Supporting Information

Cascade Hydroarylation/Diels−Alder Cycloaddition of Alkynylindoles with Electron-Deficient Alkynes and Alkenes

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1. General Information

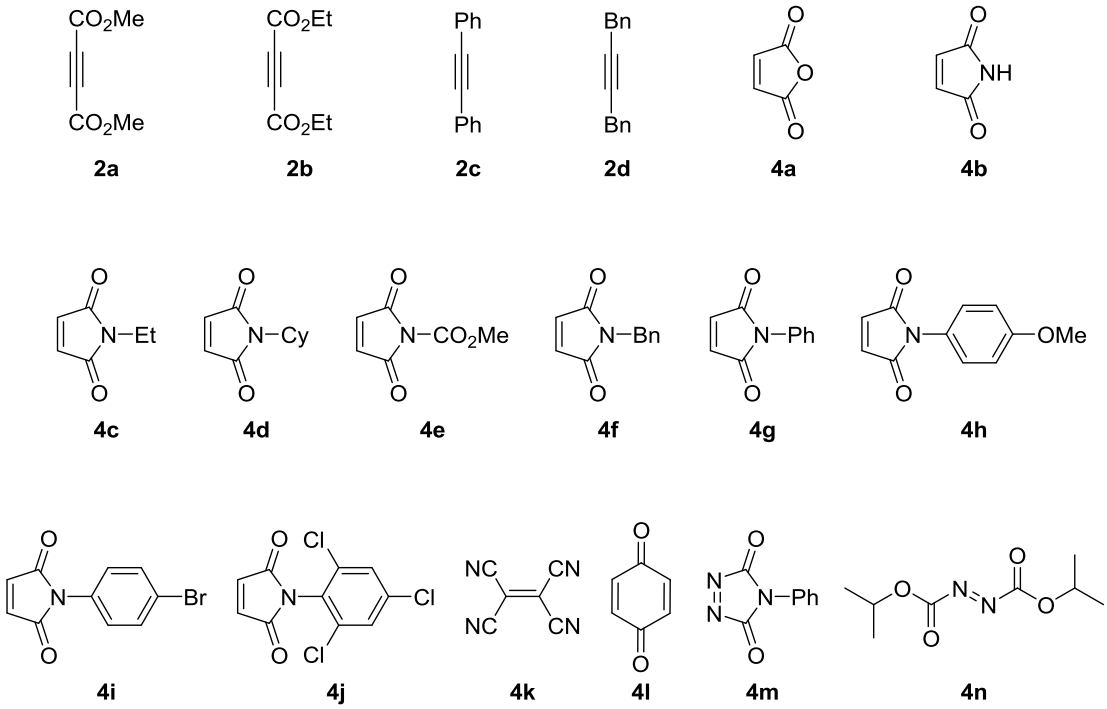
Unless otherwise stated, all reactions were performed in sealed tube (capacity 15 mL). Commercially available reagents were used without further purification. NMR spectra were recorded on Bruker Avance NEO 500 or Bruker Avance III 600 instruments and calibrated using residual solvent peaks as internal reference. Chemical shifts (δ) were expressed in ppm with reference to the solvent signals. Coupling constants *J* are given in Hz. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) [quantitative time-of-flight (Q-TOF)] ionization sources on an Agilent 6200 Q-TOF MS. Infrared (IR) spectra were obtained with a Tenor 27 spectrophotometer using KBr pellets. Melting points were determined on a SGW X-4A melting point apparatus. X-ray diffraction was obtained by Bruker D8 QUEST. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel GF254. Silica gel (Huanghai 300 – 400 mesh) was used for flash column chromatography.

2. Experimental Section

2.1 Preparation of 2 and 4

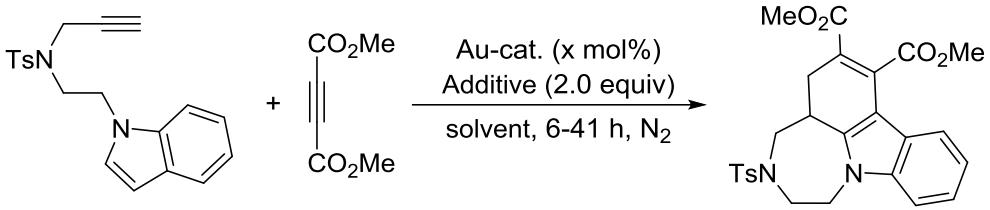
Substrate **2a-c**, **4a-n** were purchased and 1,4-diphenylbut-2-yne **2d** were synthesized from commercially available benzylacetylene and benzyl bromide followed by literature report.

List of substrates **2** and **4**:



2.2 Optimization of Reaction Conditions.

Table S1: Selected Examples of the Optimizations.

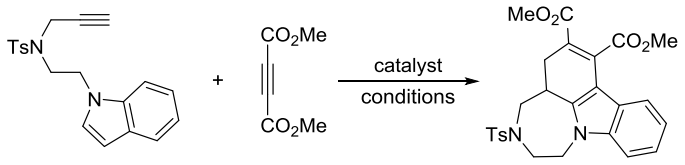


1a **2a** (2.0 equiv) **3a**

entry	catalyst (0.5 mol%)	additive	solvent	time (h)	temp. (^{o}C)	yield[b] (%)
1	^{t}BuXPhosAuNTf$_2$	-	toluene	9	80	(46)
2	^{t}BuXPhosAuNTf$_2$	-	toluene	9	100	(45)
3	^{t}BuXPhosAuNTf$_2$	-	toluene	9	120	(69)
4	^{t}BuXPhosAuNTf$_2$	-	toluene	9	150	(46)
5	^{t}BuXPhosAuNTf$_2$	-	PhCl	5	120	74 (72)
6	^{t}BuXPhosAuNTf$_2$	-	PhF	7	120	(70)
7	XPhosAuNTf$_2$	-	PhCl	10	120	69
8	JohnPhosAu(MeCN)SbF$_6$	-	PhCl	10	120	57
9	AuCl$_3$	-	PhCl	5	120	NR
10[c]	^{t}BuXPhosAuNTf$_2$	-	PhCl	7	120	(56)
11	^{t}BuXPhosAuNTf$_2$	Ac$_2$O	PhCl	9	120	78
12	^{t}BuXPhosAuNTf$_2$	Piv$_2$O	PhCl	9	120	78
13	^{t}BuXPhosAuNTf$_2$	Boc$_2$O	PhCl	6	120	78 (75)
14	-	Boc$_2$O	PhCl	12	120	NR

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (0.5 mol%), additive (0.2 mmol), dry solvent (0.1 M) under N_2. [b]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard. Isolated yields were given in parentheses. [c]1.0 mol% of catalyst. NR = no reaction.

Table S2: Optimization of the Reaction Conditions.

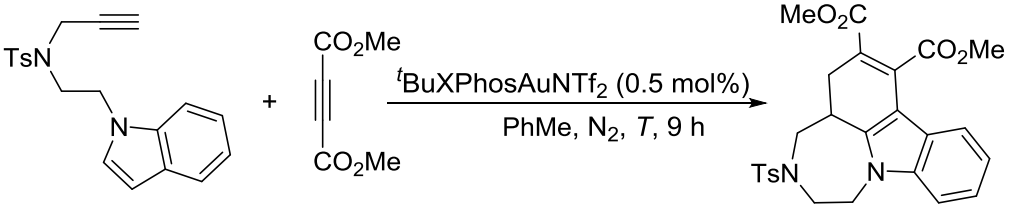


1a **2a** **3a**

Entry	Catalyst	Solvent	Additive	*T* (°C)	Yield (%)[b]
1	^{t}BuXPhosAuNTf$_2$	toluene	–	80	(46)
2	^{t}BuXPhosAuNTf$_2$	toluene	–	100	(45)
3	^{t}BuXPhosAuNTf$_2$	toluene	–	110	(61)
4	^{t}BuXPhosAuNTf$_2$	toluene	–	120	(69)
5	^{t}BuXPhosAuNTf$_2$	toluene	–	150	(46)
6	***^{t}BuXPhosAuNTf$_2$***	***PhCl***	–	***120***	***74 (72)***
7	^{t}BuXPhosAuNTf$_2$	$PhCF_3$	–	120	(50)
8	^{t}BuXPhosAuNTf$_2$	PhF	–	120	(70)
9	^{t}BuXPhosAuNTf$_2$	HFIP	–	120	67
10	^{t}BuXPhosAuNTf$_2$	Xylene	–	150	17
11	XPhosAuNTf$_2$	PhCl	–	120	69
12	JohnPhosAu(MeCN)SbF$_6$	PhCl	–	120	57
13	JohnPhosAuCl	PhCl	–	120	trace
14	DTBPAuCl + AgSbF$_6$	PhCl	–	120	9
15	PPh_3AuCl + AgSbF$_6$	PhCl	–	120	0
16	$AuCl_3$	PhCl	–	120	NR
17[c]	^{t}BuXPhosAuNTf$_2$	PhCl	–	120	(56)
18[d]	^{t}BuXPhosAuNTf$_2$	PhCl	–	120	50
19[e]	^{t}BuXPhosAuNTf$_2$	PhCl	–	120	72
20	^{t}BuXPhosAuNTf$_2$	PhCl	Ac_2O (2.0 eq)	120	78
21	^{t}BuXPhosAuNTf$_2$	PhCl	Piv_2O (2.0 eq)	120	78
22	^{t}BuXPhosAuNTf$_2$	PhCl	Boc_2O (2.0 eq)	120	78 (75)
23	^{t}BuXPhosAuNTf$_2$	PhCl	Boc_2O (1.0 eq)	120	74
24	^{t}BuXPhosAuNTf$_2$	PhCl	Boc_2O (4.0 eq)	120	69
25[f]	^{t}BuXPhosAuNTf$_2$	PhCl	Boc_2O (2.0 eq)	120	61
26[g]	^{t}BuXPhosAuNTf$_2$	PhCl	Boc_2O (2.0 eq)	120	54
27	–	PhCl	Boc_2O (2.0 eq)	120	NR

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (0.5 mol%), additive (0.2 mmol), dry solvent (0.1 M) under N_2 for 5-34 h. [b]The yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard, and the isolated yields were given in parentheses. [c]1.0 mol% of ^{t}BuXPhosAuNTf$_2$. [d]under the oxygen. [e]Under the air. [f]1.0 equiv of **2a**. [g]3.0 equiv of **2a**. NR = no reaction.

Table S3: Screening of Temperature.

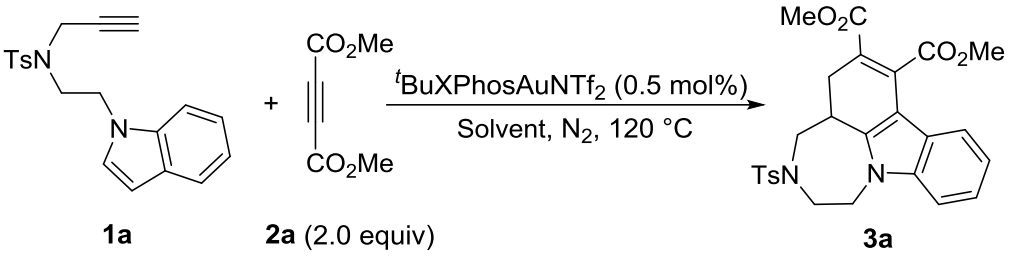


1a **2a** (2.0 equiv) **3a**

Entry	*T* (°C)	Yield[a] (%)
1	80	46
2	100	45
3	110	61
4	120	69
5	150	46

[a]Isolated yield.

Table S4: Screening of Solvents.

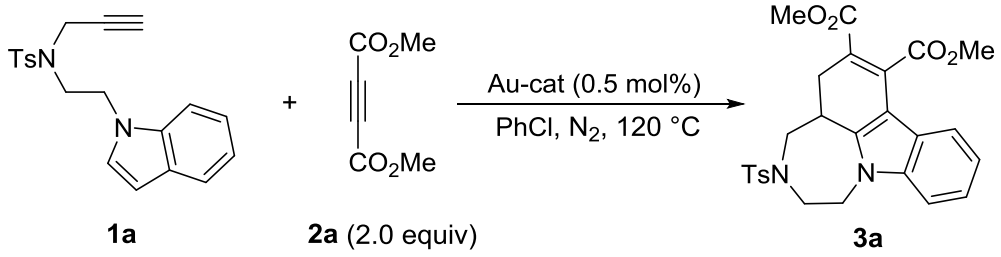


1a **2a** (2.0 equiv) **3a**

Entry	Solvent	Time (h)	Yield[a] (%)
1	toluene	9	(69)
2	PhCl	5	(72)
3	$PhCF_3$	16	(50)
4	PhF	7	(70)
5	HFIP	9	67
6	Xylene	9	17

[a]The yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard, and the isolated yields were given in parentheses.

Table S5: Screening of Catalyst.

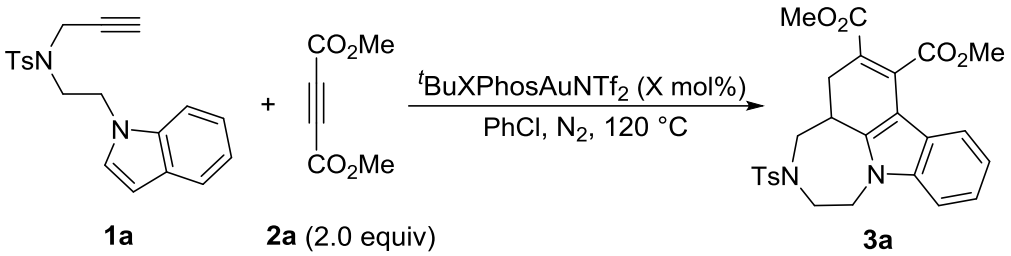


1a **2a** (2.0 equiv) **3a**

Entry	Catalyst	Time (h)	Yield[a] (%)
1	^{t}BuXPhosAuNTf$_2$	5	74
2	XPhosAuNTf$_2$	10	69
3	JohnPhosAu(MeCN)SbF$_6$	10	57
4	JohnPhosAuCl	34	trace
5	DTBPAuCl + AgSbF$_6$	10	9
6	PPh_3AuCl + AgSbF$_6$	12	0
7	$AuCl_3$	5	NR

[a]The yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard. NR = no reaction.

Table S6: Screening of the Catalyst Loading.

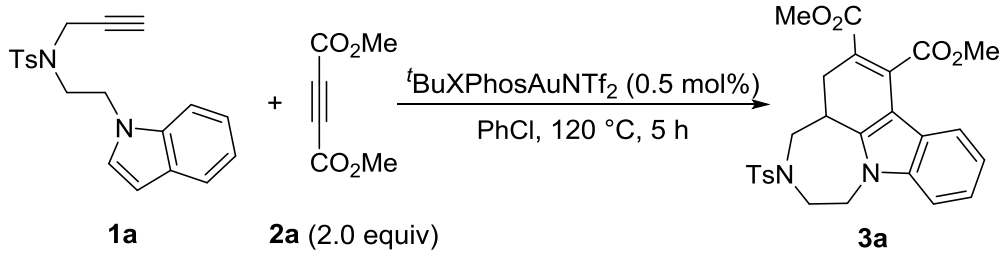


1a **2a** (2.0 equiv) **3a**

Entry	X mol%	Time (h)	Yield[a] (%)
1	0.5	5	72
2	1.0	7	56

[a]Isolated yields.

Table S7: Screening of Atmosphere.

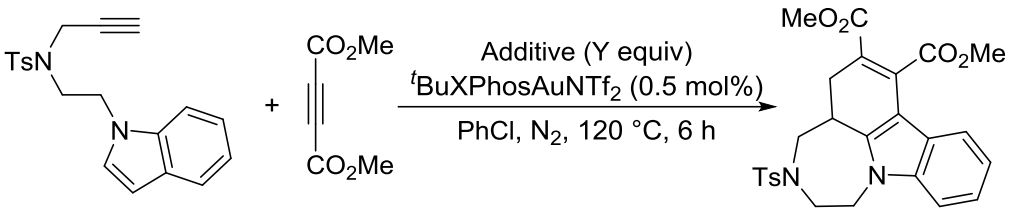


1a **2a** (2.0 equiv) **3a**

Entry	Atmosphere	Yield[a] (%)
1	N_2	74
2	O_2	50
3	Air	72

[a]The yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.

Table S8: Screening of Additives.

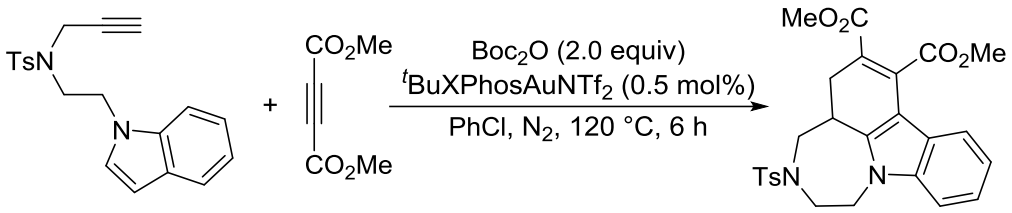


1a **2a** (2.0 equiv) **3a**

Entry	Additive	Y equiv	Yield[a] (%)
1	–	–	74
2	Ac_2O	2.0	78
3	Piv_2O	2.0	78
4	Boc_2O	2.0	78
5	Boc_2O	1.0	74
6	Boc_2O	4.0	69

[a]The yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.

Table S9: Screening of the Equivalent of **2a**.

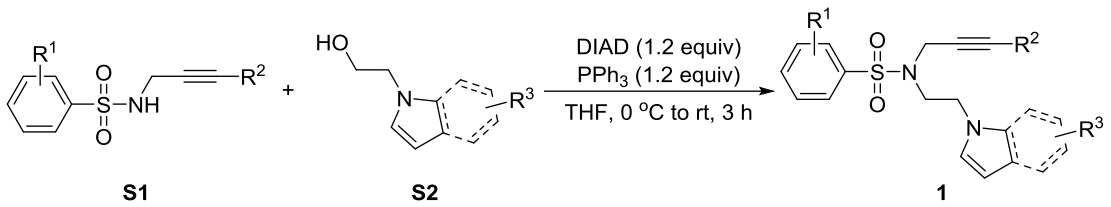


1a **2a** (Z equiv) **3a**

Entry	Z (equiv)	Yield[a] (%)
1	1.0	61
2	2.0	78
3	3.0	54

[a]The yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.

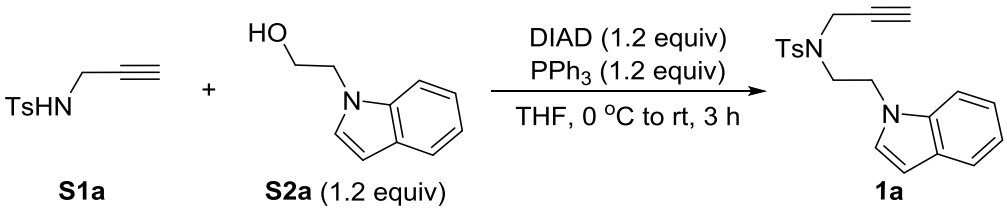
3. Synthesis of Compounds 1a-1w, 2d



S1 **S2** **1**

General Procedure A: To a round-bottom flask were added **S1** (1.0 equiv), PPh_3 (1.2 equiv) in THF. The mixture was cooled to 0 °C before diisopropylazodicarboxylate (DIAD) (1.2 equiv) was added dropwise. Then, corresponding **S2** (1.2 equiv) was added to the mixture. Then, the ice-water bath was removed and the mixture was naturally warmed up to room temperature. After stirred at room temperature for 3 h, the mixture was concentrated under vacuum and purified by flash column chromatography using petroleum ether/ethyl acetate as eluent to give the corresponding **1a-1r, 1v**.

***N*-(2-(1*H*-indol-1-yl)ethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1a)**



S1a **S2a** (1.2 equiv) **1a**

The compound **1a** (yellow solid, 935.9 mg, 82% yield) was obtained following General Procedure A from **S1a** (675.4 mg, 3.23 mmol, 1.0 equiv) and **S2a** (624.8 mg, 3.88 mmol, 1.2 equiv) using PPh_3 (1.02 g, 3.88 mmol, 1.2 equiv) and DIAD (0.76 mL, 3.88 mmol, 1.2 equiv) after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.26) as eluent.

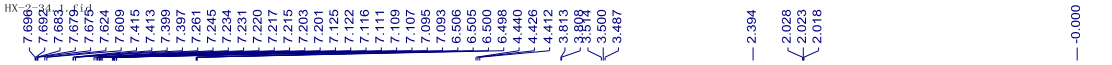
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.69 (dt, J = 8.5, 2.0 Hz, 2H), 7.62 (d, J = 7.5 Hz, 1H), 7.41 (dd, J = 8.0, 1.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.23-7.20 (m, 1H), 7.13-7.09 (m, 2H), 6.50 (dd, J = 3.0, 1.0 Hz, 1H), 4.43 (t, J = 7.0 Hz, 2H), 3.81 (d, J = 2.5 Hz, 2H), 3.50 (t, J = 7.0 Hz, 2H), 2.39 (s, 3H), 2.02 (t, J = 2.5 Hz, 1H).

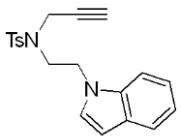
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 135.9, 135.4, 129.8, 128.8, 128.0, 127.7, 122.0, 121.2, 119.8, 109.3, 102.1, 76.8, 74.1, 46.6, 46.0, 38.4, 21.7.

IR (KBr) ν (cm^{-1}): 3262, 1631, 1597, 1344, 1320, 1161, 1103, 740 cm^{-1}.

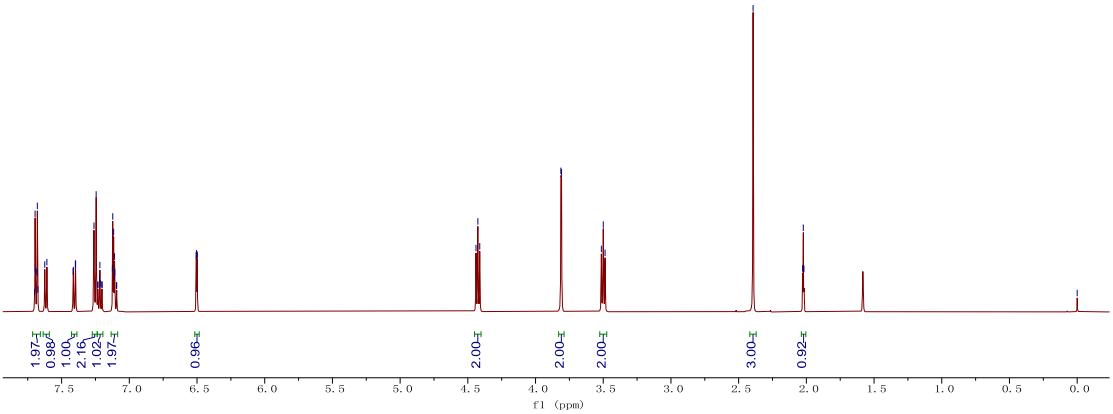
HRMS (ESI): calcd for $C_{20}H_{21}N_2O_2S$ $[M+H]^+$: 353.13183, found: 353.13181.

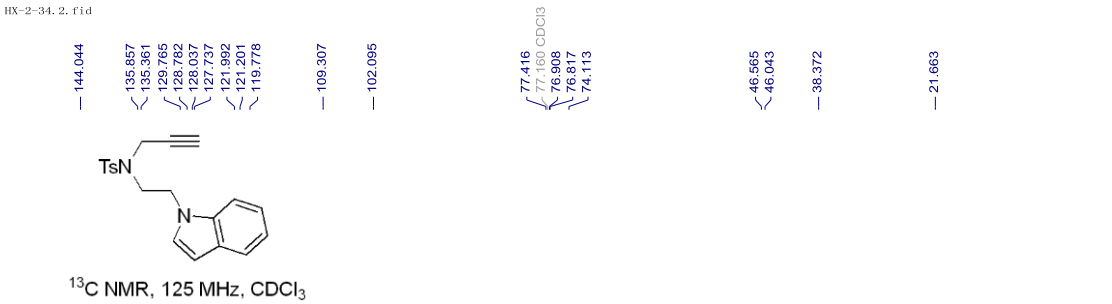
MP: 79-81 ºC.



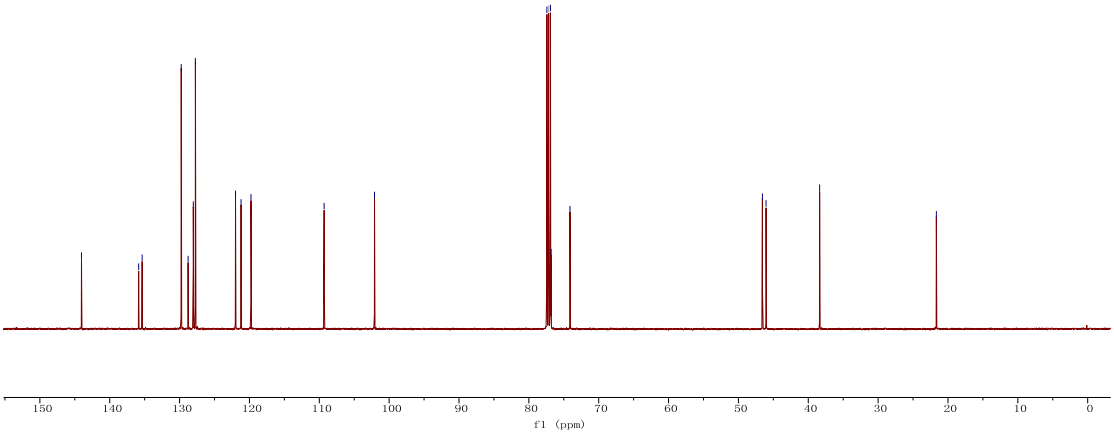


^{1}H NMR, 500 MHz, $CDCl_3$

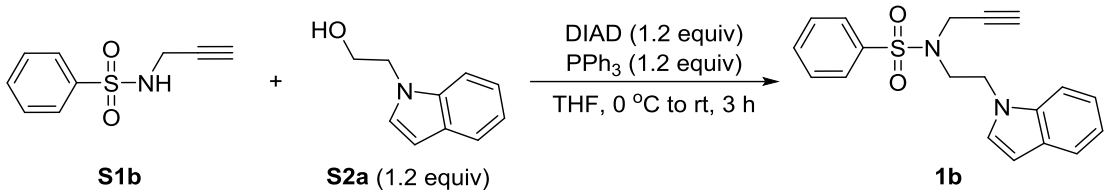




^{13}C NMR, 125 MHz, $CDCl_3$



***N*-(2-(1*H*-indol-1-yl)ethyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1b)**



The compound **1b** (white solid, 810.8 mg, 97% yield) was obtained following General Procedure A from **S1b** (482.7 mg, 2.47 mmol, 1.0 equiv) and **S2a** (477.2 mg, 2.96 mmol, 1.2 equiv) using PPh_3 (777.5 mg, 2.96 mmol, 1.2 equiv) and DIAD (0.58 mL, 2.96 mmol, 1.2 equiv) after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.21) as eluent.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.80 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 7.5 Hz, 1H), 7.54 (tt, J = 7.5, 1.5 Hz, 1H), 7.47-7.43 (m, 2H), 7.40 (d, J = 8.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.12-7.09 (m, 2H), 6.50 (d, J = 3.0 Hz, 1H), 4.41 (t, J = 7.0 Hz, 2H), 3.79 (d, J = 2.5 Hz, 2H), 3.51 (t, J = 7.0 Hz, 2H), 1.99-1.98 (m, 1H).

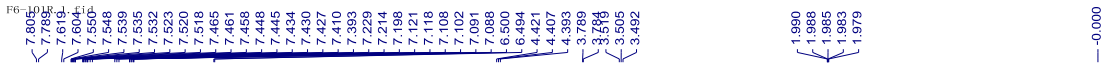
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 135.8, 133.1, 129.1, 128.7, 128.0, 127.6, 122.0, 121.2, 119.8, 109.3, 102.1, 76.6, 74.1, 46.5, 46.0, 38.3.

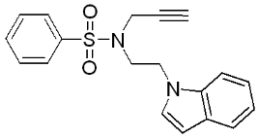
IR (KBr) ν (cm^{-1}): 3253, 1737, 1690, 1526, 1386, 1258, 1165, 1109, 927, 741 cm^{-1}.

HRMS (ESI): calcd for $C_{19}H_{18}N_2NaO_2S$ $[M+Na]^+$: 361.09812, found: 361.09811.

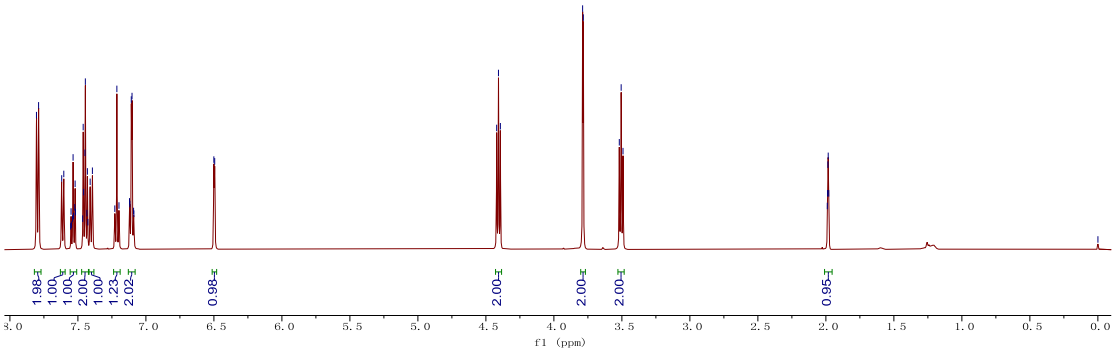
MP: 82-85 °C.

F6-101R.1.fid

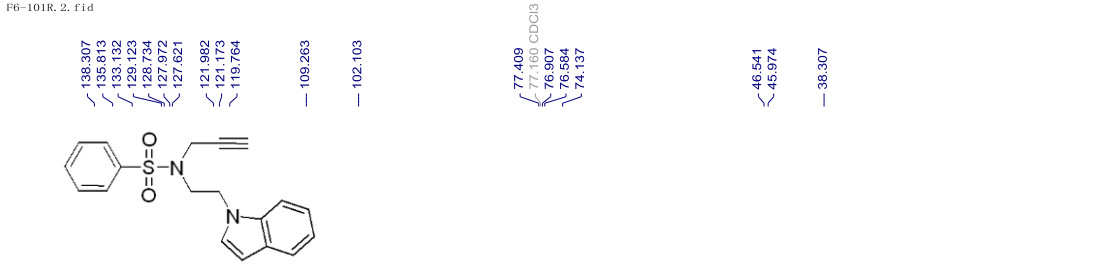




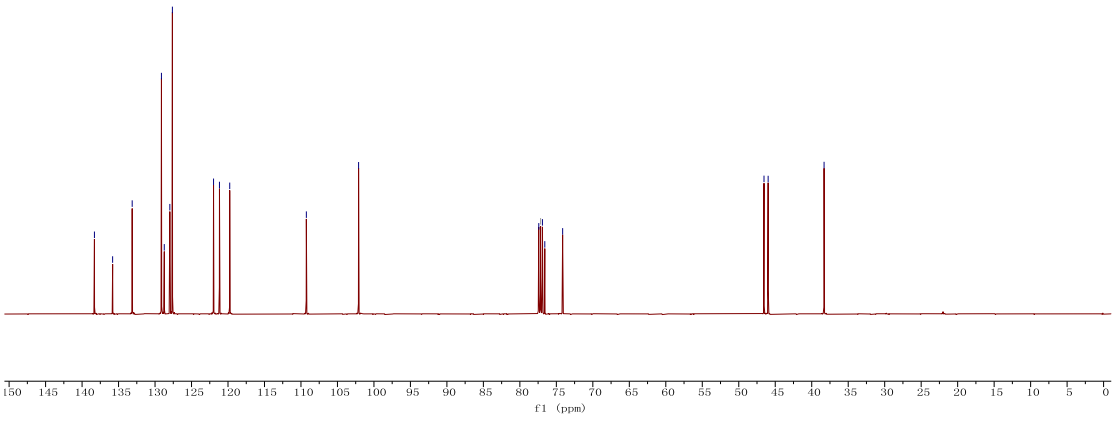
^{1}H NMR, 500 MHz, $CDCl_3$



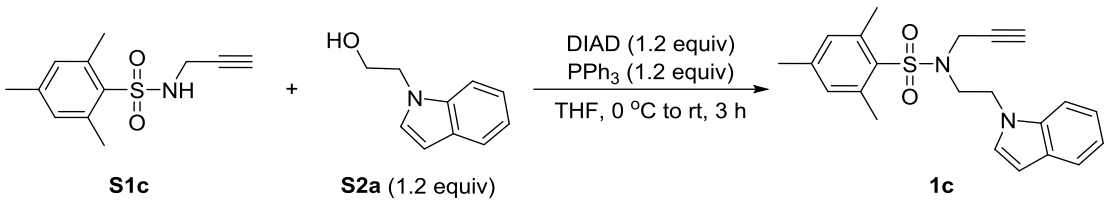
F6-101R.2.fid



^{13}C NMR, 125 MHz, $CDCl_3$



***N*-(2-(1*H*-indol-1-yl)ethyl)-2,4,6-trimethyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1c)**



S1c **S2a** (1.2 equiv) **1c**

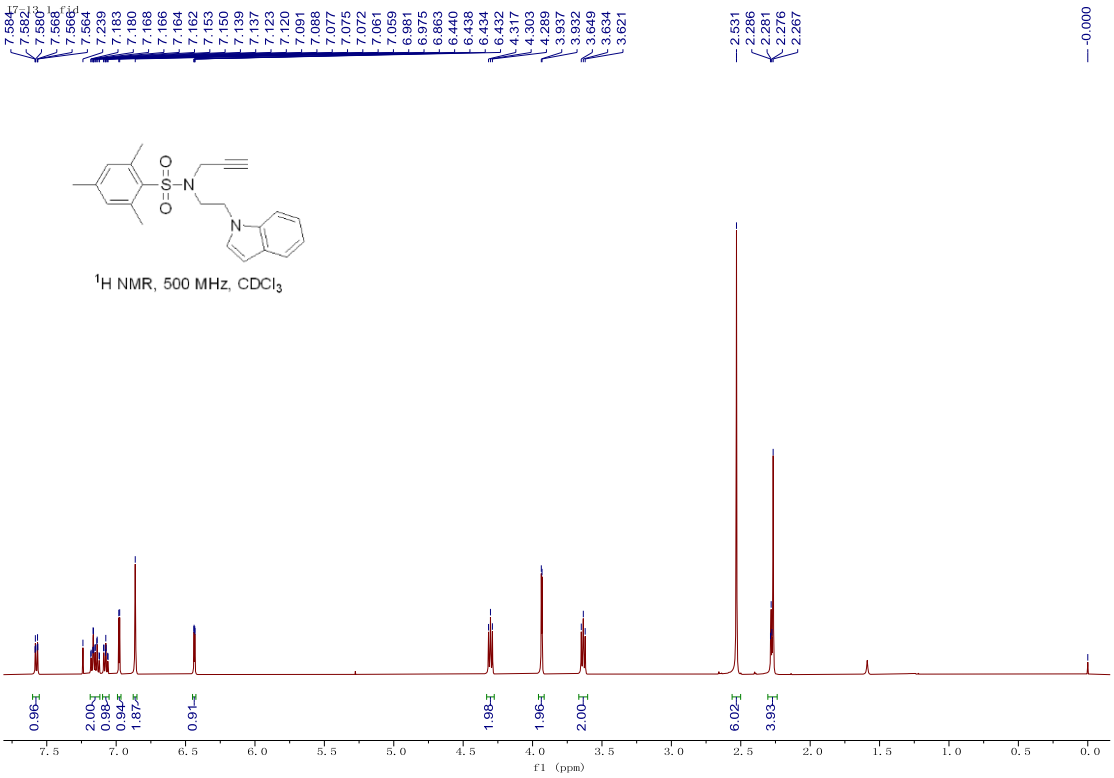
The compound **1c** (yellow oil, 291.0 mg, 76% yield) was obtained following General Procedure A from **S1c** (237.1 mg, 1.0 mmol, 1.0 equiv) and **S2a** (193.4 mg, 1.2 mmol, 1.2 equiv) using PPh_3 (314.8 mg, 1.2 mmol, 1.2 equiv) and DIAD (0.24 mL, 1.2 mmol, 1.2 equiv) after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.29) as eluent.

