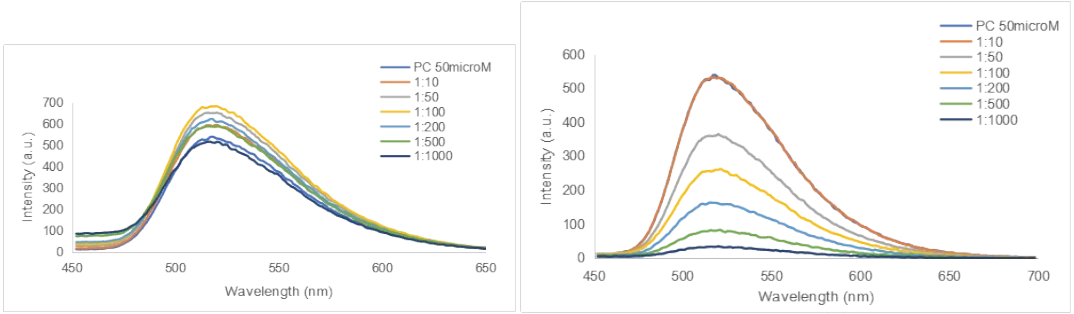


1a **2a** **3a**

Entry	6 W blue LEDs	photocatalyst	yield[b] (%)
1	+	+	82%
2	w/o	+	0
3	+	w/o	0

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.4 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) , Acetone (2.0 mL), 6 W blue LEDs, r.t. 24 h. [b]isolated yield. w/o = without

4.2 Luminescence quenching experiments



(a) Quenching of *fac*-Ir(ppy)$_3$ by **1a** in acetone (b) Quenching of *fac*-Ir(ppy)$_3$ by **2a** in acetone

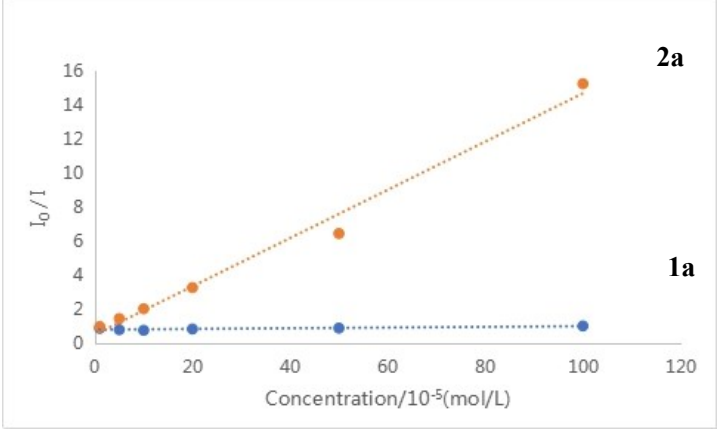


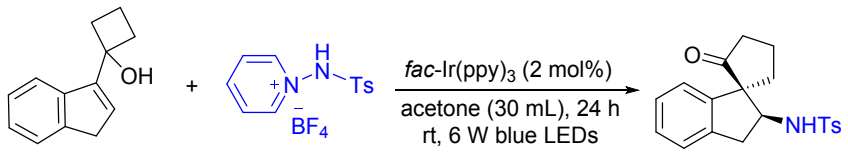
Figure S1. Luminescence Quenching Experiments

Fluorescence spectra were collected on Cary Eclipse Fluorescence Spectrophotometer. All the *fac*-Ir(ppy)$_3$ solutions were excited at 366 nm and the emission intensity at 515 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of *fac*-Ir(ppy)$_3$ in acetone was collected.

As shown in **Figure S1**, substrate **2a** can quench the Luminescence of *fac*-Ir(ppy)$_3$* more quickly than substrate **1a**.

5. Preparative Utility of the Methodology

5.1 Gram-scale reaction

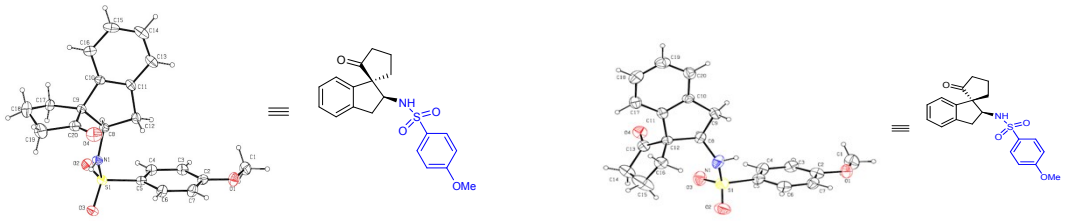


1a **2a** **3a**

1.3 g, 63% yield

To a dried Schlenk tube was treated with **1a** (6 mmol), **2a** (12 mmol), and *fac*-Ir(ppy)$_3$ (78.6 mg, 0.12 mmol). Then, acetone (30 mL) was added. The resulting mixture solution was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred under the irradiation of 6 W blue LEDs (450-460 nm) at ambient temperature and monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give the desired product **3a** as a white solid (1.3 g, 63 % yield).

6. X-Ray structures of two diastereomers of 3p



X-ray structure of diastereomer (major) of 3p (ccdc: 1956000) X-ray structure of diastereomer (minor) of 3p (ccdc: 1956001)

Figure S2. ORTEP diagram of the X-ray crystal structures of *cis*- and *trans*-isomer of 3p.

Platon plot of 3x(298 k) with thermal ellipsoids at the 50% probability level.

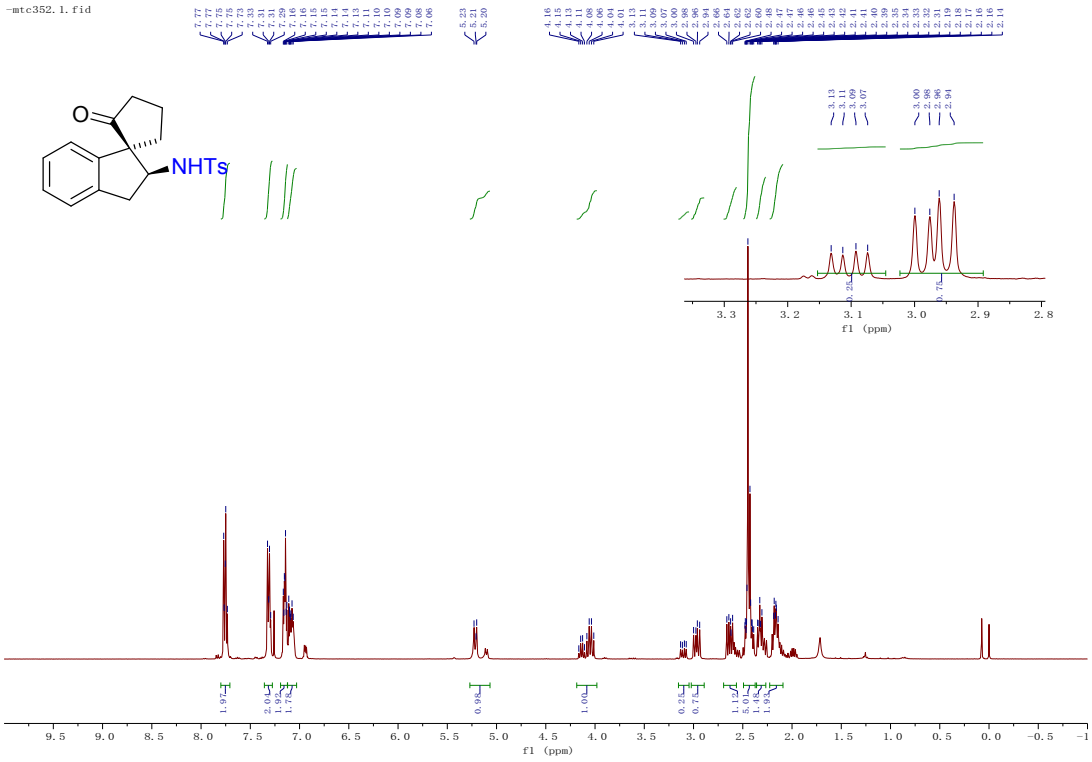
Single crystals of two diastereomers of compound **3p** were obtained from the mixed petroleum ether and ethyl acetate. CCDC 1956000, 1956001 contain the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data (CCDC 1956000)**.** C_{20} H_{21} N O_4 S, M = 371.44, triclinic, a = 9.205(2) Å, b = 10.114(2) Å, c = 10.147(2) Å, V = 909.1(4) Å^3.

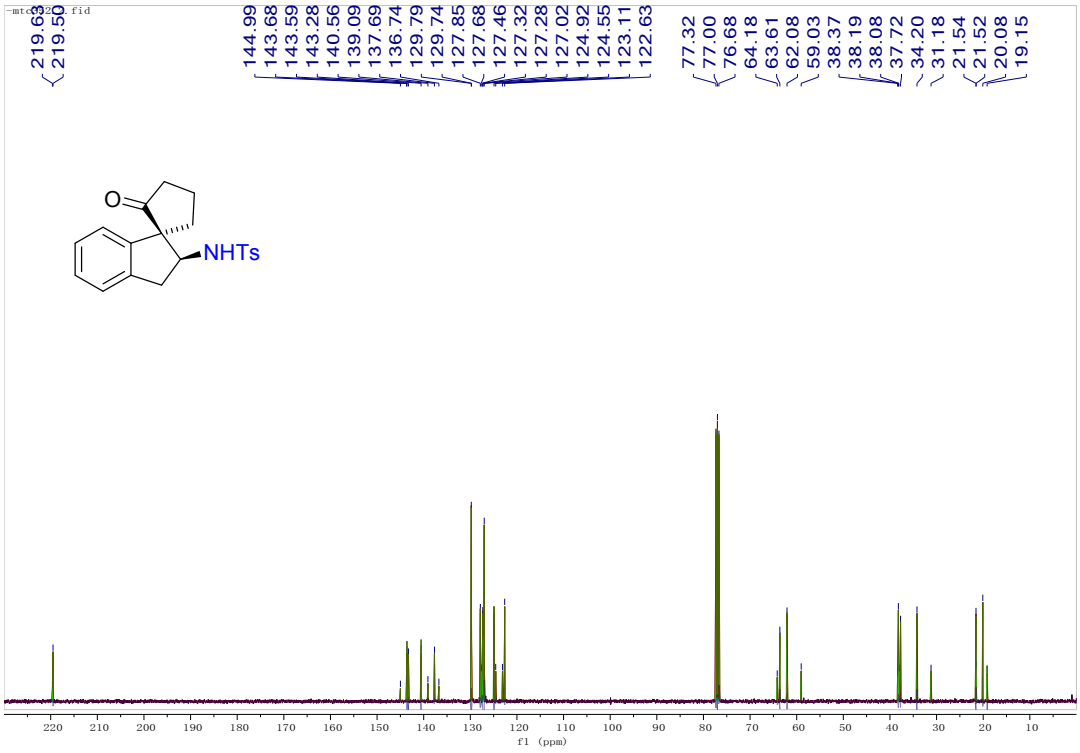
Crystal data (CCDC 1956001). C_{20} H_{21} N O_4 S, M = 371.44, monoclinic, a = 11.275(1) Å, b = 14.112(1) Å, c = 11.635(1) Å, V = 1844.9(3) Å^3.

7. NMR Spectra of products 3a-3q and 5a-5g.

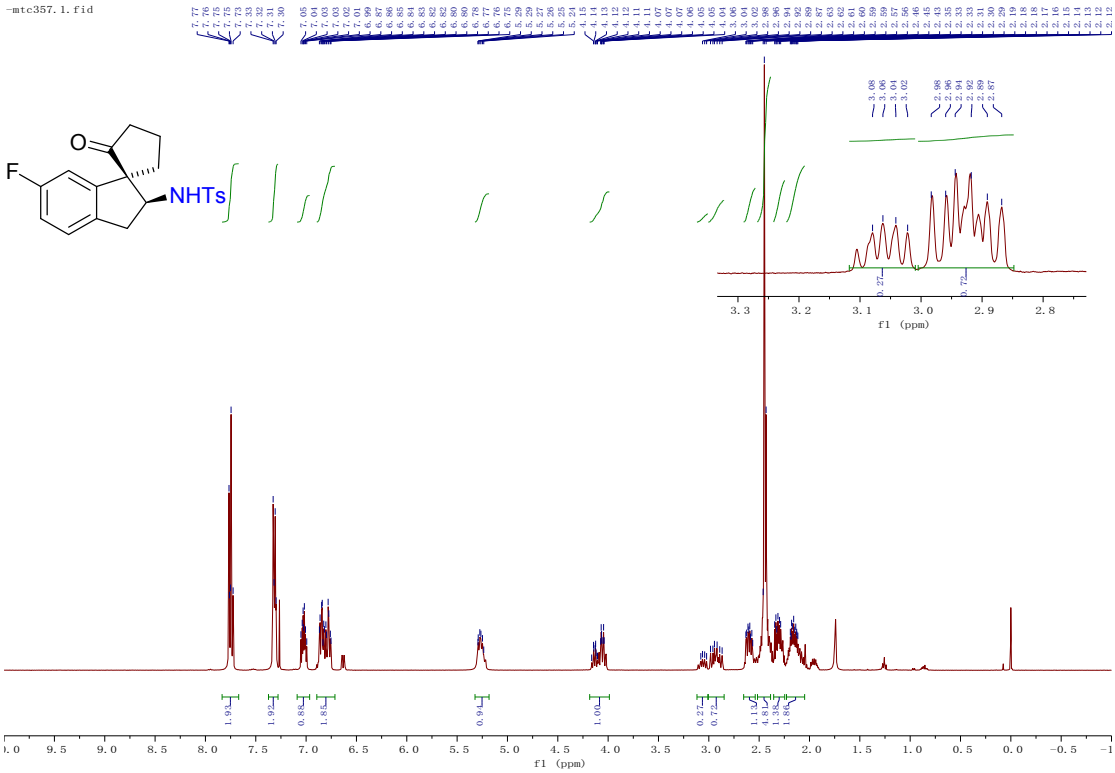
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3a



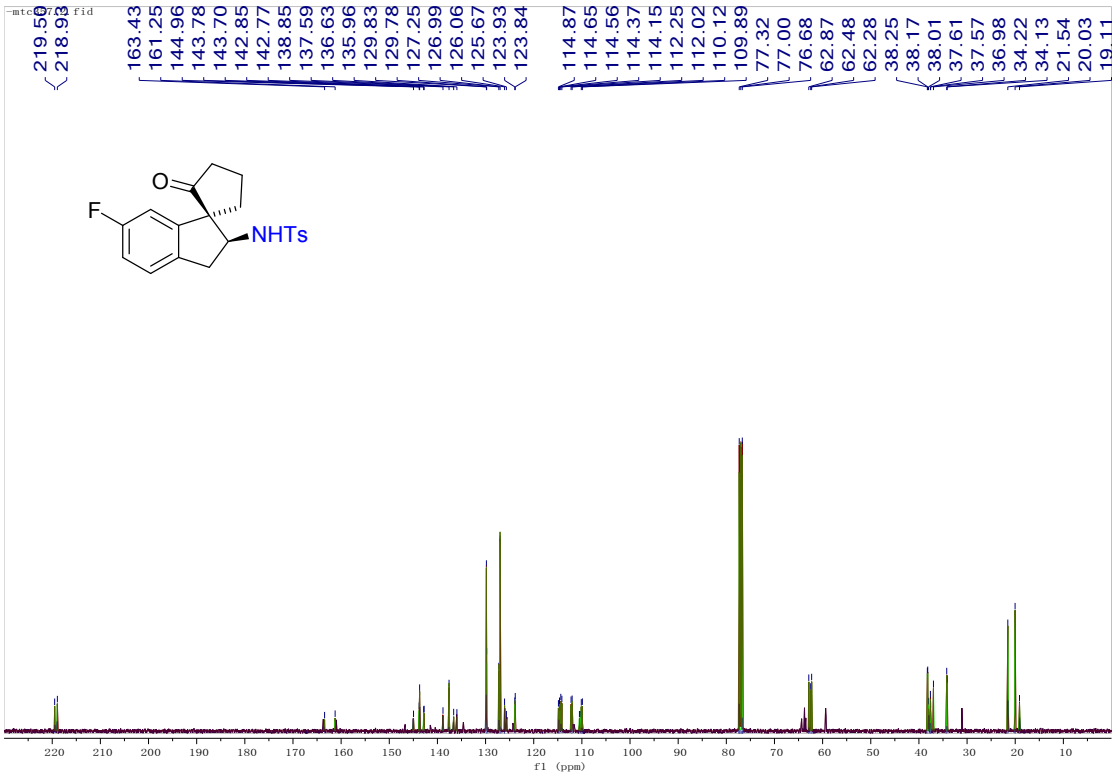
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3a