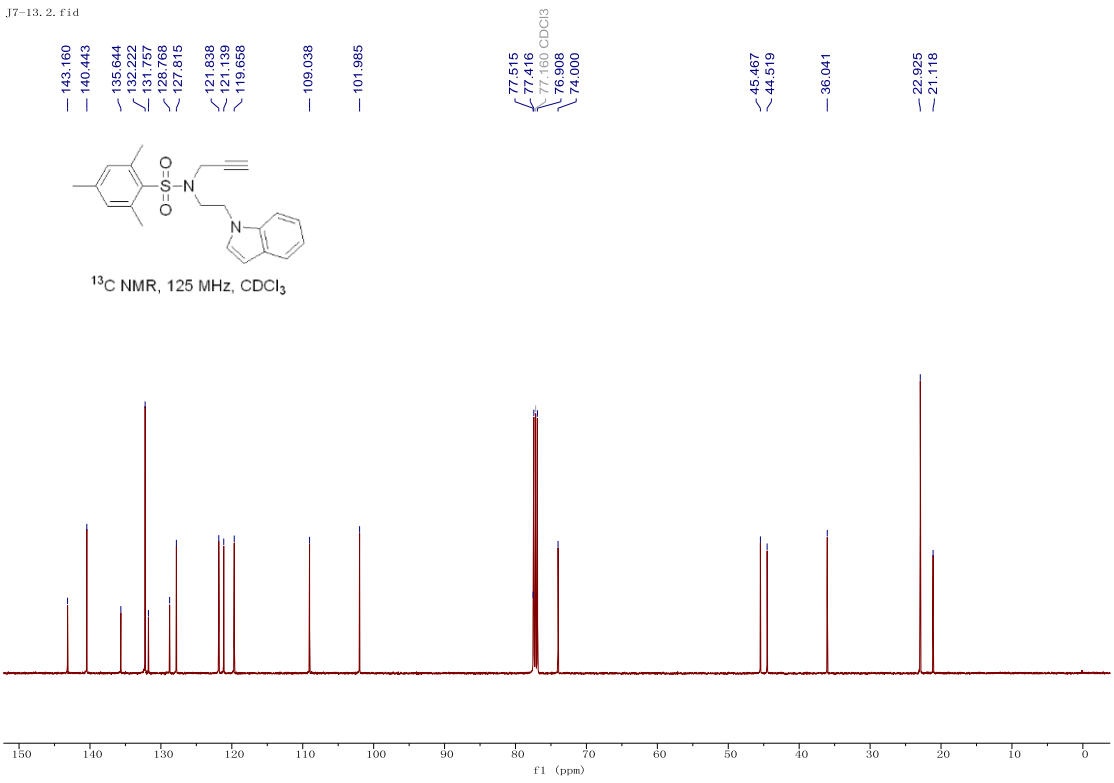
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.57 (dt, J = 8.0, 1.0 Hz, 1H), 7.18-7.12 (m, 2H), 7.09-7.06 (m, 1H), 6.98 (d, J = 3.0 Hz, 1H), 6.86 (s, 2H), 6.44 (dd, J = 3.0, 1.0 Hz, 1H), 4.30 (t, J = 7.0 Hz, 2H), 3.93 (d, J = 2.5 Hz, 2H), 3.63 (t, J = 7.0 Hz, 2H), 2.53 (s, 6H), 2.28 (t, J = 2.5 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 140.4, 135.6, 132.2, 131.8, 128.8, 127.8, 121.8, 121.1, 119.7, 109.0, 102.0, 77.5, 74.0, 45.5, 44.5, 36.0, 22.9, 21.1.

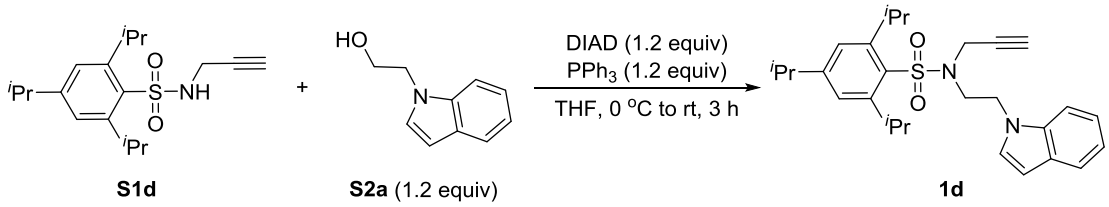
IR (KBr) ν (cm^{-1}): 3280, 2938, 1604, 1464, 1319, 1155, 742, 654 cm^{-1}.

HRMS (ESI): calcd for $C_{22}H_{25}N_2O_2S$ $[M+H]^+$: 381.16313, found: 381.16299.


J7-13-1.fid
7.584
7.582
7.580
7.568
7.566
7.564
7.239
7.183
7.180
7.168
7.166
7.164
7.162
7.153
7.150
7.139
7.137
7.123
7.120
7.091
7.088
7.077
7.075
7.072
7.061
7.059
6.981
6.975
6.863
6.440
6.438
6.434
6.432
4.317
4.303
4.289
3.937
3.932
3.649
3.634
3.621
2.531
2.286
2.281
2.276
2.267
-0.000
O
S
N
N
1H NMR, 500 MHz, CDCl3
0.96
2.00
0.98
0.94
1.87
0.91
1.98
1.96
2.00
6.02
3.93
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


J7-13.2.fid
143.160
140.443
135.644
132.222
131.757
128.768
127.815
121.838
121.139
119.658
109.038
101.985
77.515
77.416
77.160 CDCl3
76.908
74.000
45.467
44.519
36.041
22.925
21.118
O
S
N
N
13C NMR, 125 MHz, CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

***N*-(2-(1*H*-indol-1-yl)ethyl)-2,4,6-triisopropyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1d)**



S1d **S2a** (1.2 equiv) **1d**

The compound **1d** (yellow solid, 238.0 mg, 74% yield) was obtained following General Procedure A from **S1d** (221.8 mg, 0.69 mmol, 1.0 equiv) and **S2a** (133.8 mg, 0.83 mmol, 1.2 equiv) using PPh_3 (217.7 mg, 0.83 mmol, 1.2 equiv) and DIAD (0.16 mL, 0.83 mmol, 1.2 equiv) after purification by flash column chromatography using petroleum ether/ethyl acetate = 15/1 (R_f = 0.32) as eluent.

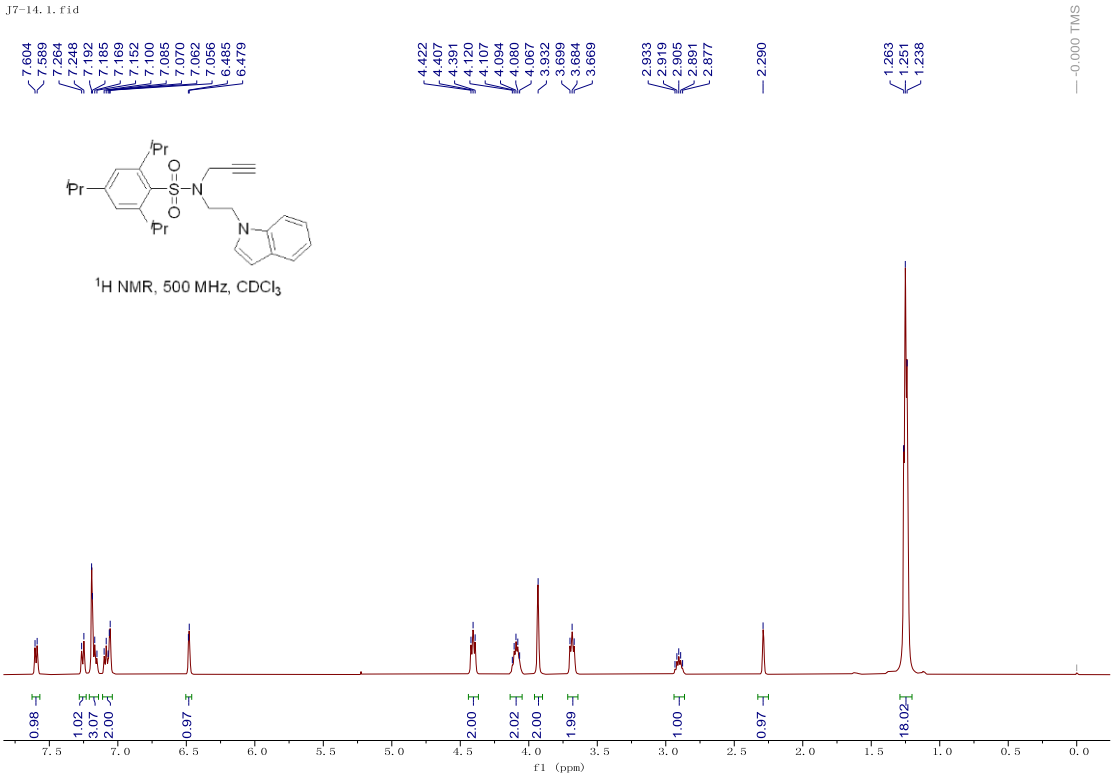
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.60 (d, J = 7.5 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.19-7.15 (m, 3H), 7.10-7.06 (m, 2H), 6.48 (d, J = 3.0 Hz, 1H), 4.41 (t, J = 7.5 Hz, 2H), 4.12-4.07 (m, 2H), 3.93 (s, 2H), 3.68 (t, J = 7.5 Hz, 2H), 2.93-2.88 (m, 1H), 2.29 (s, 1H), 1.26-1.24 (m, 18H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 151.9, 135.8, 130.2, 128.7, 127.8, 124.2, 121.9, 121.1, 119.7, 109.2, 102.0, 77.5, 74.2, 45.3, 44.5, 36.4, 34.3, 29.5, 24.9, 23.6.

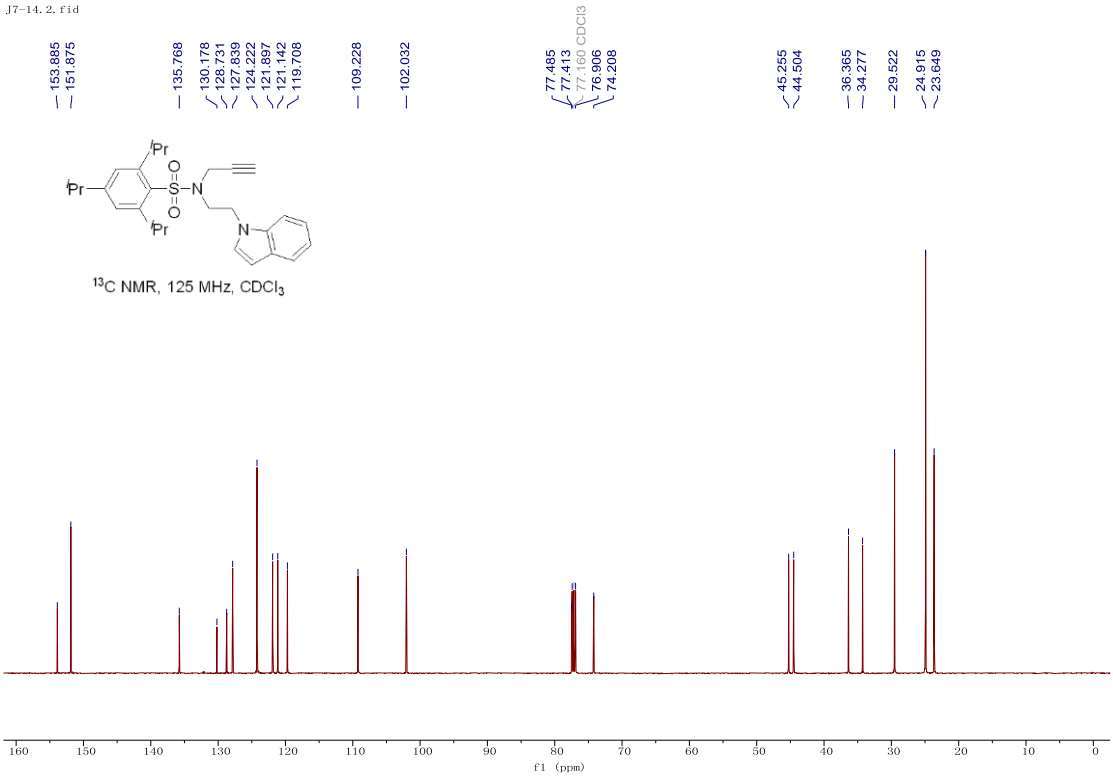
IR (KBr) ν (cm^{-1}): 3304, 2960, 1464, 1361, 1314, 1299, 1254, 1149, 911, 744 cm^{-1}.

HRMS (ESI): calcd for $C_{28}H_{37}N_2O_2S$ $[M+H]^+$: 465.25703, found: 465.25702.

MP: 96-99 °C.

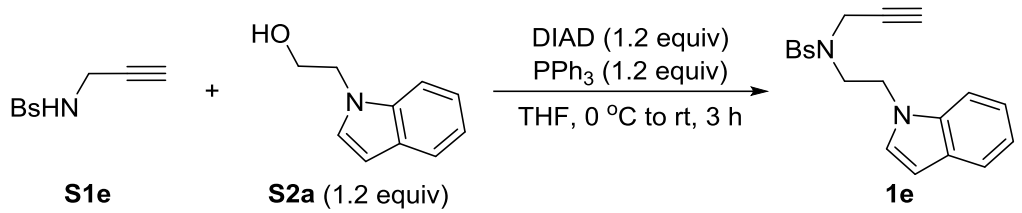


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

***N*-(2-(1*H*-indol-1-yl)ethyl)-4-bromo-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1e)**



S1e **S2a** (1.2 equiv) **1e**

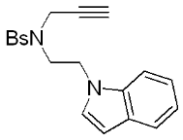
The compound **1e** (yellow oil, 388.5 mg, 93% yield) was obtained following General Procedure A from **S1e** (274.1 mg, 1.0 mmol, 1.0 equiv) and **S2a** (193.4 mg, 1.2 mmol, 1.2 equiv) using PPh_3 (314.8 mg, 1.2 mmol, 1.2 equiv) and DIAD (0.24 mL, 1.2 mmol, 1.2 equiv) after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.28) as eluent.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.66-7.61 (m, 3H), 7.58 (dt, J = 8.5, 2.0 Hz, 2H), 7.39 (dd, J = 8.0, 0.5 Hz, 1H), 7.24-7.21 (m, 1H), 7.14-7.10 (m, 2H), 6.51 (dd, J = 3.0, 0.5 Hz, 1H), 4.42 (t, J = 6.5 Hz, 2H), 3.78 (d, J = 2.5 Hz, 2H), 3.52 (t, J = 6.5 Hz, 2H), 2.04 (t, J = 2.5 Hz, 1H).

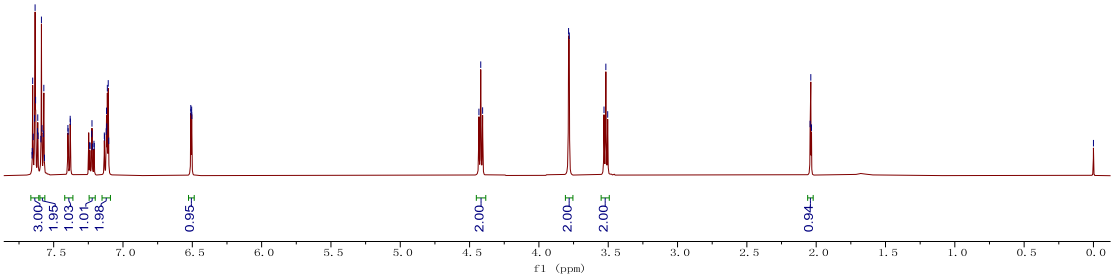
^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 135.8, 132.4, 129.2, 128.8, 128.2, 127.9, 122.1, 121.3, 119.9, 109.2, 102.3, 76.4, 74.5, 46.5, 45.9, 38.2.

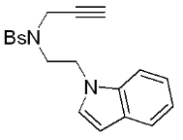
IR (KBr) ν (cm^{-1}): 3279, 1575, 1464, 1390, 1351, 1162, 1108, 1088, 1010 cm^{-1}.

HRMS (ESI): calcd for $C_{19}H_{18}BrN_2O_2S$ $[M+H]^+$: 417.02669, found: 417.02686.

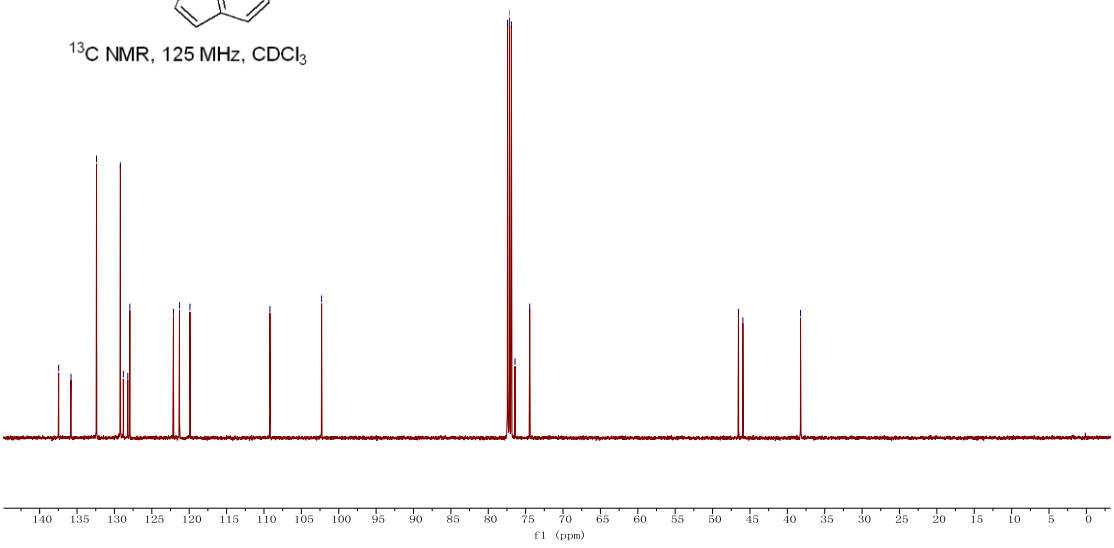


^{1}H NMR, 500 MHz, $CDCl_3$

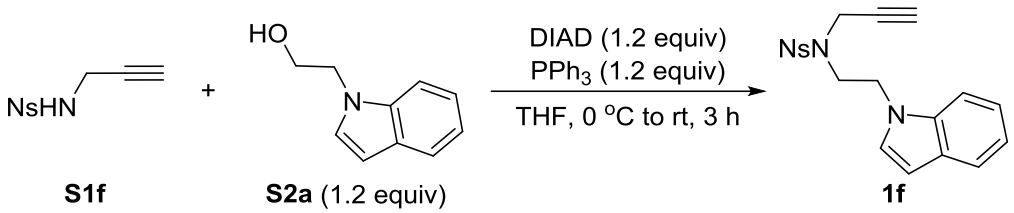




^{13}C NMR, 125 MHz, $CDCl_3$



***N*-(2-(1*H*-indol-1-yl)ethyl)-4-nitro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1f)**



S1f **S2a** (1.2 equiv) **1f**

The compound **1f** (yellow solid, 375.2 mg, 98% yield) was obtained following General Procedure A from **S1f** (240.2 mg, 1.0 mmol, 1.0 equiv) and **S2a** (193.4 mg, 1.2 mmol, 1.2 equiv) using PPh_3 (314.8 mg, 1.2 mmol, 1.2 equiv) and DIAD (0.24 mL, 1.2 mmol, 1.2 equiv) after purification by flash column chromatography using petroleum ether/ethyl acetate = 4/1 (R_f = 0.32) as eluent.

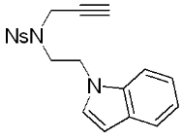
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.20 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.59 (dt, J = 8.0, 1.0 Hz, 1H), 7.34 (dd, J = 8.0, 1.0 Hz, 1H), 7.22-7.19 (m, 1H), 7.12-7.08 (m, 2H), 6.49 (dd, J = 3.0, 1.0 Hz, 1H), 4.41 (t, J = 6.0 Hz, 2H), 3.84 (d, J = 2.5 Hz, 2H), 3.59 (t, J = 6.0 Hz, 2H), 2.07 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 144.2, 135.7, 128.80, 128.75, 127.8, 124.2, 122.2, 121.3, 120.0, 109.0, 102.5, 76.2, 74.8, 46.6, 45.7, 38.0.

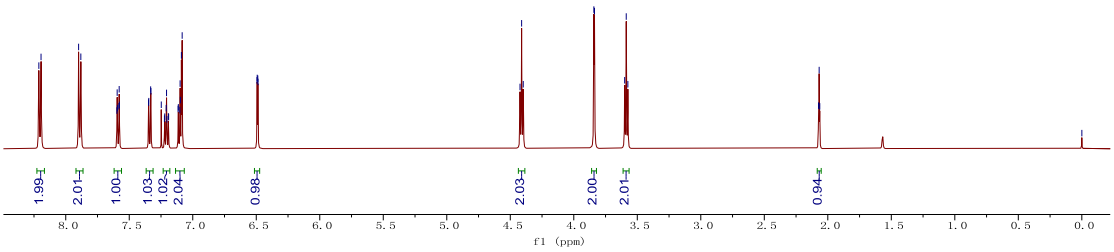
IR (KBr) ν (cm^{-1}): 3266, 1532, 1464, 1349, 1255, 1109,750, 620 cm^{-1}.

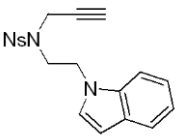
HRMS (ESI): calcd for $C_{19}H_{18}N_3O_4S$ $[M+H]^+$: 384.10125, found: 384.10144.

MP: 80-84 °C.

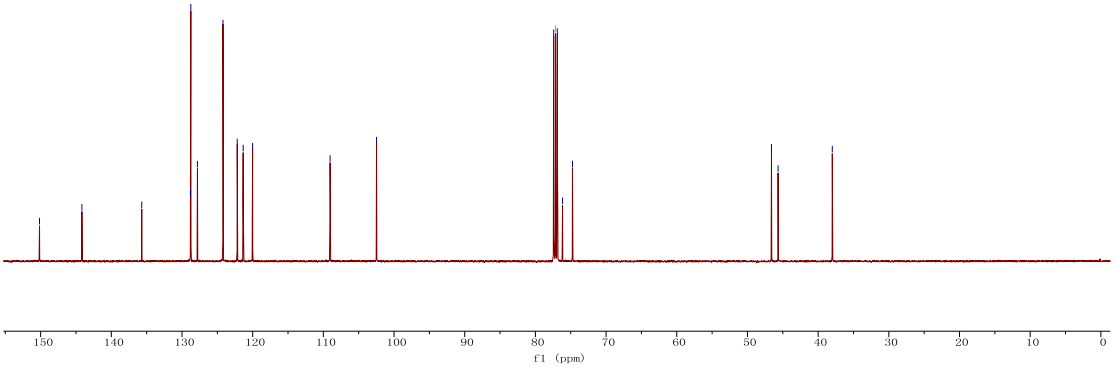


^{1}H NMR, 500 MHz, $CDCl_3$

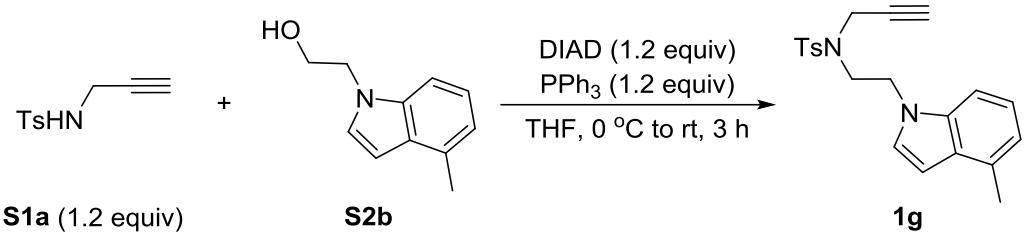




^{13}C NMR, 125 MHz, $CDCl_3$



4-methyl-*N*-(2-(4-methyl-1*H*-indol-1-yl)ethyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1g)



S1a (1.2 equiv) **S2b** **1g**

The compound **1g** (yellow solid, 361.0 mg, 74% yield) was obtained following General Procedure A from **S1a** (336.9 mg, 1.61 mmol, 1.2 equiv) and **S2b** (235.5 mg, 1.34 mmol, 1.0 equiv) using PPh_3 (422.3 mg, 1.61 mmol, 1.2 equiv) and DIAD (0.32 mL, 1.61 mmol, 1.2 equiv) after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.25) as eluent.

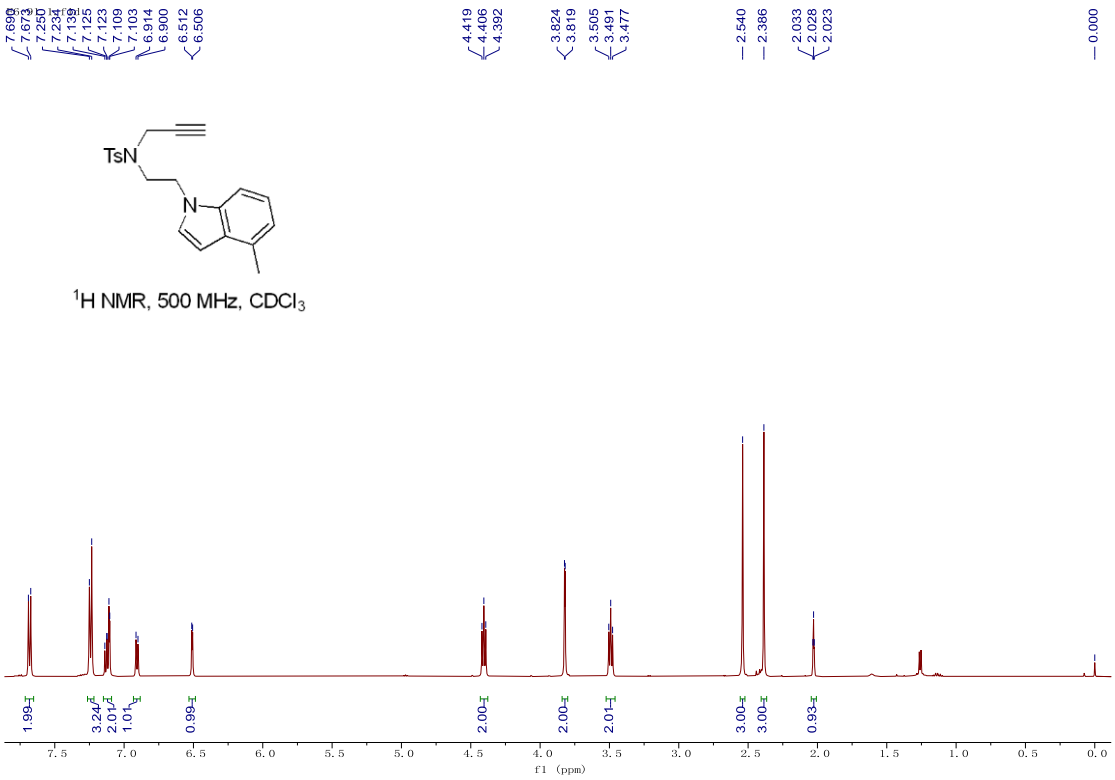
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.68 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.0 Hz, 3H), 7.14-7.10 (m, 2H), 6.91 (d, J = 7.0 Hz, 1H), 6.51 (d, J = 3.0 Hz, 1H), 4.41 (t, J = 6.5 Hz, 2H), 3.82 (d, J = 2.5 Hz, 2H), 3.49 (t, J = 6.5 Hz, 2H), 2.54 (s, 3H), 2.39 (s, 3H), 2.03 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 135.5, 135.4, 130.7, 129.7, 128.6, 127.7, 127.4, 122.1, 120.0, 106.9, 100.5, 76.8, 74.1, 46.6, 46.1, 38.3, 21.6, 18.8.

IR (KBr) ν (cm^{-1}): 3312, 1494, 1333, 1299, 1161, 1096, 753, 730 cm^{-1}.

HRMS (ESI): calcd for $C_{21}H_{23}N_2O_2S$ $[M+H]^+$: 367.14748, found: 367.14743.

MP: 63-65 °C.


7.699
7.673
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7.123
7.109
7.103
6.914
6.900
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4.406
4.392
3.824
3.819
3.505
3.491
3.477
2.540
2.386
2.033
2.028
2.023
0.000
TsN
N
1H NMR, 500 MHz, CDCl3
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3.24
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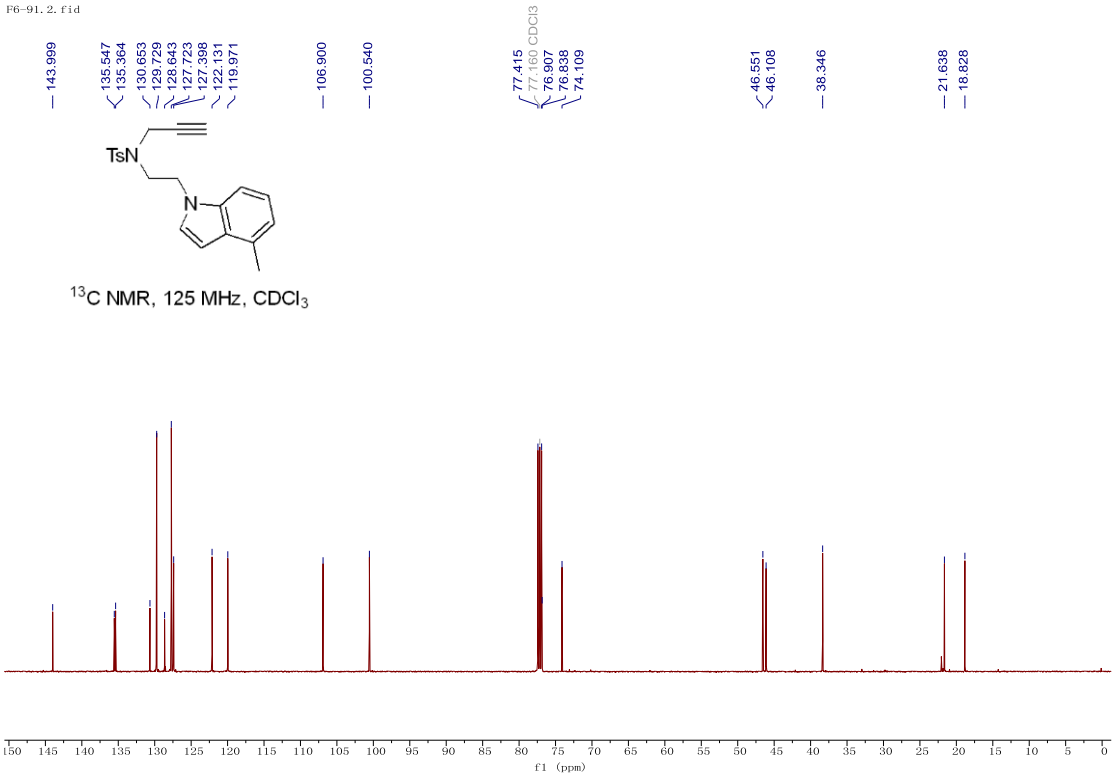
1.01
0.99
2.00
2.00
2.01
3.00
3.00
0.93
f1 (ppm)


F6-91.2.fid
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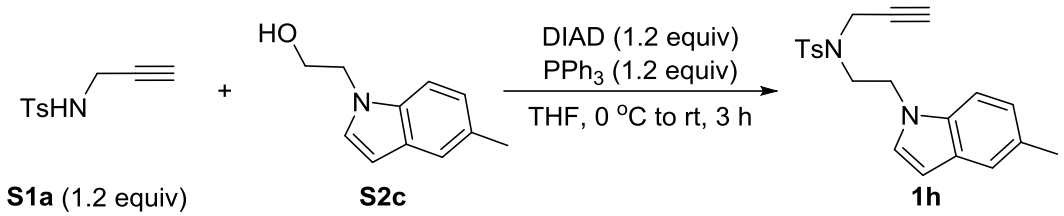
135.364
130.653
129.729
128.643
127.723
127.398
122.131
119.971
106.900
100.540
77.415
77.160 CDCl3
76.907
76.838
74.109
46.551
46.108
38.346
21.638
18.828
TsN
N
13C NMR, 125 MHz, CDCl3
f1 (ppm)

4-methyl-*N*-(2-(5-methyl-1*H*-indol-1-yl)ethyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1h)



S1a (1.2 equiv) **S2c** **1h**

The compound **1h** (white solid, 188.2 mg, 88% yield) was obtained following General Procedure A from **S1a** (146.4 mg, 0.70 mmol, 1.2 equiv) and **S2c** (101.9 mg, 0.58 mmol, 1.0 equiv) using PPh_3 (183.6 mg, 0.70 mmol, 1.2 equiv) and DIAD (0.32 mL, 0.70 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.26) as eluent.

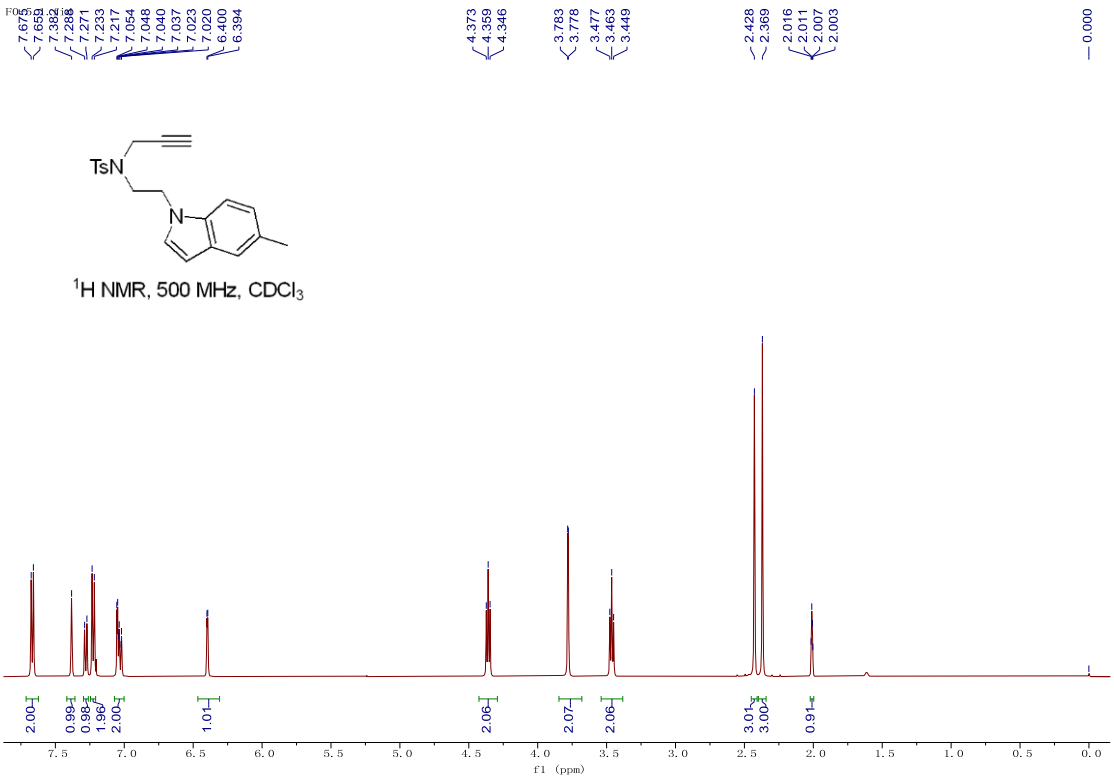
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.67 (d, J = 8.0 Hz, 2H), 7.38 (s, 1H), 7.28 (d, J = 8.5 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.05-7.02 (m, 2H), 6.40 (d, J = 3.0 Hz, 1H), 4.36 (t, J = 7.0 Hz, 2H), 3.78 (d, J = 2.5 Hz, 2H), 3.46 (t, J = 7.0 Hz, 2H), 2.43 (s, 3H), 2.37 (s, 3H), 2.02-2.00 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 135.3, 134.2, 129.7, 129.0, 128.8, 128.0, 127.6, 123.5, 120.7, 108.9, 101.4, 76.8, 74.1, 46.5, 46.0, 38.2, 21.6, 21.4.

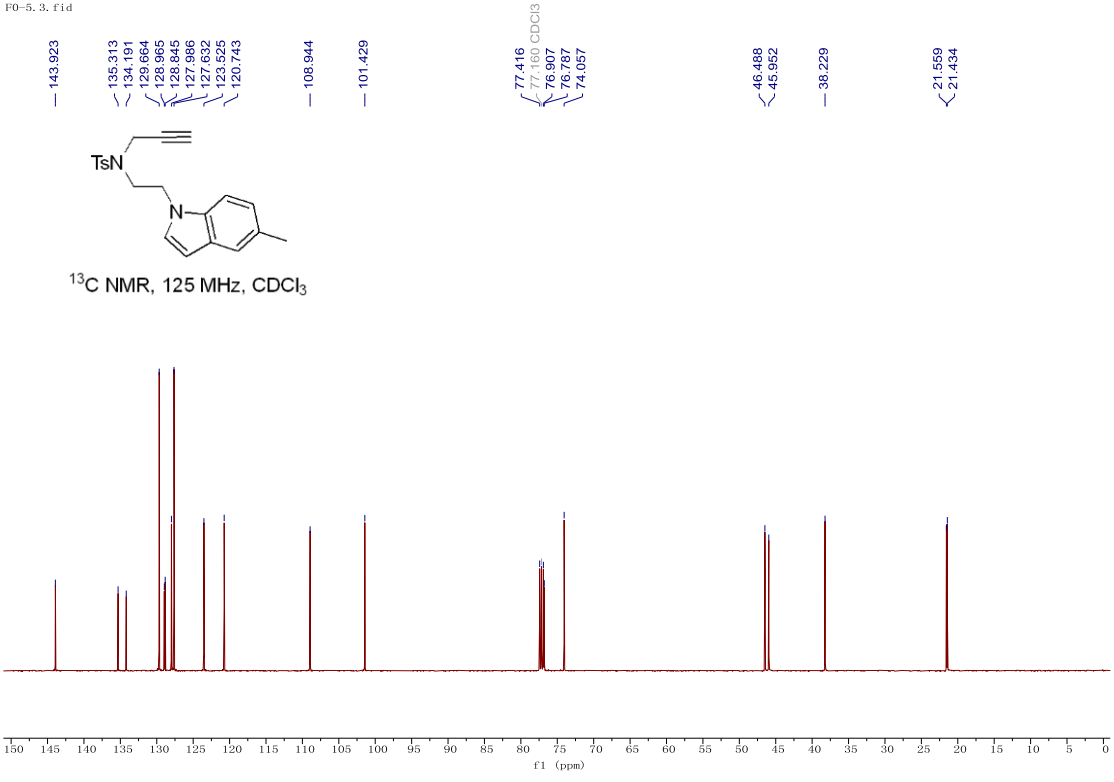
IR (KBr) ν (cm^{-1}): 3260, 1344, 1301, 1160, 880, 725, 689, 664 cm^{-1}.

HRMS (ESI): calcd for $C_{21}H_{23}N_2O_2S$ $[M+H]^+$: 367.14748, found: 367.14755.

MP: 79-82 °C.