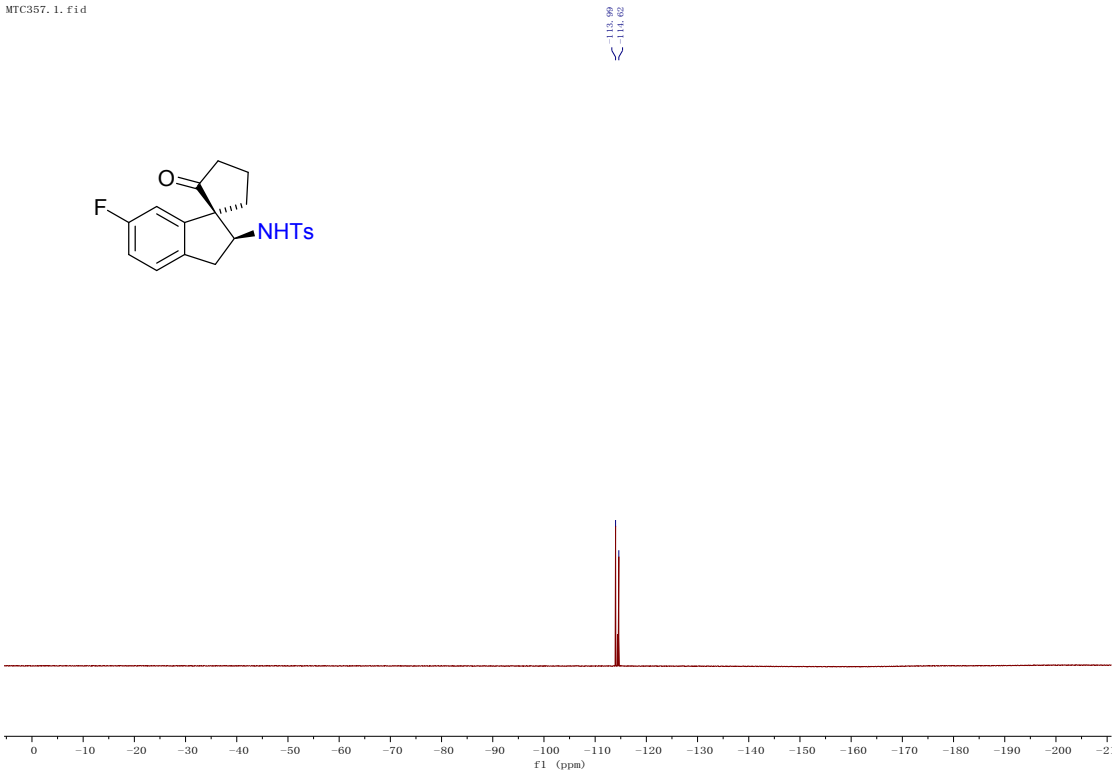
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3b



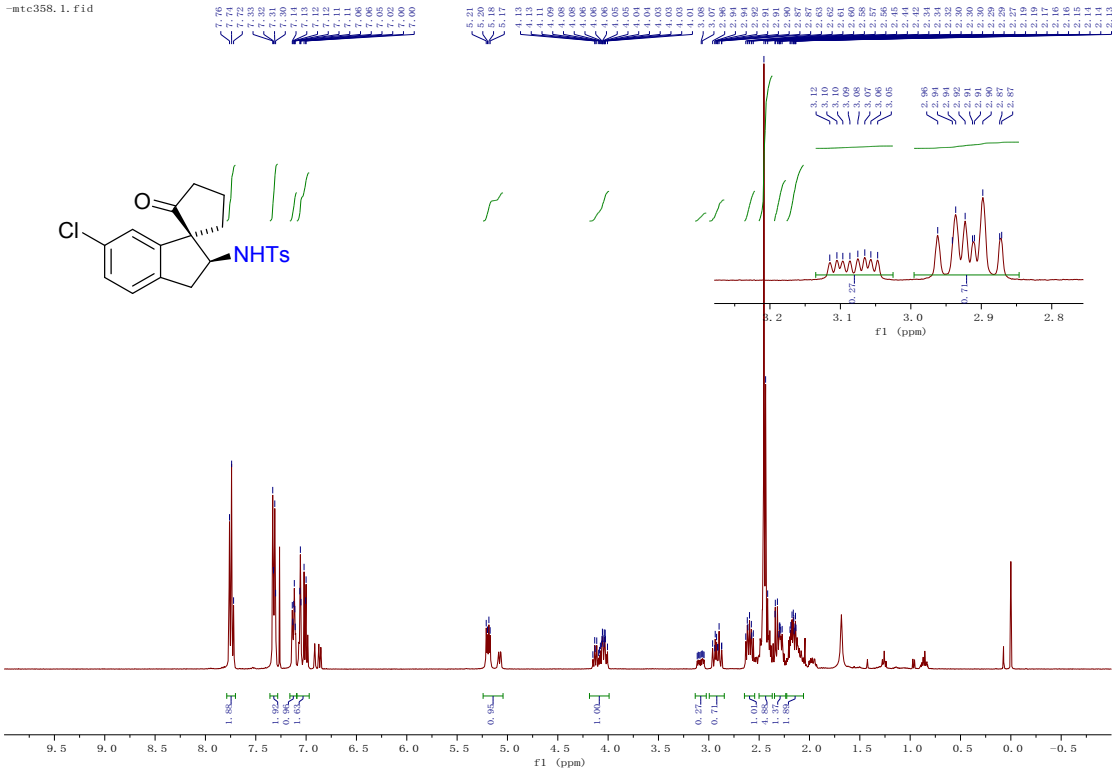
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3b



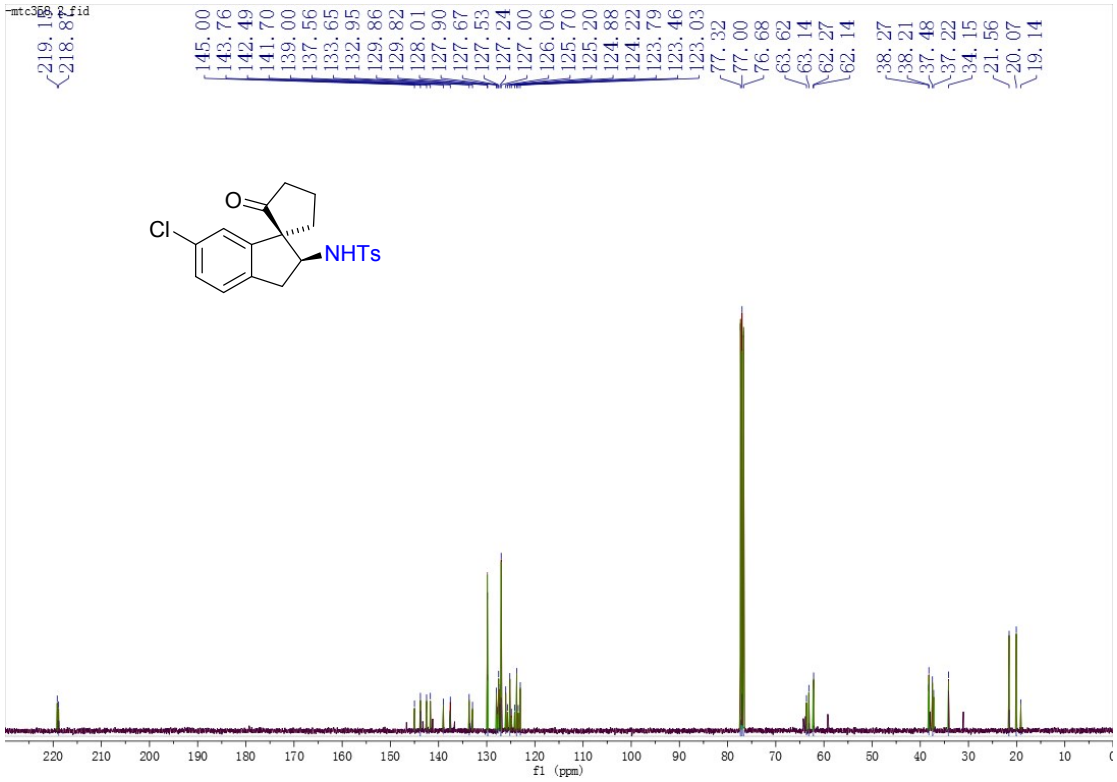
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of3b



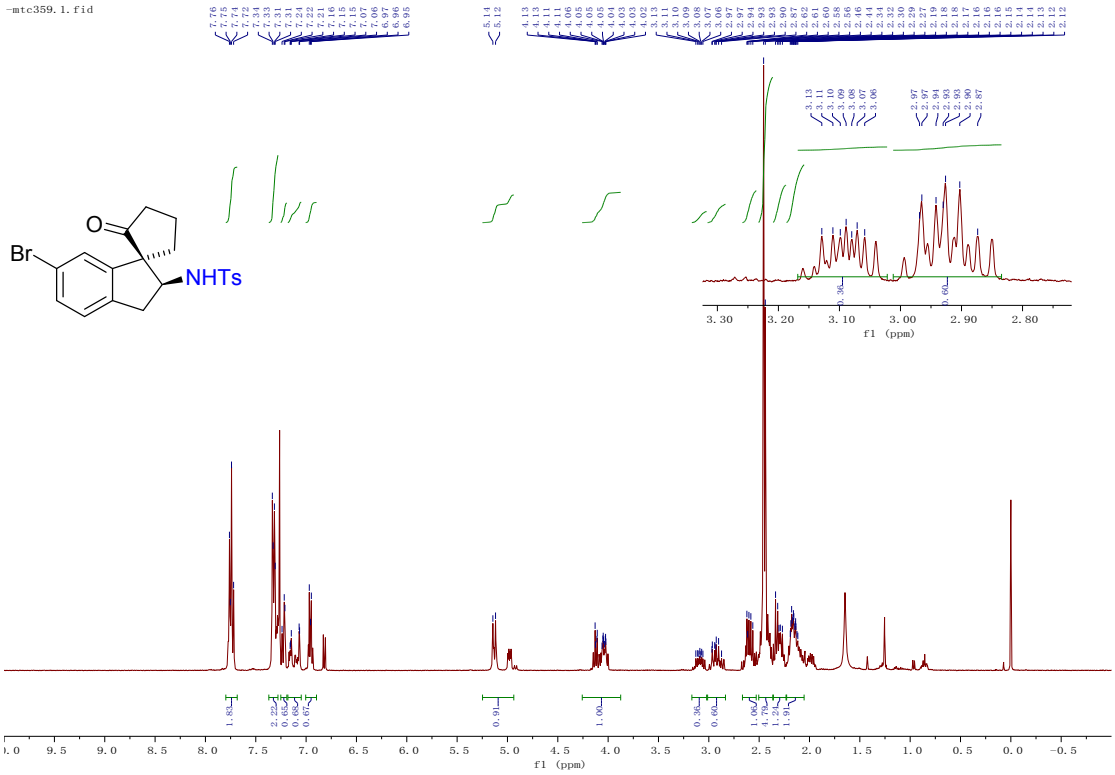
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3c



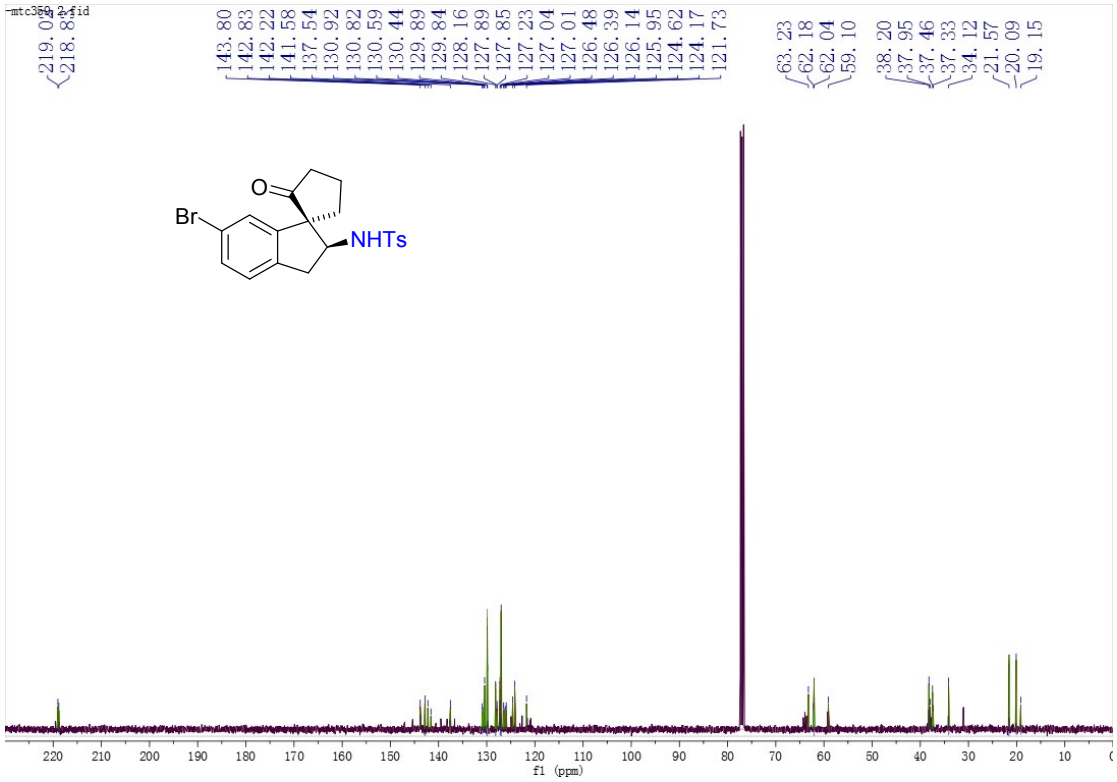
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3c



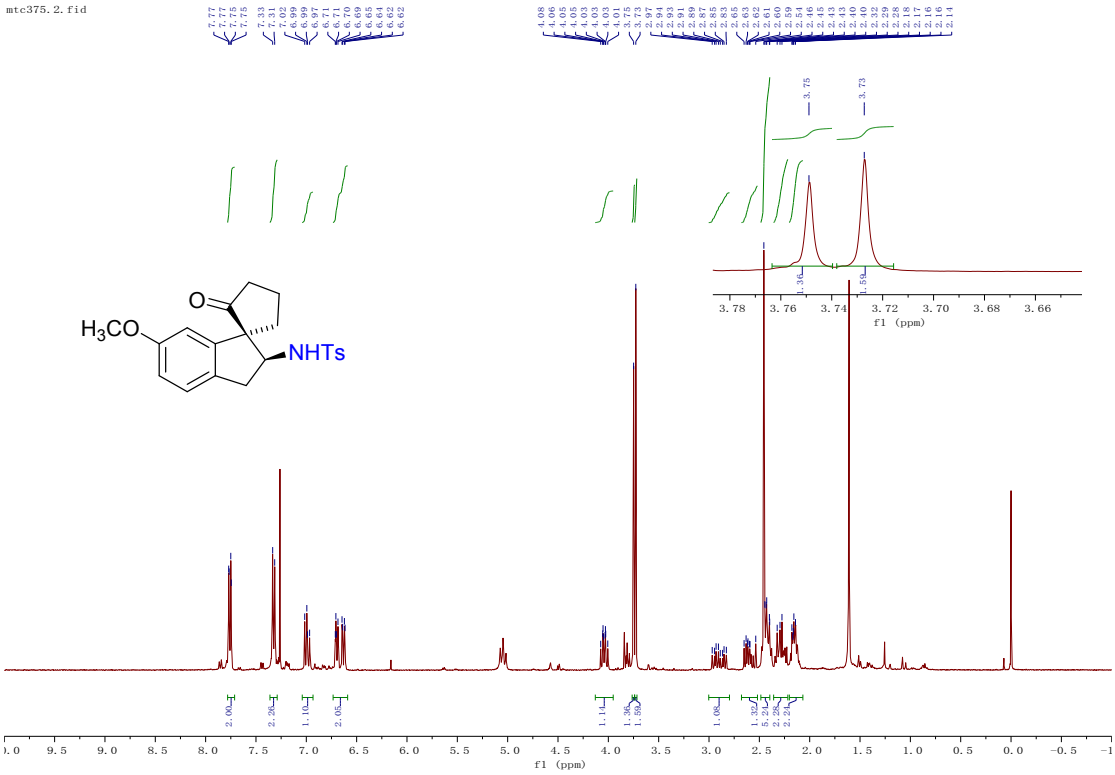
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3d



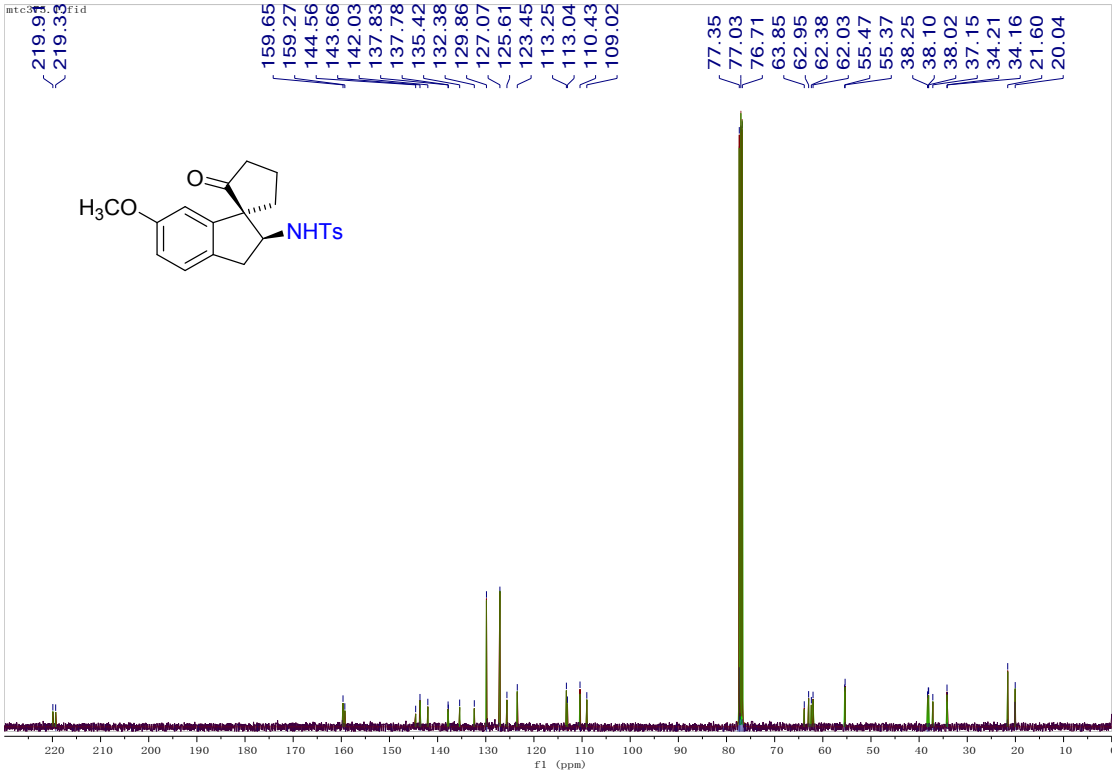
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3d



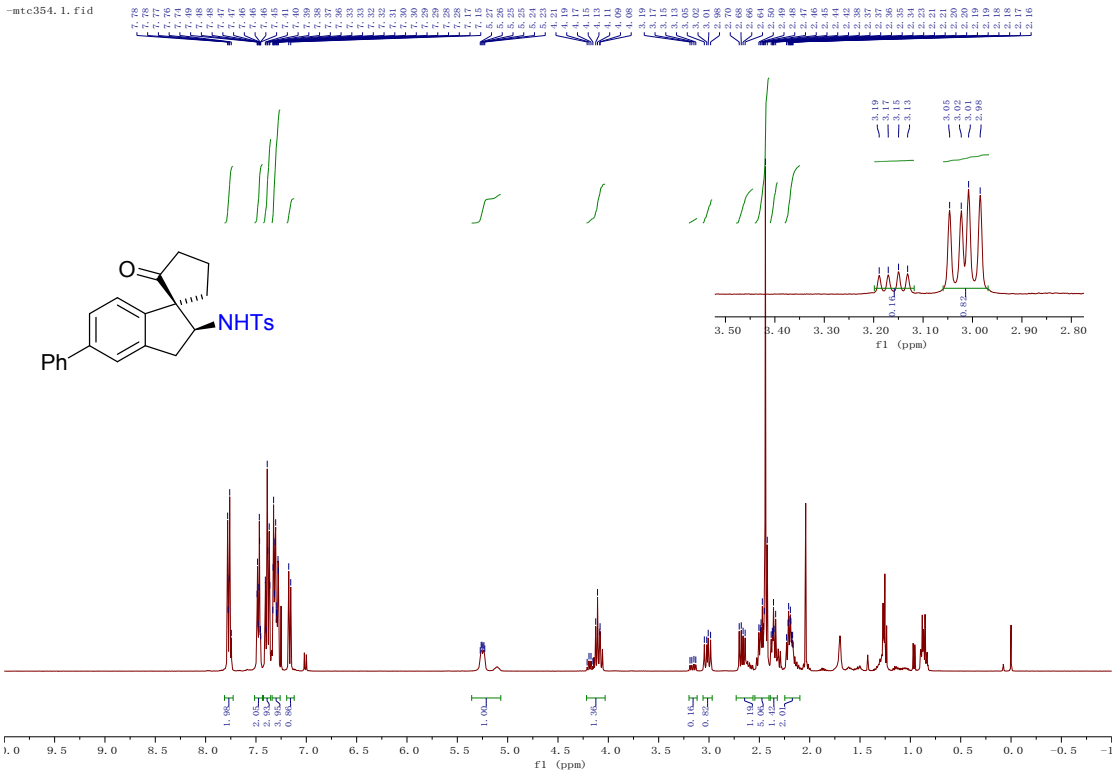
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3e



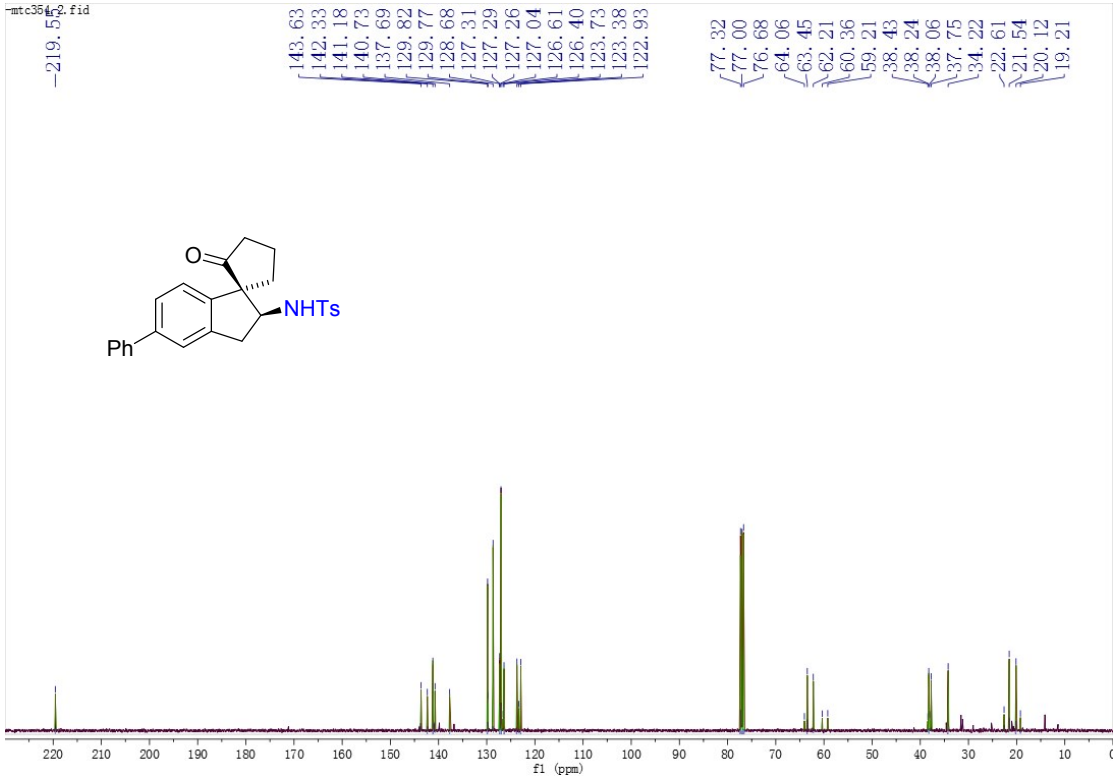
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3e



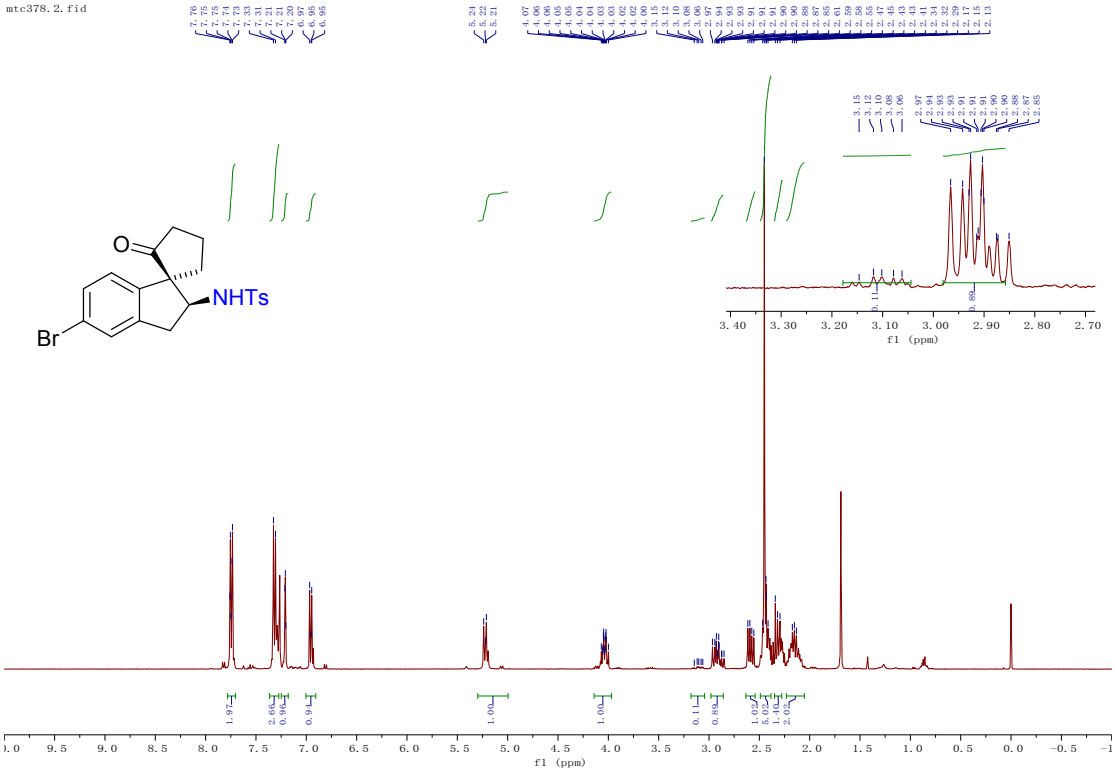
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3f



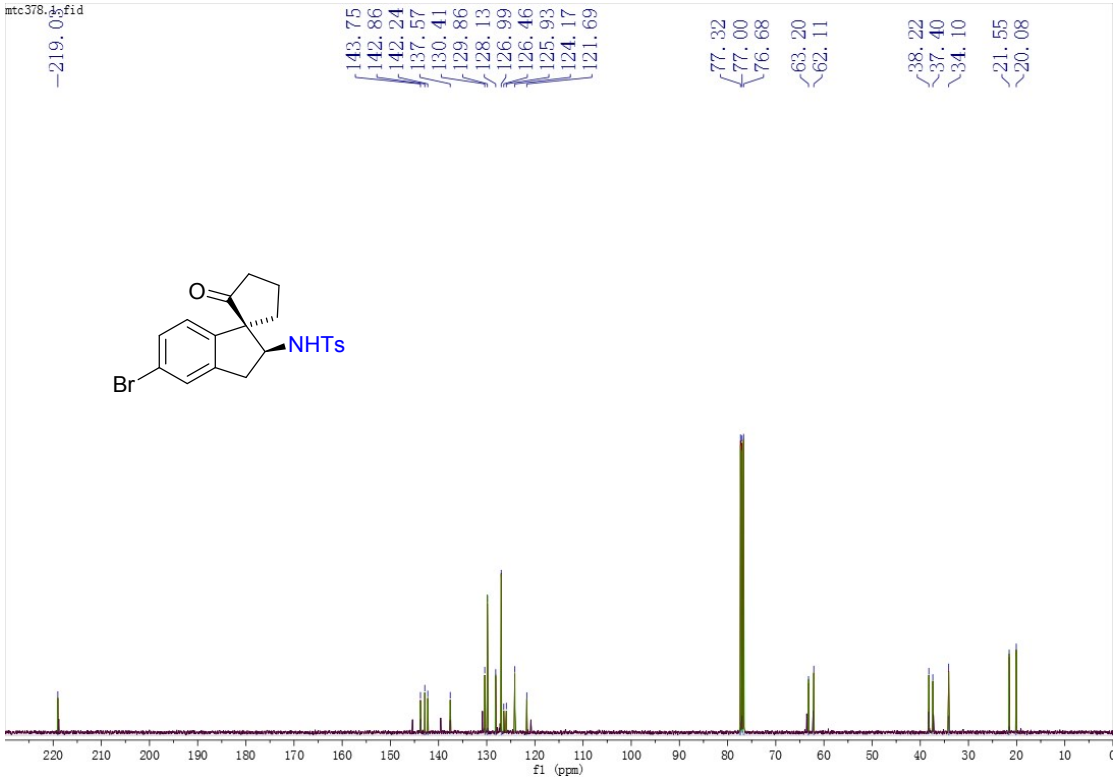
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3f



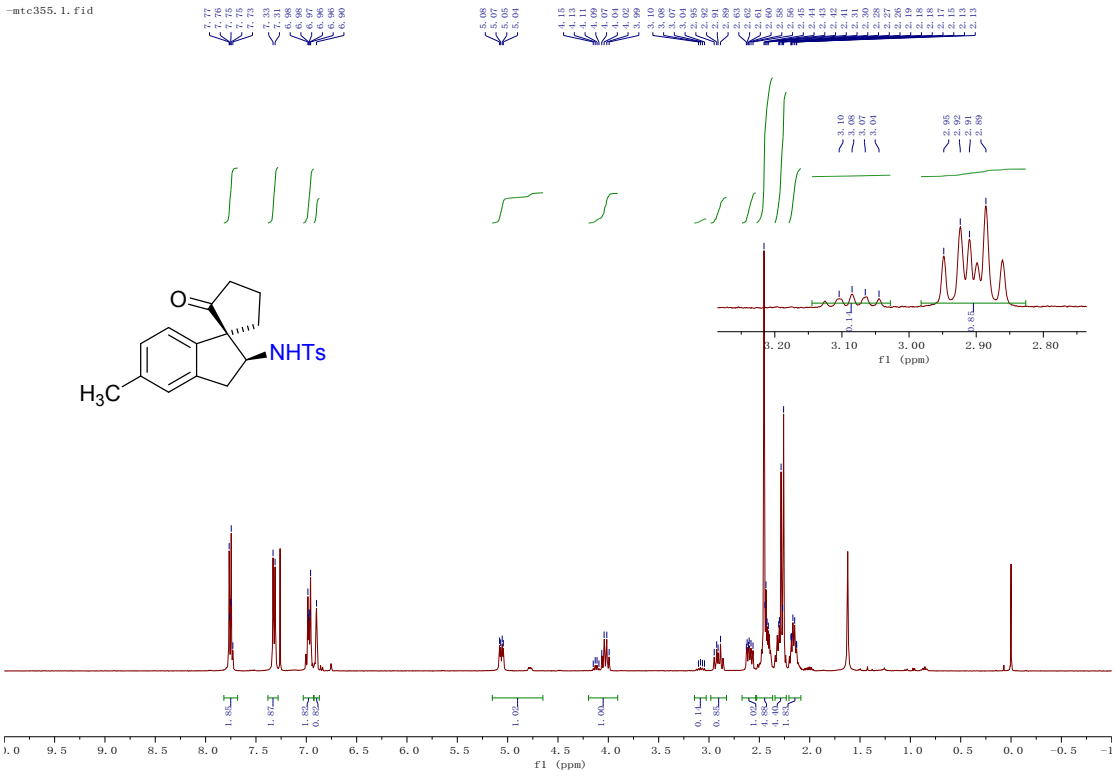
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3g



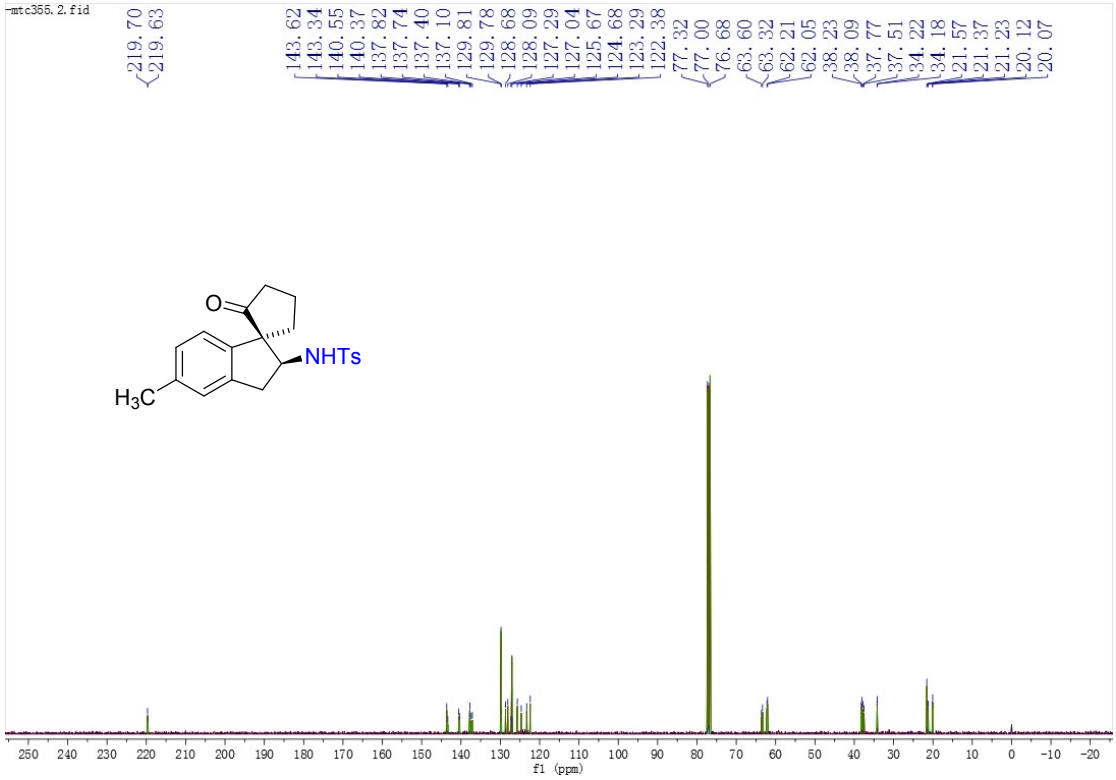
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3g



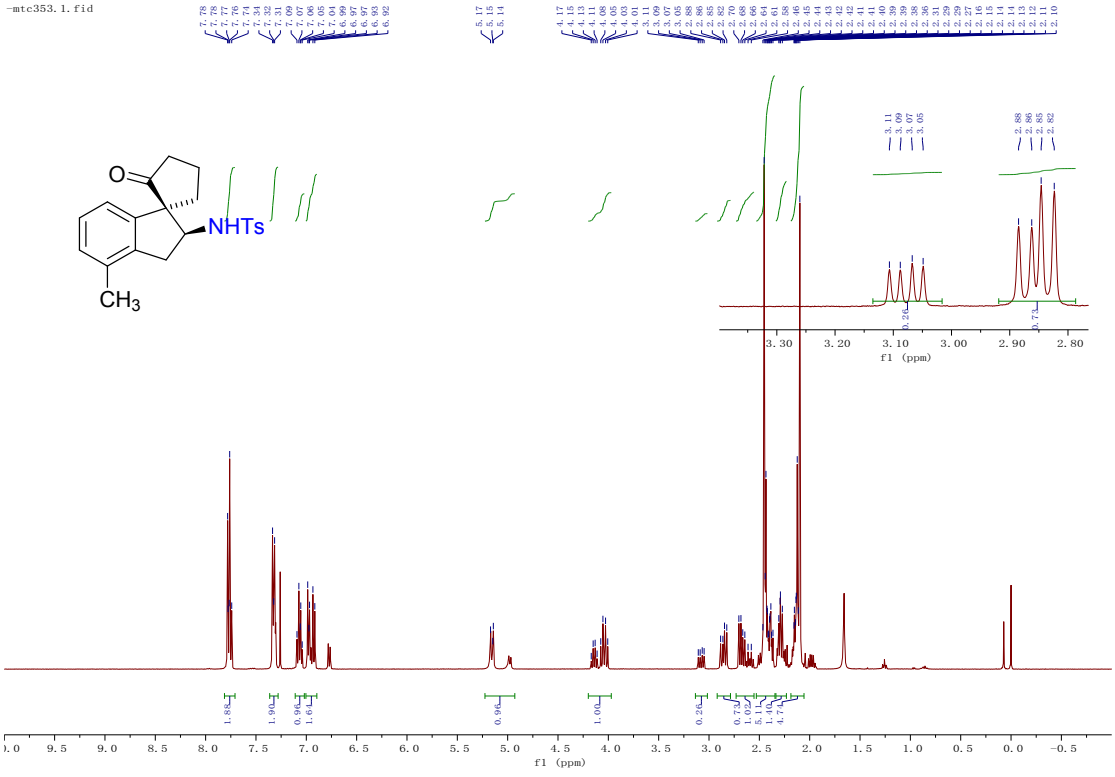
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3h