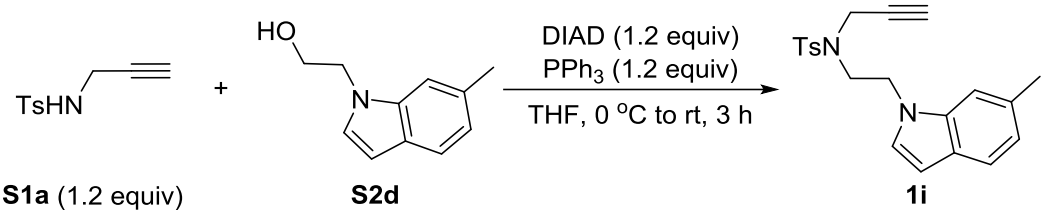


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

4-methyl-*N*-(2-(6-methyl-1*H*-indol-1-yl)ethyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1i)



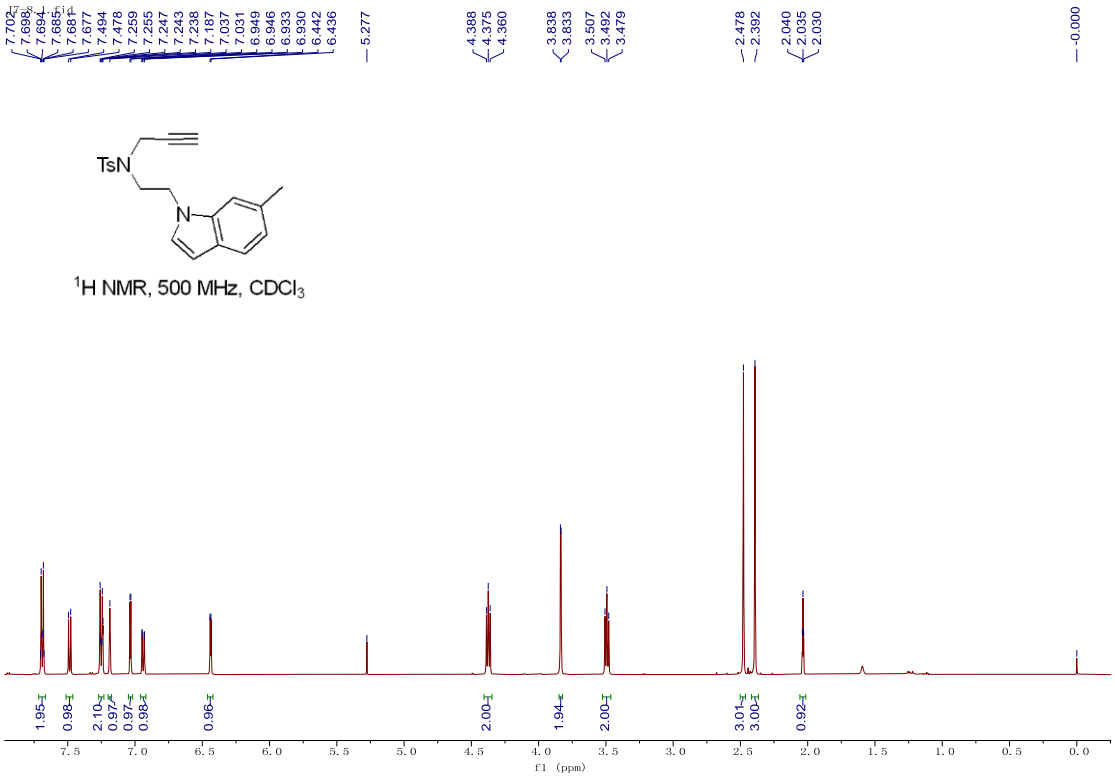
The compound **1i** (yellow oil, 301.6 mg, 82% yield) was obtained following General Procedure A from **S1a** (251.1 mg, 1.2 mmol, 1.2 equiv) and **S2d** (175.2 mg, 1.0 mmol, 1.0 equiv) using PPh_3 (314.8 mg, 1.2 mmol, 1.2 equiv) and DIAD (0.24 mL, 1.2 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.28) as eluent.

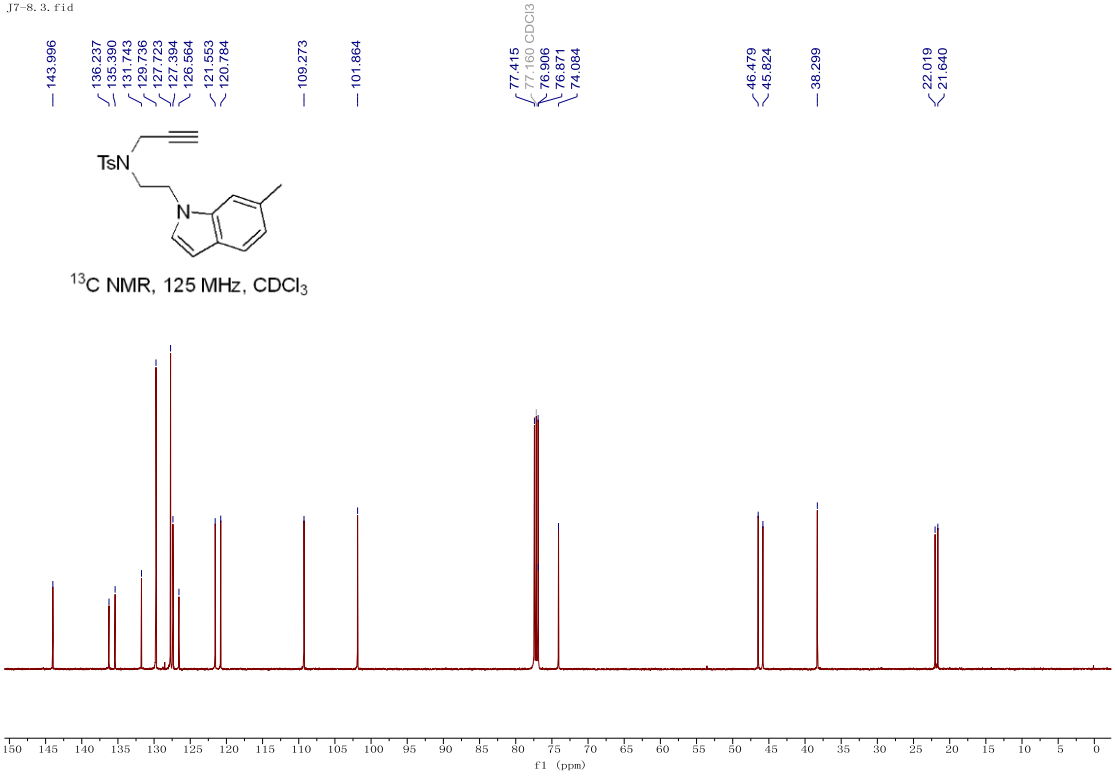
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.69 (dt, J = 8.5, 2.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.26-7.24 (m, 2H), 7.19 (s, 1H), 7.03 (d, J = 3.0 Hz, 1H), 6.94 (dd, J = 8.0, 1.5 Hz, 1H), 6.44 (d, J = 3.0 Hz, 1H), 4.38 (t, J = 6.5 Hz, 2H), 3.84 (d, J = 2.5 Hz, 2H), 3.49 (t, J = 6.5 Hz, 2H), 2.48 (s, 3H), 2.39 (s, 3H), 2.04 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 136.2, 135.4, 131.7, 129.7, 127.7, 127.4, 126.6, 121.6, 120.8, 109.3, 101.9, 76.9, 74.1, 46.5, 45.8, 38.3, 22.0, 21.6.

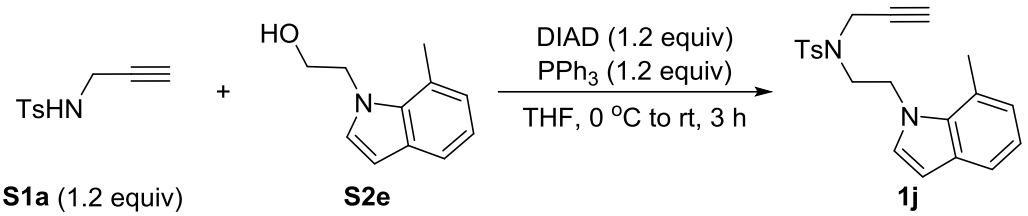
IR (KBr) ν (cm^{-1}): 3274, 1509, 1468, 1345, 1160, 1106, 804, 727, 658 cm^{-1}.

HRMS (ESI): calcd for $C_{21}H_{23}N_2O_2S$ $[M+H]^+$: 367.14748, found: 367.14746.


J7-8.1.fid
7.702
7.698
7.694
7.685
7.681
7.677
7.494
7.478
7.259
7.255
7.247
7.243
7.238
7.187
7.037
7.031
6.949
6.946
6.933
6.930
6.442
6.436
5.277
4.388
4.375
4.360
3.838
3.833
3.507
3.492
3.479
2.478
2.392
2.040
2.035
2.030
0.000
TsN
N
1H NMR, 500 MHz, CDCl3
1.95
0.98
2.10
0.97
0.97
0.98
0.96
2.00
1.94
2.00
3.01
3.00
0.92
f1 (ppm)


J7-8.3.fid
143.996
136.237
135.390
131.743
129.736
127.723
127.394
126.564
121.553
120.784
109.273
101.864
77.415
77.160 CDCl3
76.906
76.871
74.084
46.479
45.824
38.299
22.019
21.640
TsN
N
13C NMR, 125 MHz, CDCl3
f1 (ppm)

4-methyl-*N*-(2-(7-methyl-1*H*-indol-1-yl)ethyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1j)



The compound **1j** (yellow solid, 226.1 mg, 58% yield) was obtained following General Procedure A from **S1a** (265.8 mg, 1.27 mmol, 1.2 equiv) and **S2e** (185.9 mg, 1.06 mmol, 1.0 equiv) using PPh_3 (333.1 mg, 1.27 mmol, 1.2 equiv) and DIAD (0.25 mL, 1.27 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.29) as eluent.

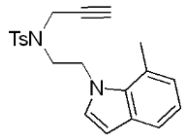
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.69 (dt, J = 8.5, 2.0 Hz, 2H), 7.45 (d, J = 7.5 Hz, 1H), 7.27-7.25 (m, 2H), 7.07 (d, J = 3.5 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.93 (dt, J = 7.0, 1.0 Hz, 1H), 6.49 (d, J = 3.0 Hz, 1H), 4.62 (t, J = 7.0 Hz, 2H), 3.82 (d, J = 2.5 Hz, 2H), 3.46 (t, J = 7.0 Hz, 2H), 2.74 (s, 3H), 2.40 (s, 3H), 1.99 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 135.4, 134.5, 130.0, 129.8, 129.7, 127.8, 125.0, 120.7, 120.0, 119.4, 102.7, 76.7, 74.2, 48.4, 48.2, 38.4, 21.7, 20.0.

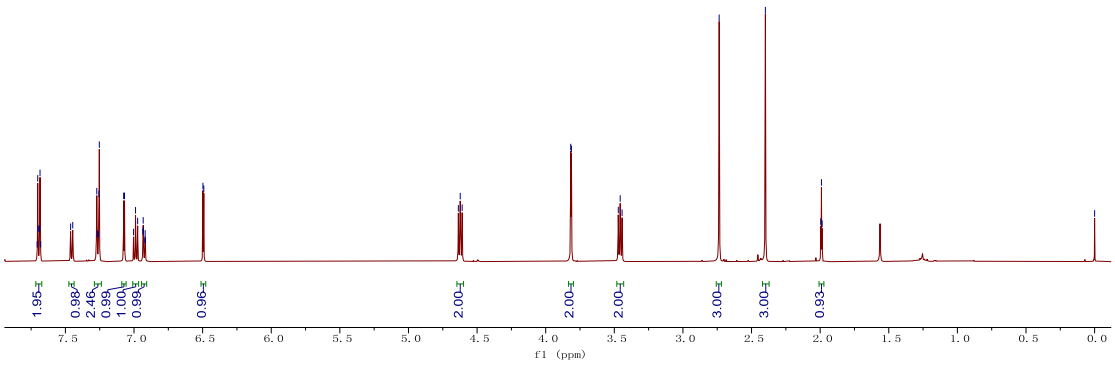
IR (KBr) ν (cm^{-1}): 3278, 1359, 1350, 1328, 1312, 1161, 1097, 880 cm^{-1}.

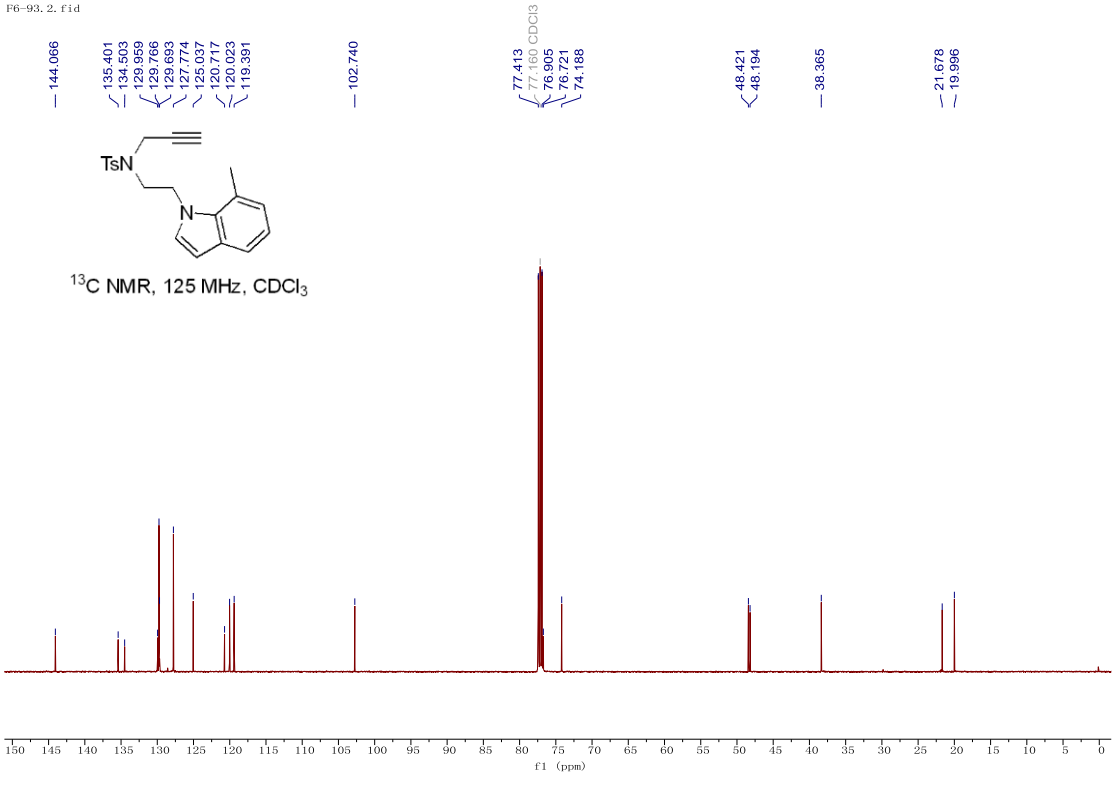
HRMS (ESI): calcd for $C_{21}H_{23}N_2O_2S$ $[M+H]^+$: 367.14748, found: 367.14746.

MP: 85-88 °C.



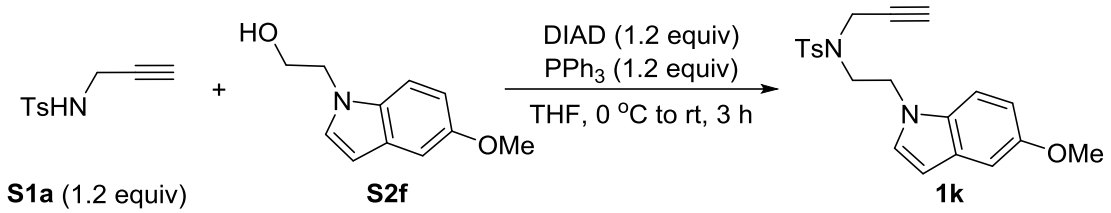
^{1}H NMR, 500 MHz, $CDCl_3$





^{13}C NMR, 125 MHz, $CDCl_3$

***N*-(2-(5-methoxy-1*H*-indol-1-yl)ethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1k)**



The compound **1k** (yellow solid, 370.1 mg, 97% yield) was obtained following General Procedure A from **S1a** (251.1 mg, 1.2 mmol, 1.2 equiv) and **S2f** (1.0 mmol, 191.2 mg, 1.0 equiv) using PPh_3 (314.8 mg, 1.2 mmol, 1.2 equiv) and DIAD (0.24 mL, 1.2 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 4/1 (R_f = 0.34) as eluent.

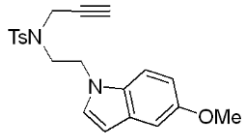
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.68 (dt, J = 7.5, 2.0 Hz, 2H), 7.29-7.24 (m, 3H), 7.08 (d, J = 3.5 Hz, 1H), 7.07 (d, J = 2.0 Hz, 1H), 6.87 (dd, J = 9.0, 2.5 Hz, 1H), 6.41 (dd, J = 3.0, 1.0 Hz, 1H), 4.38 (t, J = 6.5 Hz, 2H), 3.84 (s, 3H), 3.78 (d, J = 2.5 Hz, 2H), 3.48 (t, J = 6.5 Hz, 2H), 2.39 (s, 3H), 2.02 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 144.0, 135.4, 131.1, 129.7, 129.2, 128.6, 127.7, 112.3, 110.1, 102.7, 101.6, 76.8, 74.1, 55.9, 46.6, 46.3, 38.3, 21.6.

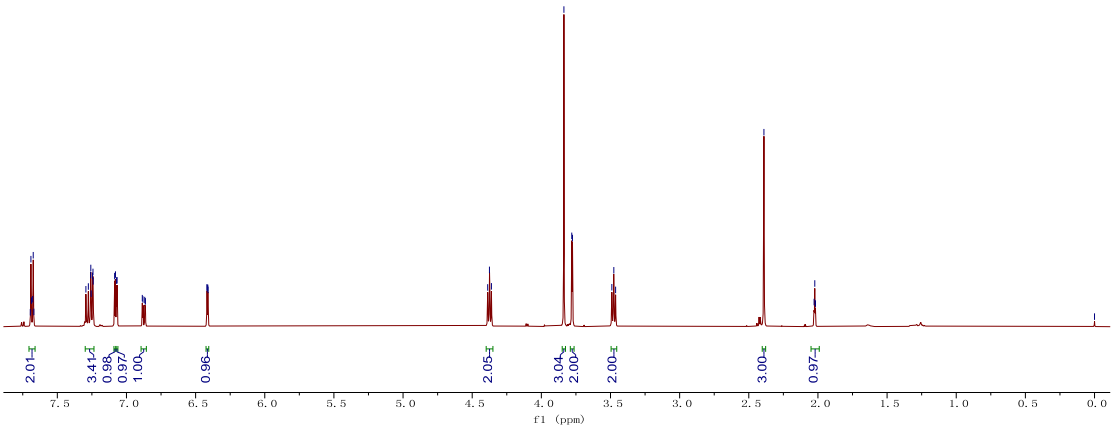
IR (KBr) ν (cm^{-1}): 3269, 1489, 1446, 1341, 1239, 1161, 1152, 797, 728 cm^{-1}.

HRMS (ESI): calcd for $C_{21}H_{23}N_2O_3S$ $[M+H]^+$: 383.14239, found: 383.14227.

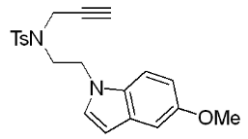
MP: 63-65 °C.



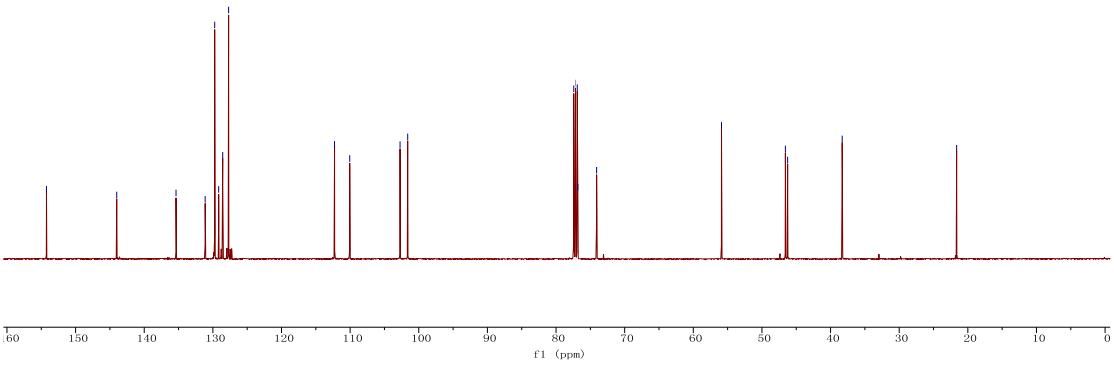
^{1}H NMR, 500 MHz, $CDCl_3$



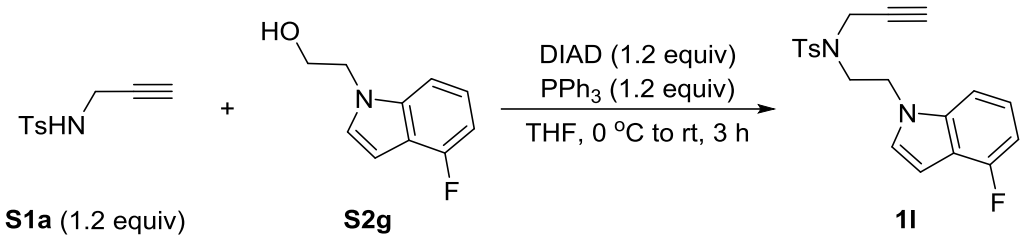
J7-16.2.fid



^{13}C NMR, 125 MHz, $CDCl_3$



***N*-(2-(4-fluoro-1*H*-indol-1-yl)ethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1l)**



S1a (1.2 equiv) **S2g** **1l**

The compound **1l** (yellow oil, 137 mg, 66% yield) was obtained following General Procedure A from **S1a** (141.2 mg, 0.67 mmol, 1.2 equiv) and **S2g** (100.4 mg, 0.56 mmol, 1.0 equiv) using PPh_3 (175.7 mg, 0.67 mmol, 1.2 equiv) and DIAD (0.13 mL, 0.67 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 6/1 (R_f = 0.24) as eluent.

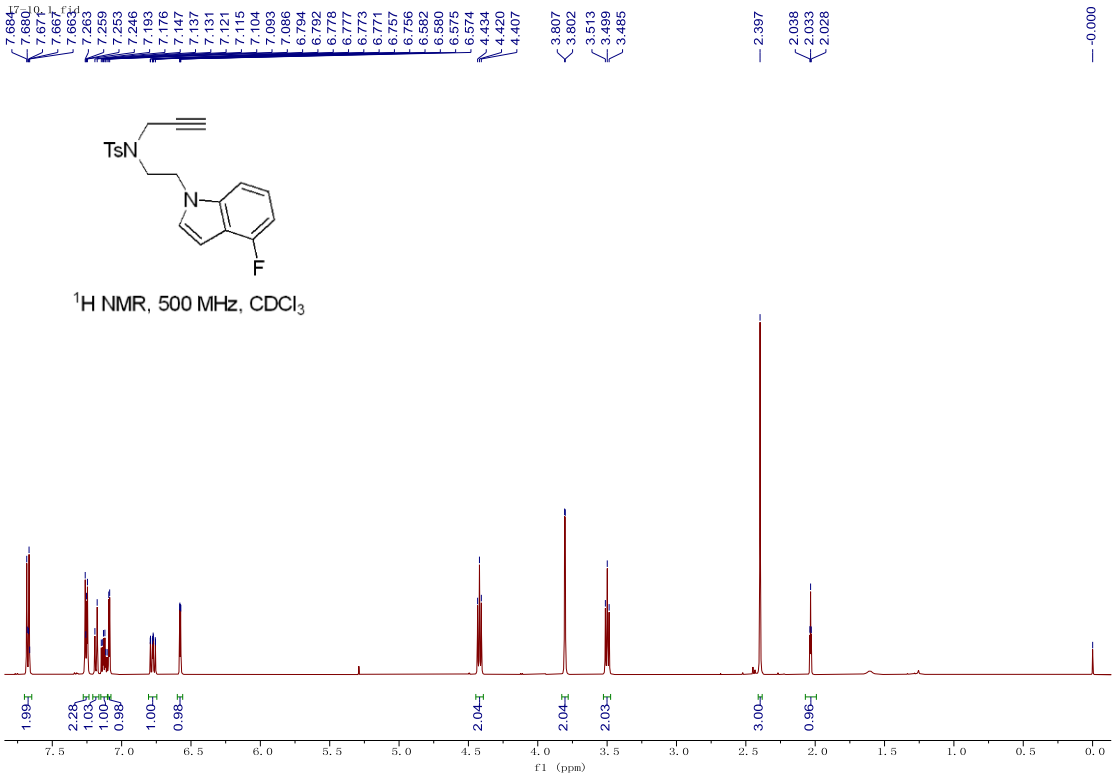
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.68 (dt, J = 8.5, 2.0 Hz, 2H), 7.26-7.25 (m, 2H), 7.18 (d, J = 8.5 Hz, 1H), 7.15-7.10 (m, 1H), 7.09 (d, J = 8.5 Hz, 1H), 6.77 (ddd, J = 10.5, 8.0, 1.0 Hz, 1H), 6.58 (dd, J = 3.5, 1.0 Hz, 1H), 4.42 (t, J = 7.0 Hz, 2H), 3.80 (d, J = 2.5 Hz, 2H), 3.50 (t, J = 7.0 Hz, 2H), 2.40 (s, 3H), 2.04 (t, J = 2.5 Hz, 1H).

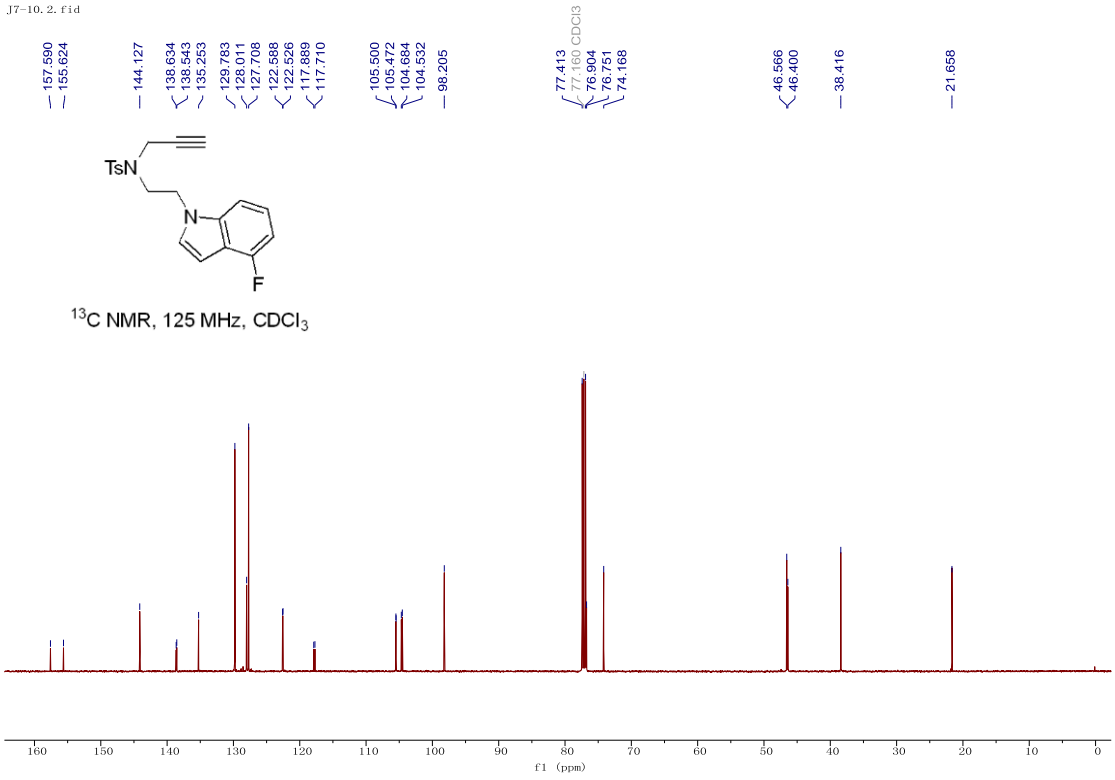
^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6 (d, J = 245.8 Hz), 144.1, 138.6 (d, J = 11.4 Hz), 135.3, 129.8, 128.0, 127.7, 122.6 (d, J = 7.8 Hz), 117.8 (d, J = 22.4 Hz), 105.5 (d, J = 3.5 Hz), 104.6 (d, J = 19.0 Hz), 98.2, 76.8, 74.2, 46.6, 46.4, 38.4, 21.7.

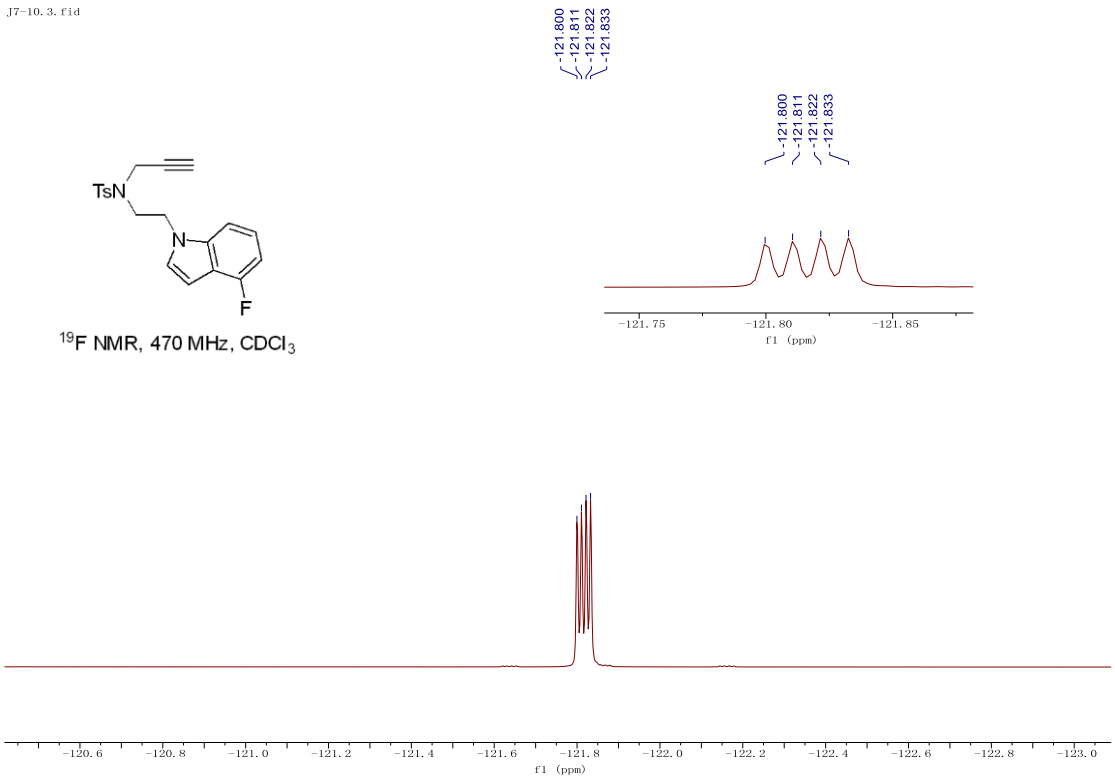
^{19}F NMR (470 MHz, $CDCl_3$) δ (-121.80) - (-121.83) (m).

IR (KBr) ν (cm^{-1}): 3292, 2926, 1496, 1347, 1227, 1160, 742, 659 cm^{-1}.

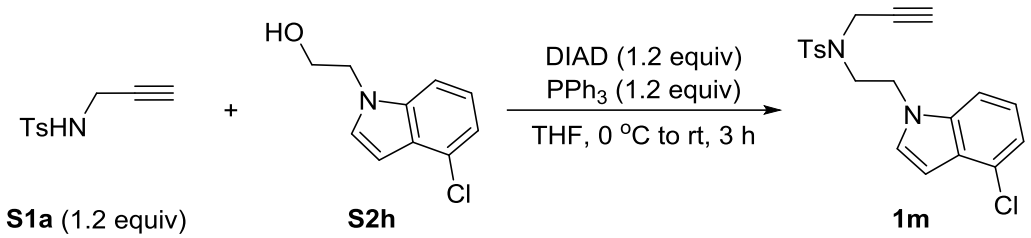
HRMS (ESI): calcd for $C_{20}H_{20}FN_2O_2S$ $[M+H]^+$: 371.12240, found: 371.12247.


J7-10-1.fid
7.684
7.680
7.671
7.667
7.663
7.263
7.259
7.253
7.246
7.193
7.176
7.147
7.137
7.131
7.121
7.115
7.104
7.093
7.086
6.794
6.792
6.778
6.777
6.773
6.771
6.757
6.756
6.582
6.580
6.575
6.574
4.434
4.420
4.407
3.807
3.802
3.513
3.499
3.485
2.397
2.038
2.033
2.028
-0.000
TsN
N
F
1H NMR, 500 MHz, CDCl3
1.99
2.28
1.03
1.00
0.98
1.00
0.98
2.04
2.04
2.03
3.00
0.96
f1 (ppm)


J7-10.2.fid
157.590
155.624
144.127
138.634
138.543
135.253
129.783
128.011
127.708
122.588
122.526
117.889
117.710
105.500
105.472
104.684
104.532
98.205
77.413
77.160 CDCl3
76.904
76.751
74.168
46.566
46.400
38.416
21.658
TsN
N
F
13C NMR, 125 MHz, CDCl3
f1 (ppm)



***N*-(2-(4-chloro-1*H*-indol-1-yl)ethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1m)**



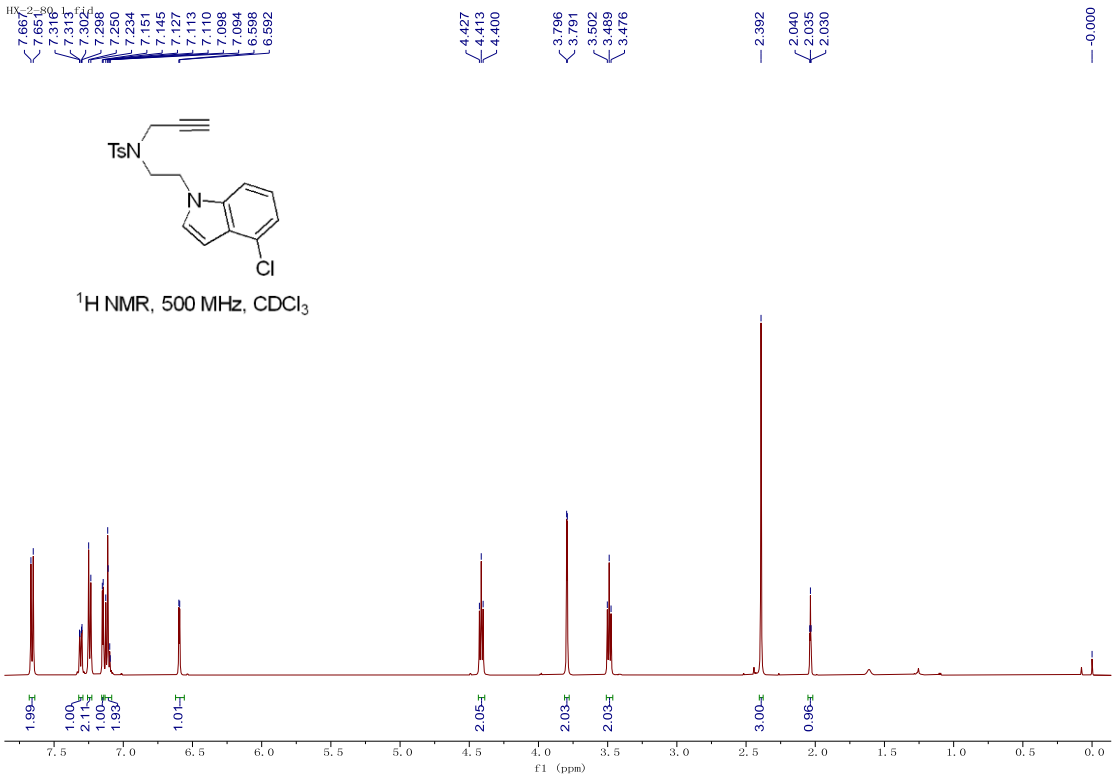
The compound **1m** (yellow oil, 159.4 mg, 87% yield) was obtained following General Procedure A from **S1a** (118.4 mg, 0.57 mmol, 1.2 equiv) and **S2h** (92.3 mg, 0.47 mmol, 1.0 equiv) using PPh_3 (148.5 mg, 0.57 mmol, 1.2 equiv) and DIAD (0.11 mL, 0.57 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 6/1 (R_f = 0.22) as eluent.