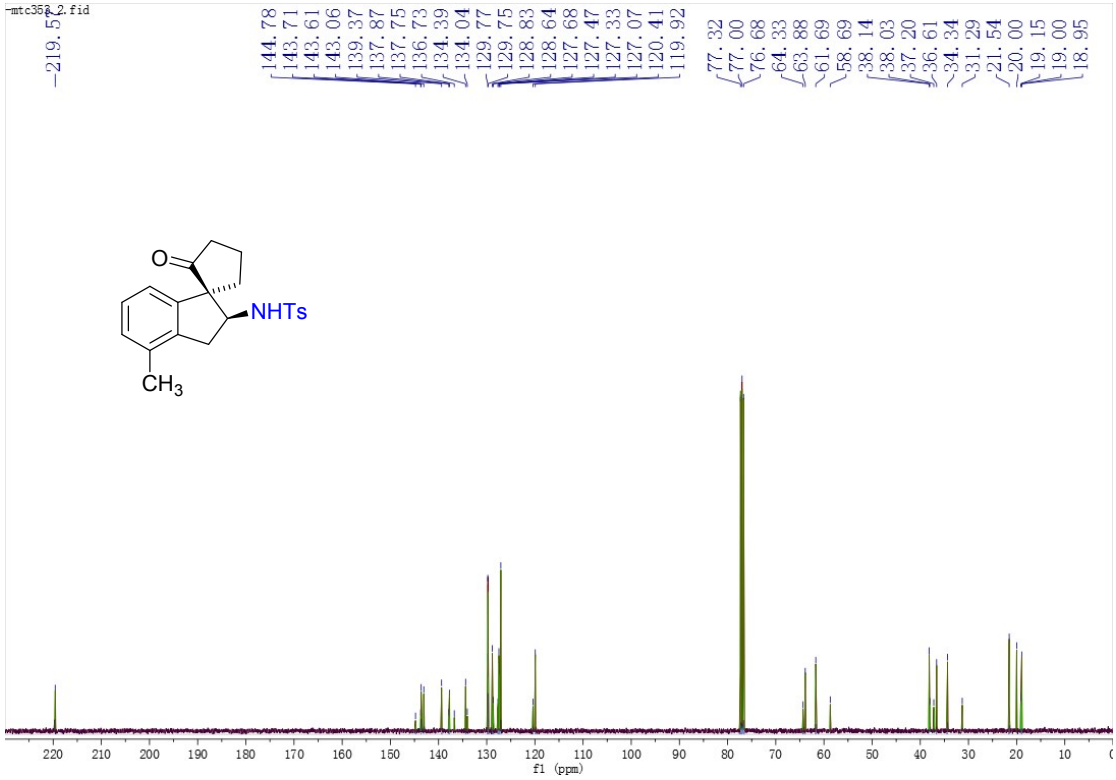
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3h



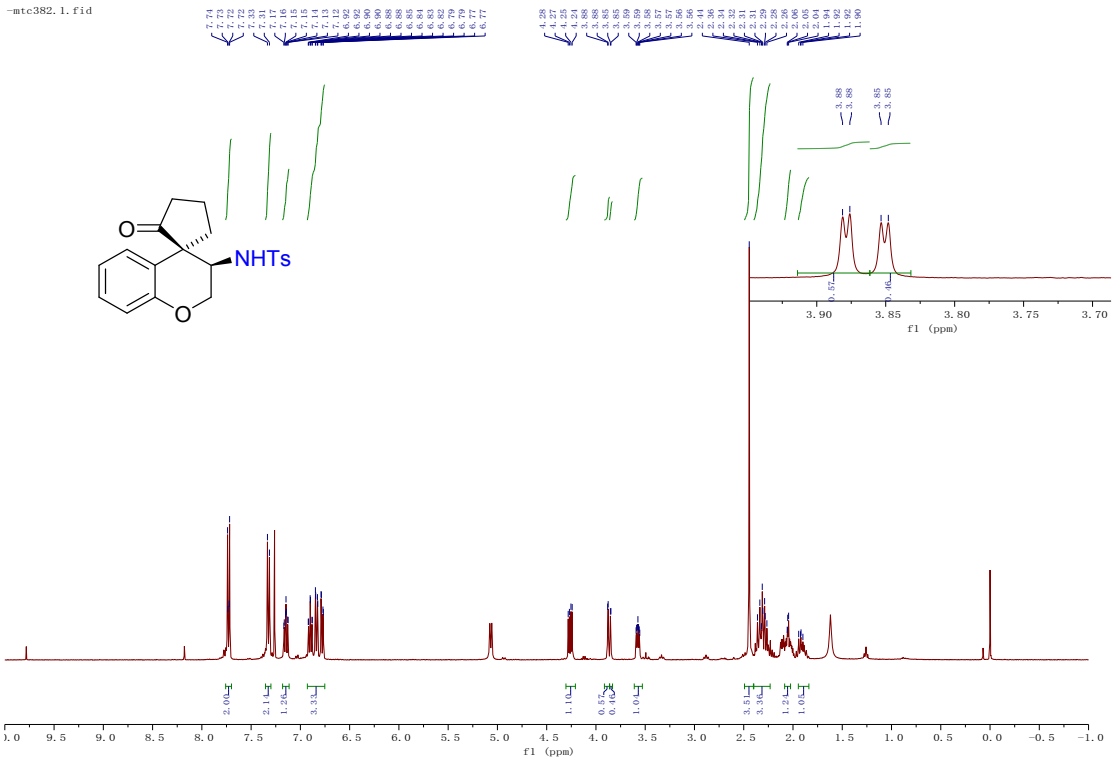
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3i



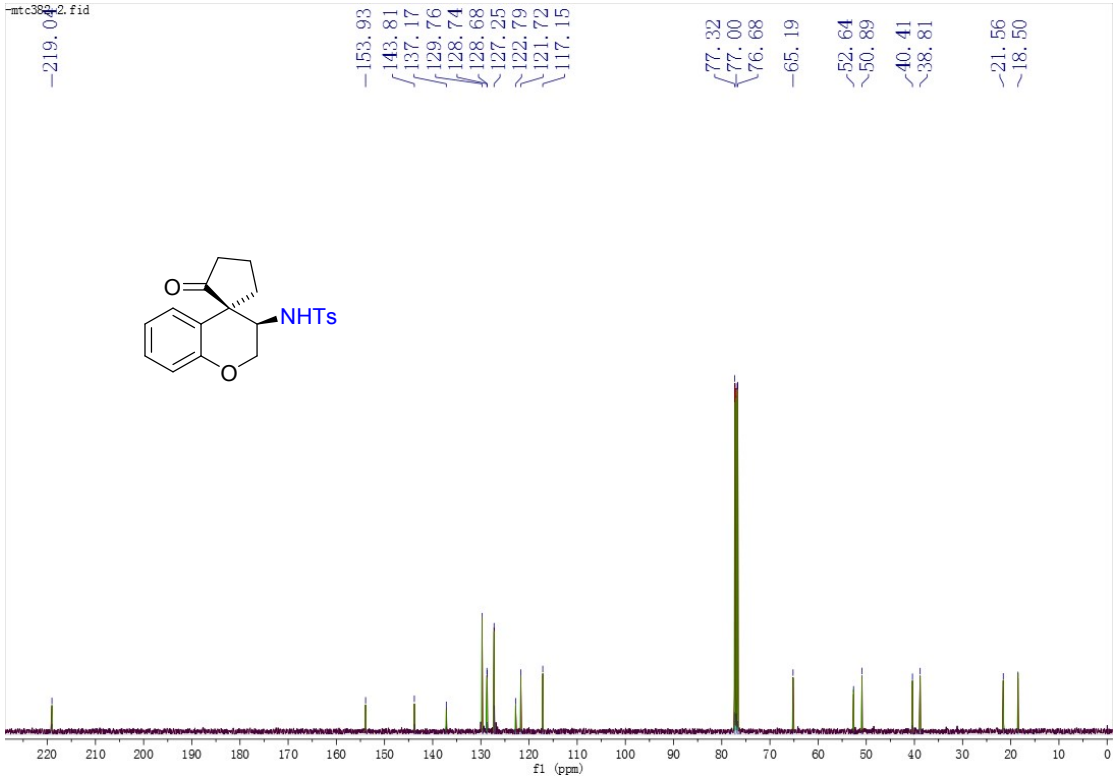
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3i



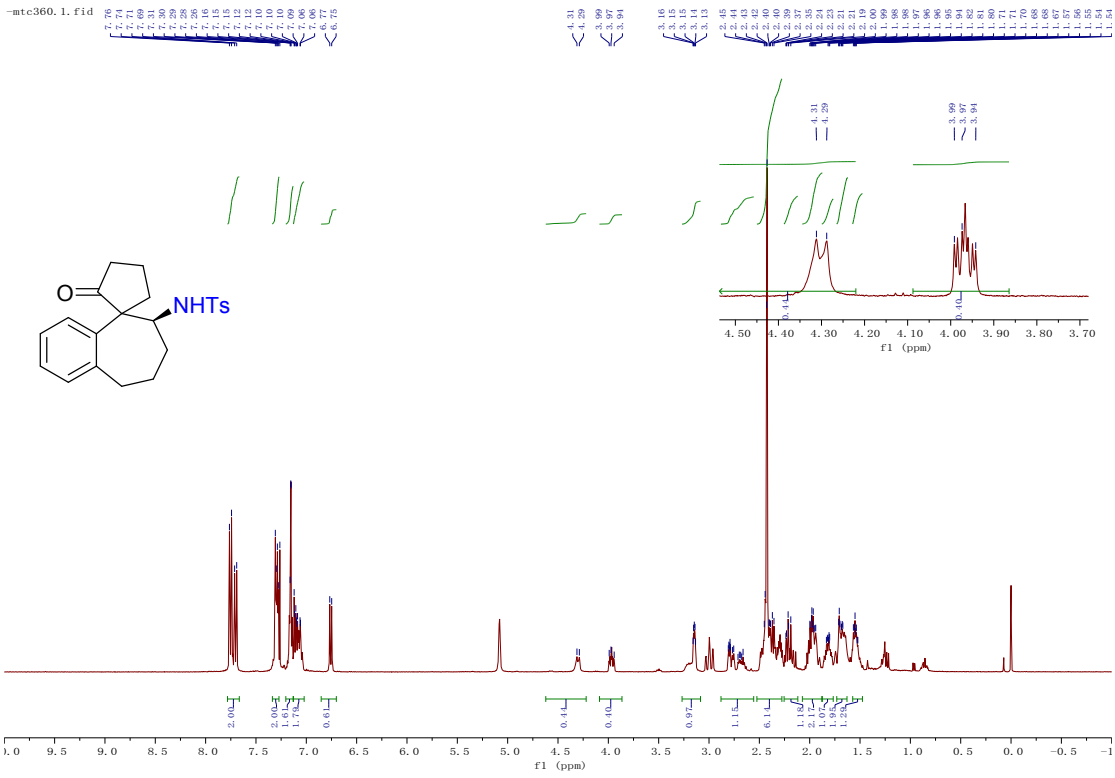
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3j



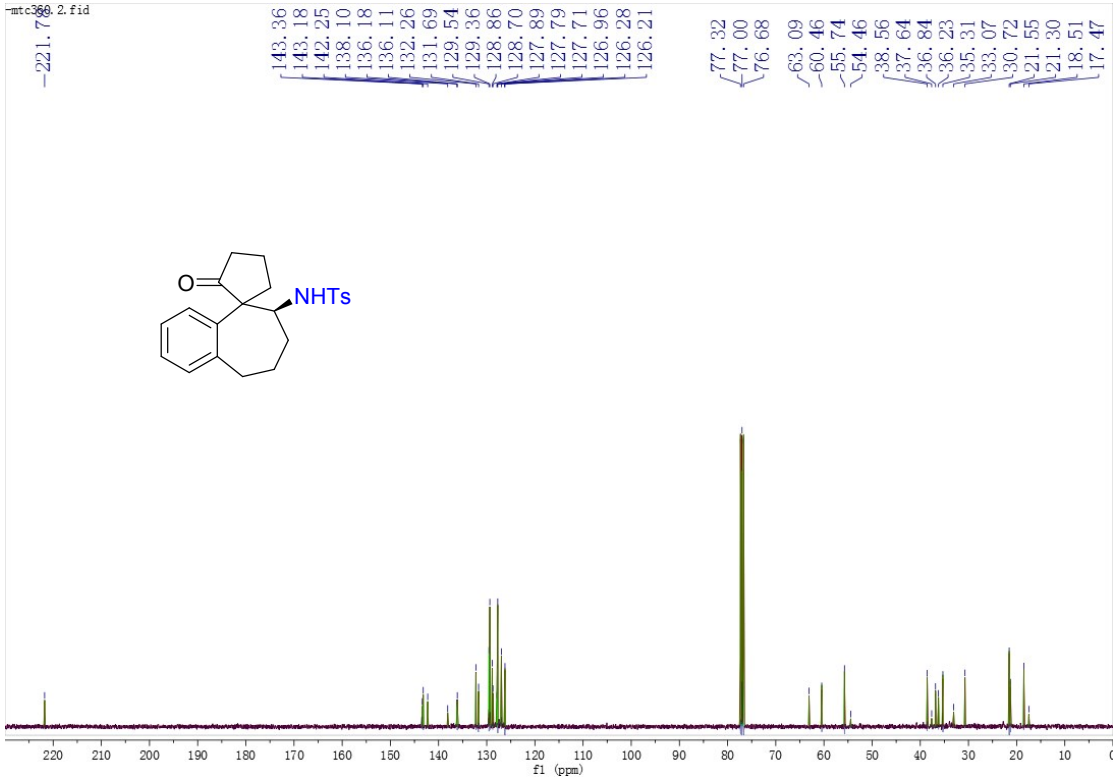
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3j



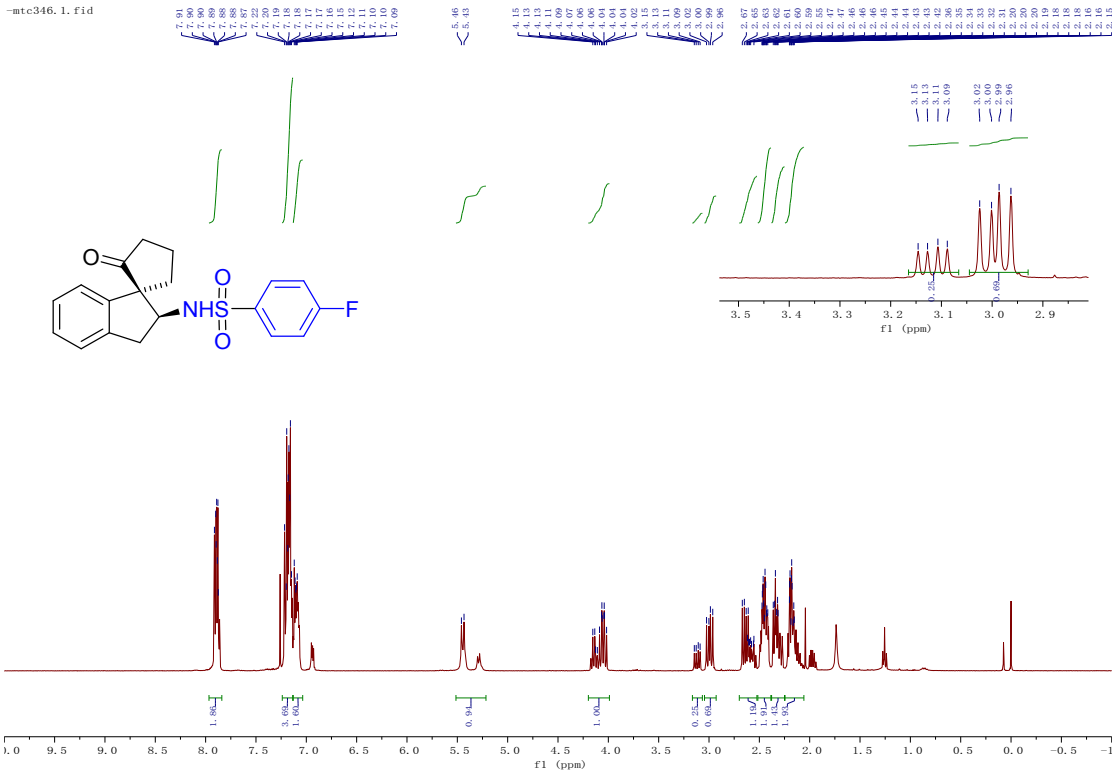
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3k