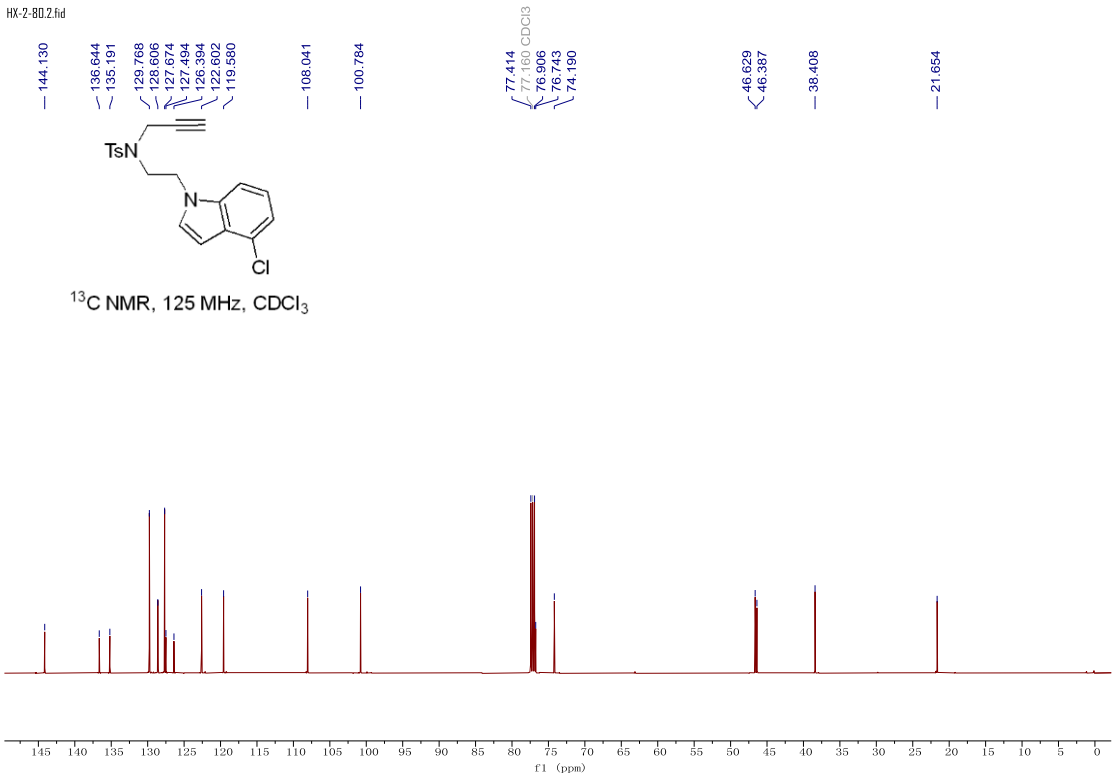
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.66 (d, J = 8.0 Hz, 2H), 7.31 (dd, J = 7.0, 1.5 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 3.0 Hz, 1H), 7.13-7.09 (m, 2H), 6.60 (d, J = 3.0 Hz, 1H), 4.41 (t, J = 7.0 Hz, 2H), 3.79 (d, J = 2.5 Hz, 2H), 3.49 (t, J = 7.0 Hz, 2H), 2.39 (s, 3H), 2.04 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 136.6, 135.2, 129.8, 128.6, 127.7, 127.5, 126.4, 122.6, 119.6, 108.0, 100.8, 76.7, 74.2, 46.6, 46.4, 38.4, 21.7.

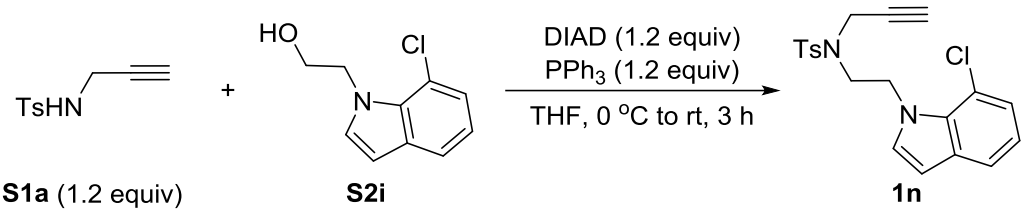
IR (KBr) ν (cm^{-1}): 3290, 1442, 1352, 1343, 1274, 1189, 1161, 910 cm^{-1}.

HRMS (ESI): calcd for $C_{20}H_{20}ClN_2O_2S$ $[M+H]^+$: 387.09285, found: 387.09268.





***N*-(2-(7-chloro-1*H*-indol-1-yl)ethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1n)**



The compound **1n** (white solid, 70.1 mg, 65% yield) was obtained following General Procedure A from **S1a** (70.3 mg, 0.34 mmol, 1.2 equiv) and **S2i** (54.9 mg, 0.28 mmol, 1.0 equiv) using PPh_3 (88.1 mg, 0.34 mmol, 1.2 equiv) and DIAD (0.07 mL, 0.34 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.30) as eluent.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.62 (d, J = 8.0 Hz, 2H), 7.40 (dd, J = 8.0, 1.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.07-7.04 (m, 2H), 6.90 (t, J = 7.5 Hz, 1H), 6.42 (d, J = 3.5 Hz, 1H), 4.69 (t, J = 6.5 Hz, 2H), 3.69 (d, J = 2.5 Hz, 2H), 3.49 (t, J = 6.5 Hz, 2H), 2.31 (s, 3H), 1.83 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 135.4, 132.2, 131.5, 130.9, 129.7, 127.8, 123.4, 120.5, 120.0, 116.4, 102.5, 76.7, 73.9, 48.5, 48.3, 38.5, 21.6.

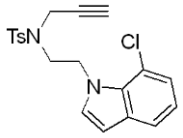
IR (KBr) ν (cm^{-1}): 3264, 1348, 1325, 1160, 1112, 880, 728, 716, 659 cm^{-1}.

HRMS (ESI): calcd for $C_{20}H_{20}ClN_2O_2S$ $[M+H]^+$: 387.09285, found: 387.09283.

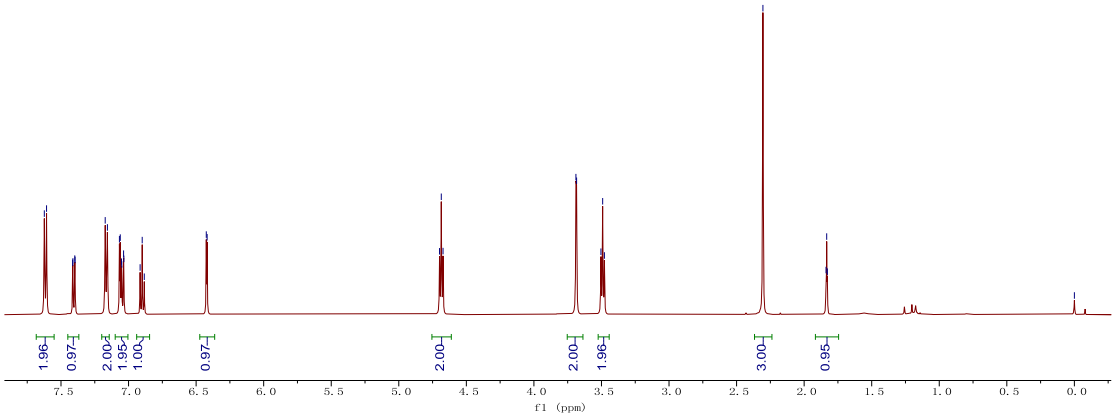
MP: 82-85 °C.

F0-7.1.fid

7.623 7.607 7.414 7.412 7.398 7.396 7.173 7.157 7.068 7.061 7.052 7.050 7.037 7.035 6.914 6.899 6.884 6.425 6.418 4.698 4.686 4.673 3.689 3.684 3.504 3.491 3.478 2.305 1.838 1.833 1.828 -0.000

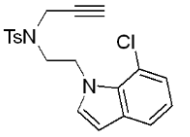


^{1}H NMR, 500 MHz, $CDCl_3$

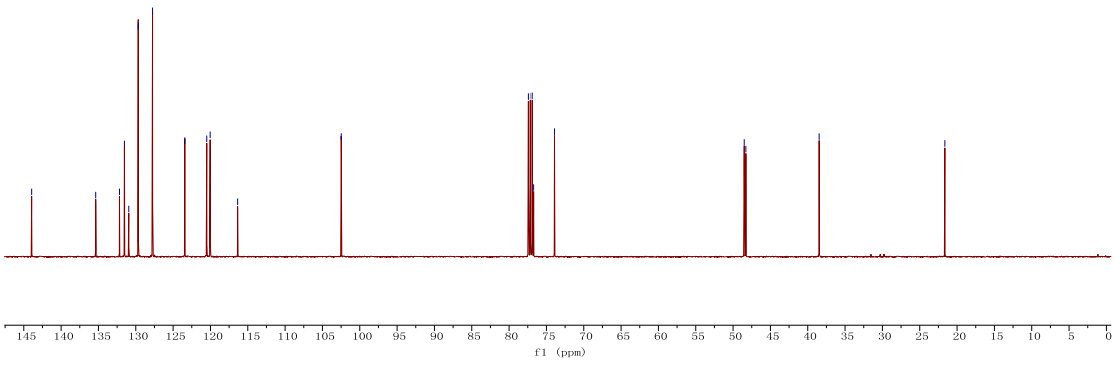


F0-7.2.fid

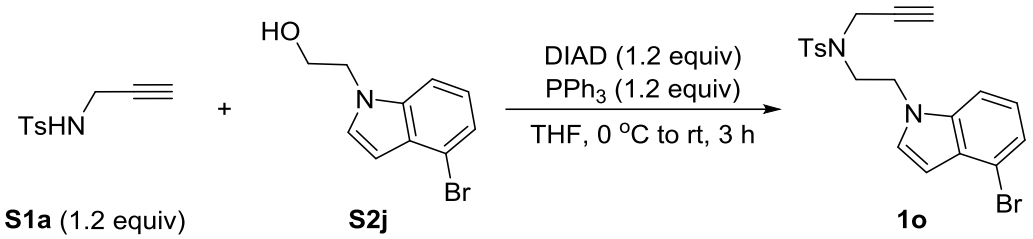
143.945 135.366 132.183 131.522 130.936 129.673 127.753 123.435 120.492 120.039 116.359 102.484 77.414 77.160 CDCl3 76.906 76.712 73.920 48.507 48.284 38.472 21.636



^{13}C NMR, 125 MHz, $CDCl_3$



***N*-(2-(4-bromo-1*H*-indol-1-yl)ethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1o)**



S1a (1.2 equiv) **S2j** **1o**

The compound **1o** (yellow solid, 107.1 mg, 83% yield) was obtained following General Procedure A from **S1a** (75.3 mg, 0.36 mmol, 1.2 equiv) and **S2j** (72.4 mg, 0.30 mmol, 1.0 equiv) using PPh_3 (94.4 mg, 0.36 mmol, 1.2 equiv) and DIAD (0.07 mL, 0.36 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 6/1 (R_f = 0.23) as eluent.

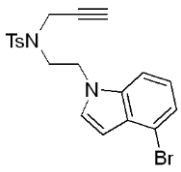
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.57 (dt, J = 8.5, 2.0 Hz, 2H), 7.27 (dt, J = 8.5, 1.0 Hz, 1H), 7.19 (dd, J = 8.0, 1.0 Hz, 1H), 7.16-7.14 (m, 2H), 7.07 (d, J = 3.5 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 6.45 (dd, J = 3.0, 1.0 Hz, 1H), 4.31 (t, J = 7.0 Hz, 2H), 3.71 (d, J = 2.5 Hz, 2H), 3.40 (t, J = 7.0 Hz, 2H), 2.30 (s, 3H), 1.96 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 136.2, 135.1, 129.7, 129.3, 128.6, 127.6, 122.9, 122.7, 115.1, 108.6, 102.4, 76.7, 74.2, 46.6, 46.4, 38.4, 21.6.

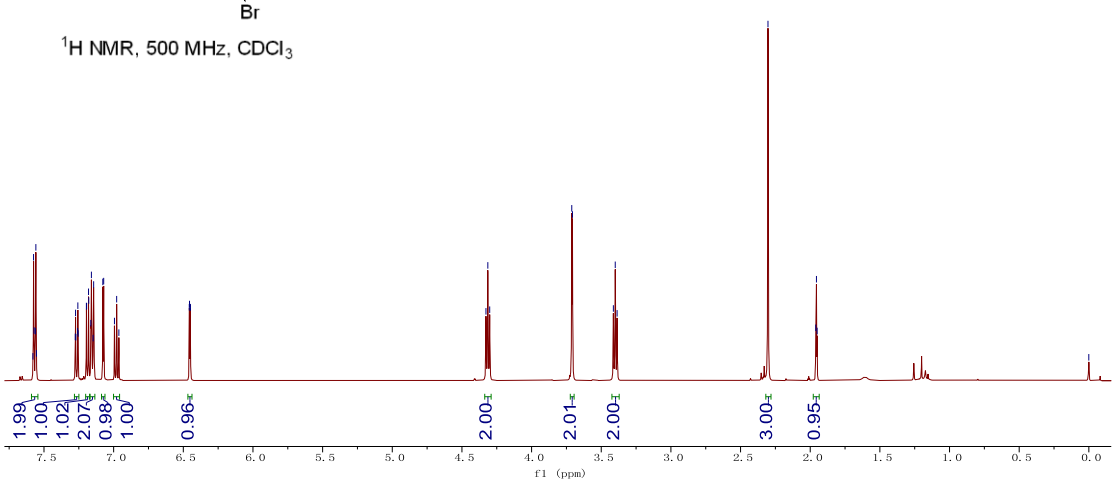
IR (KBr) ν (cm^{-1}): 3289, 1441, 1341, 1274, 911, 730, 657, 542 cm^{-1}.

HRMS (ESI): calcd for $C_{20}H_{20}BrN_2O_2S$ $[M+H]^+$: 431.04234, found: 431.04260.

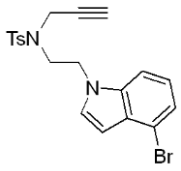
MP: 78-80 °C.



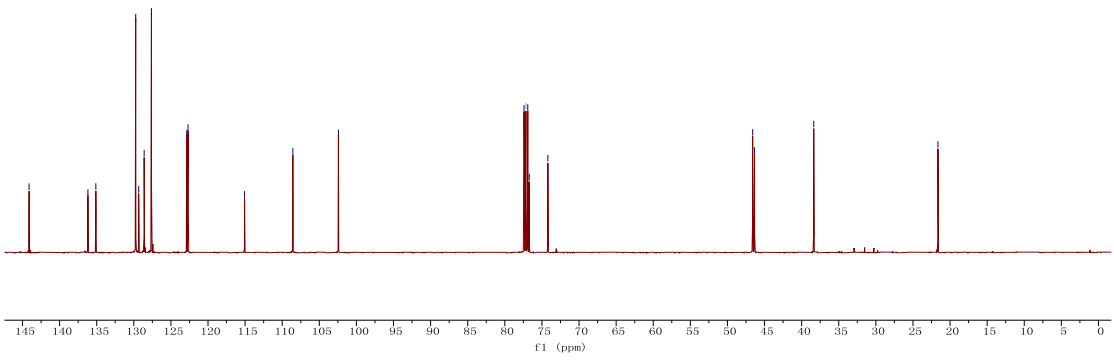
^{1}H NMR, 500 MHz, $CDCl_3$



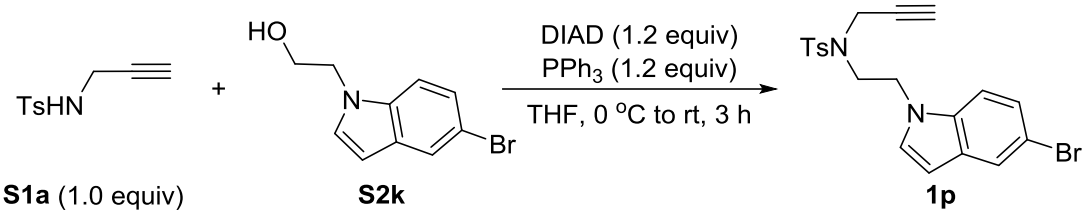
HX-2-74.2.fid



^{13}C NMR, 125 MHz, $CDCl_3$



***N*-(2-(5-bromo-1*H*-indol-1-yl)ethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1p)**



S1a (1.0 equiv) **S2k** **1p**

The compound **1p** (white solid, 446 mg, 74% yield) was obtained following General Procedure A from **S1a** (292.9 mg, 1.40 mmol, 1.0 equiv) and **S2k** (336.1 mg, 1.40 mmol, 1.0 equiv) using PPh_3 (440.7 mg, 1.68 mmol, 1.2 equiv) and DIAD (0.34 mL, 1.68 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 6/1 (R_f = 0.22) as eluent.

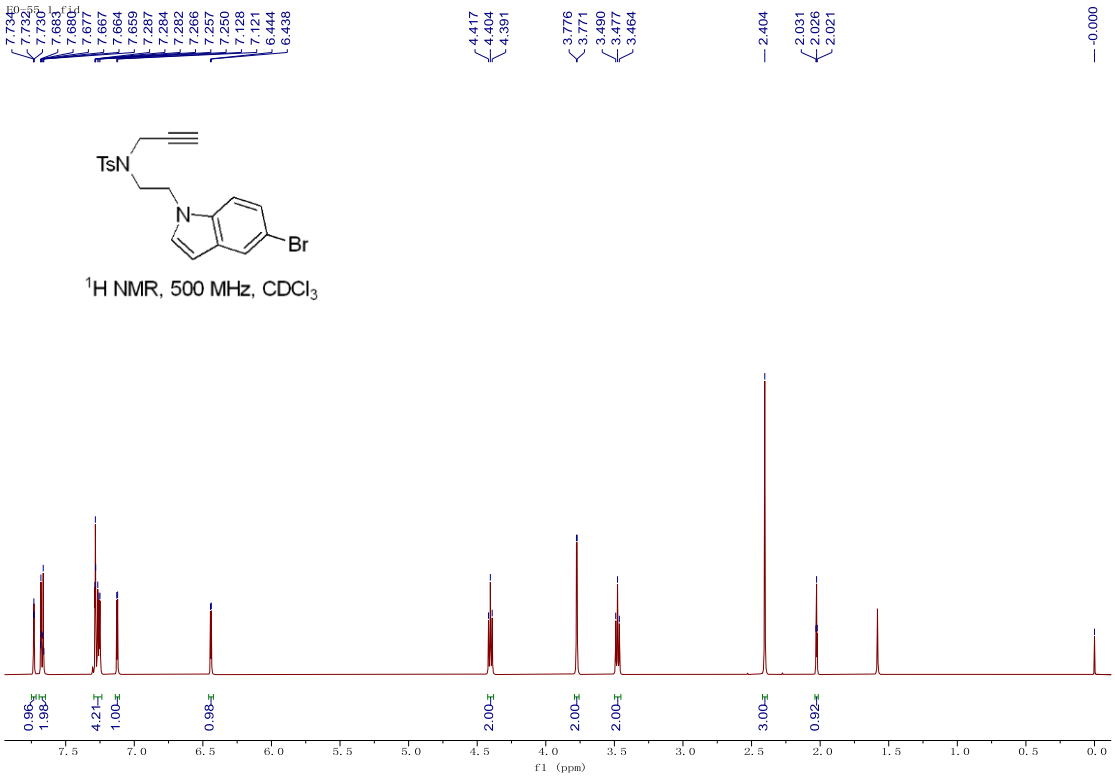
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.734-7.730 (m, 1H), 7.67 (dt, J = 8.0, 1.5 Hz, 2H), 7.29-7.25 (m, 4H), 7.12 (d, J = 3.5 Hz, 1H), 6.44 (d, J = 3.0 Hz, 1H), 4.40 (t, J = 6.5 Hz, 2H), 3.77 (d, J = 2.5 Hz, 2H), 3.48 (t, J = 6.5 Hz, 2H), 2.40 (s, 3H), 2.03 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 136.2, 135.2, 129.8, 129.4, 128.6, 127.7, 122.9, 122.8, 115.2, 108.6, 102.5, 76.8, 74.2, 46.6, 46.4, 38.4, 21.7.

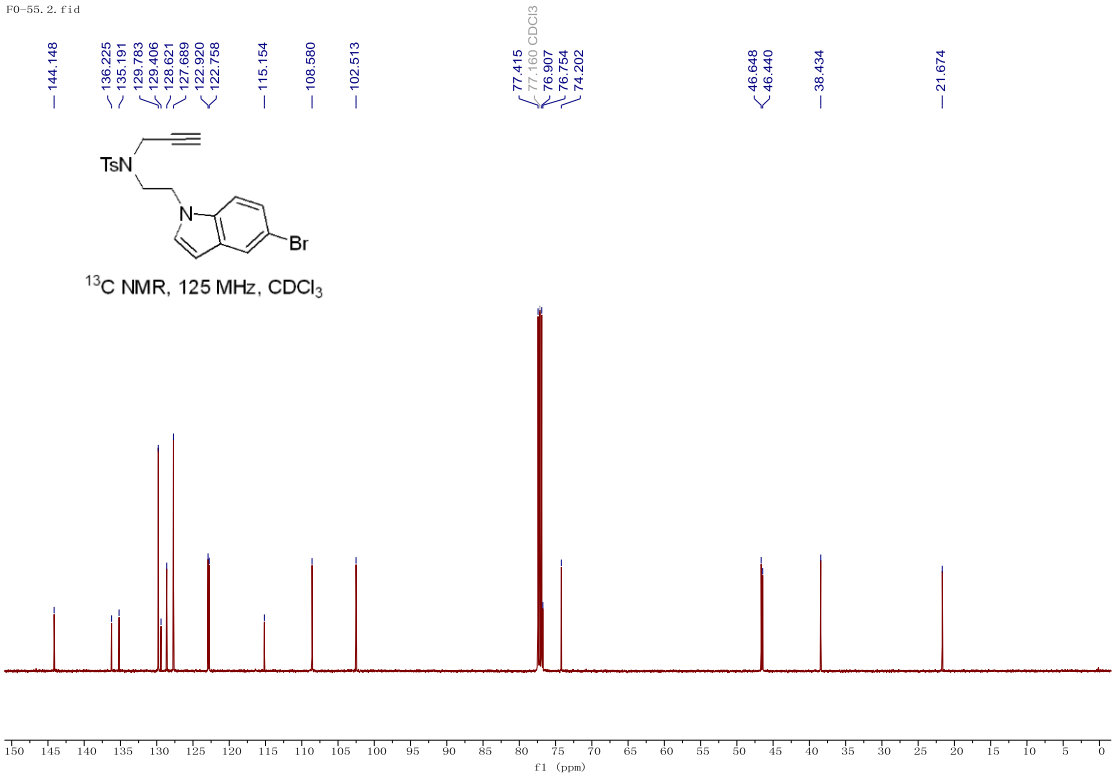
IR (KBr) ν (cm^{-1}): 3276, 1466, 1365, 1327, 1156, 1109, 873, 656 cm^{-1}.

HRMS (ESI): calcd for $C_{20}H_{20}BrN_2O_2S$ $[M+H]^+$: 431.04234, found: 431.04254.

MP: 80-82 °C.

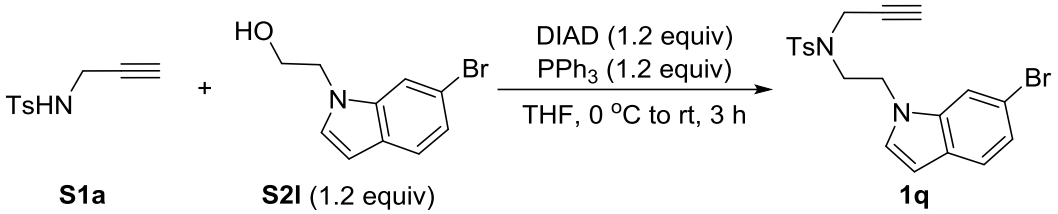


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

***N*-(2-(6-bromo-1*H*-indol-1-yl)ethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1q)**



S1a **S2l** (1.2 equiv) **1q**

The compound **1q** (yellow solid, 377.2 mg, 98% yield) was obtained following General Procedure A from **S1a** (185.8 mg, 0.88 mmol, 1.0 equiv) and **S2l** (250.6 mg, 1.05 mmol, 1.2 equiv) using PPh_3 (275.4 mg, 1.05 mmol, 1.2 equiv) and DIAD (0.21 mL, 1.05 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.21) as eluent.

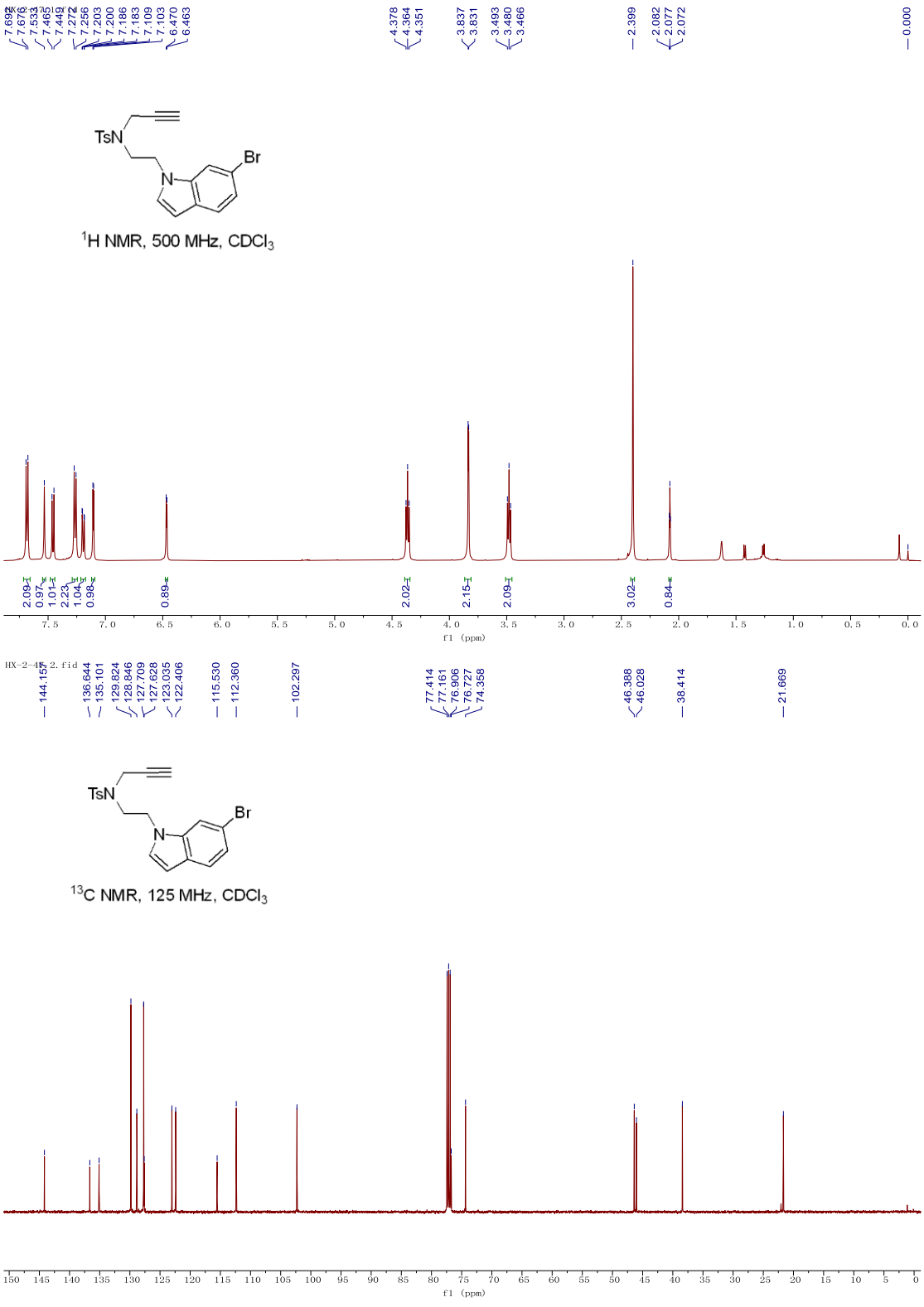
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.68 (d, J = 8.0 Hz, 2H), 7.53 (s, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.19 (dd, J = 8.5, 1.5 Hz, 1H), 7.11 (d, J = 3.0 Hz, 1H), 6.47 (d, J = 3.5 Hz, 1H), 4.36 (t, J = 7.0 Hz, 2H), 3.83 (d, J = 3.0 Hz, 2H), 3.48 (t, J = 7.0 Hz, 2H), 2.40 (s, 3H), 2.08 (t, J = 3.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 136.6, 135.1, 129.8, 128.8, 127.7, 127.6, 123.0, 122.4, 115.5, 112.4, 102.3, 76.7, 74.4, 46.4, 46.0, 38.4, 21.7.

IR (KBr) ν (cm^{-1}): 3287, 1368, 1358, 1164, 872, 817, 728, 653 cm^{-1}.

HRMS (ESI): calcd for $C_{20}H_{20}BrN_2O_2S$ $[M+H]^+$: 431.04234, found: 431.04251.

MP: 86-89 °C.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7.256
7.203
7.200
7.186
7.183
7.109
7.103
6.470
6.463
4.378
4.364
4.351
3.837
3.831
3.493
3.480
3.466
2.399
2.082
2.077
2.072
0.000
TsN
Br
N
1H NMR, 500 MHz, CDCl3
2.09
0.97
1.01
2.23
1.04
0.98
0.89
2.02
2.15
2.09
3.02
0.84
f1 (ppm)
HX-2-45 2.fid
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136.644
135.101
129.824
128.846
127.709
127.628
123.035
122.406
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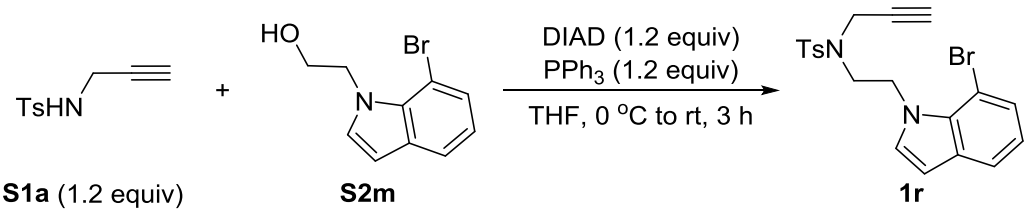
112.360
102.297
77.414
77.161
76.906
76.727
74.358
46.388
46.028
38.414
21.669
TsN
Br
N
13C NMR, 125 MHz, CDCl3
f1 (ppm)

***N*-(2-(7-bromo-1*H*-indol-1-yl)ethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1r)**



The compound **1r** (yellow solid, 125.2 mg, 30% yield) was obtained following General Procedure A from **S1a** (240.7 mg, 1.15 mmol, 1.0 equiv) and **S2m** (230.6 mg, 0.96 mmol, 1.2 equiv) using PPh_3 (302.4 mg, 1.15 mmol, 1.2 equiv) and DIAD (0.23 mL, 1.15 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 15/1 (R_f = 0.23) as eluent.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.70 (dt, J = 8.5, 2.0 Hz, 2H), 7.53 (dd, J = 8.0, 1.0 Hz, 1H), 7.32 (dd, J = 7.5, 1.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 3.0 Hz, 1H), 6.92 (t, J = 8.0 Hz, 1H), 6.50 (d, J = 3.0 Hz, 1H), 4.81 (t, J = 6.5 Hz, 2H), 3.77 (d, J = 2.5 Hz, 2H), 3.57 (t, J = 6.5 Hz, 2H), 2.39 (s, 3H), 1.91 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 135.4, 132.3, 132.0, 131.8, 129.7, 127.8, 127.0, 120.9, 120.7, 103.5, 102.4, 76.8, 74.0, 48.5, 47.9, 38.5, 21.7.

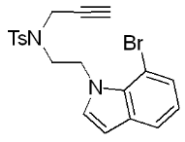
IR (KBr) ν (cm^{-1}): 3299, 1347, 1160, 1092, 879, 782, 659, 577 cm^{-1}.

HRMS (ESI): calcd for $C_{20}H_{20}BrN_2O_2S$ $[M+H]^+$: 431.04234, found: 431.04245.

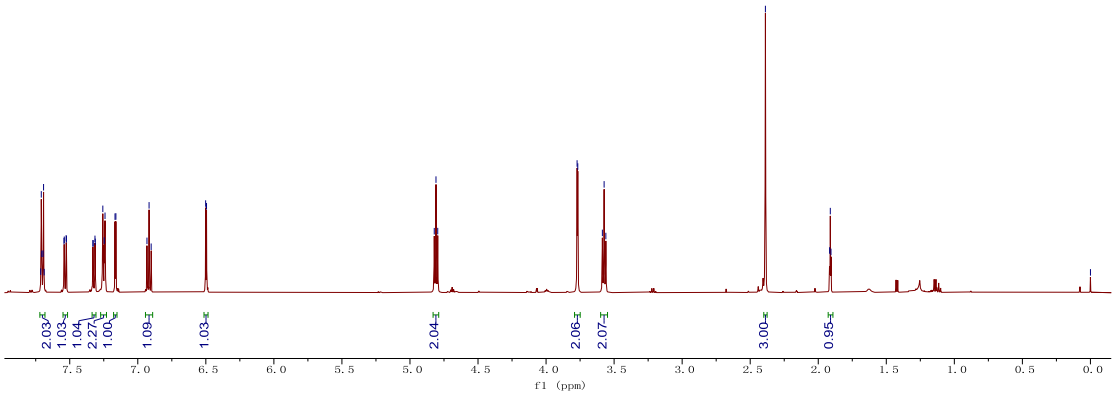
MP: 75-78 °C.

F6-94.1.fid

7.713 7.709 7.705 7.696 7.692 7.688 7.542 7.540 7.526 7.524 7.330 7.328 7.315 7.313 7.257 7.247 7.241 7.167 7.161 6.933 6.917 6.902 6.501 6.495 4.822 4.809 4.796 3.772 3.767 3.586 3.573 3.561 2.388 1.916 1.911 1.907 -0.000

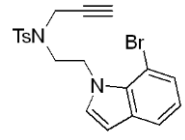


^{1}H NMR, 500 MHz, $CDCl_3$

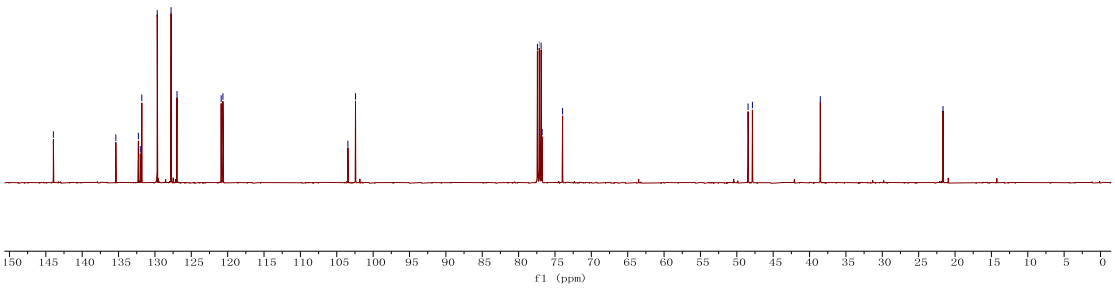


F6-94.2.fid

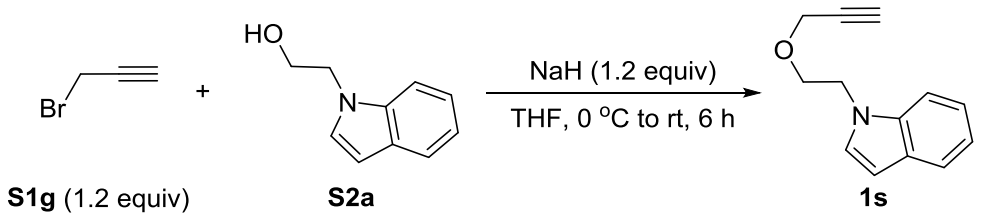
143.960 135.376 132.277 132.015 131.802 129.682 127.782 126.967 120.893 120.652 103.467 102.424 77.414 77.160 CDCl3 76.906 76.766 73.955 48.457 47.856 38.524 21.652



^{13}C NMR, 125 MHz, $CDCl_3$



1-(2-(prop-2-yn-1-yloxy)ethyl)-1*H*-indole (1s)



S1g (1.2 equiv) **S2a** **1s**

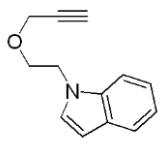
To a round-bottom flask were added **S2a** (161.2 mg, 1.0 mmol, 1.0 equiv), NaH (28.8 mg, 1.2 mmol, 1.2 equiv), and THF (3.0 mL). After stirring for 15 min, **S1g** (142.8 mg, 1.2 mmol, 1.2 equiv) was added to the mixture. After stirring at room temperature for 6 h, the mixture was filtered by using celite, concentrated under vacuum and purified by flash column chromatography using gradients of petroleum ether/ethyl acetate = 15/1 (R_f = 0.32) as eluent to give **1s** (colorless oil, 163.4 mg, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.62 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.21-7.18 (m, 1H), 7.15 (d, J = 3.5 Hz, 1H), 7.11-7.08 (m, 1H), 6.49-6.48 (m, 1H), 4.29 (t, J = 5.5 Hz, 2H), 4.06 (d, J = 2.5 Hz, 2H), 3.82 (t, J = 5.5 Hz, 2H), 2.39 (t, J = 2.5 Hz, 1H).

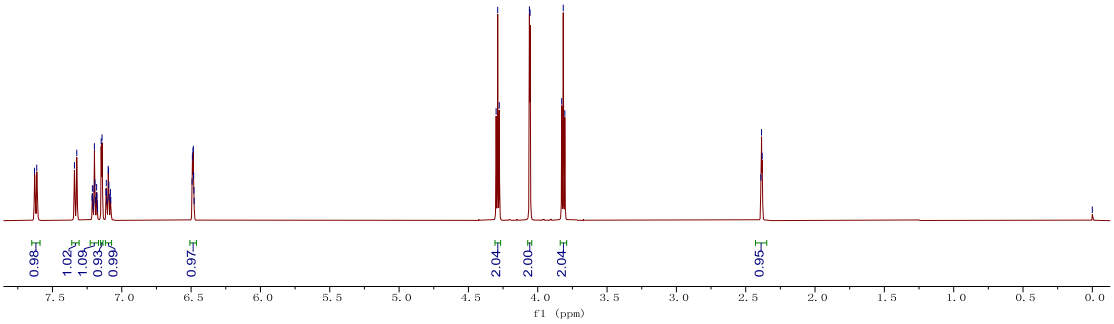
^{13}C NMR (125 MHz, $CDCl_3$) δ 136.1, 128.7, 128.5, 121.6, 121.1, 119.5, 109.3, 101.4, 79.4, 74.9, 68.8, 58.5, 46.1.

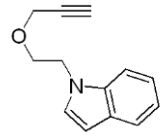
IR (KBr) ν (cm^{-1}): 3282, 1512, 1483, 1464, 1336, 1316, 1202, 1108, 764 cm^{-1}.

HRMS (ESI): calcd for $C_{13}H_{14}NO$ $[M+H]^+$: 200.10699, found: 200.10704.