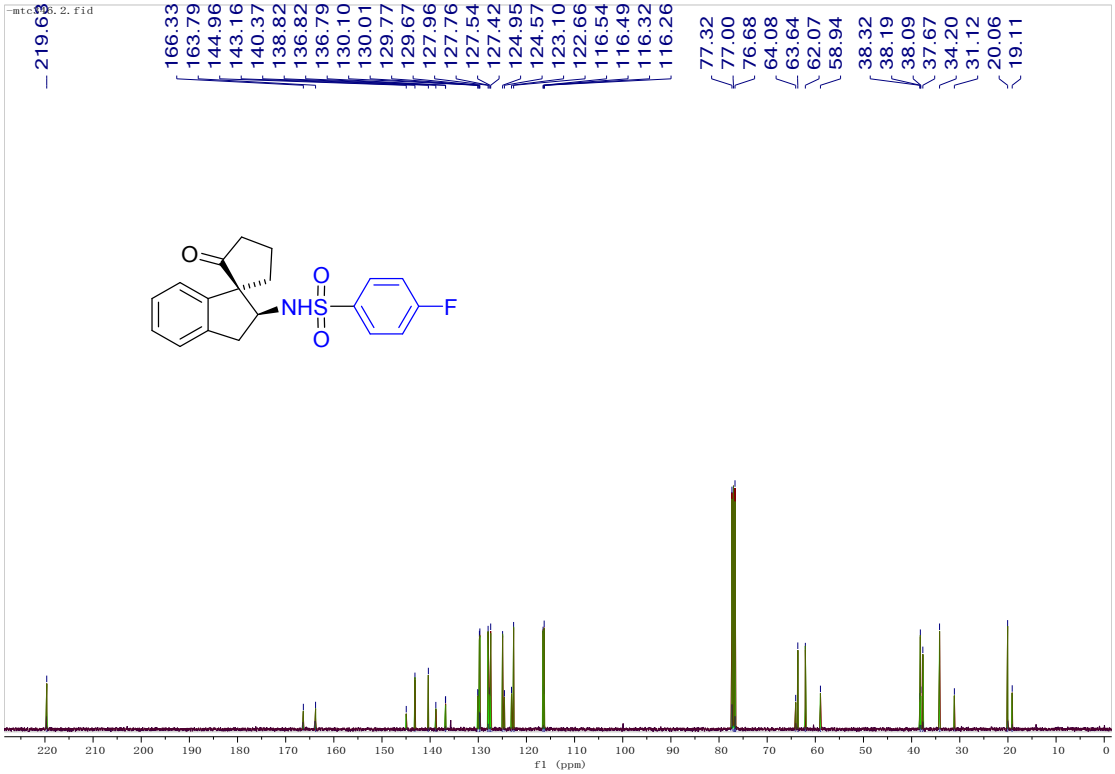
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3k



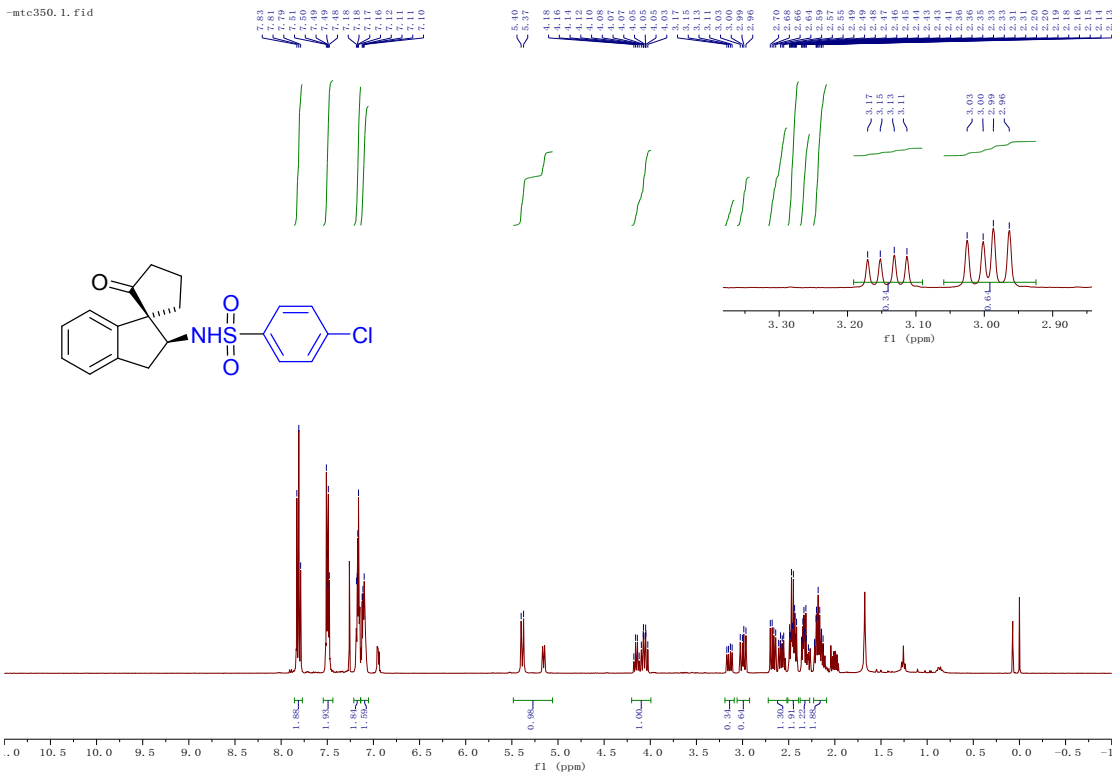
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3l



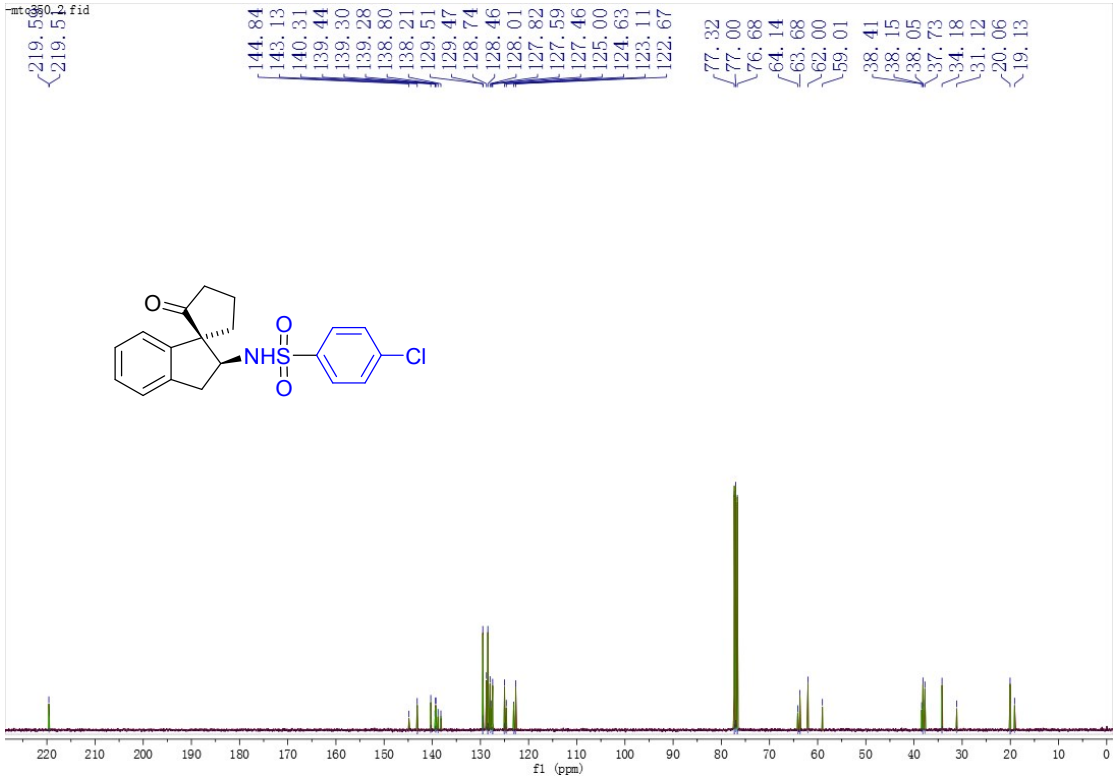
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3l



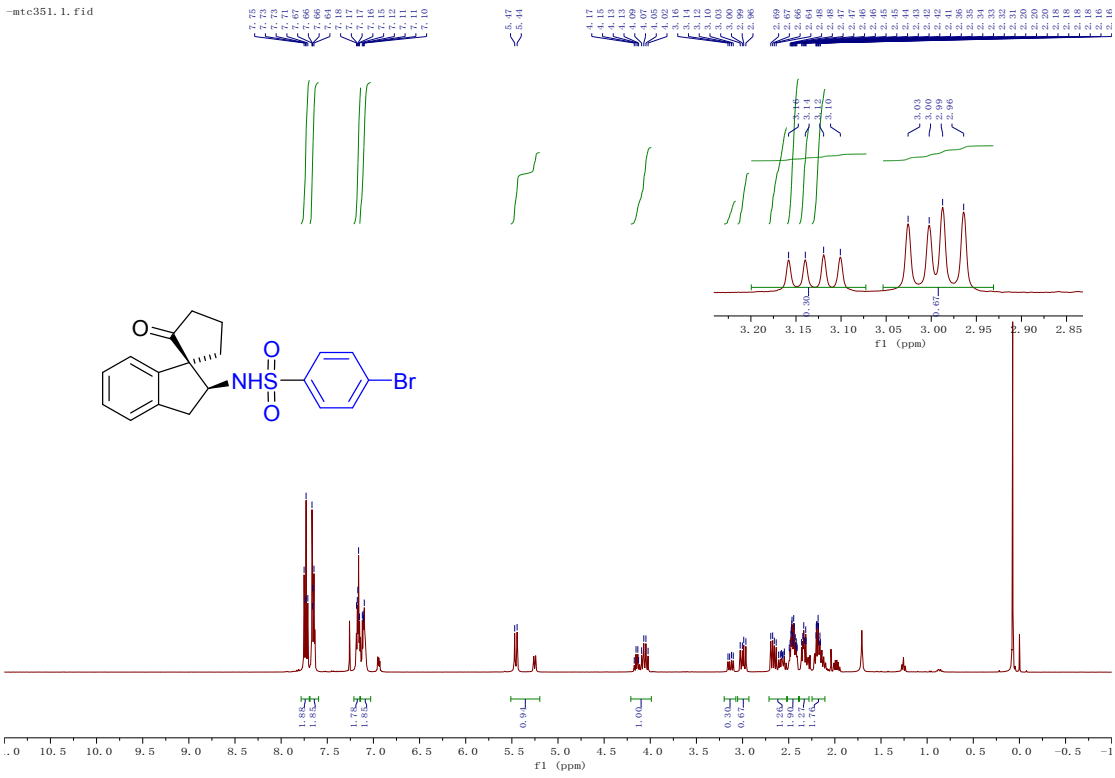
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3m



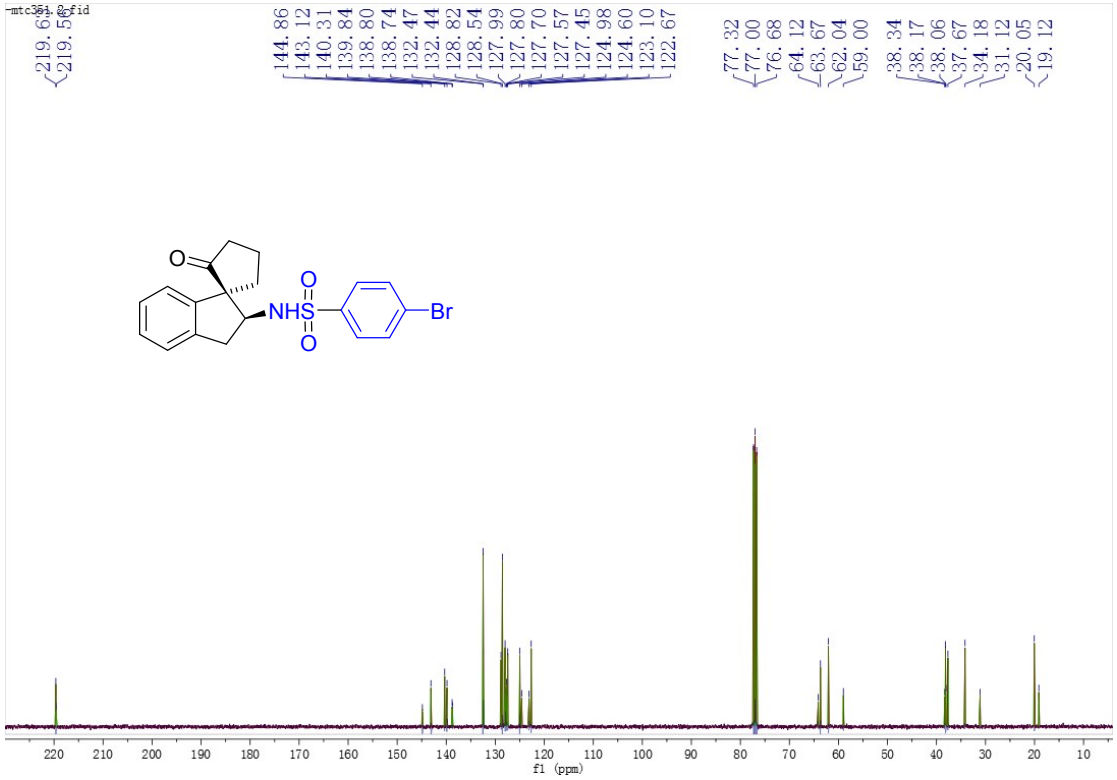
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3m



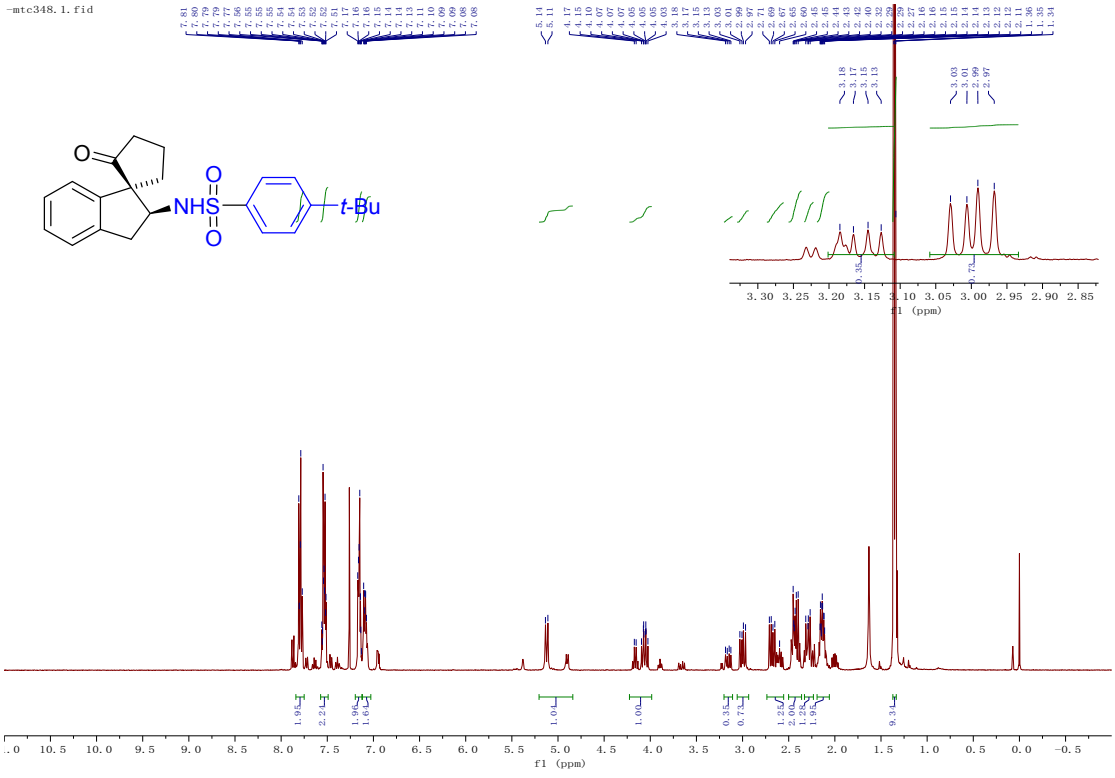
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3n



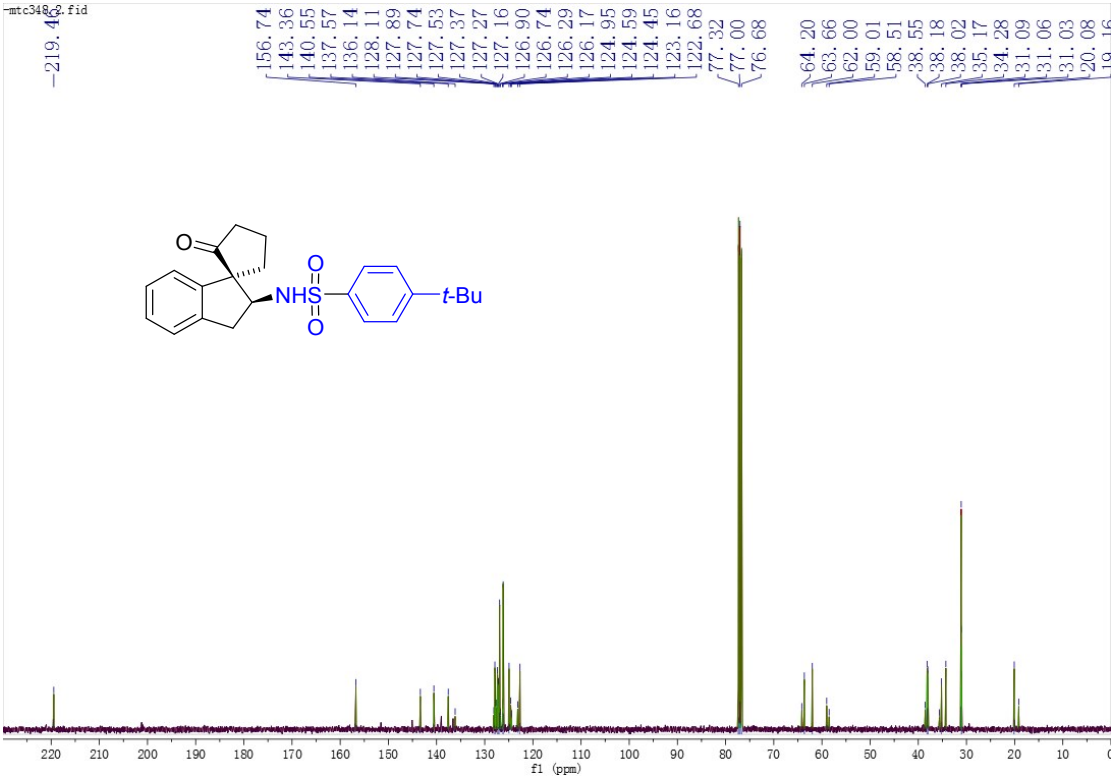
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3n



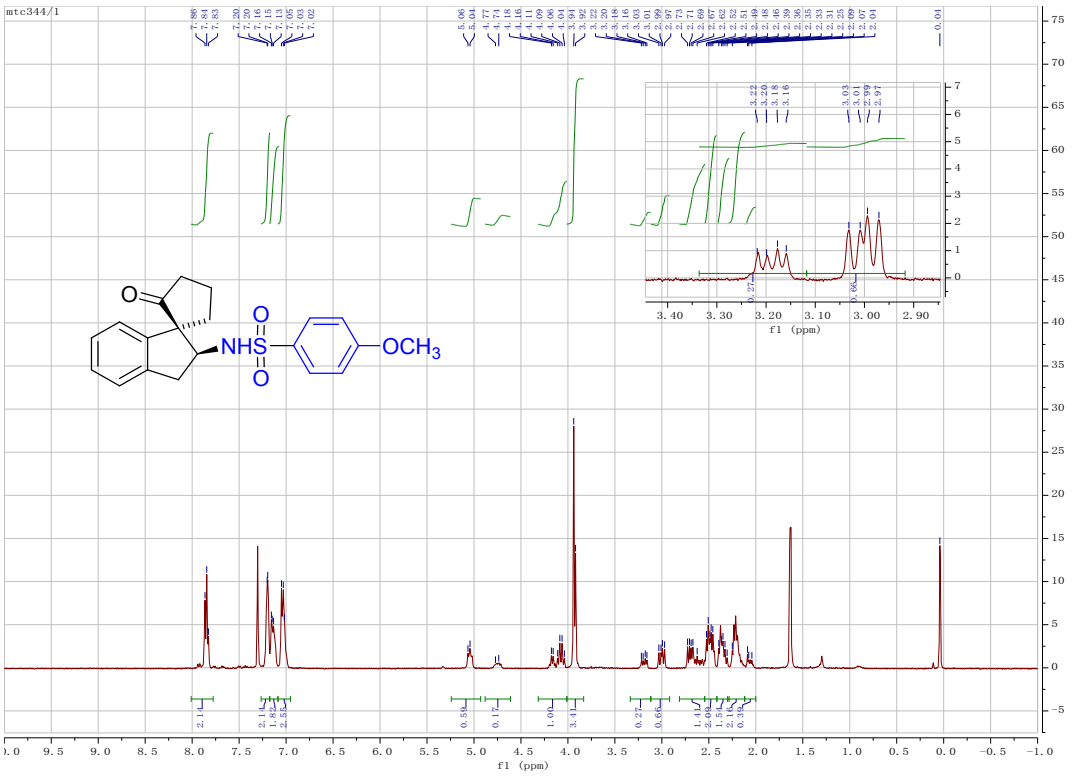
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3o

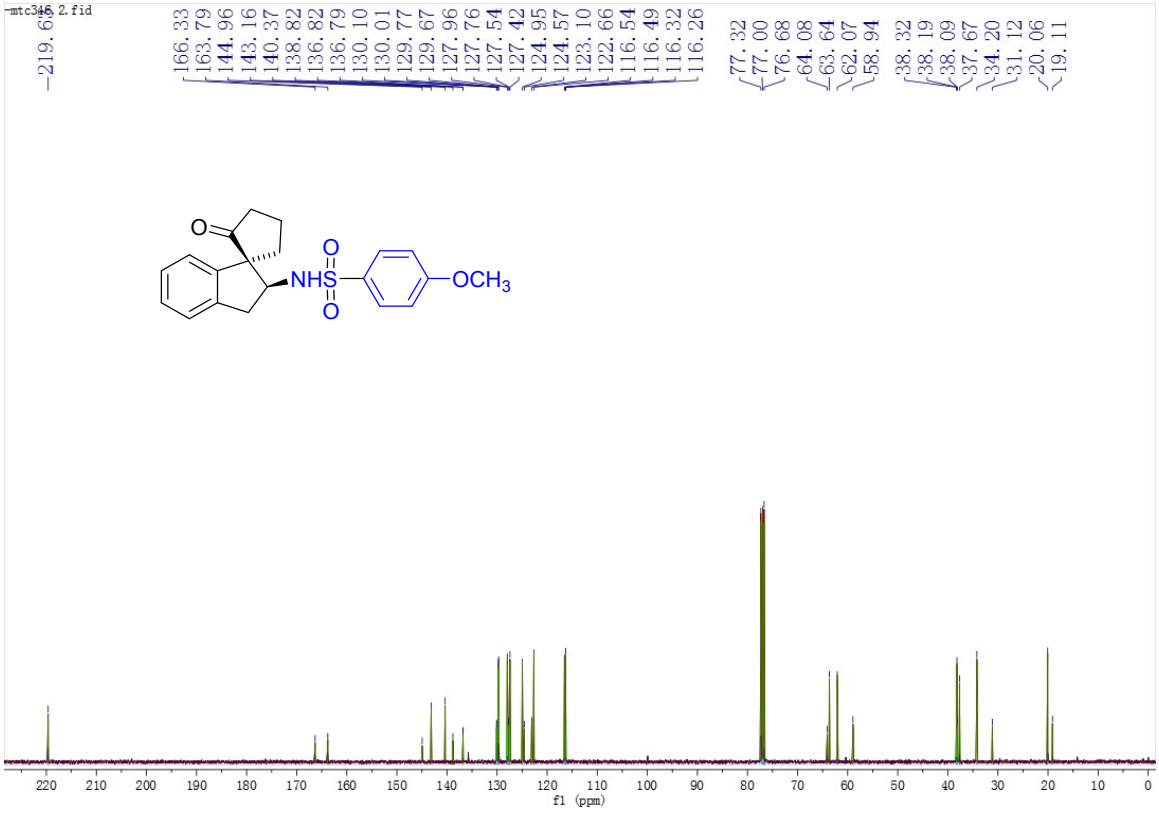


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3o

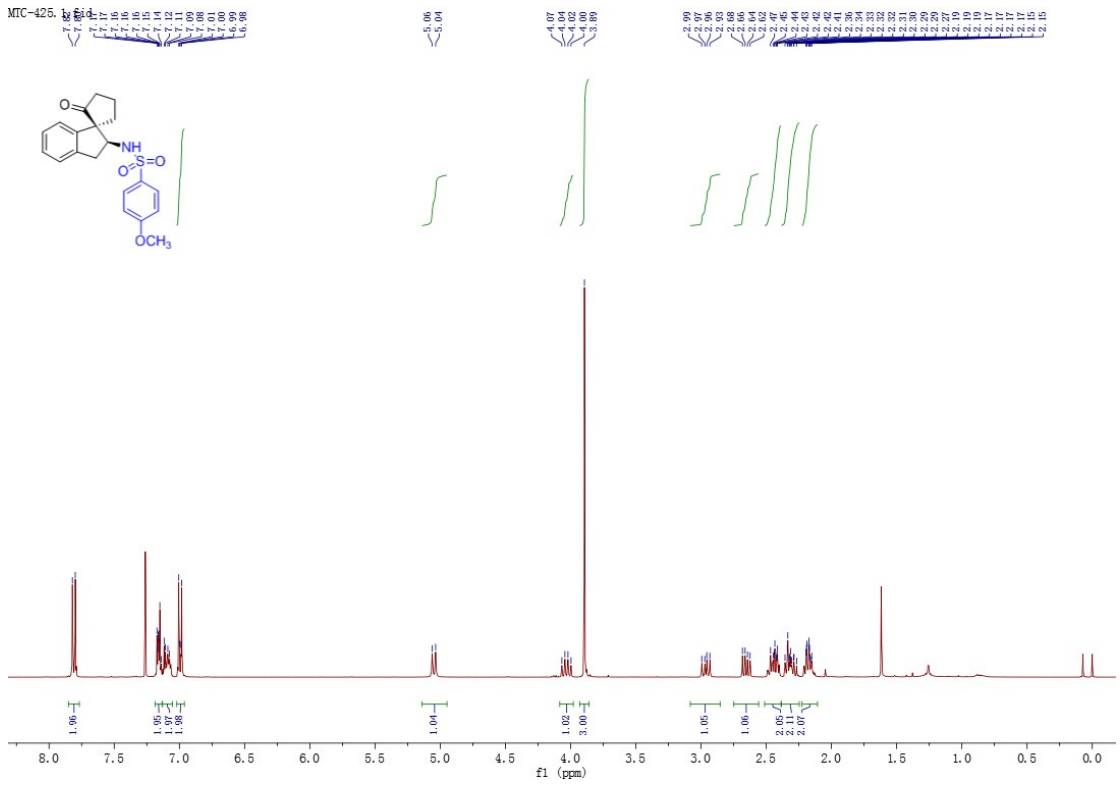


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3p

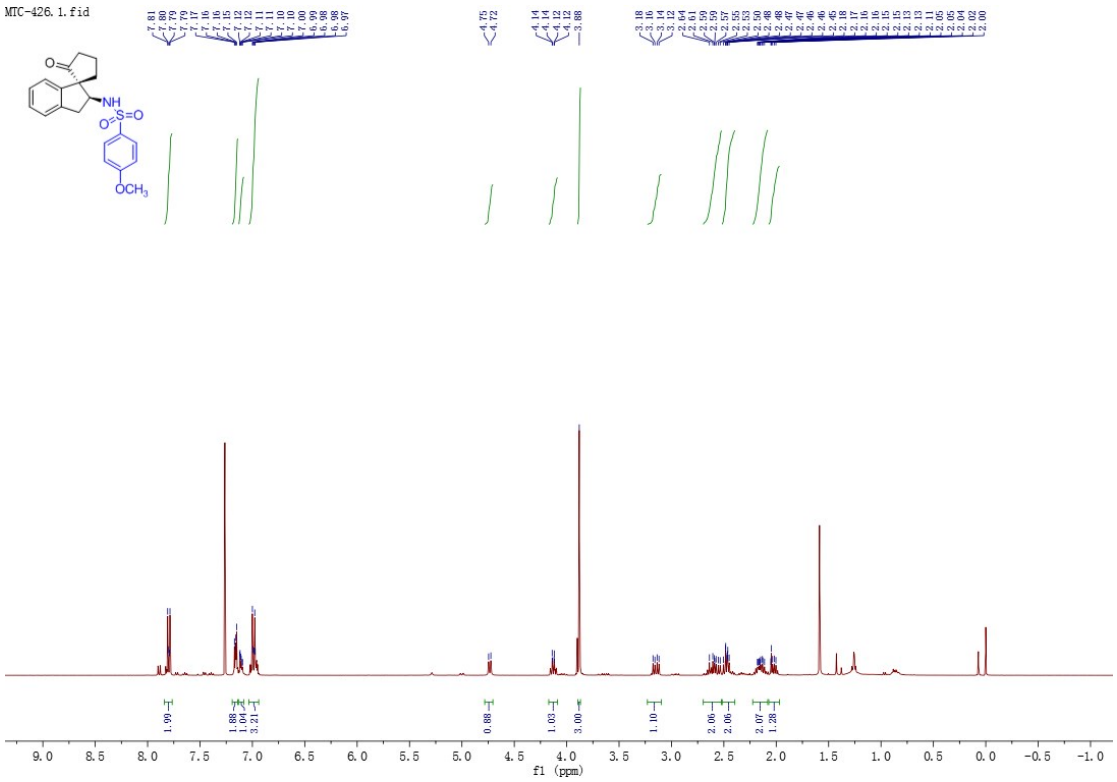




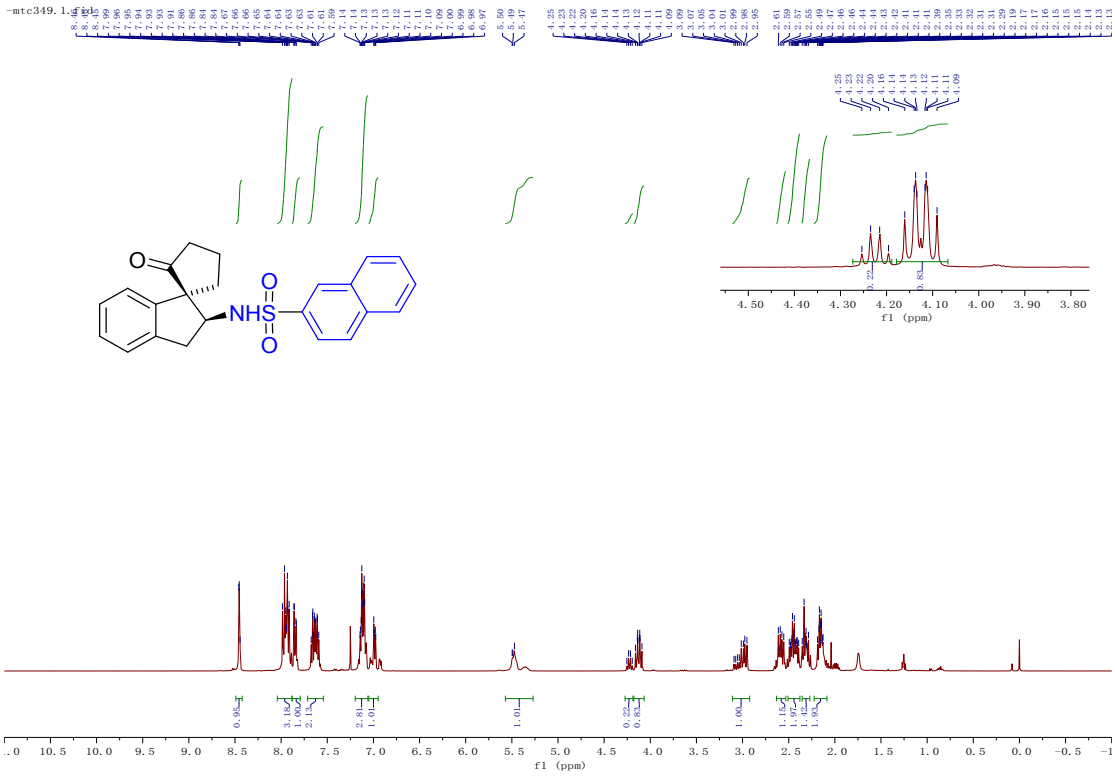
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of diastereomer of 3p (major)



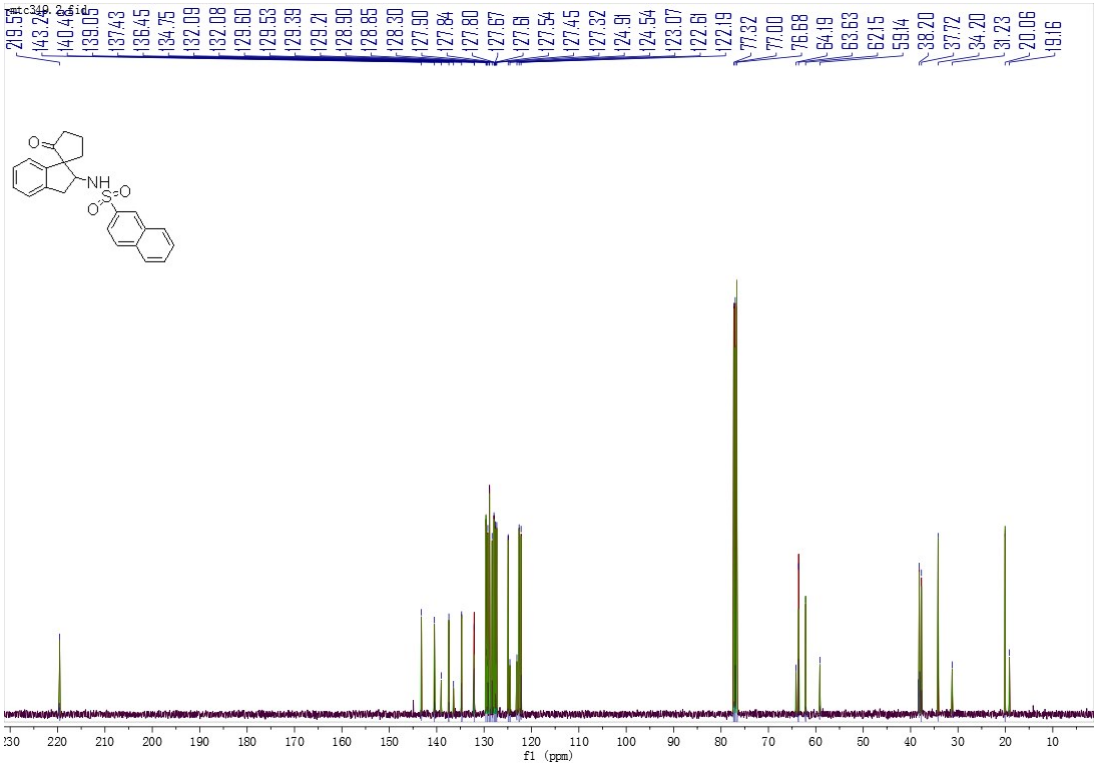
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of diastereomer of 3p (minor)