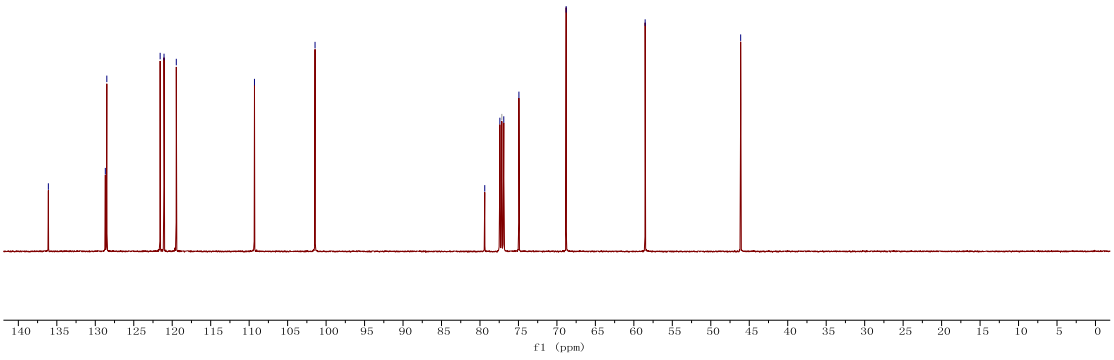


^{1}H NMR, 500 MHz, $CDCl_3$

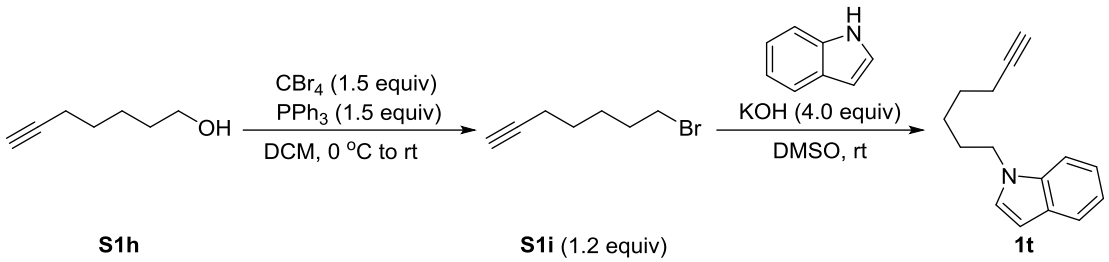




^{13}C NMR, 125 MHz, $CDCl_3$



1-(hept-6-yn-1-yl)-1*H*-indole (1t)



S1h **S1i** (1.2 equiv) **1t**

To a round-bottom flask was added **S1h** (189.6 mg, 1.69 mmol, 1.0 equiv) dissolved in dry DCM (10.0 mL), and the solution was cooled on ice. Then, triphenylphosphine (666.2 mg, 2.54 mmol, 1.5 equiv) was added, upon complete dissolution, tetrabromomethane (842.3 mg, 2.54 mmol, 1.5 equiv) was added slowly. The reaction mixture was brought to room temperature and stirred for 1 h. After completion, the solvent was removed under reduced pressure and purified by flash column chromatography using gradients of cyclohexane (R_f = 0.45) as eluent to give **S1i** (colorless oil, 274.8 mg, 93% yield)[1].

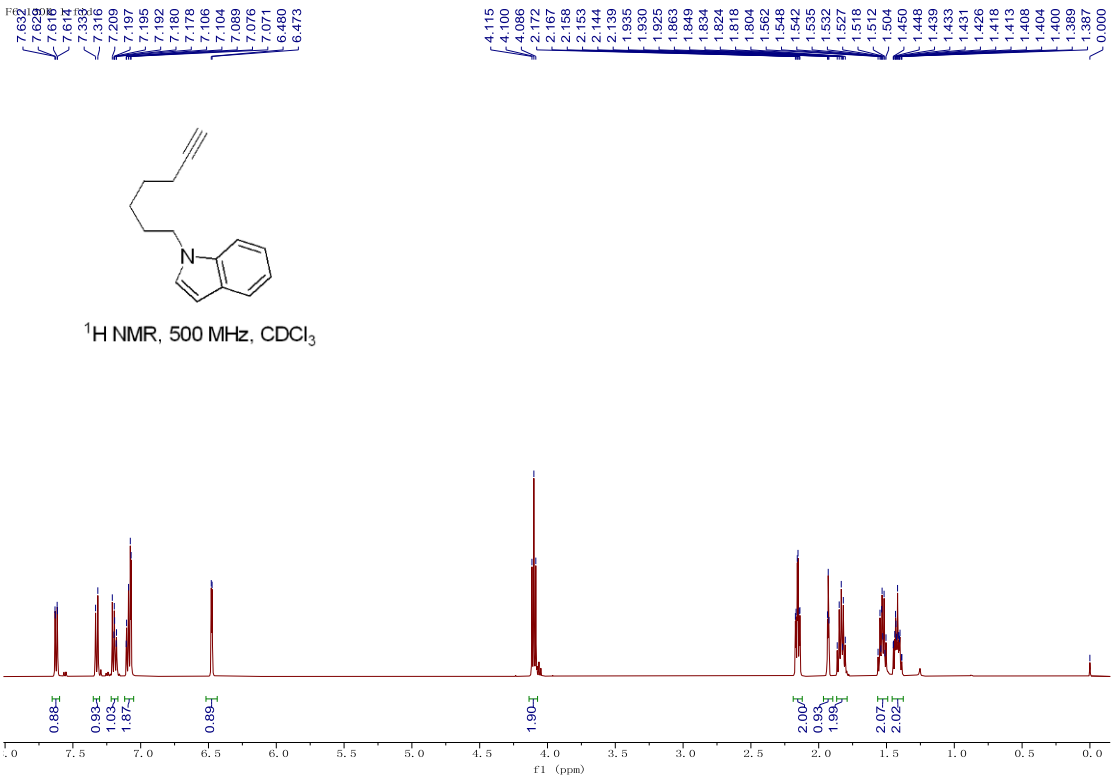
To a round-bottom flask were added 1*H*-indol (153.3 mg, 1.30 mmol, 1.0 equiv), KOH (291.8 mg, 5.20 mmol, 4.0 equiv), and DMSO (10.0 mL). After stirring for 1 h, **S1i** (1.57 mmol, 274.8 mg, 1.2 equiv) was added to the mixture. After stirring at room temperature and was complete as monitored by TLC. The mixture was extracted three times with water and ethyl acetate, dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by flash column chromatography using gradients of petroleum ether/ethyl acetate = 50/1 (R_f = 0.33) as eluent to give **1t** (yellow oil, 195.6 mg, 59% yield).

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.62 (dd, J = 8.0, 1.5 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.21-7.18 (m, 1H), 7.11-7.07 (m, 2H), 6.48 (d, J = 3.5 Hz, 1H), 4.10 (t, J = 7.5 Hz, 2H), 2.16 (td, J = 7.5, 2.5 Hz, 2H), 1.93 (t, J = 2.5 Hz, 1H), 1.86-1.80 (m, 2H), 1.56-1.50 (m, 2H), 1.45-1.39 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.0, 128.7, 127.9, 121.5, 121.1, 119.3, 109.4, 101.0, 84.3, 68.6, 46.3, 29.9, 28.1, 26.2, 18.4.

IR (KBr) ν (cm^{-1}): 3299, 1632, 1608, 1602, 1596, 1463, 1353, 743 cm^{-1}.

HRMS (ESI): calcd for $C_{15}H_{18}N$ $[M+H]^+$: 212.14338, found: 212.14340.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N
1H NMR, 500 MHz, CDCl3
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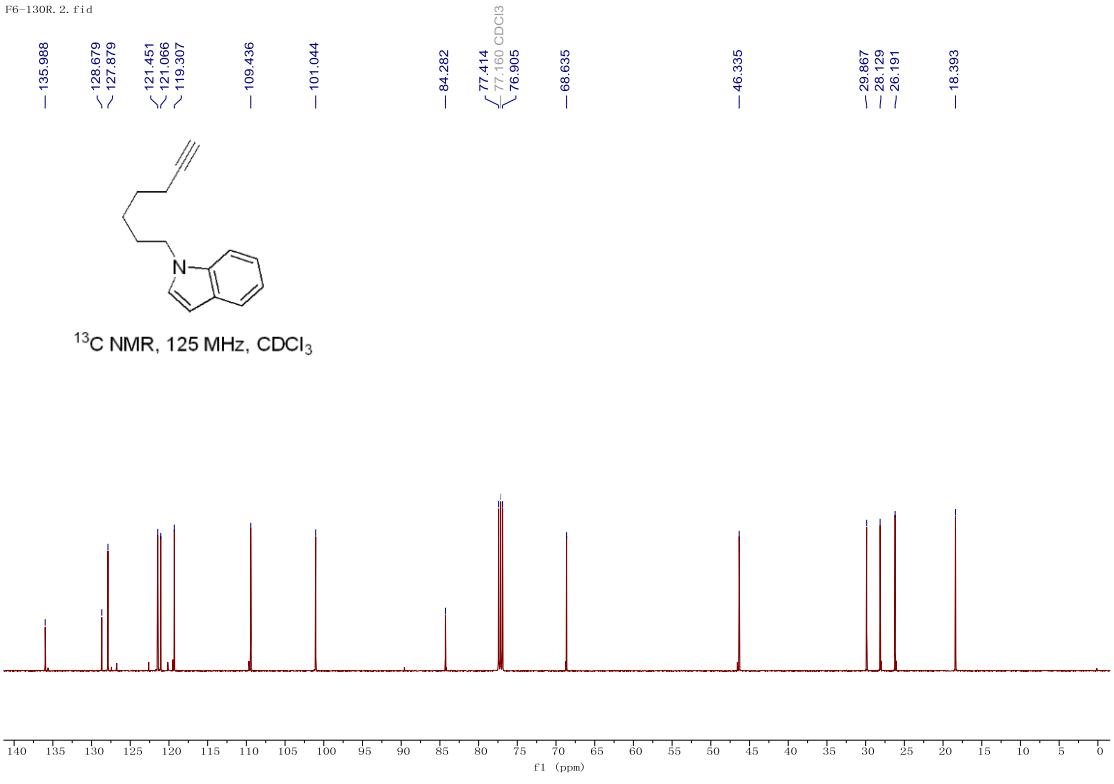
1.90
2.00
0.93
1.99
2.07
2.02
f1 (ppm)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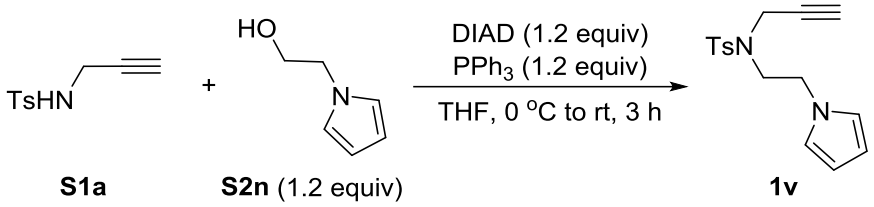
77.160 CDCl3
76.905
68.635
46.335
29.867
28.129
26.191
18.393
N
13C NMR, 125 MHz, CDCl3
f1 (ppm)

***N*-(2-(1*H*-pyrrol-1-yl)ethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1v)**



S1a **S2n** (1.2 equiv) **1v**

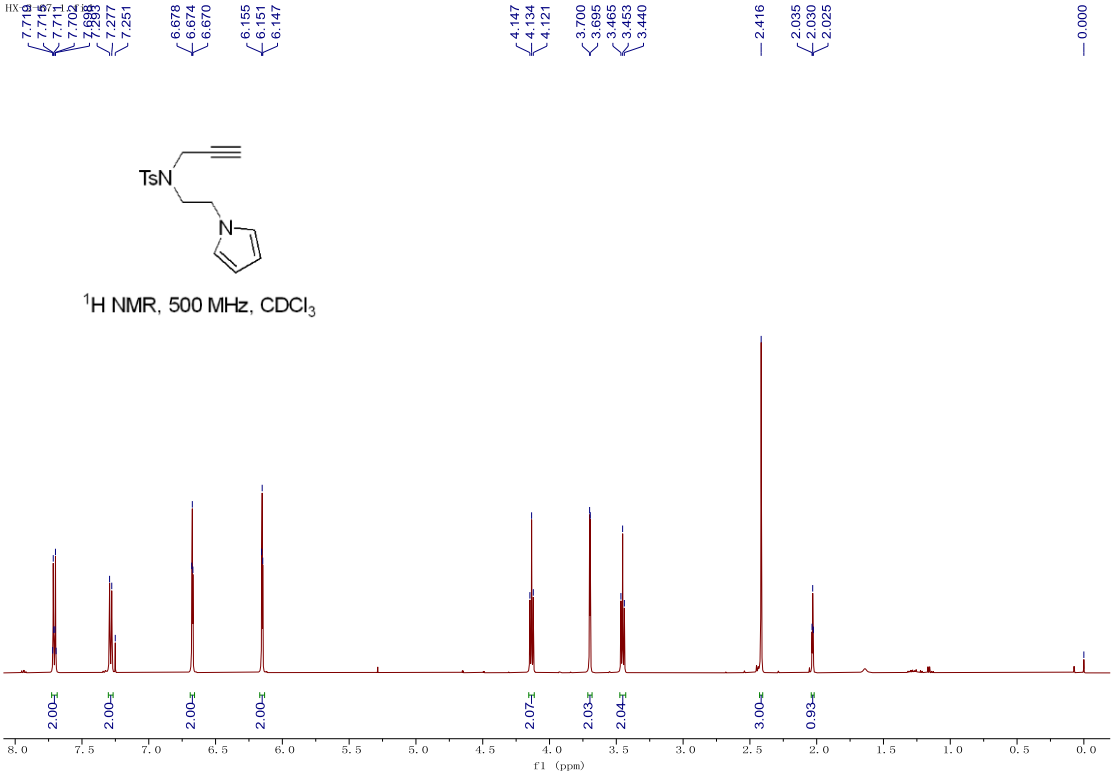
The compound **1v** (yellow oil, 364.3 mg, 48% yield) was obtained following General Procedure A from **S1a** (522.8 mg, 2.5 mmol, 1.0 equiv) and **S2n** (333.4 mg, 3.0 mmol, 1.2 equiv) using PPh_3 (786.9 mg, 3.0 mmol, 1.2 equiv) and DIAD (0.59 mL, 3.0 mmol, 1.2 equiv), after purification by flash column chromatography using petroleum ether/ethyl acetate = 8/1 (R_f = 0.24) as eluent.

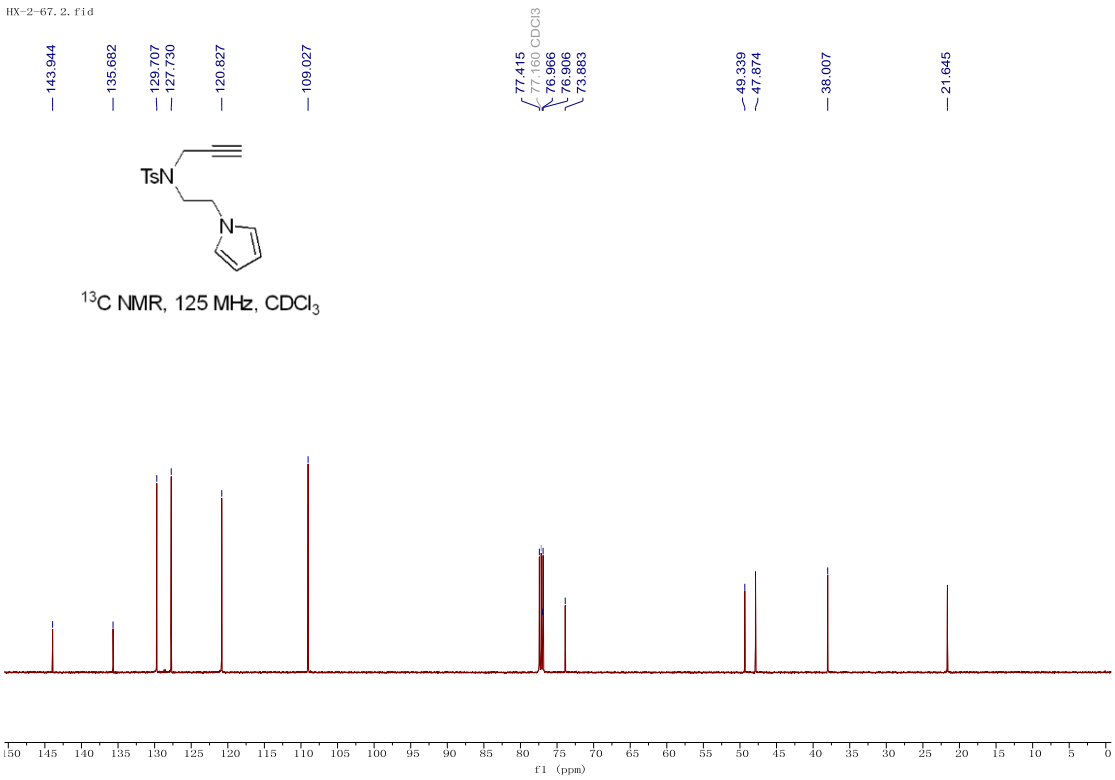
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.71 (dt, J = 8.5, 2.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.67 (t, J = 2.0 Hz, 2H), 6.15 (t, J = 2.0 Hz, 2H), 4.13 (t, J = 6.5 Hz, 2H), 3.70 (d, J = 2.5 Hz, 2H), 3.45 (t, J = 6.5 Hz, 2H), 2.42 (s, 3H), 2.03 (t, J = 2.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 135.7, 129.7, 127.7, 120.8, 109.0, 77.0, 73.9, 49.3, 47.9, 38.0, 21.6.

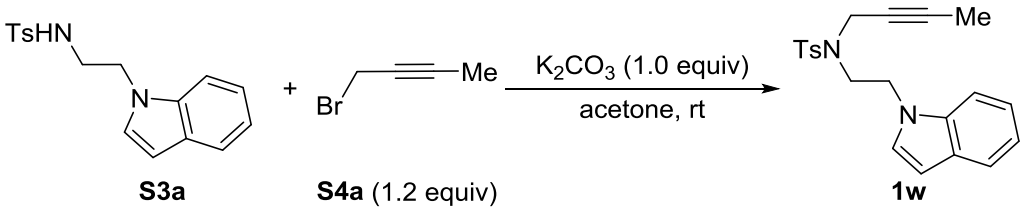
IR (KBr) ν (cm^{-1}): 3274, 2926, 1500, 1347, 1287, 1160, 1090, 728 cm^{-1}.

HRMS (ESI): calcd for $C_{16}H_{19}N_2O_2S$ $[M+H]^+$: 303.11617, found: 303.11612.





_N_-(2-(1_H_-indol-1-yl)ethyl)-_N_-(but-2-yn-1-yl)-4-methylbenzenesulfonamide (1w)

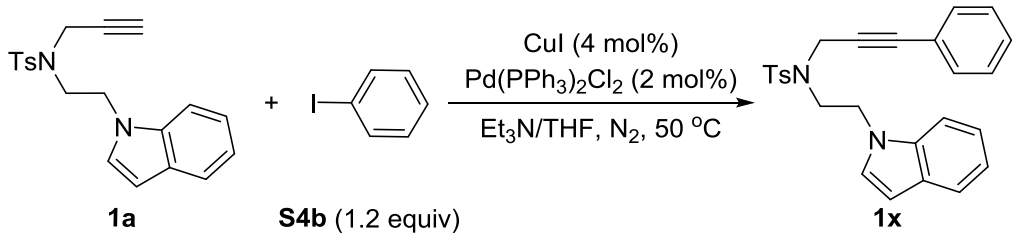


To a round-bottom flask were added **S3a** (157.2 mg, 0.5 mmol, 1.0 equiv), K_2CO_3 (69.1 mg, 0.5 mmol, 1.0 equiv), and acetone (2.0 mL). After stirring for 15 min, **S4a** (79.8 mg, 0.6 mmol, 1.2 equiv) was added to the mixture. After stirring at room temperature for 3 h, the mixture was concentrated under vacuum and purified by flash column chromatography using of petroleum ether/ethyl acetate = 8/1 (R_f = 0.29) as eluent to give **1w** (white soild, 165.9 mg, 91% yield). Characterization data match our previously reported one for this product[2].

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.69 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 8.0 Hz, 1H), 7.12-7.09 (m, 2H), 6.50 (d, J = 3.0 Hz, 1H), 4.41 (t, J = 7.0 Hz, 2H), 3.81 (q, J = 2.5 Hz, 2H), 3.47 (t, J = 7.0 Hz, 2H), 2.39 (s, 3H), 1.54 (t, J = 2.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 135.9, 135.5, 129.6, 128.8, 128.1, 127.8, 121.9, 121.2, 119.7, 109.3, 102.0, 82.1, 72.0, 46.6, 46.0, 39.0, 21.6, 3.4.

_N_-(2-(1_H_-indol-1-yl)ethyl)-4-methyl-_N_-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1x)



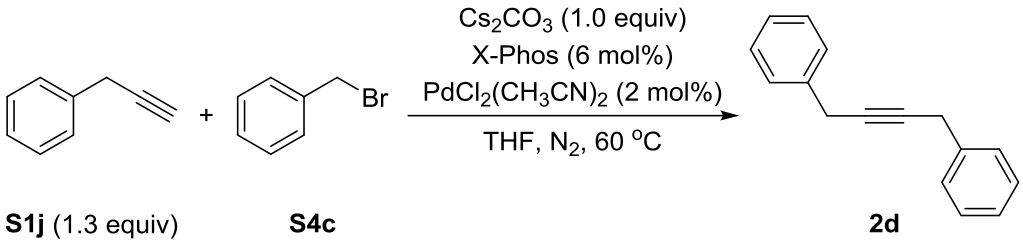
1a **S4b** (1.2 equiv) **1x**

Under N_2, Et_3N (3.0 mL) and THF (2.0 mL) was added to a round-bottom flask with **1a** (178.2 mg, 0.5 mmol, 1.0 equiv), iodobenzene (122.4 mg, 0.6 mmol, 1.2 equiv), $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol, 2 mol%), and CuI (3.8 mg, 0.02 mmol, 4 mol%). Then, the reaction was stirred at 50 °C and was complete as monitored by TLC. Upon completion, the mixture was concentrated under reduced pressure, and was purified by flash column chromatography using petroleum ether/ethyl acetate = 5/1 (R_f = 0.35) as eluent to give **1x** (white solid, 142.3 mg, 66% yield). Characterization data match the previously reported one for this product[2].

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.74 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.43 (dd, J = 8.0, 1.0 Hz, 1H), 7.30 -7.27 (m, 1H), 7.25-7.21 (m, 4H), 7.19-7.15 (m, 1H), 7.15 (d, J = 3.5 Hz, 1H), 7.12 -7.09 (m, 1H), 7.07-7.05 (m, 2H), 6.51 (dd, J = 3.5, 1.0 Hz, 1H), 4.47 (t, J = 6.5 Hz, 2H), 4.05 (s, 2H), 3.57 (t, J = 6.5 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 135.9, 135.5, 131.7, 129.8, 128.8, 128.7, 128.3, 128.1, 127.8, 122.01, 121.96, 121.2, 119.8, 109.4, 102.1, 85.9, 81.9, 46.7, 46.2, 39.3, 21.6.

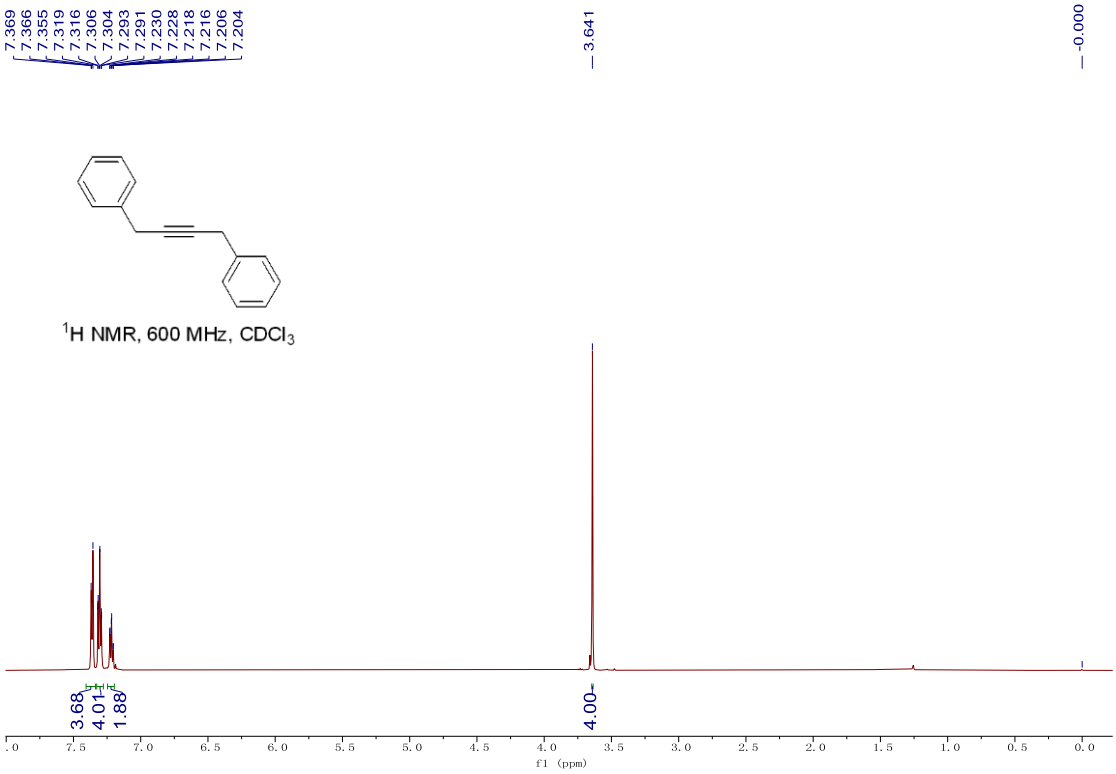
1,4-diphenylbut-2-yne (2d)



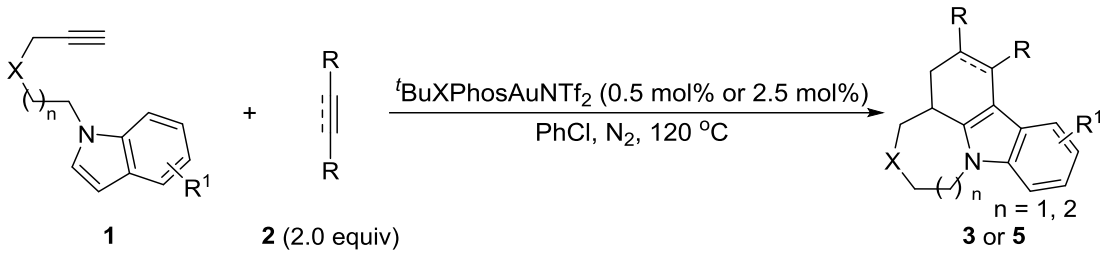
S1j (1.3 equiv) **S4c** **2d**

Under nitrogen atmosphere, THF (10.0 mL) and **S4c** (342.1 mg, 2.0 mmol, 1.0 equiv) were added to a round-bottom flask which equipped with $PdCl_2(CH_3CN)_2$ (10.4 mg, 0.04 mmol, 2 mol%), X-Phos (57.2 mg, 0.12 mmol, 6 mol%) and Cs_2CO_3 (684.2 mg, 2.1 mmol, 1.1 equiv). Then, the **S1j** (302.0 mg, 2.6 mmol, 1.3 equiv) was added and the mixture was heated to 60 °C and stirred at this temperature overnight. After cooling to room temperature, the mixture was concentrated under reduced pressure, and was purified by flash column chromatography using petroleum ether (R_f = 0.67) as eluent to give **2d** (colorless oil, 100.9 mg, 24% yield). Characterization data match the previously reported one for this product[3].

^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.37-7.36 (m, 4H), 7.32-7.29 (m, 4H), 7.23-7.20 (m, 2H), 3.64 (s, 4H).

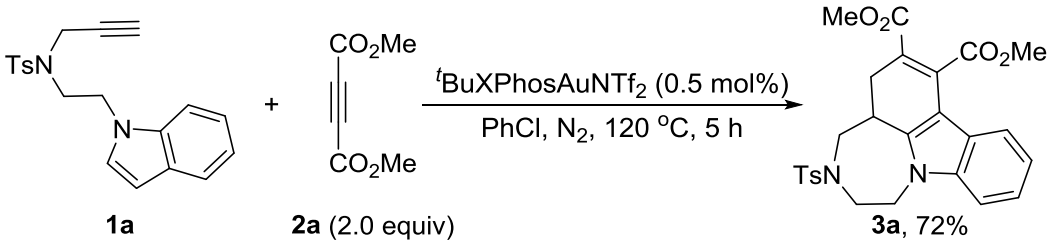


4. General Procedure B for the Synthesis of 3 and 5



Under nitrogen atmosphere, anhydrous PhCl (1.0 mL) was added to a sealed tube which equipped with the corresponding substrates **1** (1.0 equiv), **2** (2.0 equiv) and [^{t}BuXPhosAuNTf$_2$] (0.5 mol% or 2.5 mol%). The mixture was stirred at 120 °C and was complete as monitored by TLC. The mixture was concentrated under vacuum and purified by flash column chromatography on silica gel to afford **3** or **5**.

Dimethyl 3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3a)



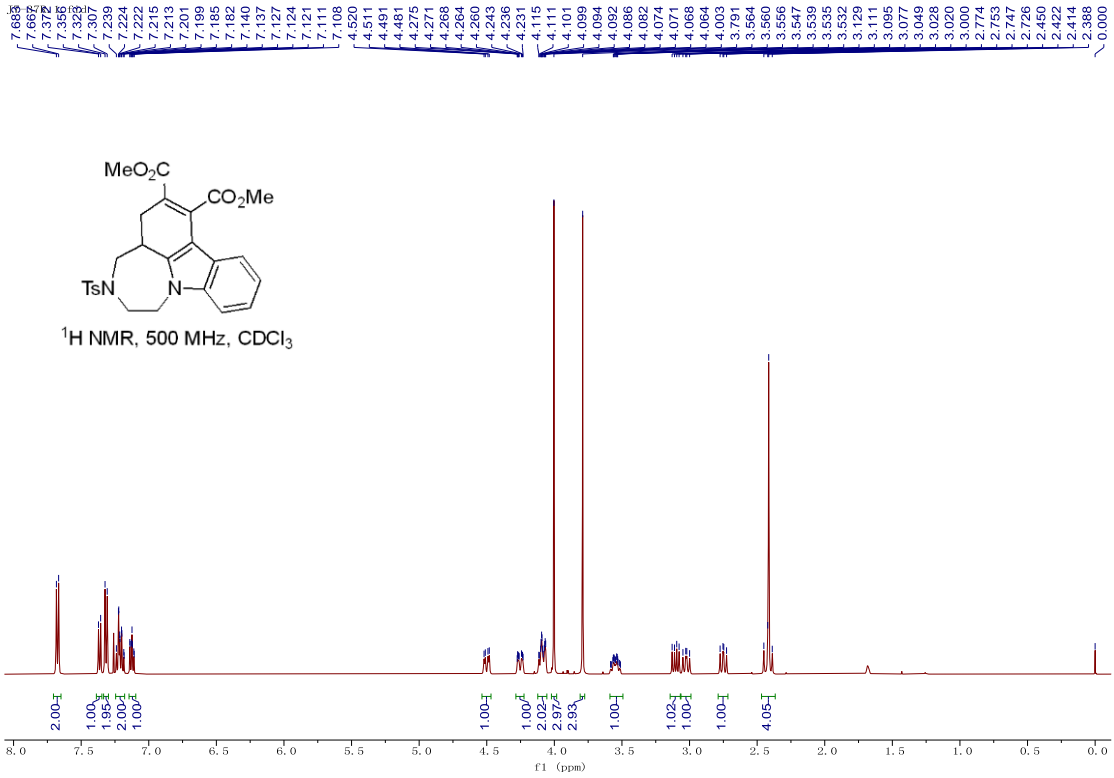
The compound **3a** (yellow solid, 35.6 mg, 72% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.33) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS) δ 7.67 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.24-7.18 (m, 2H), 7.14-7.11 (m, 1H), 4.50 (dd, J = 14.5, 4.5 Hz, 1H), 4.28-4.23 (m, 1H), 4.12-4.06 (m, 2H), 4.00 (s, 3H), 3.79 (s, 3H), 3.58-3.51 (m, 1H), 3.10 (dd, J = 17.0, 9.0 Hz, 1H), 3.02 (dd, J = 14.5, 10.5 Hz, 1H), 2.75 (dd, J = 13.5, 10.5 Hz, 1H), 2.45-2.39 (m, 4H).

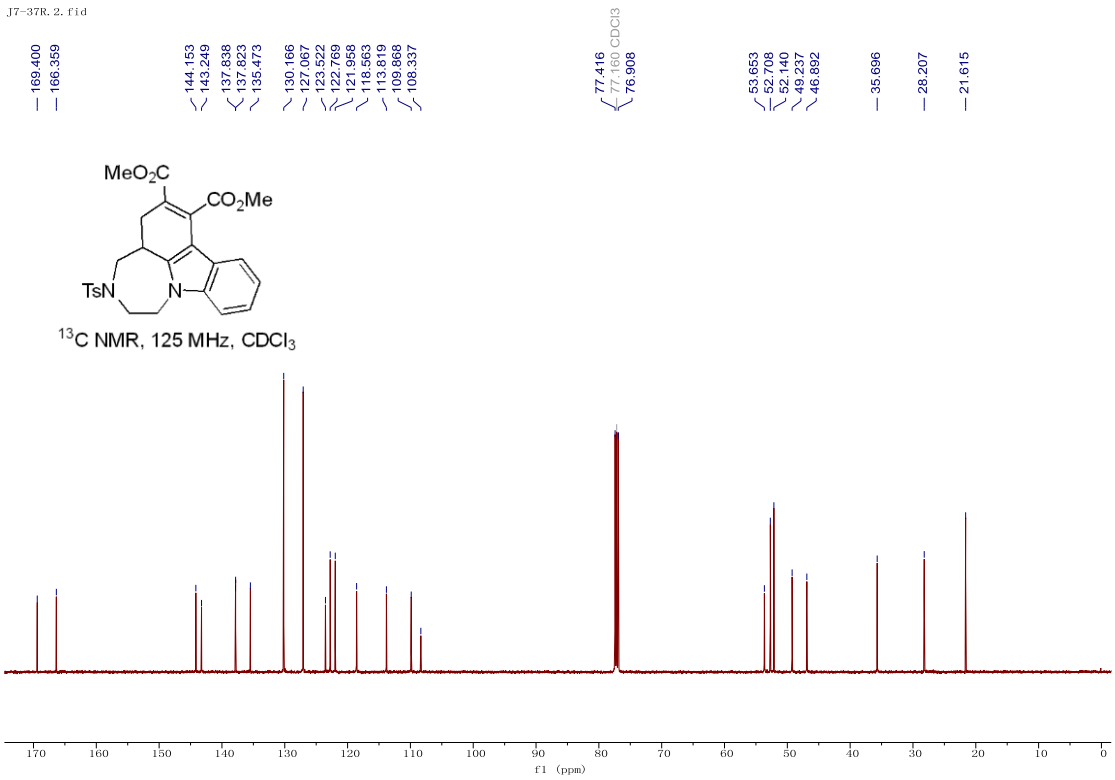
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 166.4, 144.2, 143.2, 137.84, 137.82, 135.5, 130.2, 127.1, 123.5, 122.8, 122.0, 118.6, 113.8, 109.9, 108.3, 53.7, 52.7, 52.1, 49.2, 46.9, 35.7, 28.2, 21.6.

IR (KBr) ν (cm^{-1}): 1733, 1707, 1460, 1435, 1332, 1257, 1203, 1107, 748 cm^{-1}.

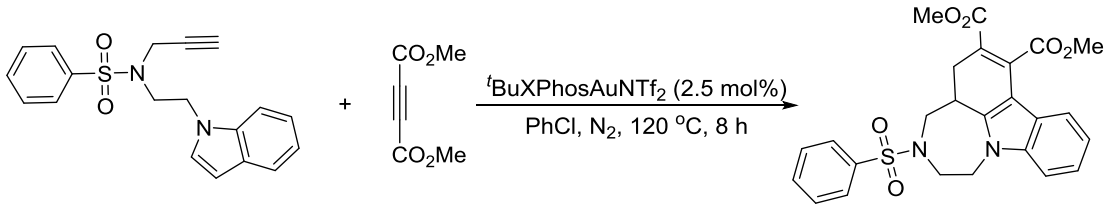
HRMS (ESI): calcd for $C_{26}H_{27}N_2O_6S$ $[M+H]^+$: 495.15843, found: 495.15884.

MP: 192-194 ºC.





Dimethyl 3-(phenylsulfonyl)-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*] carbazole-6,7-dicarboxylate (3b)



1b **2a** (2.0 equiv) **3b**, 44%

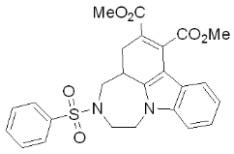
The compound **3b** (white solid, 21.1 mg, 44% yield) was obtained following General Procedure B from **1b** (33.8 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (2.25 mg, 2.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 15/4/1 (R_f = 0.30) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS) δ 7.84-7.81 (m, 2H), 7.62 (tt, J = 7.5, 1.0 Hz, 1H), 7.55 (tt, J = 8.0, 1.5 Hz, 2H), 7.38 (dt, J = 8.0, 1.0 Hz, 1H), 7.24-7.20 (m, 2H), 7.16-7.13 (m, 1H), 4.55 (ddd, J = 14.5, 5.0, 1.0 Hz, 1H), 4.34-4.29 (m, 1H), 4.16-4.12 (m, 2H), 4.01 (s, 3H), 3.80 (s, 3H), 3.65-3.58 (m, 1H), 3.14 (dd, J = 17.0, 9.0 Hz, 1H), 3.07 (ddd, J = 14.5, 10.5, 1.5 Hz, 1H), 2.80 (dd, J = 13.5, 10.5 Hz, 1H), 2.45 (dd, J = 17.0, 14.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 166.4, 143.2, 138.6, 137.9, 133.3, 129.6, 127.1, 123.6, 122.9, 122.1, 118.7, 113.9, 109.8, 108.6, 53.8, 52.8, 52.2, 49.4, 47.1, 36.0, 28.3.

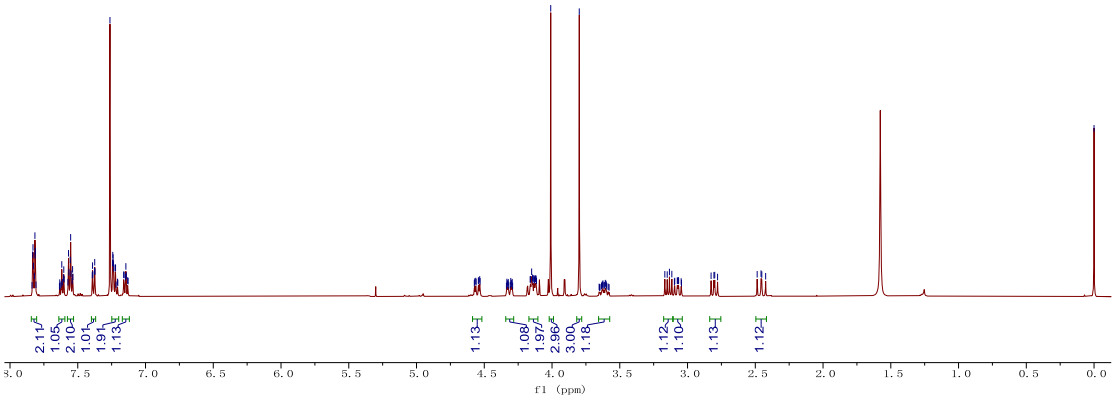
IR (KBr) ν (cm^{-1}): 1731, 1694, 1463, 1434, 1331, 1257, 1164, 1107, 739 cm^{-1}.

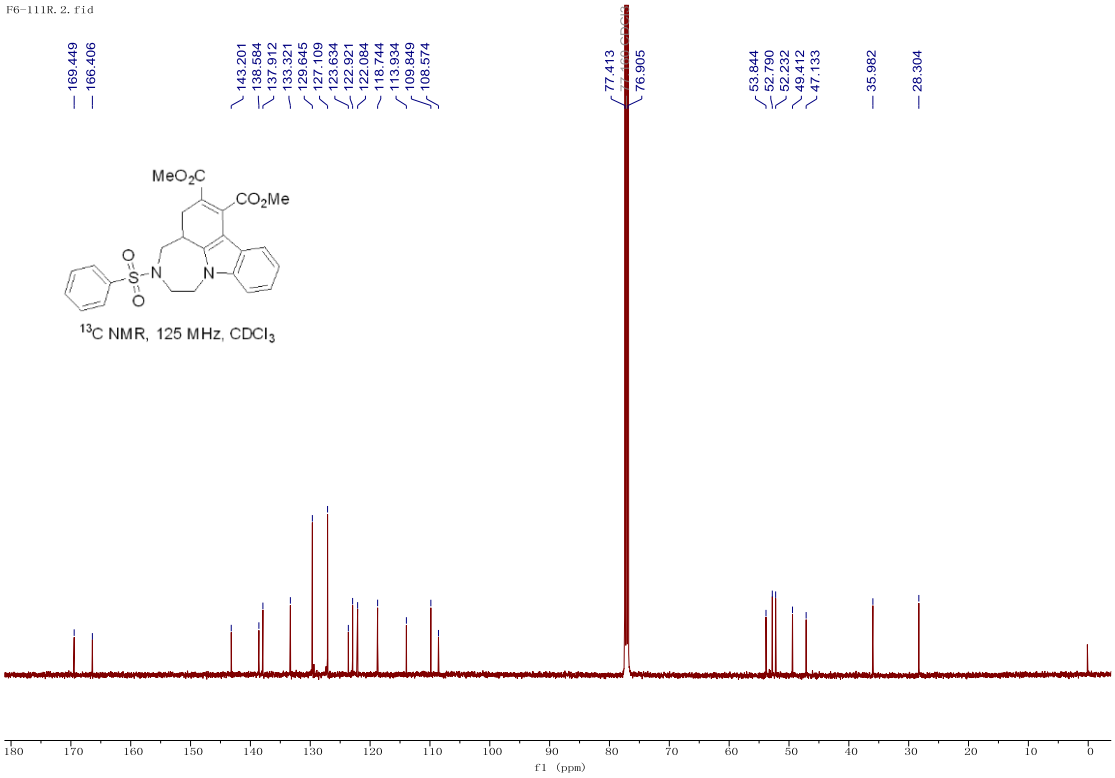
HRMS (ESI): calcd for $C_{25}H_{25}N_2O_6S$ $[M+H]^+$: 481.14278, found: 481.14313.

MP: 89-91 ºC.

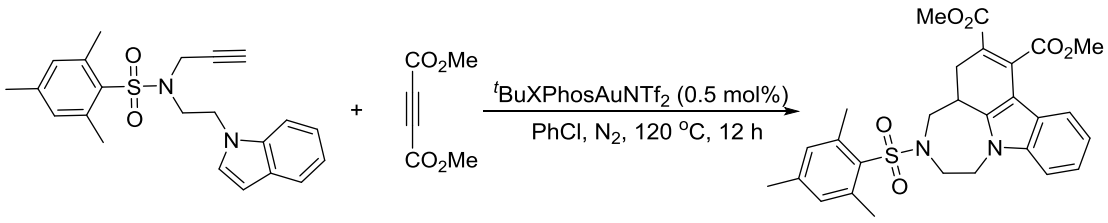


^{1}H NMR, 500 MHz, $CDCl_3$





Dimethyl 3-(mesitylsulfonyl)-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*] carbazole-6,7-dicarboxylate (3c)



1c **2a** (2.0 equiv) **3c**, 68%

The compound **3c** (yellow solid, 35.6 mg, 68% yield) was obtained following General Procedure B from **1c** (38.0 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF =15/4/1 (R_f = 0.20) as eluent.

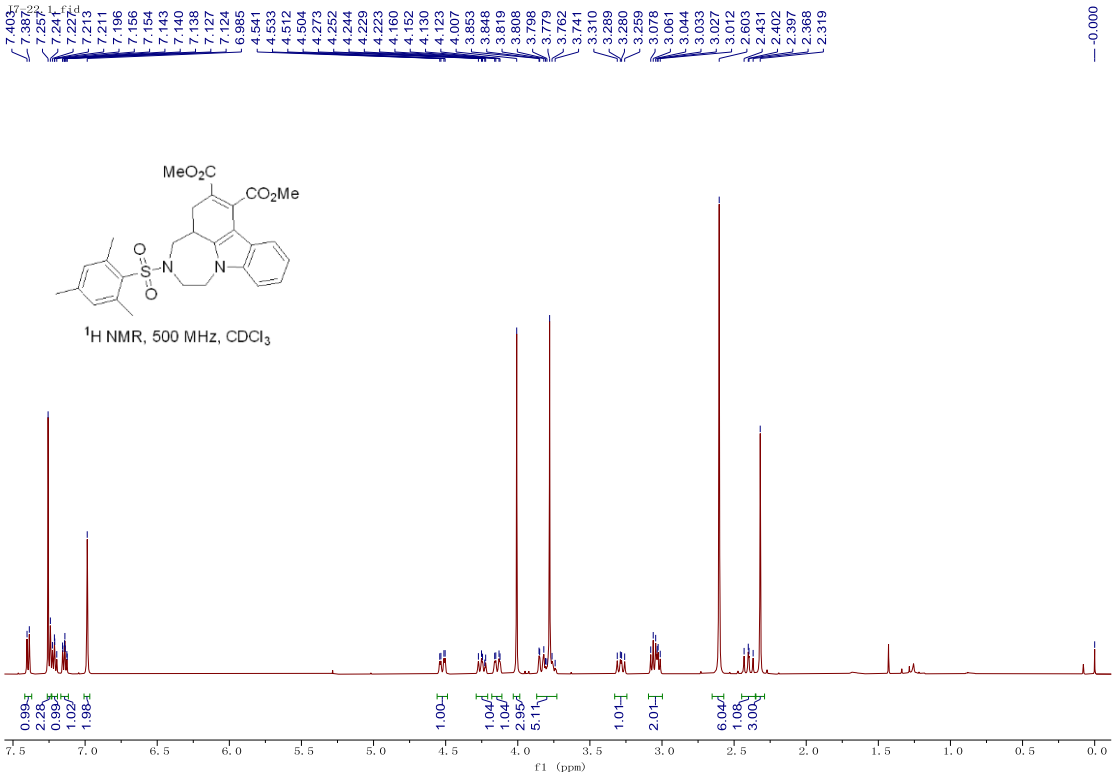
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.39 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.23-7.20 (m, 1H), 7.16-7.12 (m, 1H), 6.99 (s, 2H), 4.52 (dd, J = 14.5, 4.0 Hz, 1H), 4.27-4.22 (m, 1H), 4.14 (dd, J = 14.5, 4.0 Hz, 1H), 4.01 (s, 3H), 3.85-3.74 (m, 5H), 3.28 (dd, J = 15.0, 10.5 Hz, 1H), 3.08-3.01 (m, 2H), 2.60 (s, 6H), 2.40 (dd, J = 17.0, 14.5 Hz, 1H), 2.32 (s, 3H).

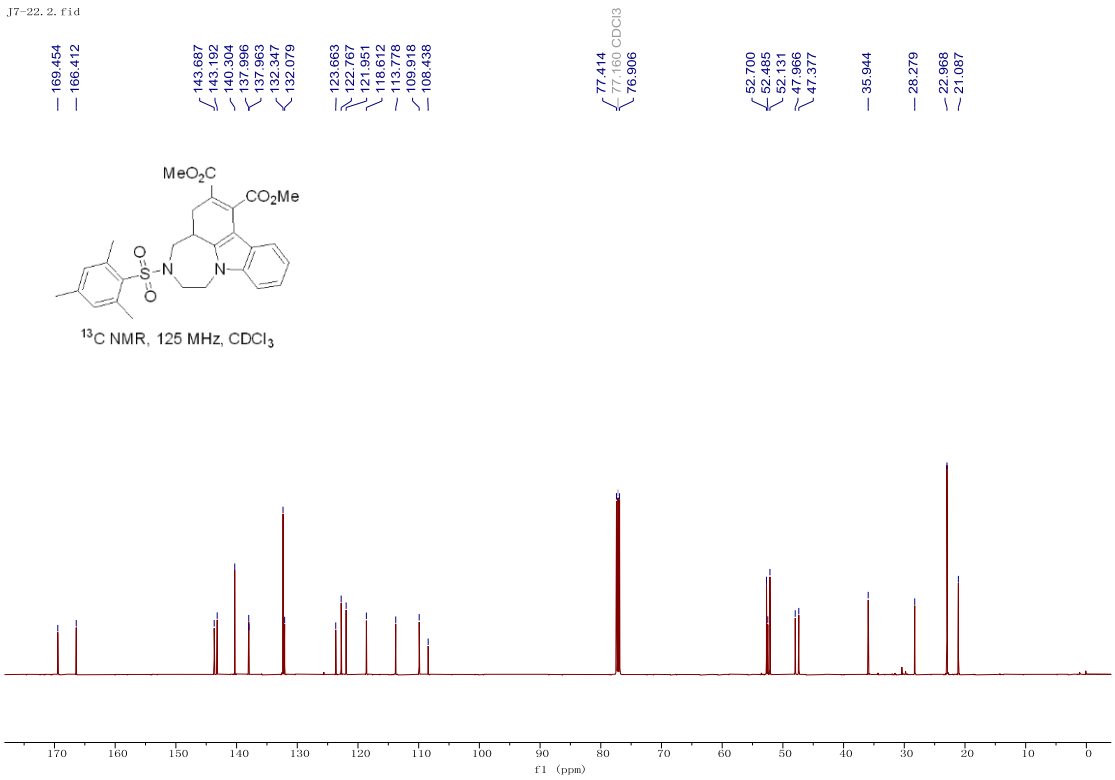
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 166.4, 143.7, 143.2, 140.3, 138.00, 137.96, 132.3, 132.1, 123.7, 122.8, 122.0, 118.6, 113.8, 109.9, 108.4, 52.7, 52.5, 52.1, 48.0, 47.4, 35.9, 28.3, 23.0, 21.1.

IR (KBr) ν (cm^{-1}): 1703, 1459, 1427, 1320, 1238, 1156, 1098, 1026, 734 cm^{-1}.

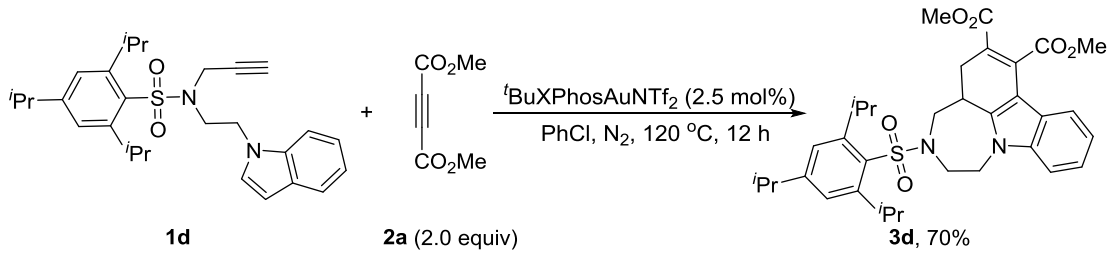
HRMS (ESI): calcd for $C_{28}H_{31}N_2O_6S$ $[M+H]^+$: 523.18973, found: 523.19012.

MP: 94-98 °C.





Dimethyl 3-((2,4,6-triisopropylphenyl)sulfonyl)-1,2,3,4,4a,5-hexahydro-[1,4] diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3d)



The compound **3d** (yellow solid, 42.5 mg, 70% yield) was obtained following General Procedure B from **1d** (46.1 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (2.25 mg, 2.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 15/4/1 (R_f = 0.25) as eluent.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.41 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 9.0 Hz, 1H), 7.24-7.20 (m, 3H), 7.17-7.14 (m, 1H), 4.54 (dd, J = 15.0, 4.0 Hz, 1H), 4.29 (dd, J = 14.0, 10.5 Hz, 1H), 4.19 (dd, J = 15.0, 4.5 Hz, 1H), 4.12-4.07 (m, 2H), 4.01 (s, 3H),

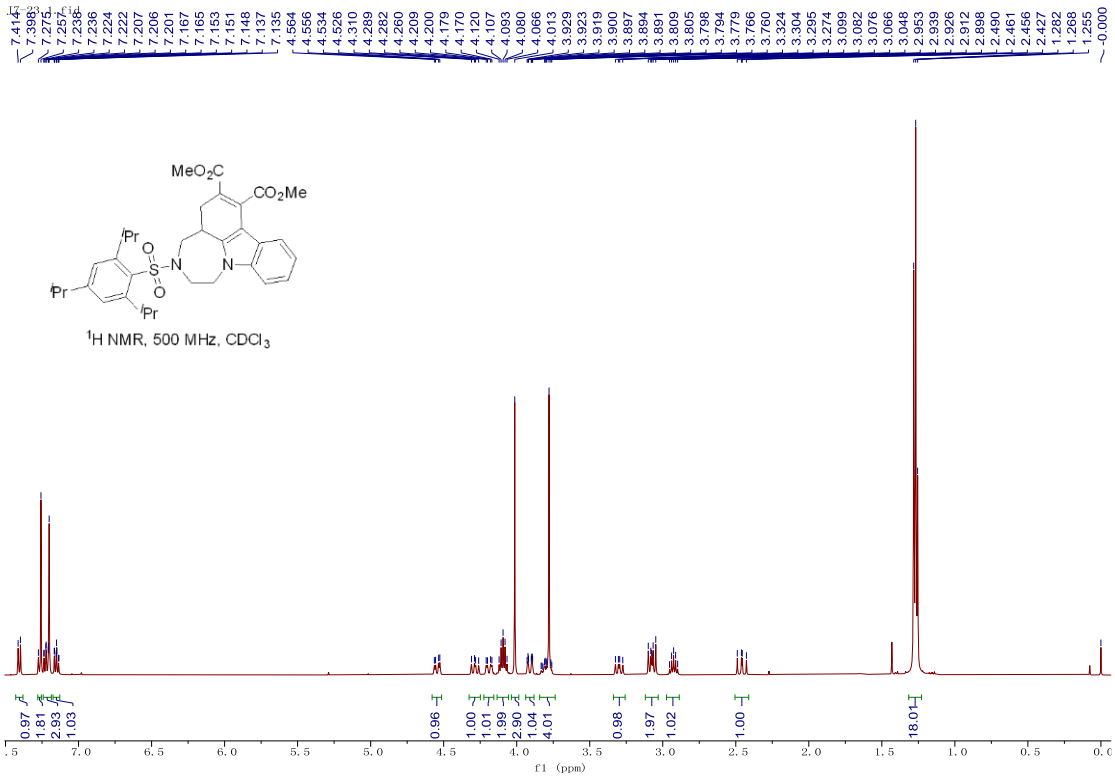
3.93-3.89 (m, 1H), 3.83-3.76 (m, 4H), 3.30 (dd, *J* = 14.5, 10.0 Hz, 1H), 3.10-3.05 (m, 2H), 2.95-2.90 (m, 1H), 2.46 (dd, *J* = 17.0, 14.5 Hz, 1H), 1.28-1.26 (m, 18H).

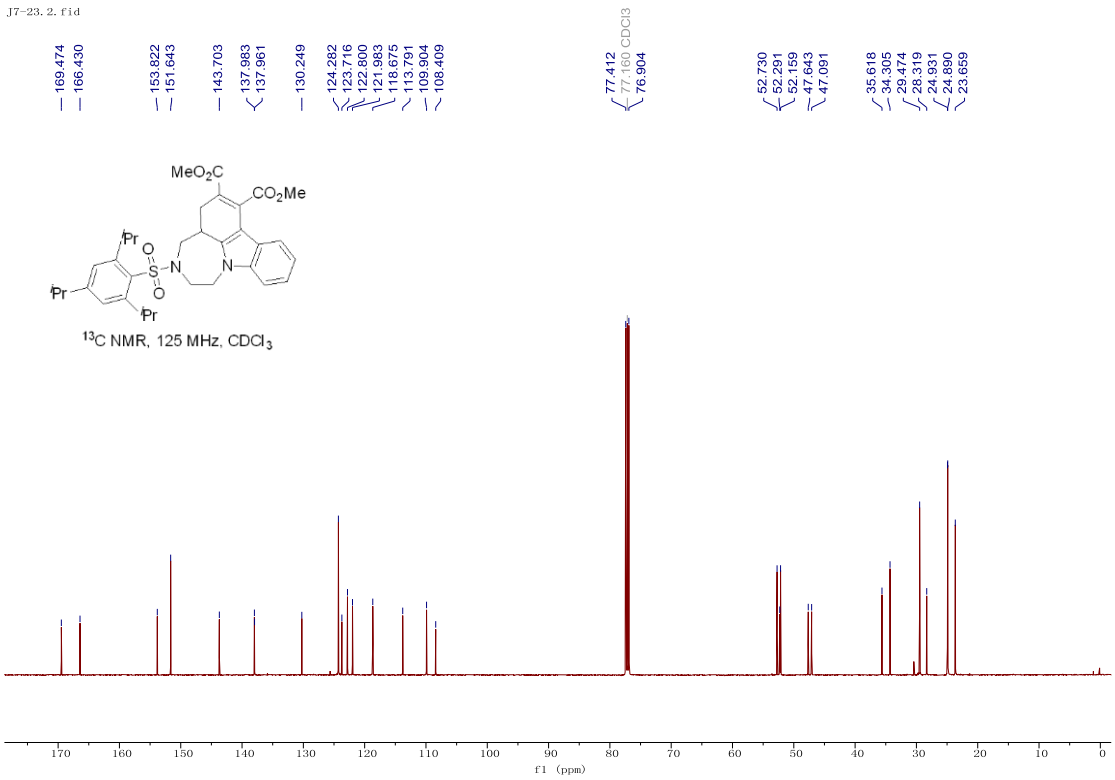
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 166.4, 153.8, 151.6, 143.7, 137.98, 137.96, 130.2, 124.3, 123.7, 122.8, 122.0, 118.7, 113.8, 109.9, 108.4, 52.7, 52.3, 52.2, 47.6, 47.1, 35.6, 34.3, 29.5, 28.3, 24.93, 24.89, 23.7.

IR (KBr) ν (cm^{-1}): 1732, 1698, 1600, 1460, 1433, 1255, 1151, 1084, 738 cm^{-1}.

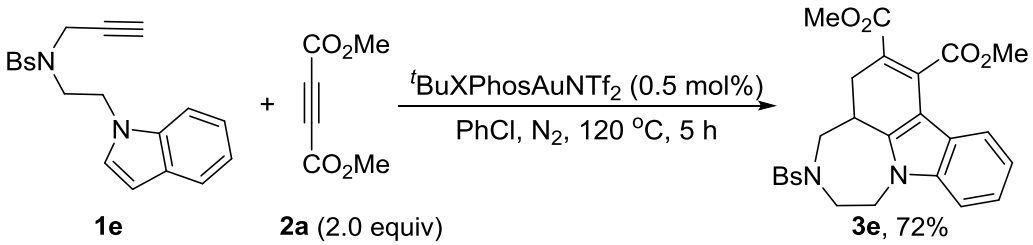
HRMS (ESI): calcd for $C_{34}H_{43}N_2O_6S$ $[M+H]^+$: 607.28363, found: 607.28406.

MP: 103-105 ºC.





Dimethyl 3-((4-bromophenyl)sulfonyl)-1,2,3,4,4a,5-hexahydro-[1,4]diazepino [6,7,1-*jk*]carbazole-6,7-dicarboxylate (3e)



1e **2a** (2.0 equiv) **3e**, 72%

The compound **3e** (yellow solid, 40.2 mg, 72% yield) was obtained following General Procedure B from **1e** (41.7 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 12/4/1 (R_f = 0.17) as eluent.

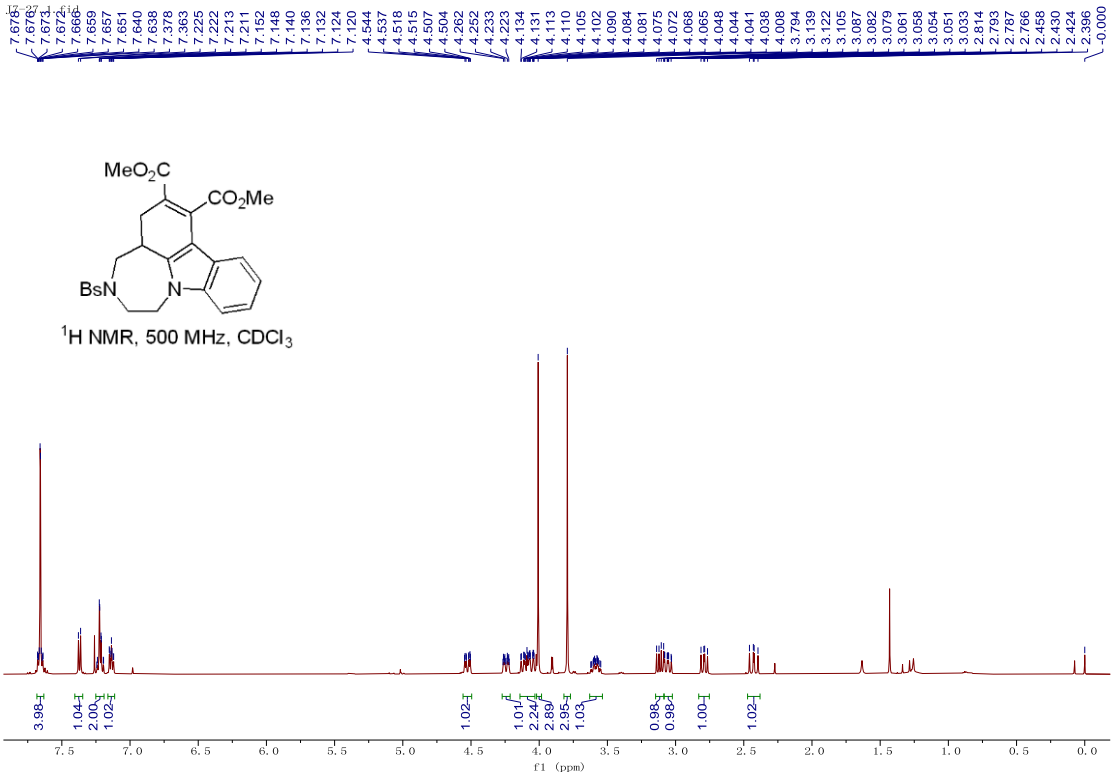
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.68-7.64 (m, 4H), 7.37 (d, J = 7.5 Hz, 1H), 7.24-7.19 (m, 2H), 7.15-7.12 (m, 1H), 4.53 (ddd, J = 14.5, 5.0, 1.5 Hz, 1H), 4.27-4.22 (m, 1H), 4.13-4.04 (m, 2H), 4.01 (s, 3H), 3.79 (s, 3H), 3.62-3.55 (m, 1H), 3.11 (dd, J = 17.0, 8.5 Hz, 1H), 3.06 (ddd, J = 14.0, 10.5, 1.5 Hz, 1H), 2.79 (dd, J = 13.5, 10.5 Hz, 1H), 2.43 (dd, J = 17.0, 14.0 Hz, 1H).

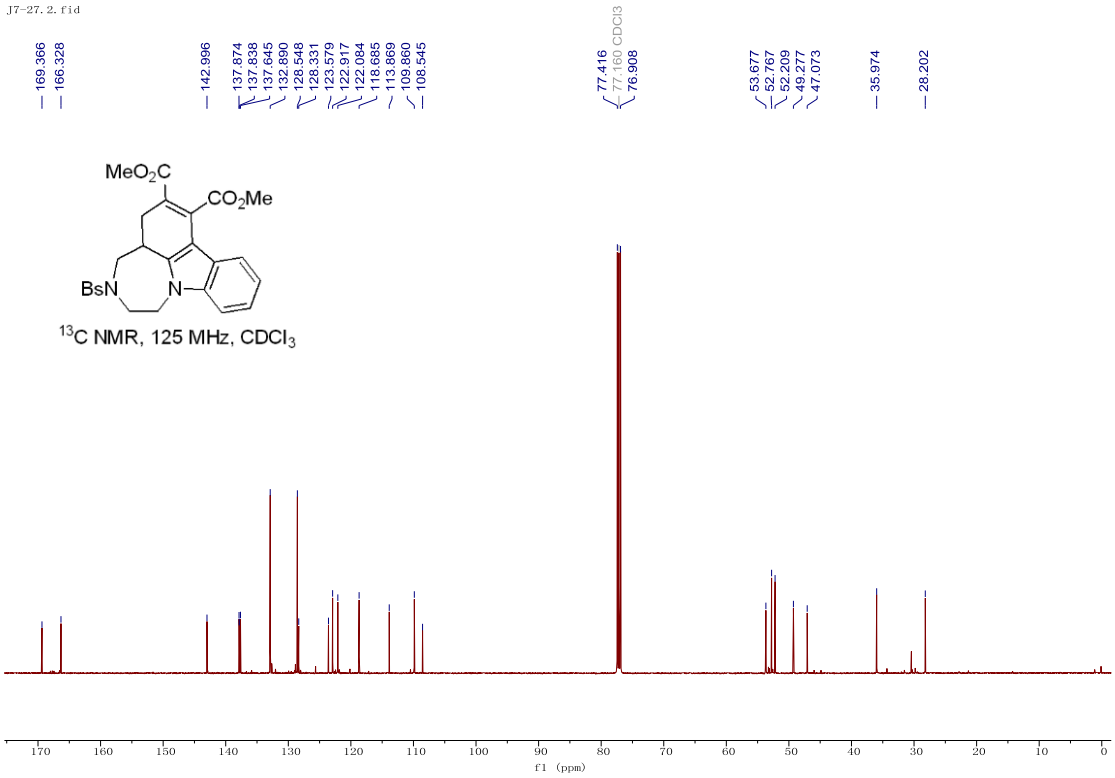
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 166.3, 143.0, 137.9, 137.8, 137.6, 132.9, 128.5, 128.3, 123.6, 122.9, 122.1, 118.7, 113.9, 109.9, 108.5, 53.7, 52.8, 52.2, 49.3, 47.1, 36.0, 28.2.

IR (KBr) ν (cm^{-1}): 1724, 1698, 1461, 1344, 1259, 1240, 1206, 1159, 752, 597 cm^{-1}.

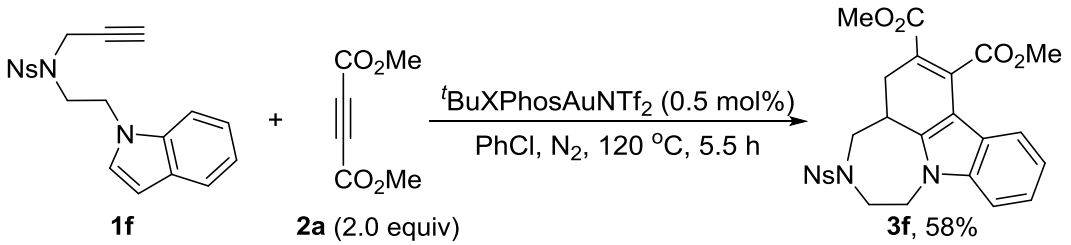
HRMS (ESI): calcd for $C_{25}H_{23}BrN_2NaO_6S$ $[M+Na]^+$: 581.03524, found: 581.03552.

MP: 202-204 °C.





Dimethyl 3-((4-nitrophenyl)sulfonyl)-1,2,3,4,4a,5-hexahydro-[1,4]diazepino [6,7,1-*jk*]carbazole-6,7-dicarboxylate (3f)



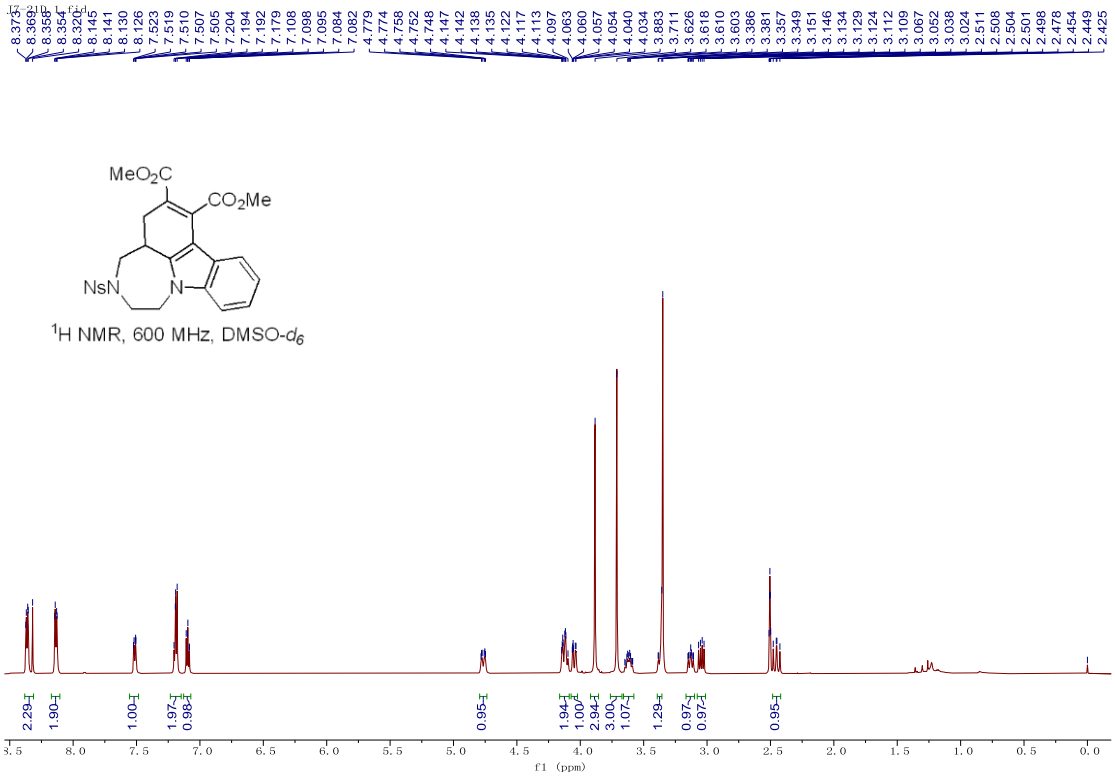
The compound **3f** (yellow solid, 30.5 mg, 58% yield) was obtained following General Procedure B from **1f** (38.3 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.20) as eluent. **^{1}H NMR** (600 MHz, DMSO-d_6, TMS) δ 8.37-8.32 (m, 2H), 8.15-8.13 (m, 2H), 7.52-7.51 (m, 1H), 7.20-7.18 (m, 2H), 7.11-7.08 (m, 1H), 4.78-4.75 (m, 1H), 4.15-4.10 (m, 2H), 4.06-4.03 (m, 1H), 3.88 (s, 3H), 3.71 (s, 3H), 3.65-3.59 (m, 1H), 3.39-3.36 (m, 1H), 3.15-3.11 (m, 1H), 3.05 (dd, J = 17.4, 9.0 Hz, 1H), 2.45 (dd, J = 17.4, 14.4 Hz, 1H).

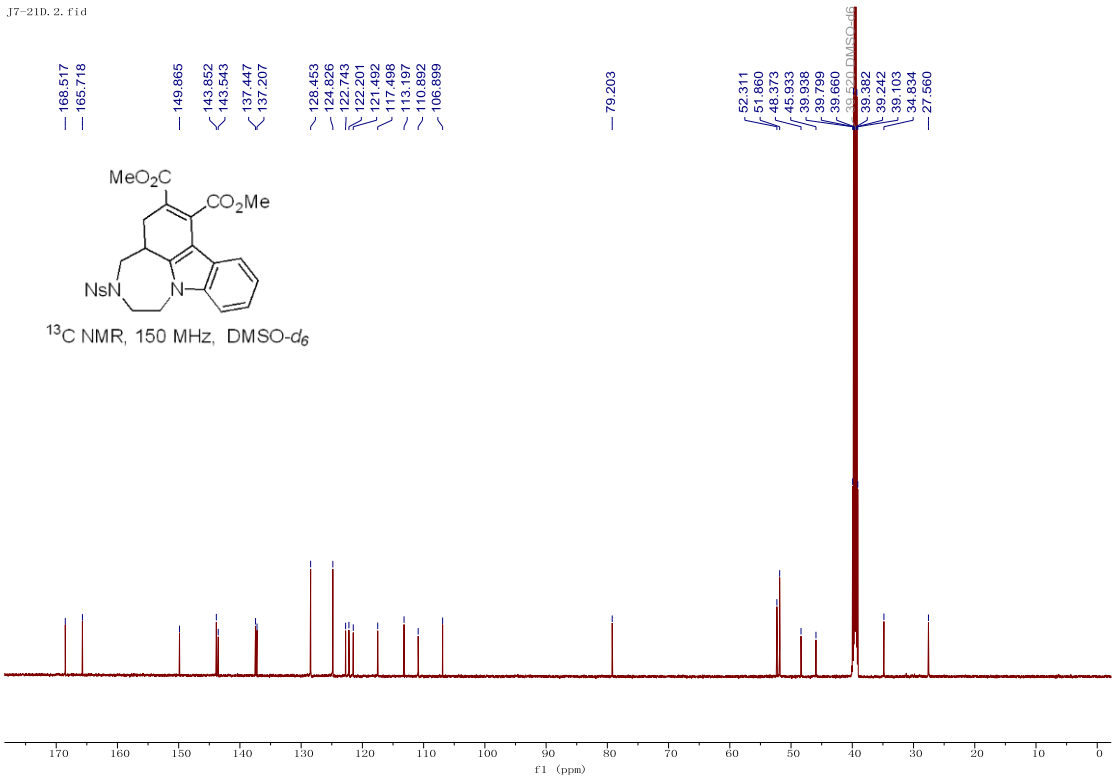
^{13}C NMR (150 MHz, DMSO-d_6) δ 168.5, 165.7, 149.9, 143.9, 143.5, 137.4, 137.2, 128.5, 124.8, 122.7, 122.2, 121.5, 117.5, 113.2, 110.9, 106.9, 79.2, 52.3, 51.9, 48.4, 45.9, 34.8, 27.6.

IR (KBr) ν (cm^{-1}): 1733, 1348, 1254, 1238, 1203, 1163, 1026, 1007, 741 cm^{-1}.

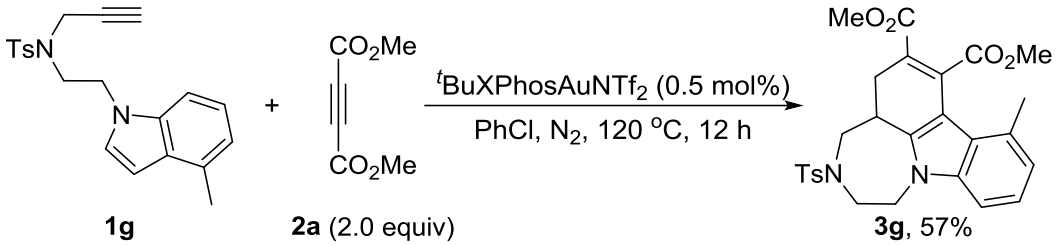
HRMS (ESI): calc for $C_{25}H_{24}N_3O_8S$ $[M+H]^+$: 526.12786, found: 526.12842.

MP: 113-116 ºC.





Dimethyl 8-methyl-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3g)



The compound **3g** (yellow solid, 29.0 mg, 57% yield) was obtained following General Procedure B from **1g** (36.7 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 15/4/1 (R_f = 0.15) as eluent.