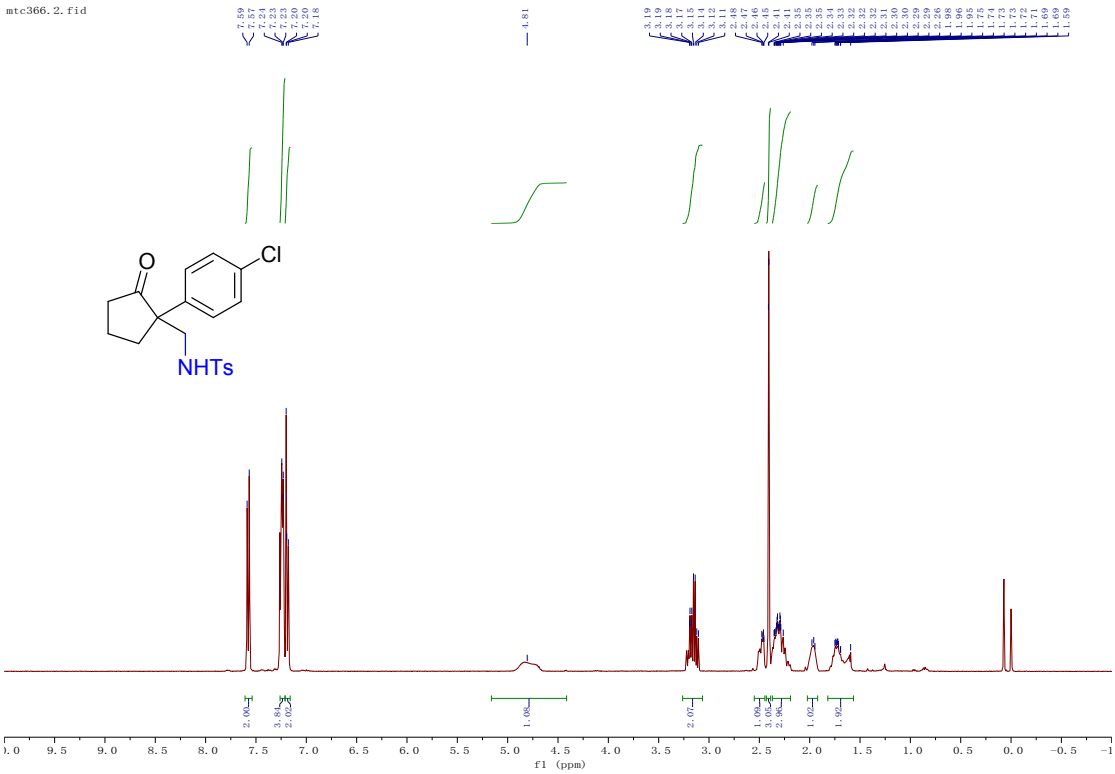
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3q



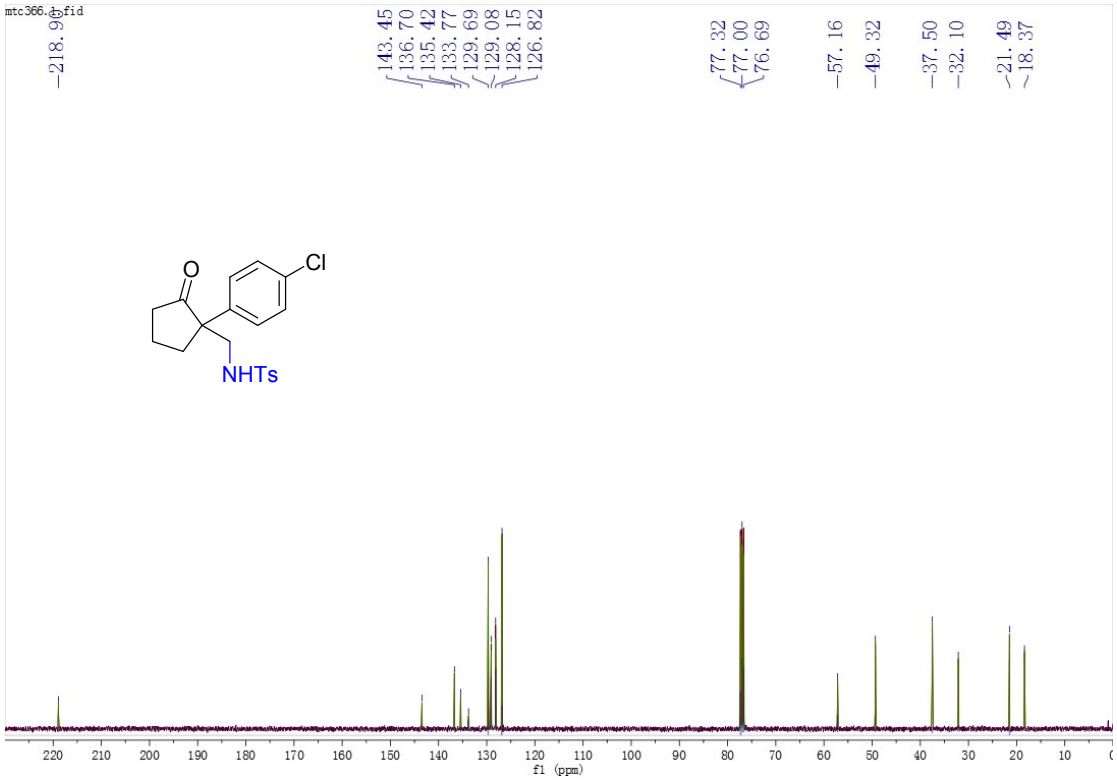
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3q



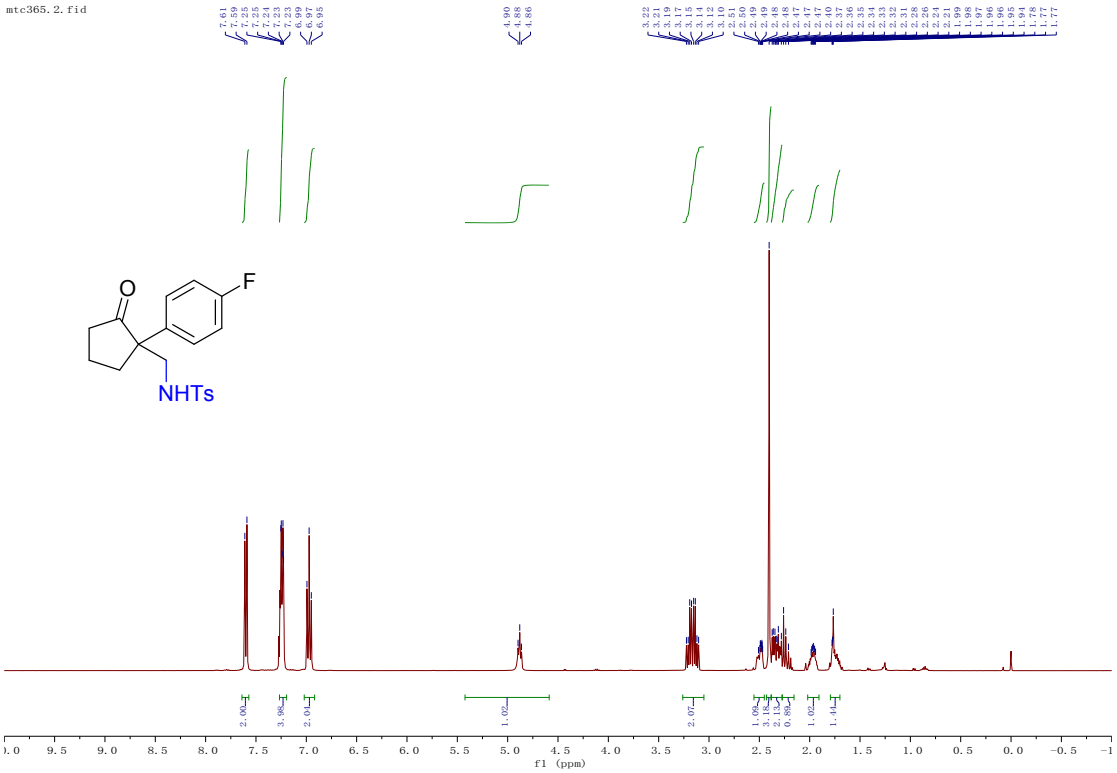
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5a



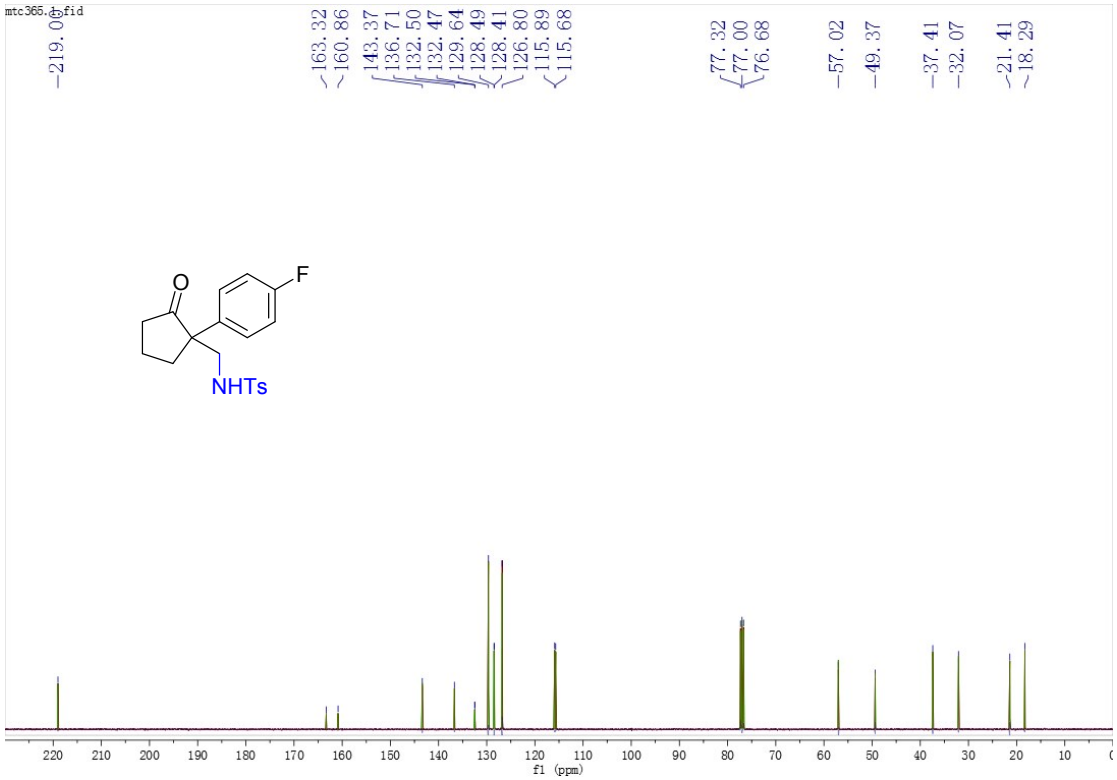
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5a



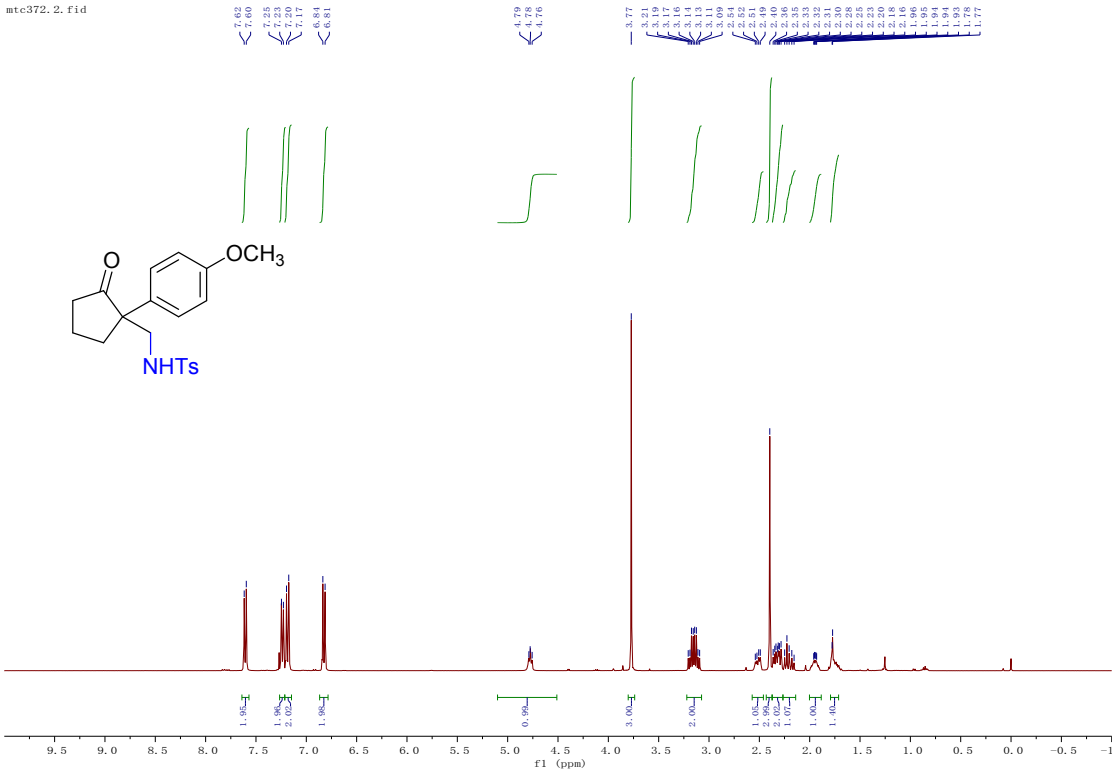
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5b



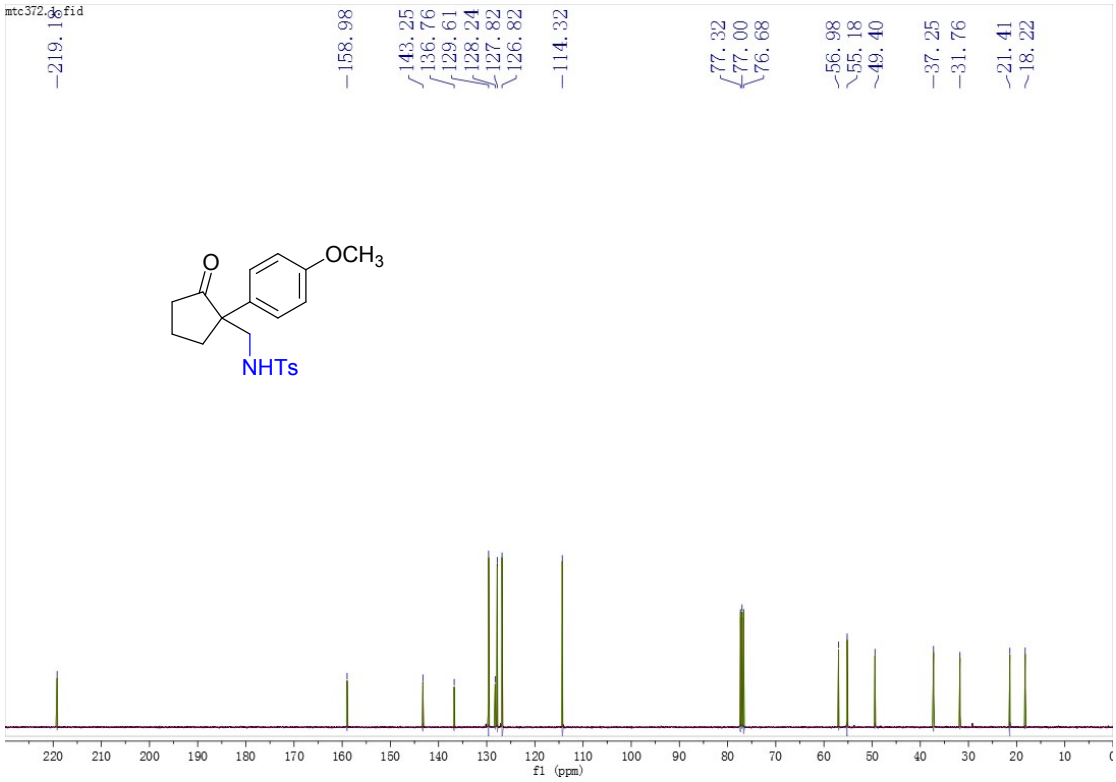
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5b



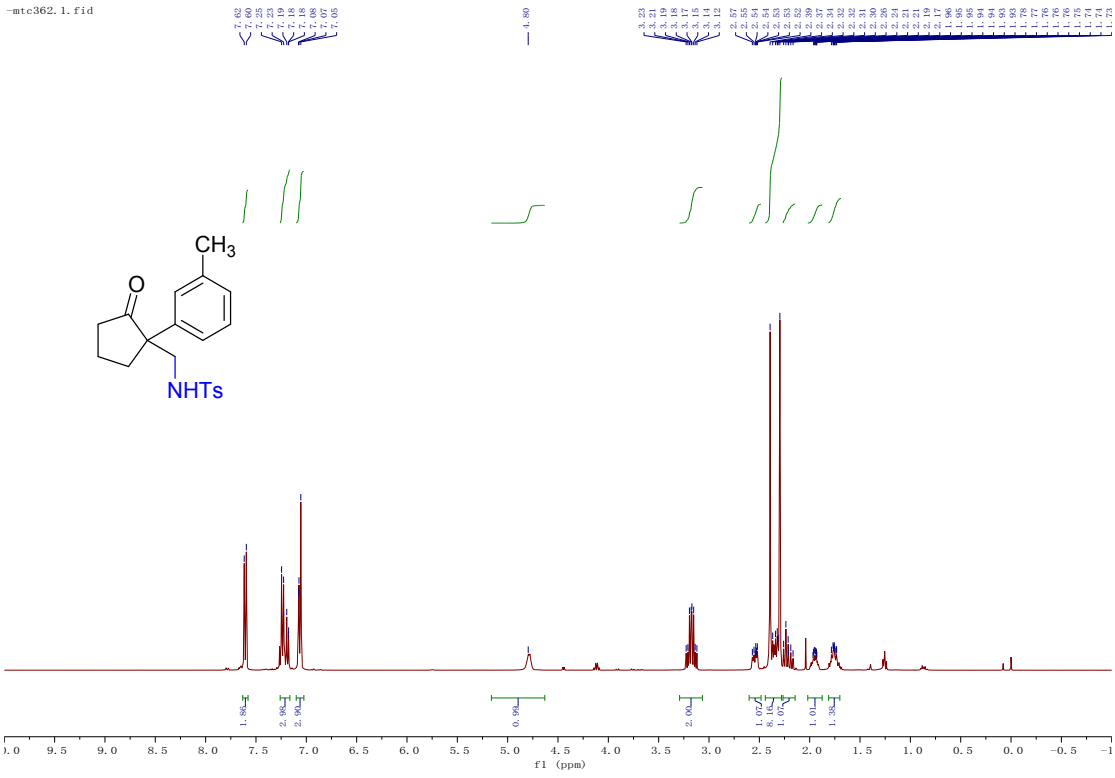
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5c



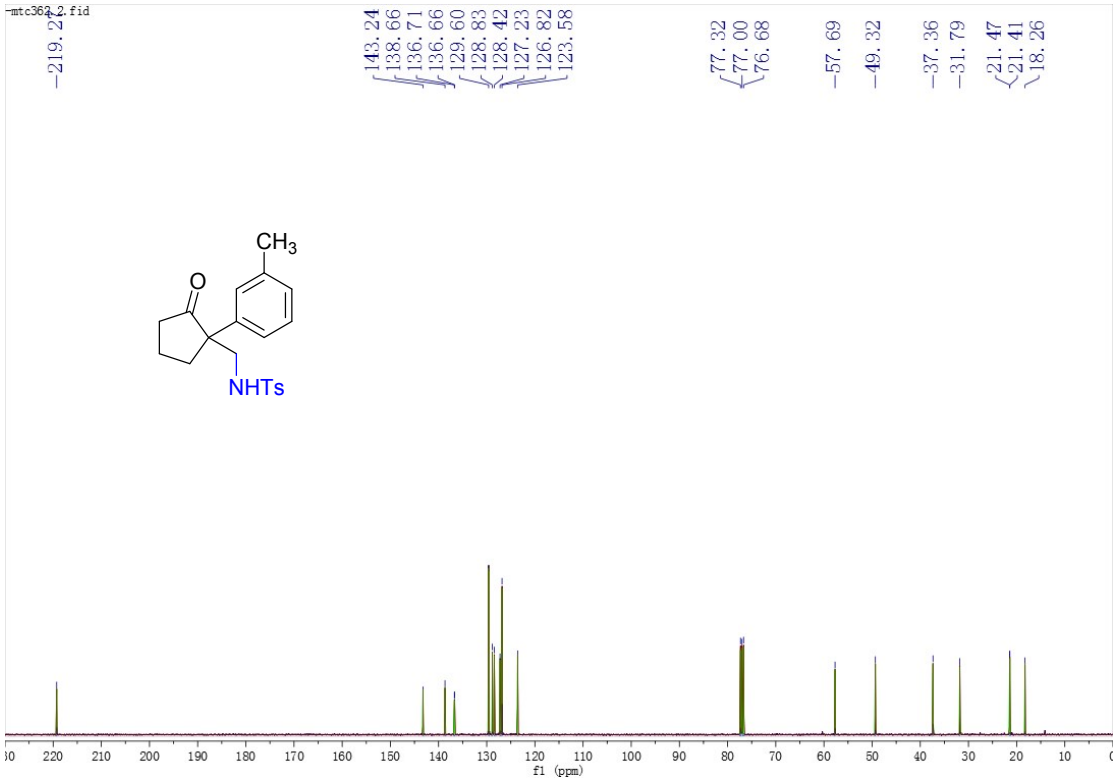
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5c



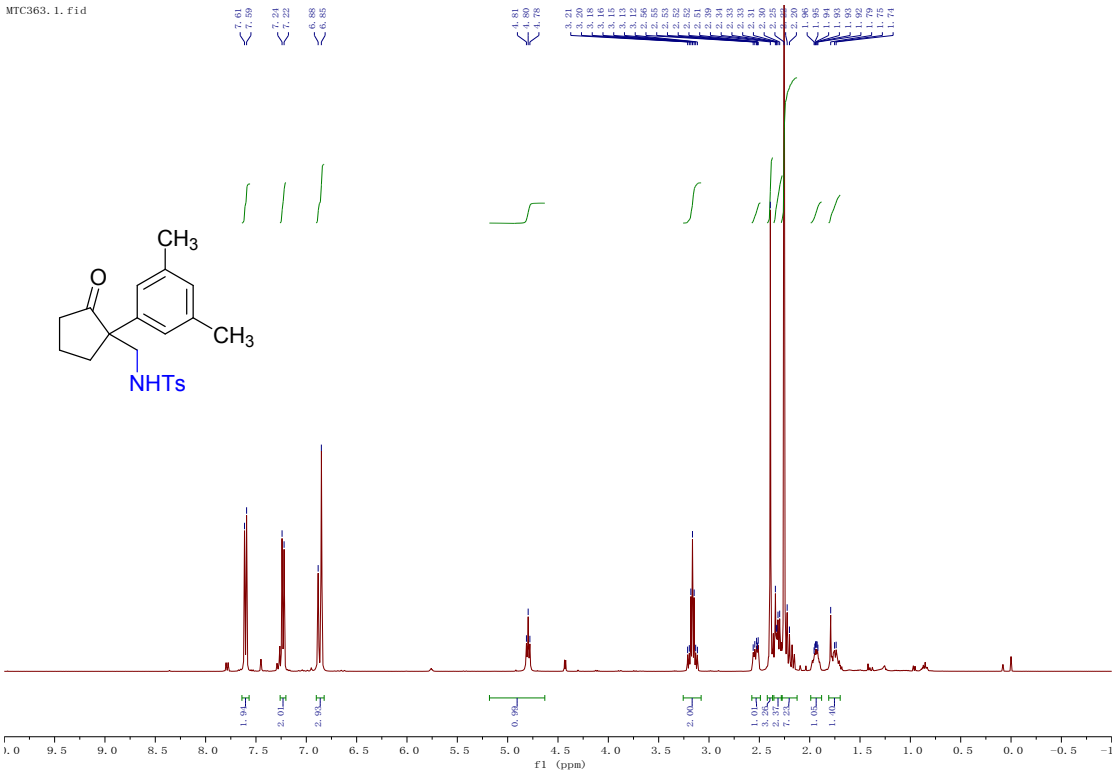
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5d



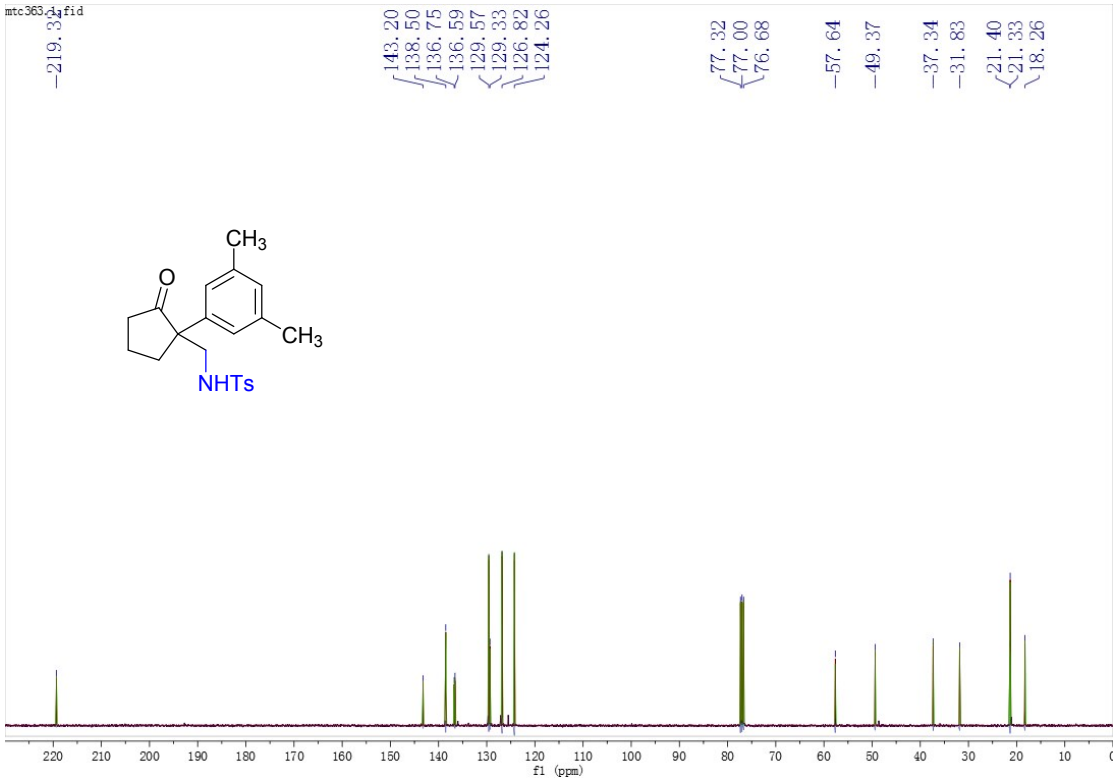
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5d



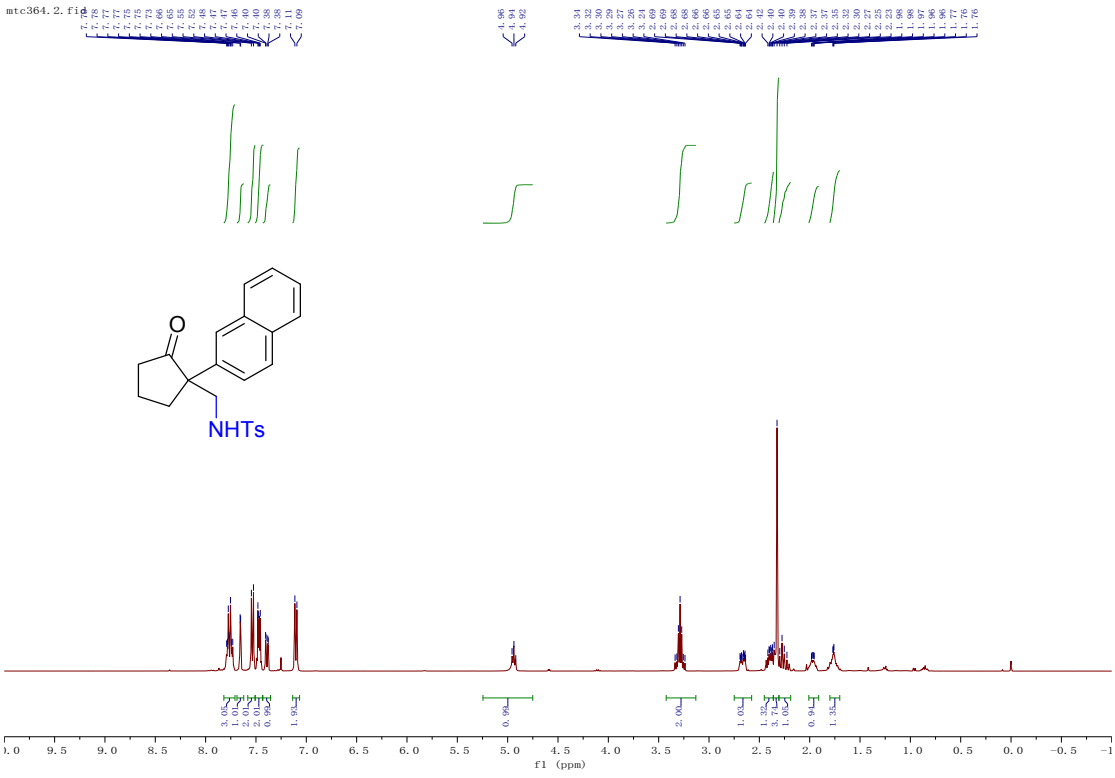
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5e



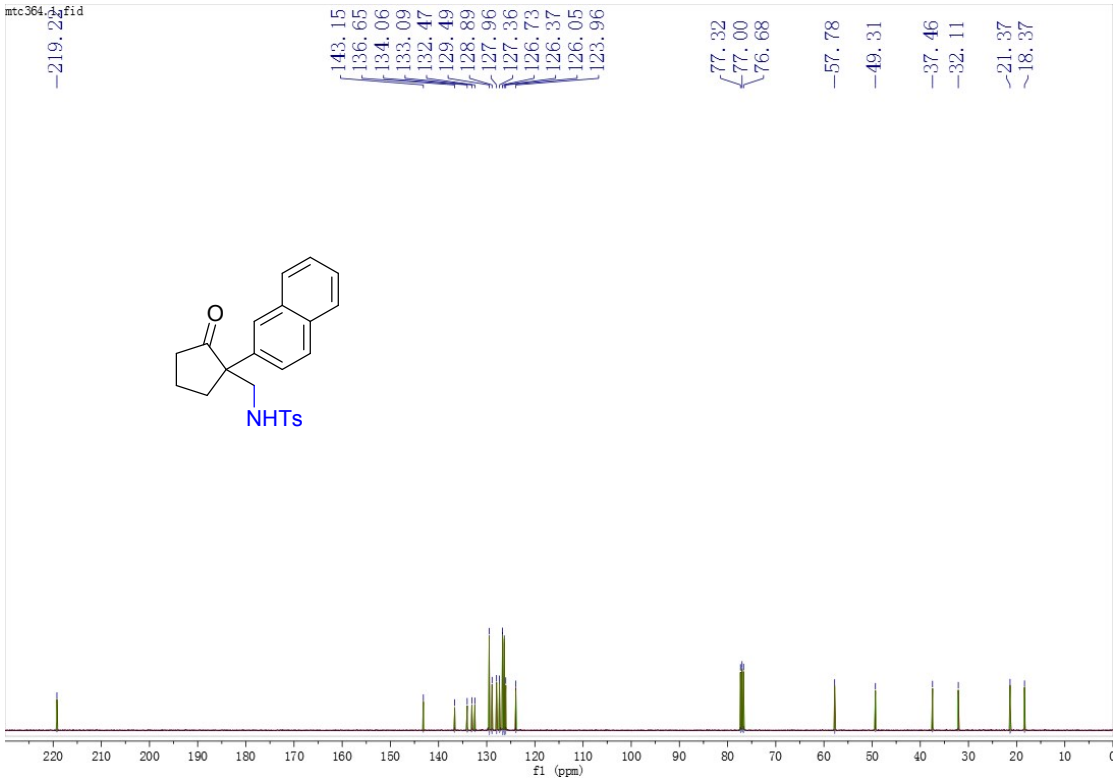
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5e



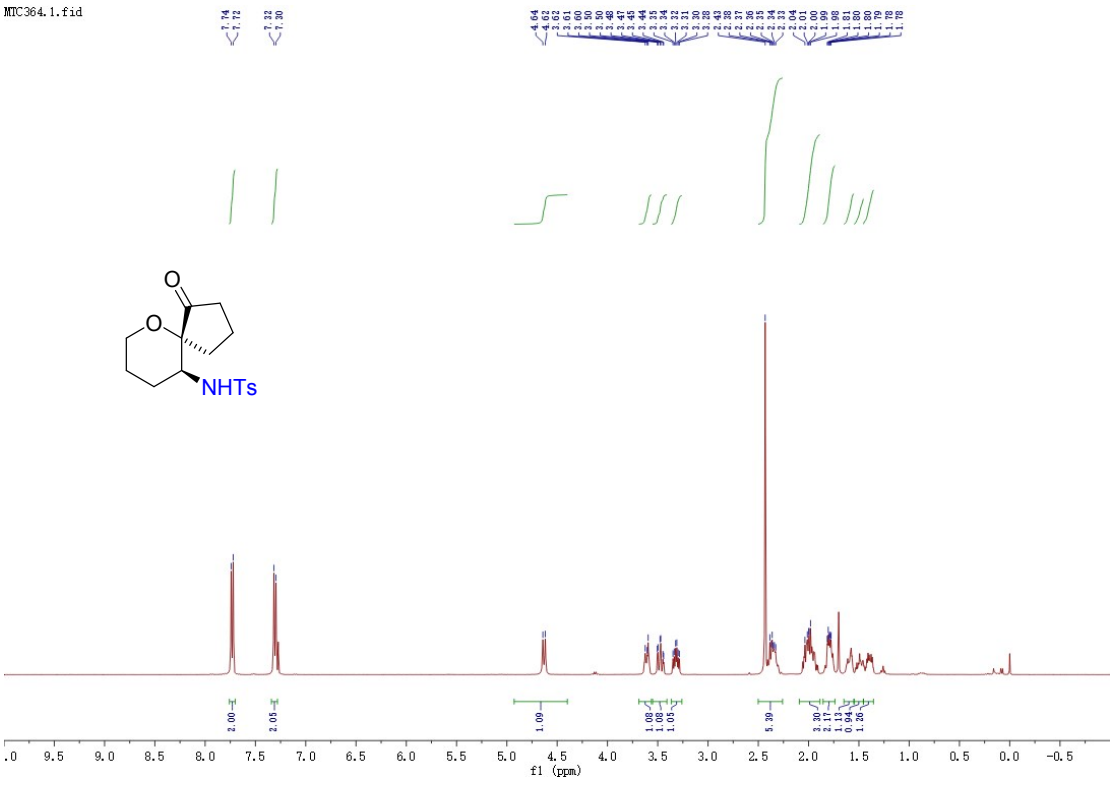
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5f



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5f



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5g



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5g