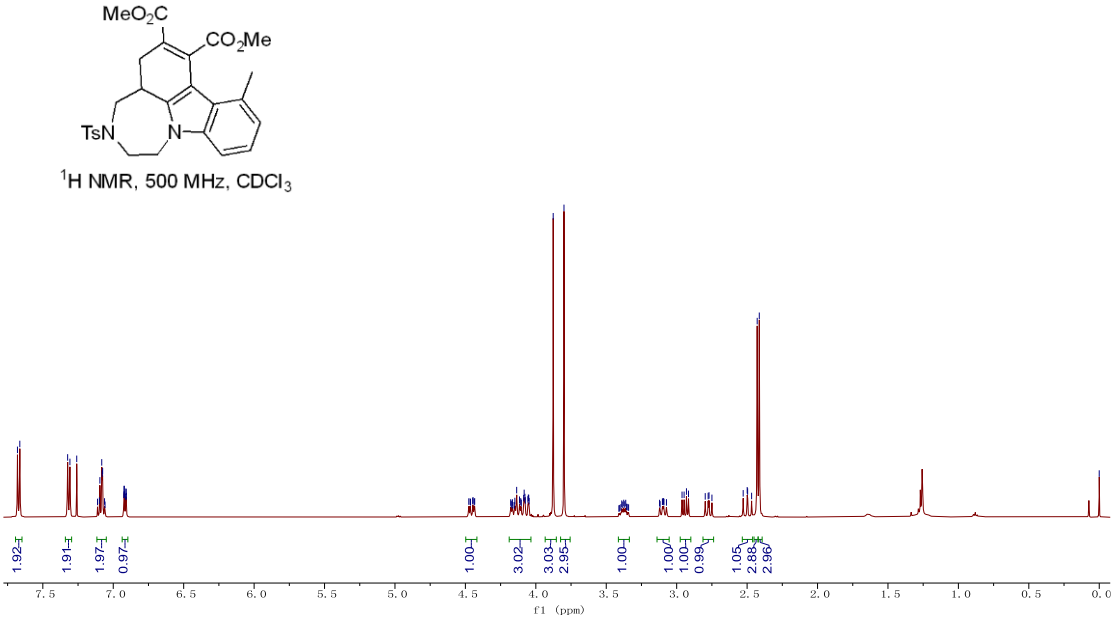
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.67 (dt, J = 8.5, 2.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.11-7.06 (m, 2H), 6.93-6.91 (m, 1H), 4.48-4.43 (m, 1H), 4.18-4.05 (m, 3H), 3.88 (s, 3H), 3.80 (s, 3H), 3.41-3.34 (m, 1H), 3.12-3.07 (m, 1H), 2.94 (dd, J = 15.5, 7.5 Hz, 1H), 2.77 (dd, J = 13.5, 10.0 Hz, 1H), 2.50 (dd, J = 16.0, 14.5 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H).

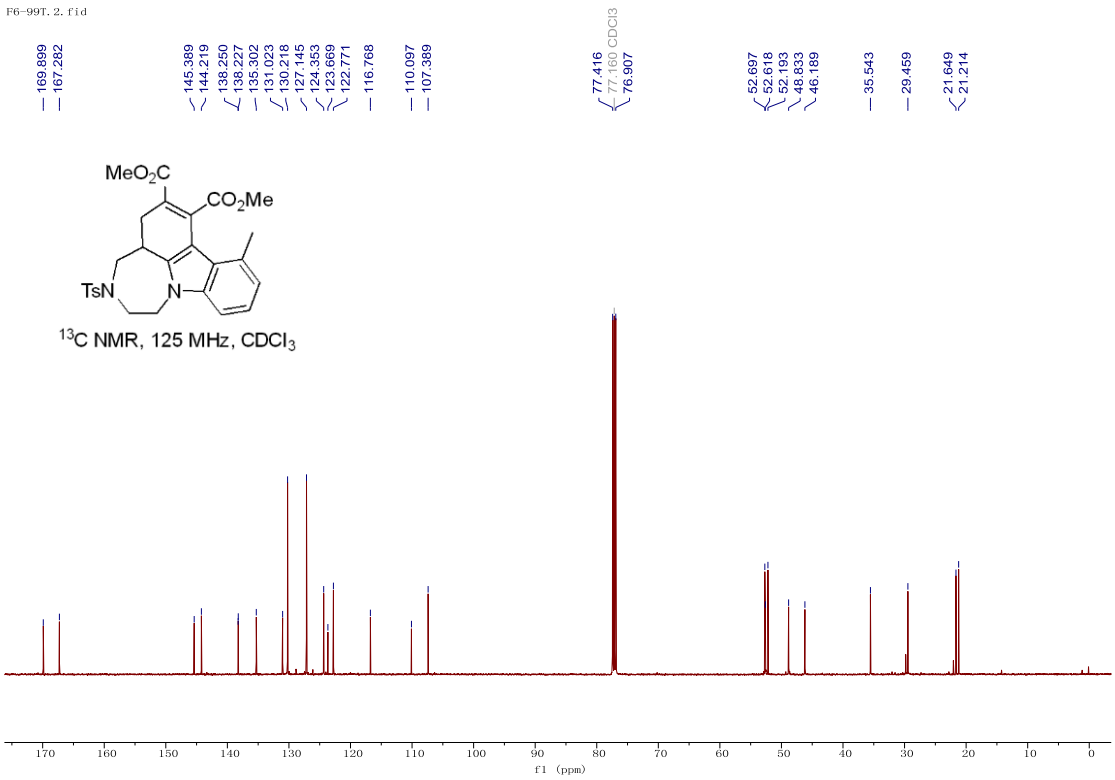
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 167.3, 145.4, 144.2, 138.3, 138.2, 135.3, 131.0, 130.2, 127.1, 124.4, 123.7, 122.8, 116.8, 110.1, 107.4, 52.7, 52.6, 52.2, 48.8, 46.2, 35.5, 29.5, 21.6, 21.2.

IR (KBr) ν (cm^{-1}): 1734, 1695, 1593, 1472, 1339, 1293, 1196, 1160, 733 cm^{-1}.

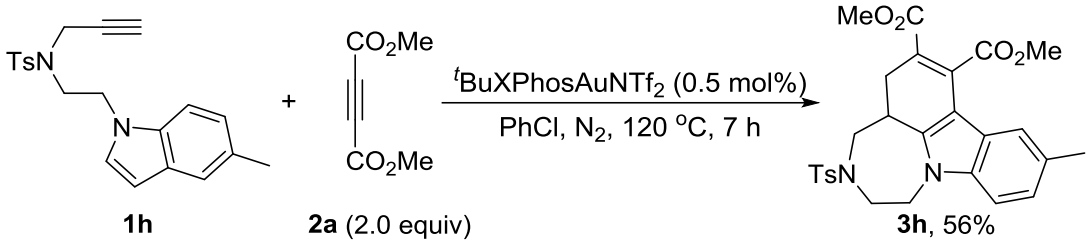
HRMS (ESI): calcd for $C_{27}H_{29}N_2O_6S$ $[M+H]^+$: 509.17408, found: 509.17462.

MP: 186-188 ºC.





Dimethyl 9-methyl-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3h)



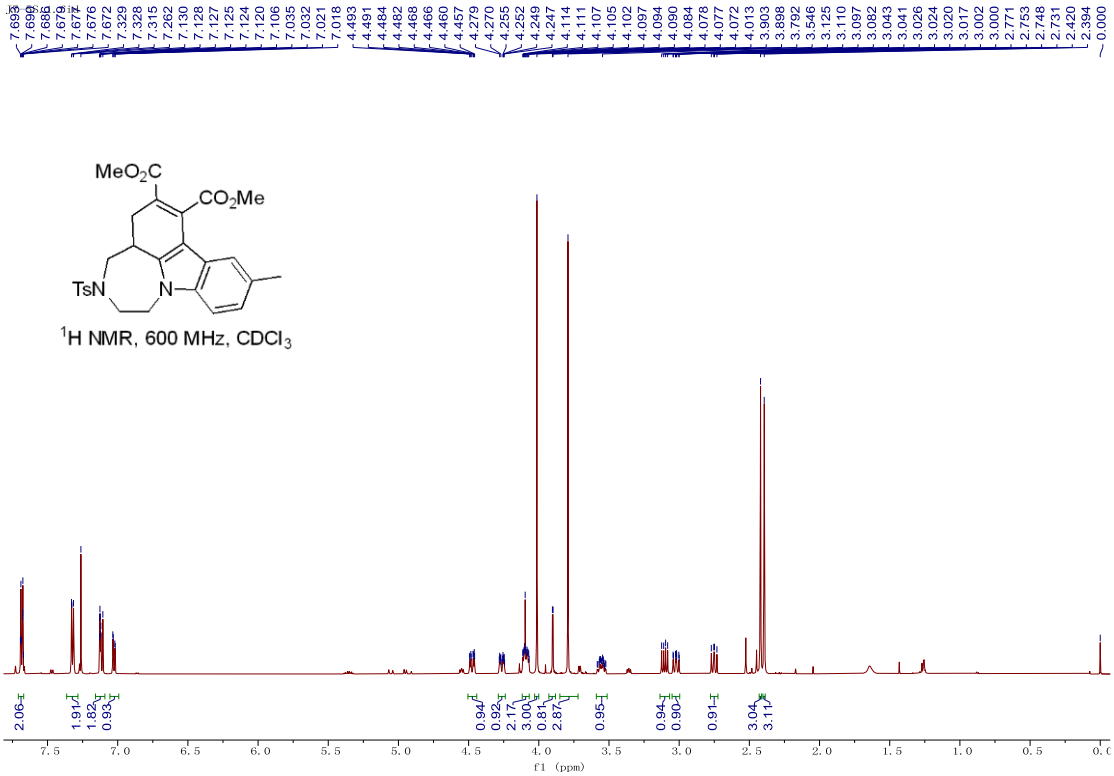
The compound **3h** (yellow solid, 28.7 mg, 56% yield) was obtained following General Procedure B from **1h** (36.7 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.27) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$, TMS) δ 7.69-7.67 (m, 2H), 7.33-7.32 (m, 2H), 7.13-7.11 (m, 2H), 7.03 (dd, J = 8.4, 1.8 Hz, 1H), 4.48 (ddd, J = 15.0, 5.4, 1.2 Hz, 1H), 4.28-4.24 (m, 1H), 4.11-4.07 (m, 2H), 4.01 (s, 3H), 3.90 (d, J = 3.0 Hz, 1H), 3.79 (s, 3H), 3.58-3.52 (m, 1H), 3.10 (dd, J = 16.8, 9.0 Hz, 1H), 3.02 (ddd, J = 13.8, 10.2, 1.2 Hz, 1H), 2.75 (dd, J = 13.8, 10.8 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H).

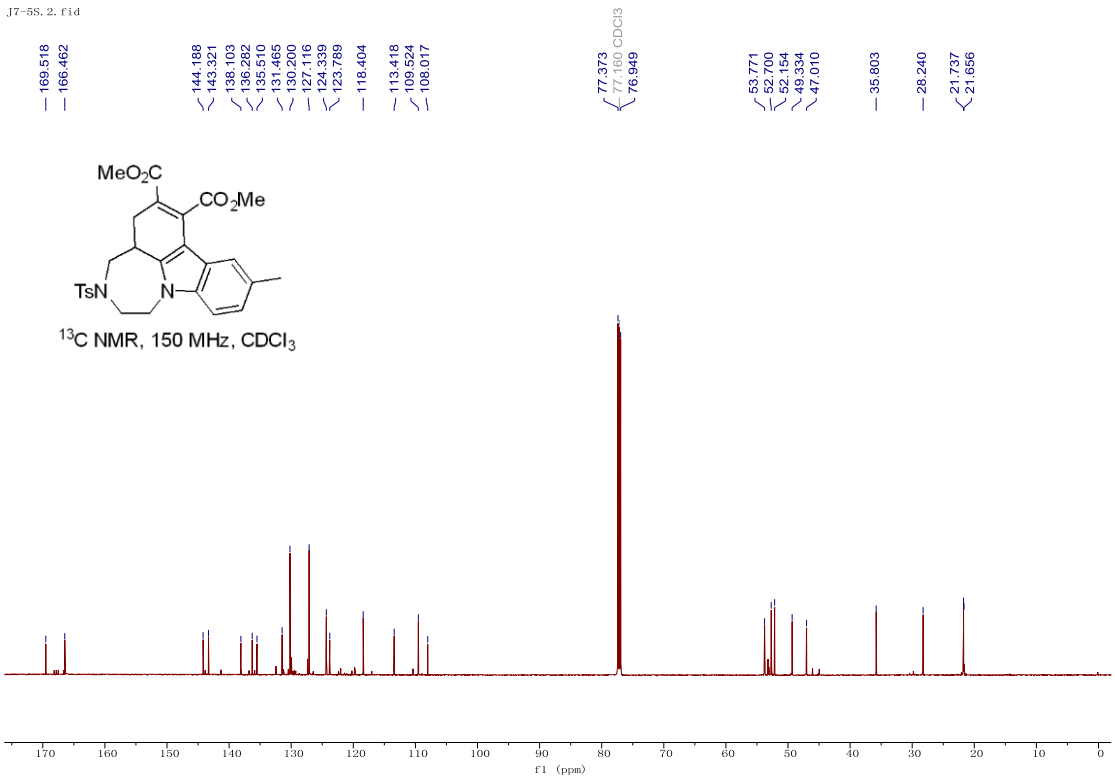
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 166.5, 144.2, 143.3, 138.1, 136.3, 135.5, 131.5, 130.2, 127.1, 124.3, 123.8, 118.4, 113.4, 109.5, 108.0, 53.8, 52.7, 52.2, 49.3, 47.0, 35.8, 28.2, 21.74, 21.66.

IR (KBr) ν (cm^{-1}): 1702, 1426, 1329, 1270, 1238, 1219, 1108, 740, 548 cm^{-1}.

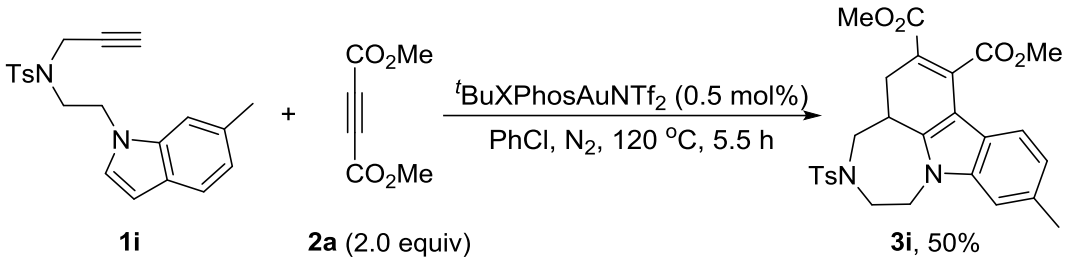
HRMS (ESI): calcd for $C_{27}H_{29}N_2O_6S$ $[M+H]^+$: 509.17408, found: 509.17465.

MP: 169-172 °C.





Dimethyl 10-methyl-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3i)



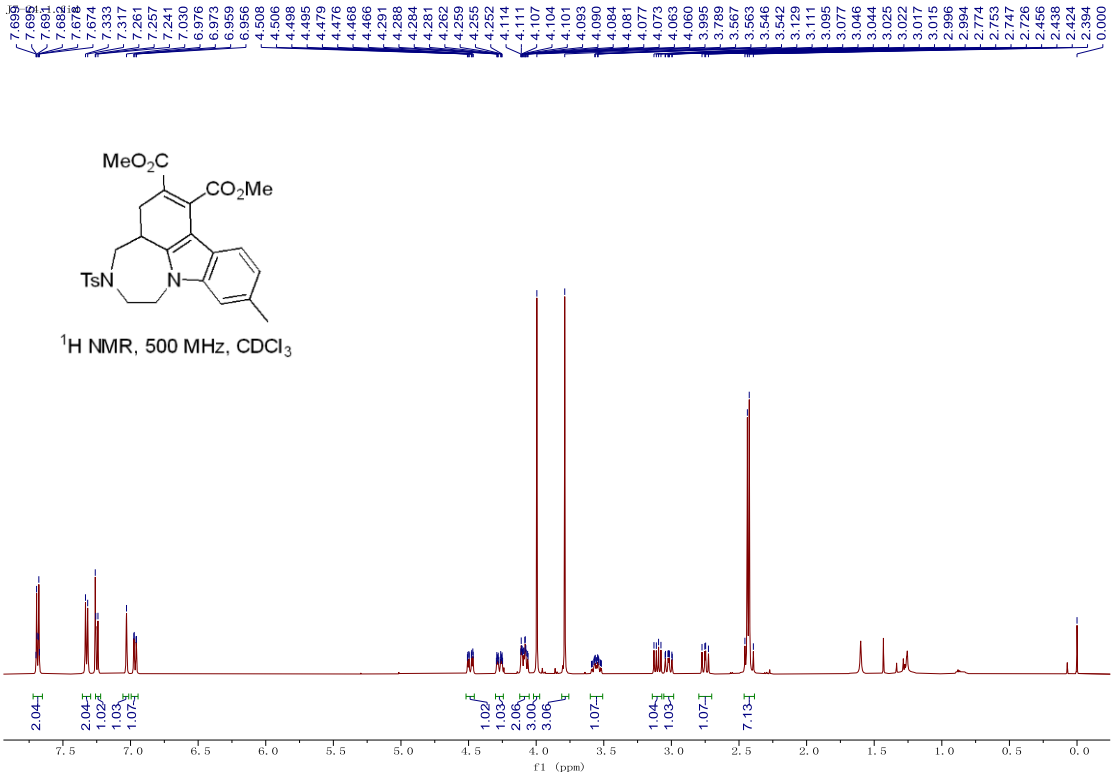
The compound **3i** (yellow solid, 25.4 mg, 50% yield) was obtained following General Procedure B from **1i** (36.6 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 12/4/1 (R_f = 0.27) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS) δ 7.69 (dt, J = 8.5, 2.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 1H), 7.03 (s, 1H), 6.97 (dd, J = 8.5, 1.5 Hz, 1H), 4.49 (ddd, J = 14.5, 5.0, 1.0 Hz, 1H), 4.29-4.25 (m, 1H), 4.11-4.06 (m, 2H), 4.00 (s, 3H), 3.79 (s, 3H), 3.59-3.52 (m, 1H), 3.10 (dd, J = 17.0, 9.0 Hz, 1H), 3.02 (ddd, J = 14.5, 10.5, 1.0 Hz, 1H), 2.75 (dd, J = 13.5, 10.5 Hz, 1H), 2.46-2.39 (m, 7H).

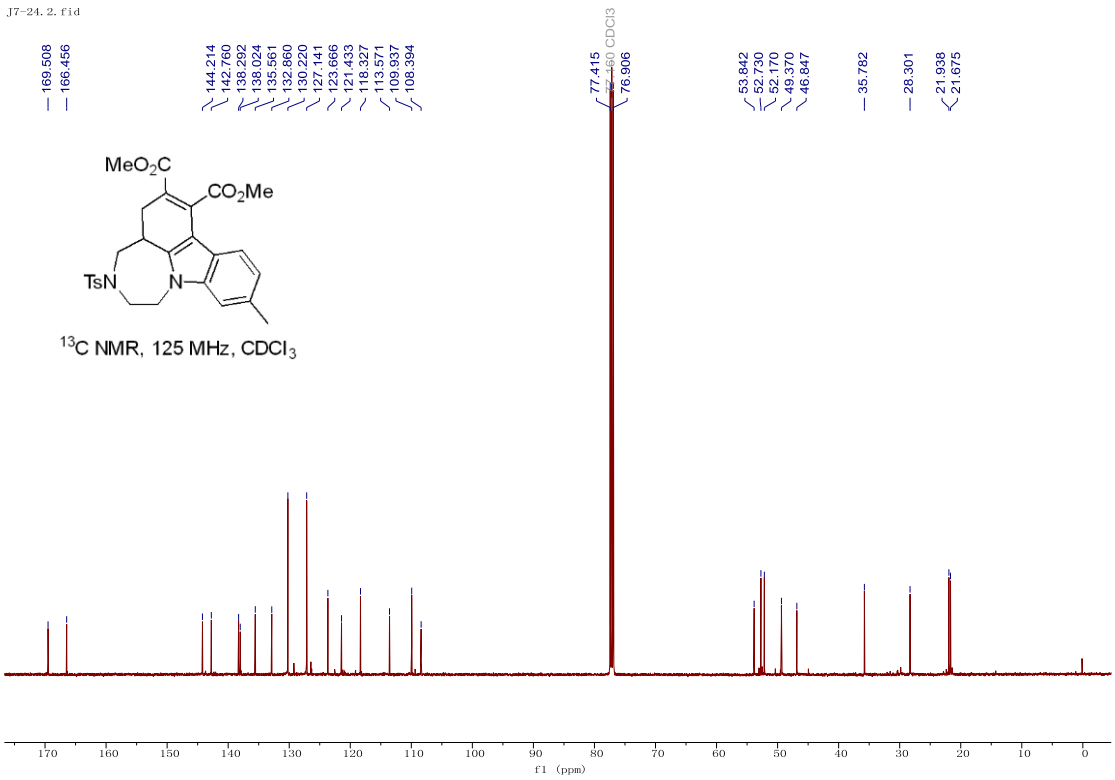
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 166.5, 144.2, 142.8, 138.3, 138.0, 135.6, 132.9, 130.2, 127.1, 123.7, 121.4, 118.3, 113.6, 109.9, 108.4, 53.8, 52.7, 52.2, 49.4, 46.8, 35.8, 28.3, 21.9, 21.7.

IR (KBr) ν (cm^{-1}): 1733, 1435, 1341, 1268, 1236, 1090, 813, 654, 546 cm^{-1}.

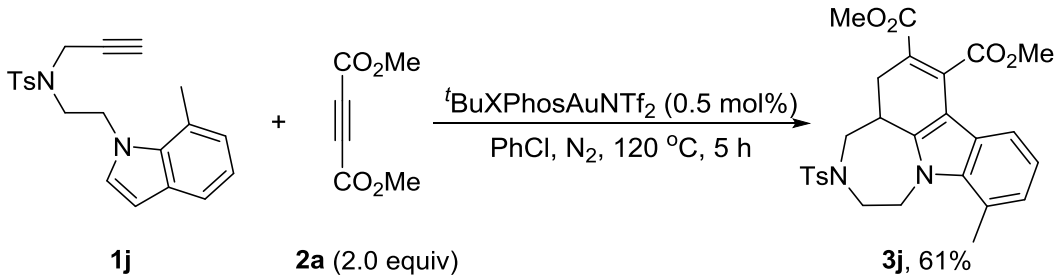
HRMS (ESI): calcd for $C_{27}H_{29}N_2O_6S$ $[M+H]^+$: 509.17408, found: 509.17496.

MP: 204-206 ºC.





Dimethyl 11-methyl-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3j)



1j **2a** (2.0 equiv) **3j**, 61%

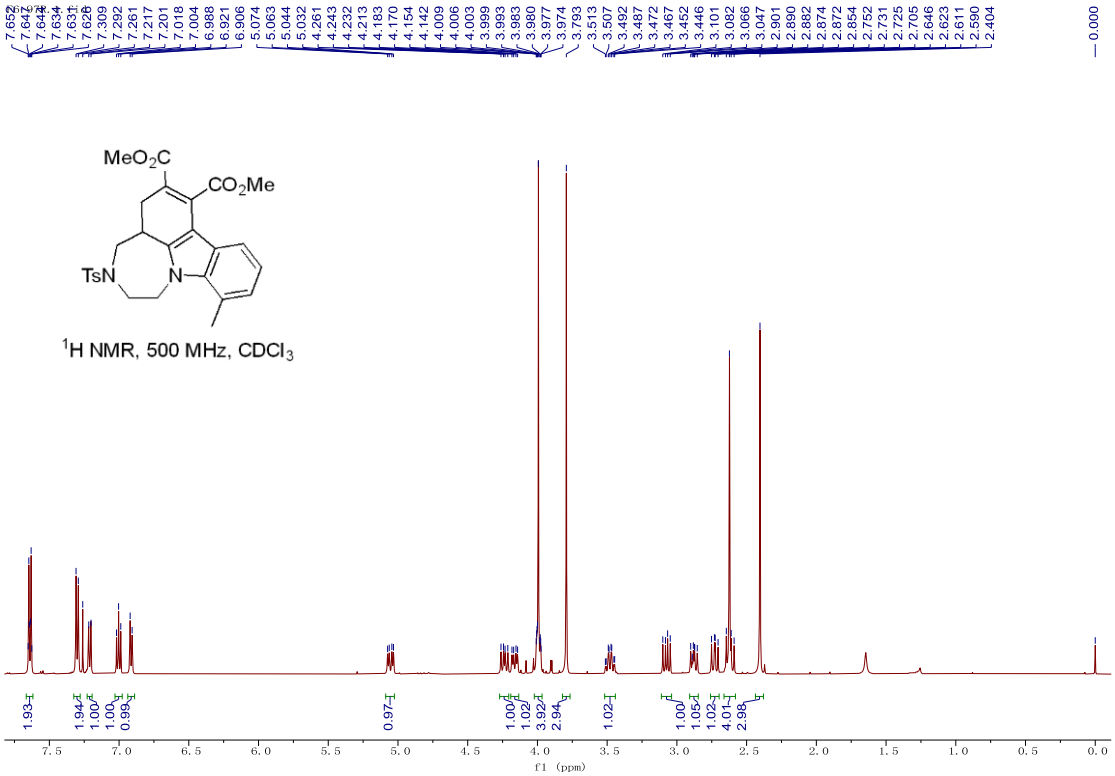
The compound **3j** (yellow solid, 30.8 mg, 61% yield) was obtained following General Procedure B from **1j** (36.7 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.19) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS) δ 7.64 (dt, J = 8.0, 1.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.0 Hz, 1H), 7.00 (t, J = 7.0 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 5.05 (dd, J = 15.0, 5.5 Hz, 1H), 4.24 (dd, J = 14.5, 9.0 Hz, 1H), 4.16 (dd, J = 14.5, 6.5 Hz, 1H), 4.01-3.97 (m, 4H), 3.79 (s, 3H), 3.51-3.45 (m, 1H), 3.07 (dd, J = 17.5, 9.5 Hz, 1H), 2.90-2.85 (m, 1H), 2.73 (dd, J = 13.5, 10.5 Hz, 1H), 2.65-2.59 (m, 4H), 2.40 (s, 3H).

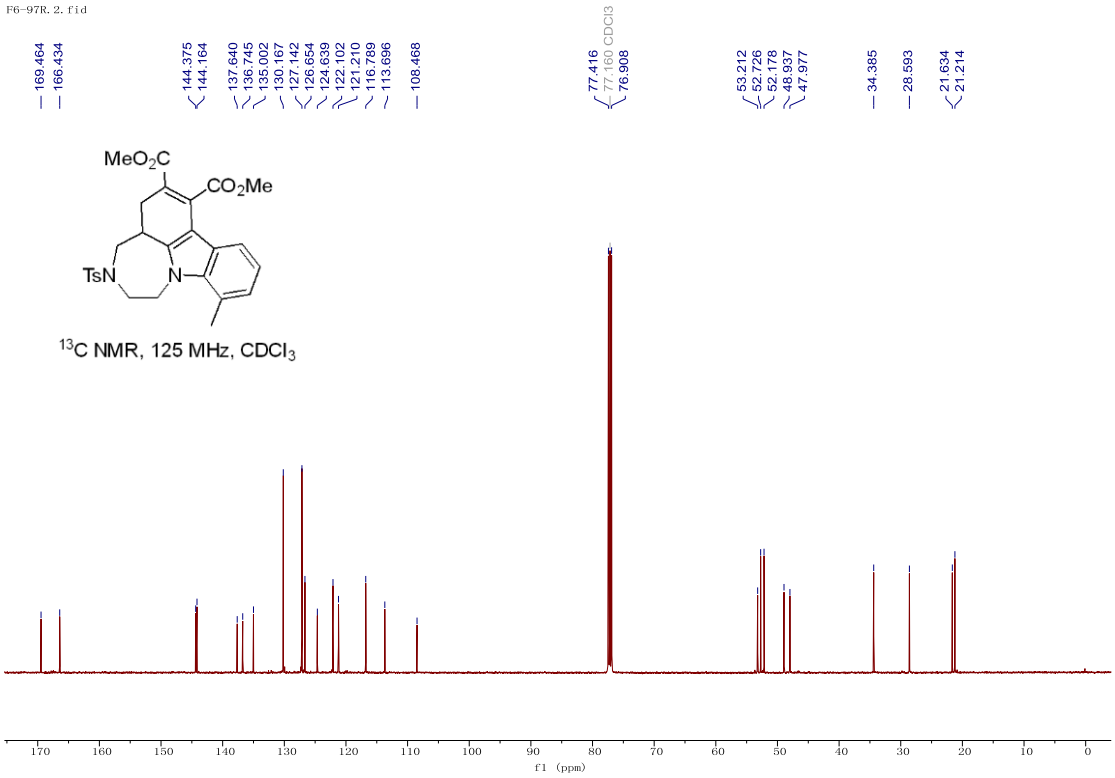
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 166.4, 144.4, 144.2, 137.6, 136.7, 135.0, 130.2, 127.1, 126.7, 124.6, 122.1, 121.2, 116.8, 113.7, 108.5, 53.2, 52.7, 52.2, 48.9, 48.0, 34.4, 28.6, 21.6, 21.2.

IR (KBr) ν (cm^{-1}): 1734, 1700, 1296, 1260, 1241, 1206, 1160, 1099, 732 cm^{-1}.

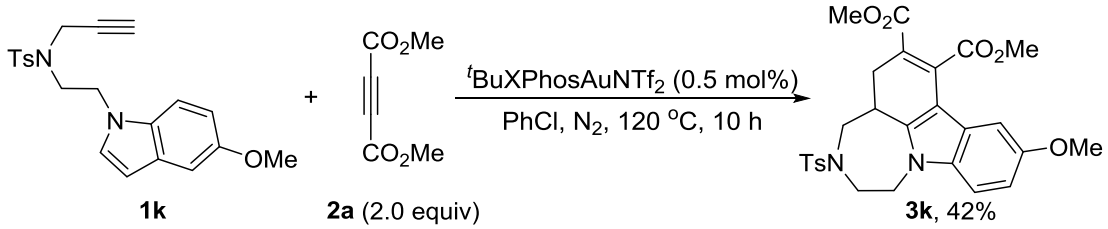
HRMS (ESI): calcd for $C_{27}H_{29}N_2O_6S$ $[M+H]^+$: 509.17408, found: 509.17474.

MP: 202-204 ºC.





Dimethyl 9-methoxy-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3k)



The compound **3k** (yellow solid, 22.0 mg, 42% yield) was obtained following General Procedure B from **1k** (38.2 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 12/4/1 (R_f = 0.17) as eluent.

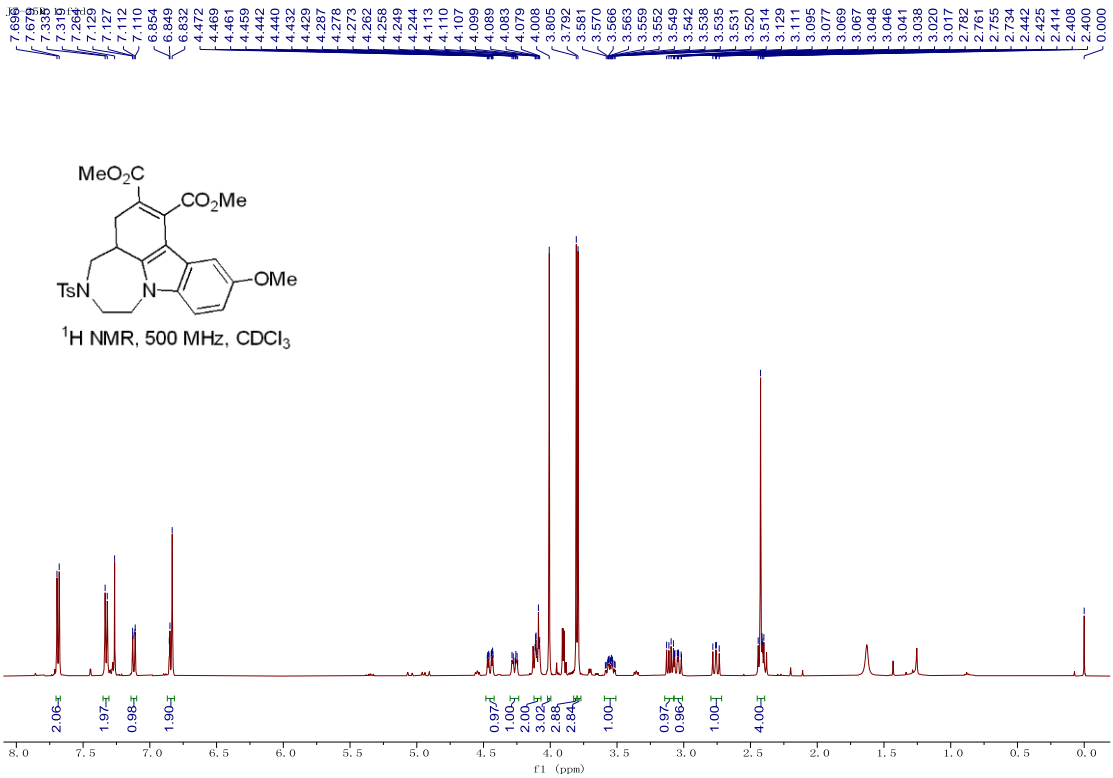
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.69 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.12 (dd, J = 8.5, 1.0 Hz, 1H), 6.85-6.83 (m, 2H), 4.45 (ddd, J = 15.0, 5.5, 1.5 Hz, 1H), 4.29-4.24 (m, 1H), 4.11-4.08 (m, 2H), 4.01 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.59-3.51 (m, 1H), 3.10 (dd, J = 17.0, 8.5 Hz, 1H), 3.04 (ddd, J = 14.0, 10.5, 1.0 Hz, 1H), 2.76 (dd, J = 13.5, 10.5 Hz, 1H), 2.44-2.40 (m, 4H).

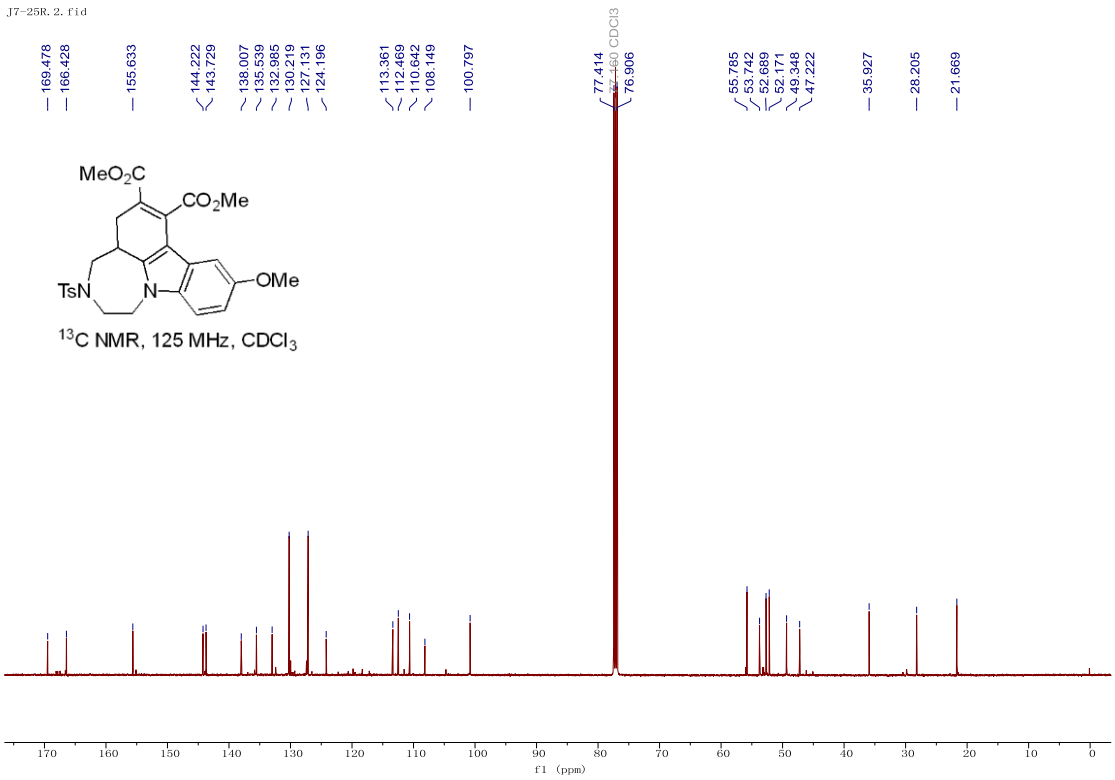
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 166.4, 155.6, 144.2, 143.7, 138.0, 135.5, 133.0, 130.2, 127.1, 124.2, 113.4, 112.5, 110.6, 108.1, 100.8, 55.8, 53.7, 52.7, 52.2, 49.3, 47.2, 35.9, 28.2, 21.7.

IR (KBr) ν (cm^{-1}): 1736, 1701, 1483, 1432, 1325, 1258,1196, 1156, 740 cm^{-1}.

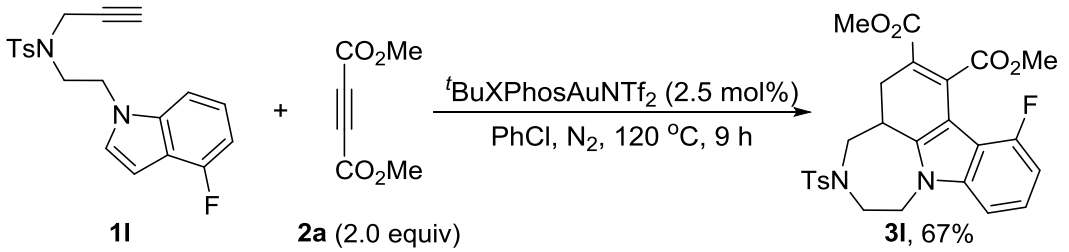
HRMS (ESI): calcd $C_{27}H_{29}N_2O_7S$ $[M+H]^+$: 525.16900, found: 525.16943.

MP: 166-168 ºC.





Dimethyl 8-fluoro-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3l)



The compound **3l** (white solid, 34.3 mg, 67% yield) was obtained following General Procedure B from **1l** (37.0 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (2.25 mg, 2.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.28) as eluent.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.68 (dt, J = 8.5, 2.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.12 (td, J = 8.5, 5.0 Hz, 1H), 7.02 (d, J = 8.5 Hz, 1H), 6.81 (dd, J = 11.0, 7.5 Hz, 1H), 4.50 (ddd, J = 15.0, 5.5, 1.5 Hz, 1H), 4.25-4.21 (m, 1H), 4.17-4.07 (m, 2H), 3.94 (s, 3H), 3.80 (s, 3H), 3.54-3.47 (m, 1H), 3.10-3.04 (m, 2H), 2.80 (dd, J = 13.5, 10.5 Hz, 1H), 2.50 (dd, J = 16.5, 13.5 Hz, 1H), 2.42 (s, 3H).

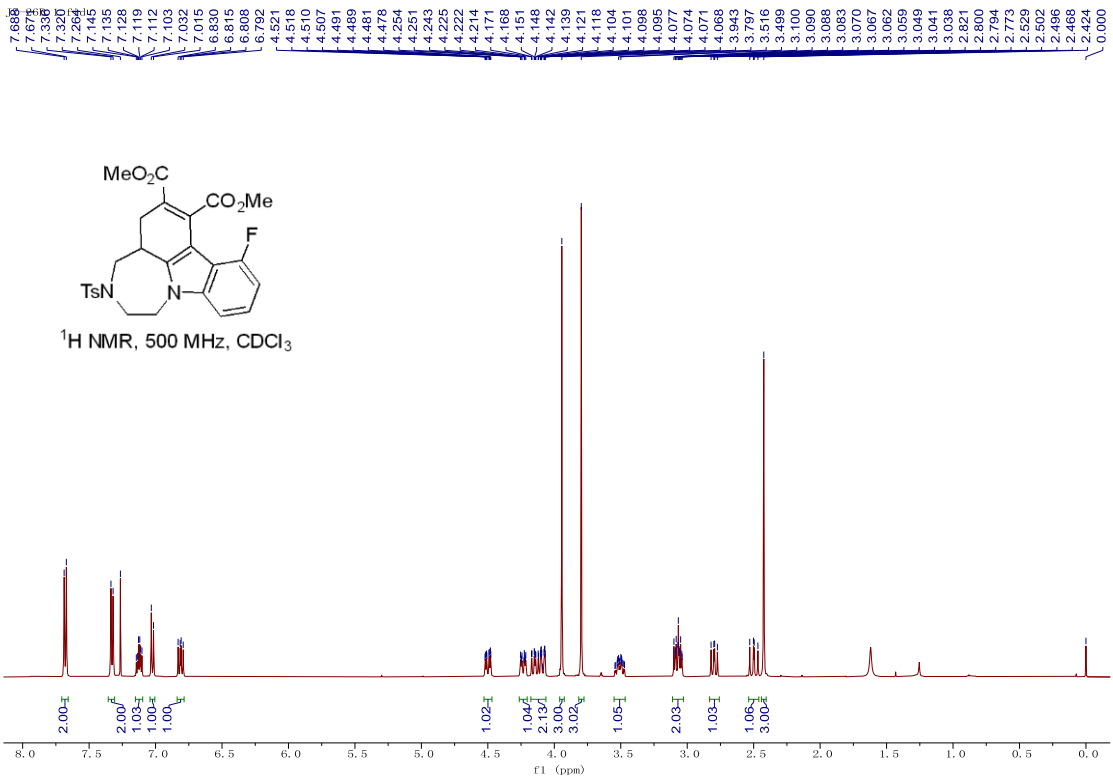
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 166.5, 156.0 (d, J = 246.6 Hz), 144.3, 143.9, 140.3 (d, J = 11.0 Hz), 138.1, 135.3, 130.3, 127.1, 123.4 (d, J = 8.3 Hz), 115.4, 112.6 (d, J = 20.4 Hz), 107.7 (d, J = 21.5 Hz), 107.6, 105.9 (d, J = 3.4 Hz), 53.3, 52.7 (d, J = 3.8 Hz), 52.3, 49.0, 47.1, 35.3, 28.7, 21.7.

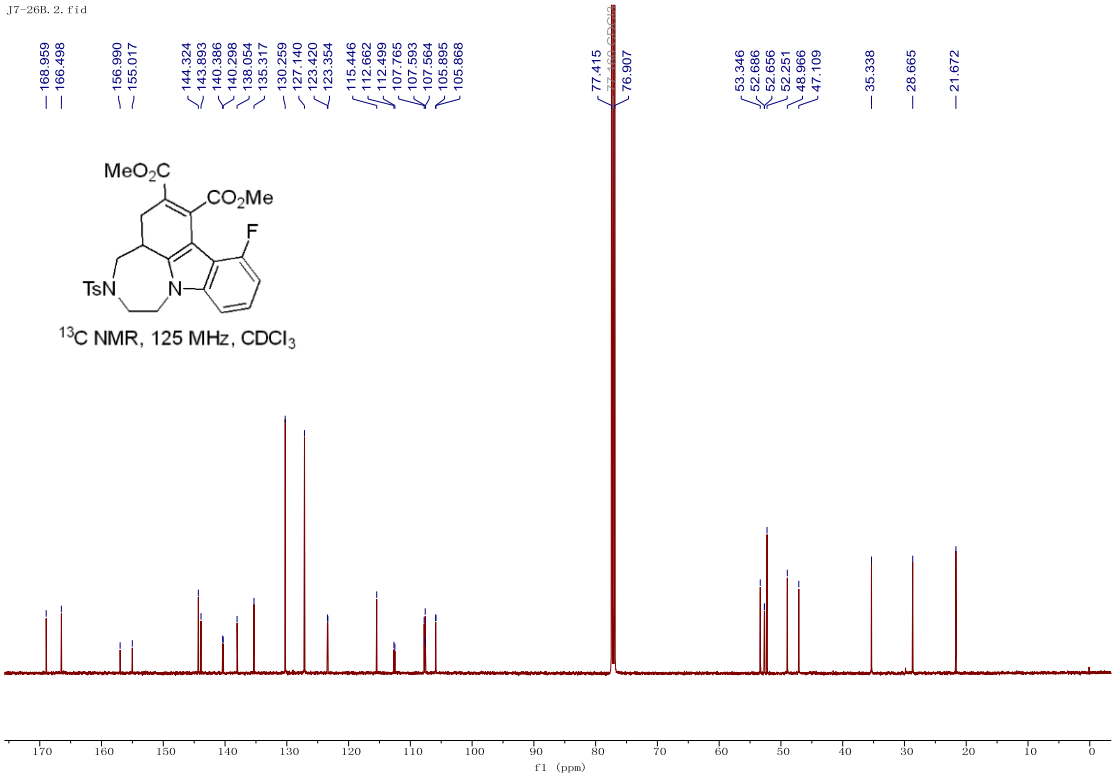
^{19}F NMR (470 MHz, $CDCl_3$) δ (-116.17) - (-116.21) (m).

IR (KBr) ν (cm^{-1}): 1737, 1699, 1433, 1329, 1314, 1296, 1236, 1152, 735 cm^{-1}.

HRMS (ESI): calcd for $C_{26}H_{26}FN_2O_6S$ $[M+H]^+$: 513.14901, found: 513.14954.

MP: 86-89 °C.

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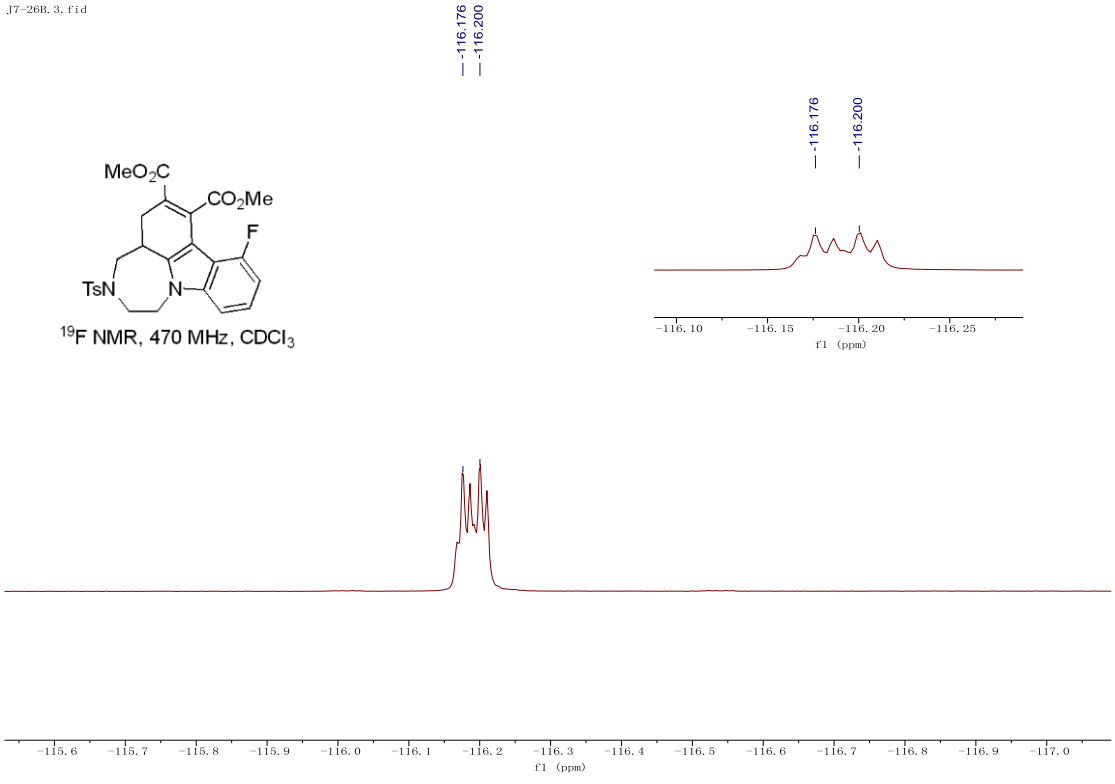
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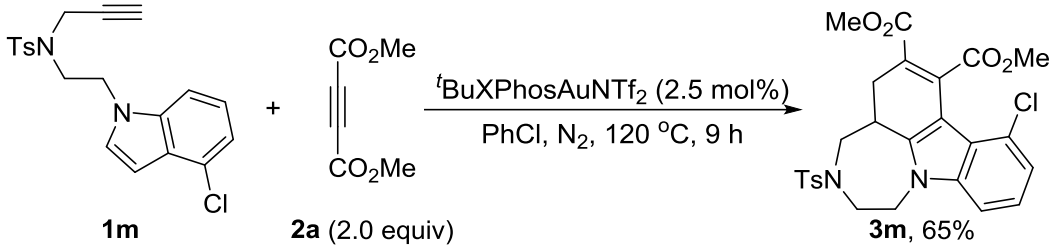
f1 (ppm)

Dimethyl 8-chloro-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3m)



The compound **3m** (yellow solid, 34.4 mg, 65% yield) was obtained following General Procedure B from **1m** (38.7 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (2.25 mg, 2.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.40) as eluent.

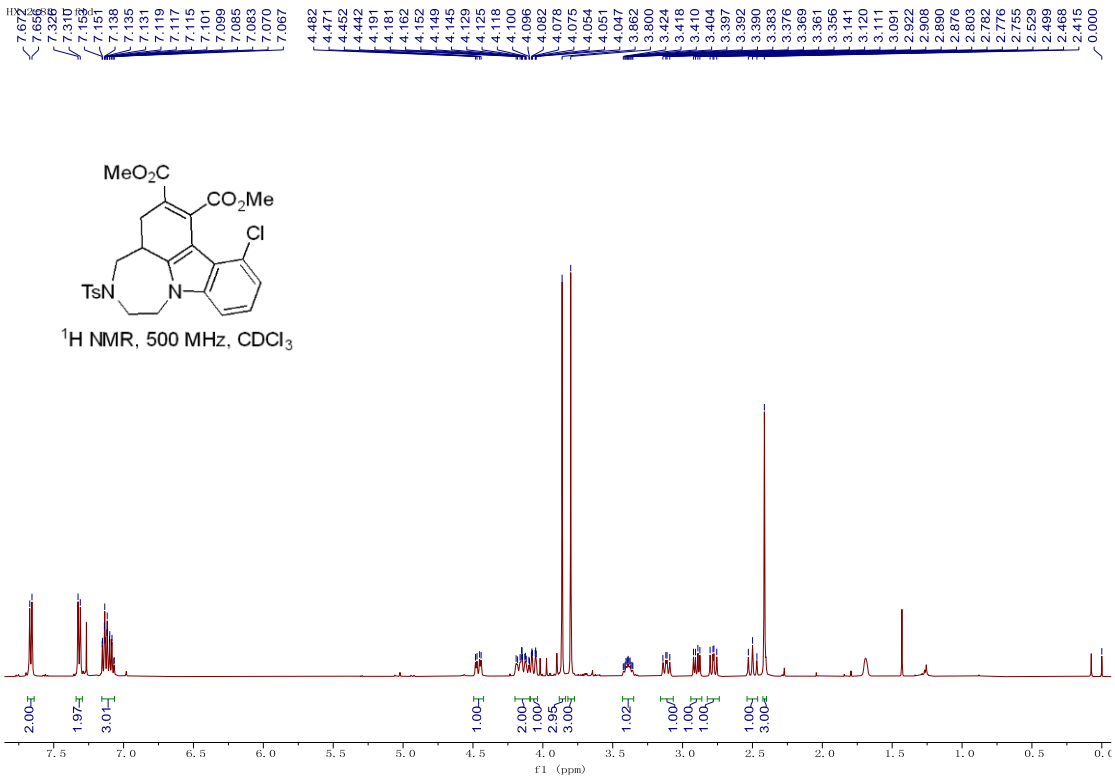
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.66 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.15-7.07 (m, 3H), 4.46 (dd, J = 15.0, 5.5 Hz, 1H), 4.19-4.10 (m, 2H), 4.06 (dt, J = 14.0, 2.0 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.42-3.36 (m, 1H), 3.11 (dd, J = 15.0, 10.5 Hz, 1H), 2.90 (dd, J = 16.0, 7.0 Hz, 1H), 2.78 (dd, J = 13.5, 10.5 Hz, 1H), 2.50 (t, J = 15.0 Hz, 1H), 2.42 (s, 3H).

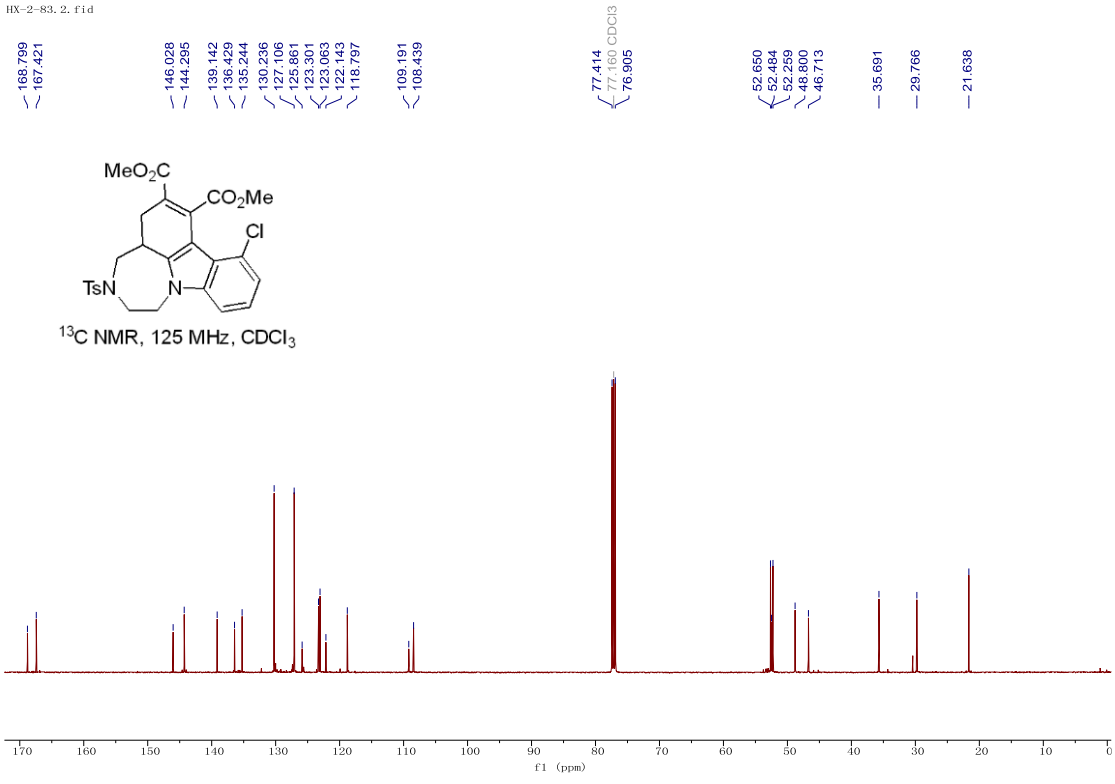
^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 167.4, 146.0, 144.3, 139.1, 136.4, 135.2, 130.2, 127.1, 125.9, 123.3, 123.1, 122.1, 118.8, 109.2, 108.4, 52.7, 52.5, 52.3, 48.8, 46.7, 35.7, 29.8, 21.6.

IR (KBr) ν (cm^{-1}): 1732, 1710, 1433, 1327, 1292, 1252, 1207, 1161, 1094, 740 cm^{-1}.

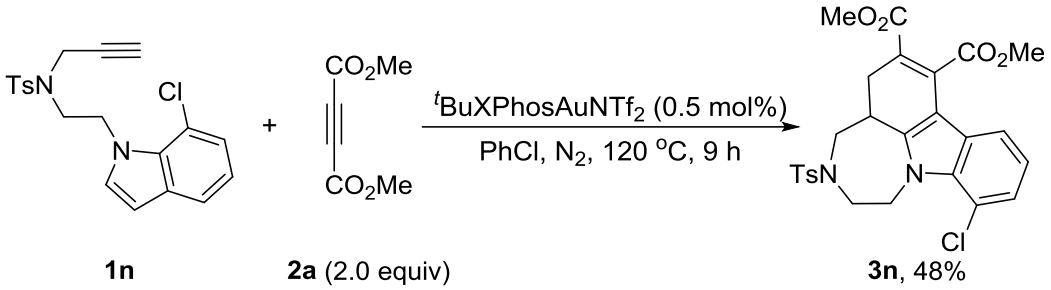
HRMS (ESI): calcd for $C_{26}H_{26}ClN_2O_6S$ $[M+H]^+$: 529.11946, found: 529.11987.

MP: 174-177 °C.


MeO2C
CO2Me
Cl
TsN
N
1H NMR, 500 MHz, CDCl3
f1 (ppm)


MeO2C
CO2Me
Cl
TsN
N
13C NMR, 125 MHz, CDCl3
f1 (ppm)

Dimethyl 11-chloro-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3n)



1n **2a** (2.0 equiv) **3n**, 48%

The compound **3n** (yellow solid, 25.4 mg, 48% yield) was obtained following General Procedure B from **1n** (38.6 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.44) as eluent.

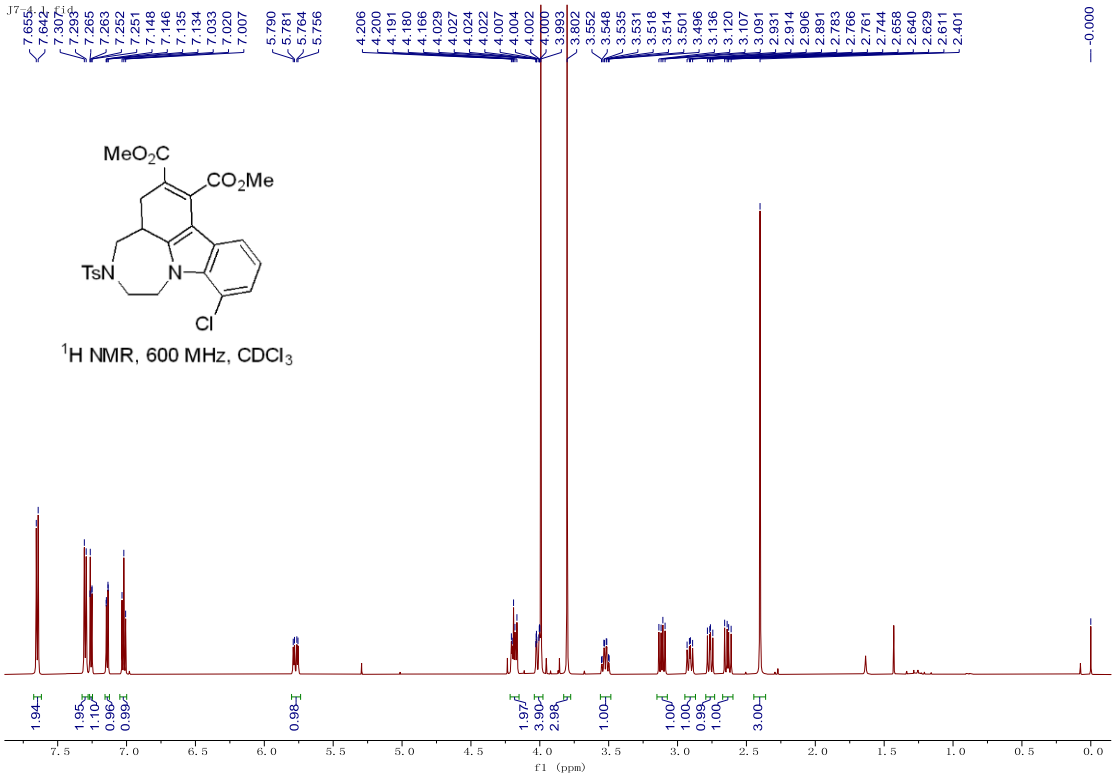
^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.65 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 7.27-7.25 (m, 1H), 7.14 (dd, J = 7.8, 1.2 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 5.77 (dd, J = 15.6, 5.4 Hz, 1H), 4.21-4.17 (m, 2H), 4.03-4.00 (m, 1H), 3.99 (s, 3H), 3.80 (s, 3H), 3.55-3.50 (m, 1H), 3.11 (dd, J = 15.0, 9.6 Hz, 1H), 2.91 (dd, J = 15.0, 10.2 Hz, 1H), 2.76 (dd, J = 13.2, 10.2 Hz, 1H), 2.63 (dd, J = 17.4, 10.8 Hz, 1H), 2.40 (s, 3H).

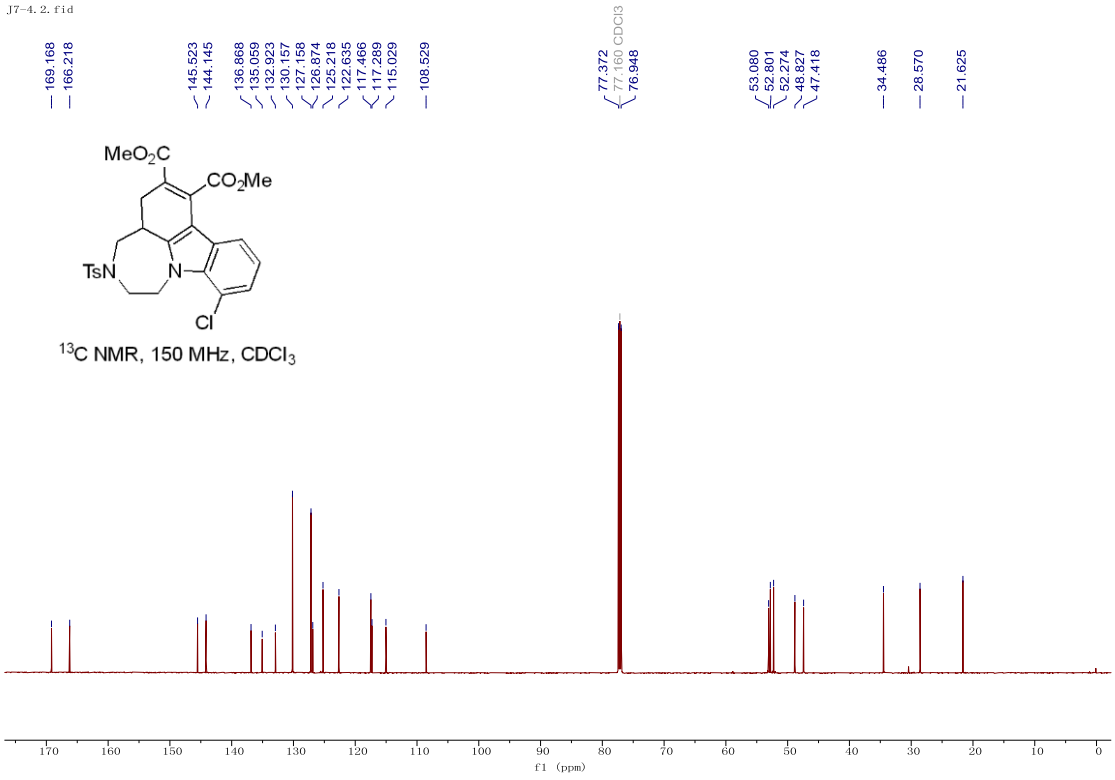
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 166.2, 145.5, 144.1, 136.9, 135.1, 132.9, 130.2, 127.2, 126.9, 125.2, 122.6, 117.5, 117.3, 115.0, 108.5, 53.1, 52.8, 52.3, 48.8, 47.4, 34.5, 28.6, 21.6.

IR (KBr) ν (cm^{-1}): 1740, 1431, 1338, 1256, 1245, 1107, 1089, 729, 547 cm^{-1}.

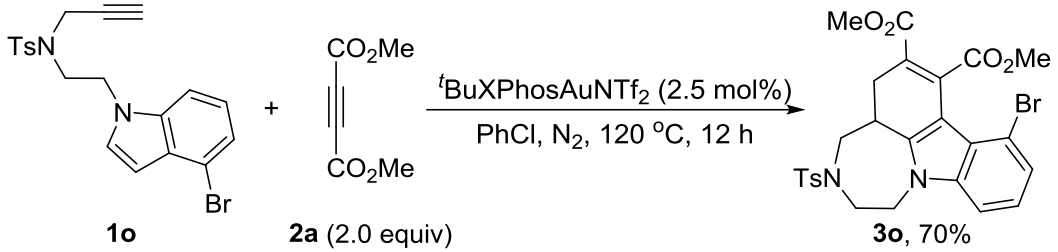
HRMS (ESI): calcd for $C_{26}H_{26}ClN_2O_6S$ $[M+H]^+$: 529.11946, found: 529.11987.

MP: 197-199 °C.


J7-4.1.fid
MeO2C
CO2Me
TsN
N
Cl
1H NMR, 600 MHz, CDCl3
f1 (ppm)


J7-4.2.fid
MeO2C
CO2Me
TsN
N
Cl
13C NMR, 150 MHz, CDCl3
f1 (ppm)

Dimethyl 8-bromo-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3o)



The compound **3o** (white solid, 40.1 mg, 70% yield) was obtained following General Procedure B from **1o** (43.0 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (2.25 mg, 2.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.27) as eluent.

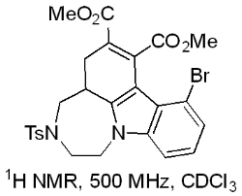
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.66 (d, J = 7.5 Hz, 2H), 7.32 (d, J = 7.5 Hz, 3H), 7.19 (d, J = 8.0 Hz, 1H), 7.01 (td, J = 8.0, 1.5 Hz, 1H), 4.45 (dd, J = 14.5, 5.0 Hz, 1H), 4.19-4.04 (m, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.40-3.33 (m, 1H), 3.12 (dd, J = 14.0, 10.0 Hz, 1H), 2.83 (dd, J = 15.5, 7.0 Hz, 1H), 2.76 (dd, J = 14.0, 10.5 Hz, 1H), 2.49 (t, J = 16.0 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 167.9, 146.3, 144.3, 139.0, 135.3, 135.0, 130.2, 127.1, 126.7, 124.0, 123.2, 120.4, 113.8, 109.8, 109.0, 52.7, 52.32, 52.27, 48.8, 46.7, 35.9, 30.2, 21.6.

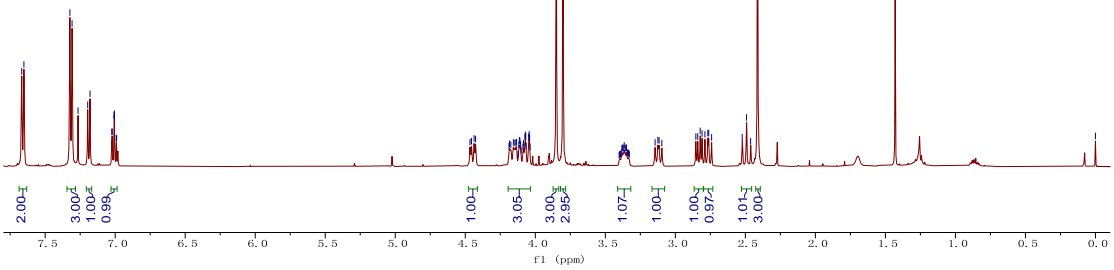
IR (KBr) ν (cm^{-1}): 1702, 1590, 1433, 1338, 1252, 1236, 1182, 1084, 741 cm^{-1}.

HRMS (ESI): calcd for $C_{26}H_{26}N_2BrO_6S$ $[M+H]^+$: 573.06895, found: 573.06946.

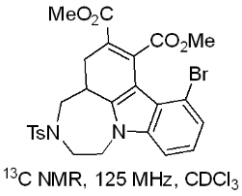
MP: 190-194 °C.



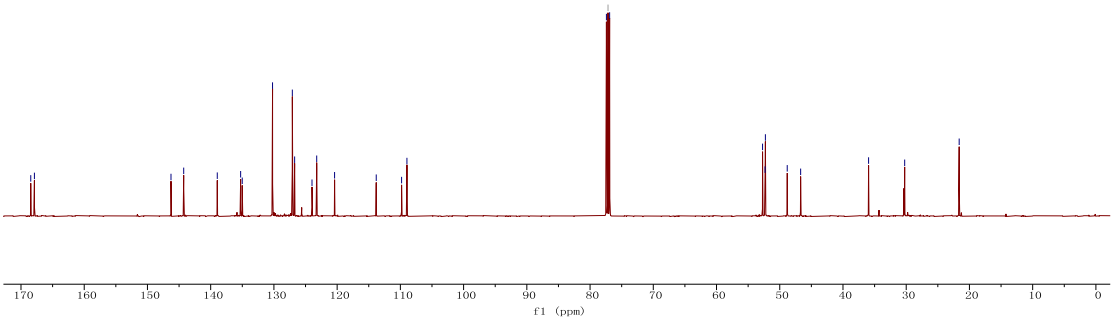
^{1}H NMR, 500 MHz, $CDCl_3$



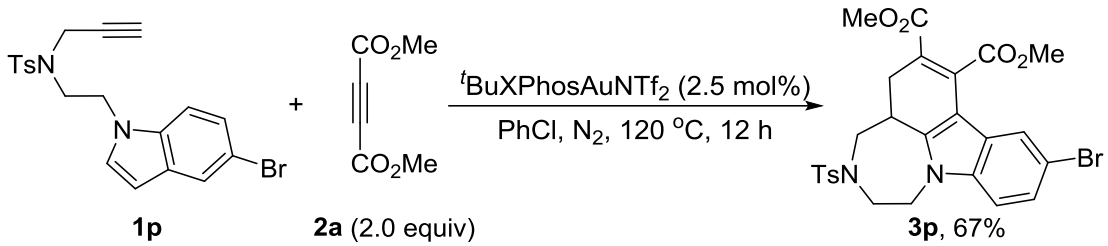
F6-140.2.fid



^{13}C NMR, 125 MHz, $CDCl_3$



Dimethyl 9-bromo-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3p)



The compound **3p** (yellow solid, 38.4 mg, 67% yield) was obtained following General Procedure B from **1p** (43.0 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (2.25 mg, 2.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.34) as eluent.

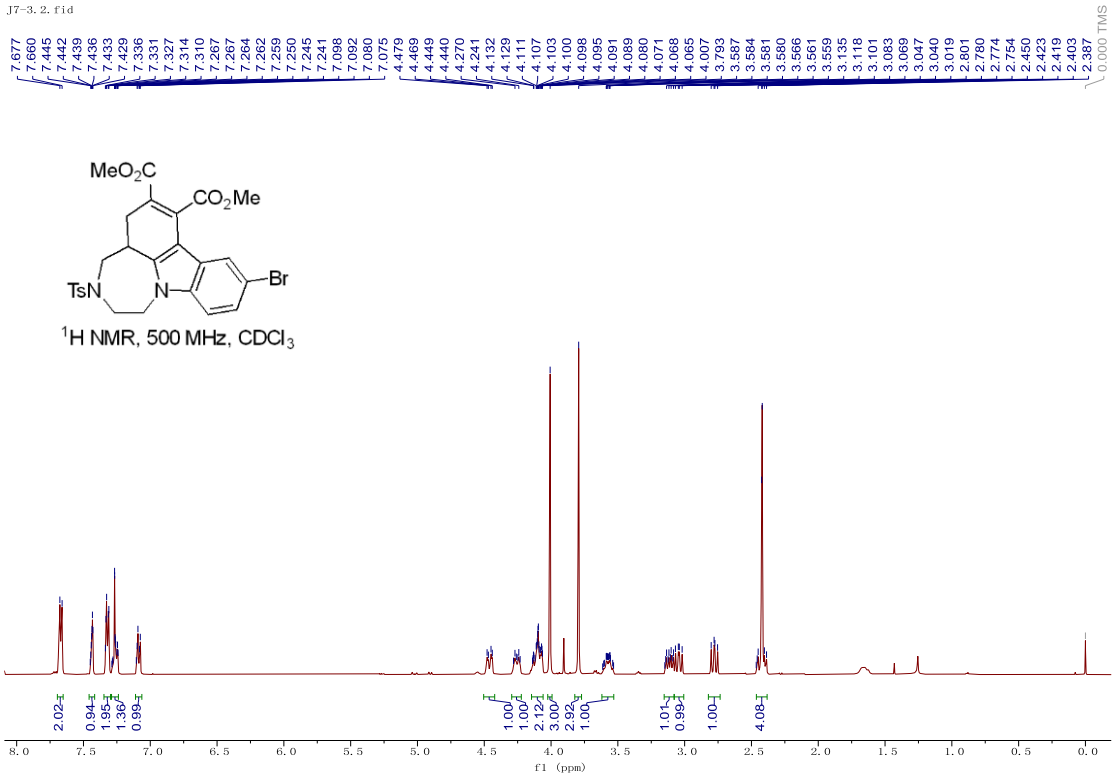
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.69-7.66 (m, 2H), 7.45-7.43 (m, 1H), 7.34-7.31 (m, 2H), 7.29-7.24 (m, 1H), 7.10-7.08 (m, 1H), 4.46 (dd, *J* = 15.0, 5.0 Hz, 1H), 4.25 (dt, *J* = 14.0, 5.0 Hz, 1H), 4.14-4.07 (m, 2H), 4.01 (s, 3H), 3.79 (s, 3H), 3.61-3.53 (m, 1H), 3.15-3.08 (m, 1H), 3.04 (dd, *J* = 14.0, 10.5 Hz, 1H), 2.78 (dd, *J* = 14.0, 10.5 Hz, 1H), 2.46-2.39 (m, 4H).

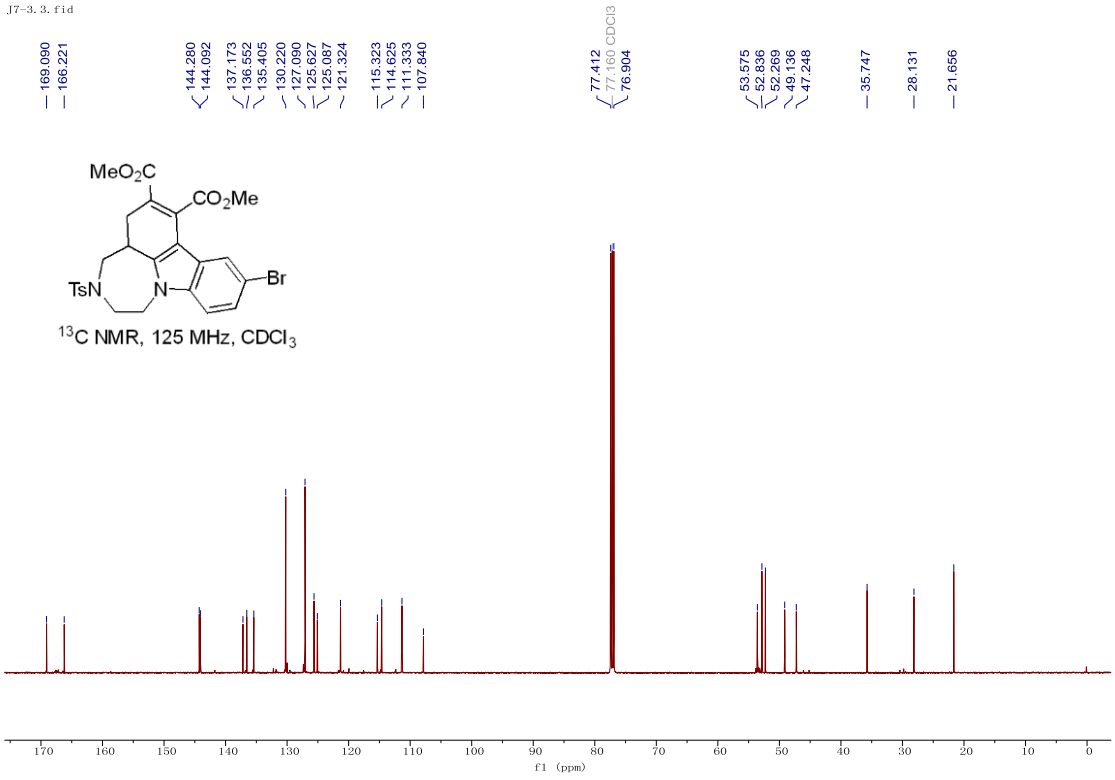
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 166.2, 144.3, 144.1, 137.2, 136.6, 135.4, 130.2, 127.1, 125.6, 125.1, 121.3, 115.3, 114.6, 111.3, 107.8, 53.6, 52.8, 52.3, 49.1, 47.2, 35.7, 28.1, 21.7.

IR (KBr) ν (cm^{-1}): 1734, 1701, 1463, 1434, 1340, 1293, 1257, 1203, 1159, 735 cm^{-1}.

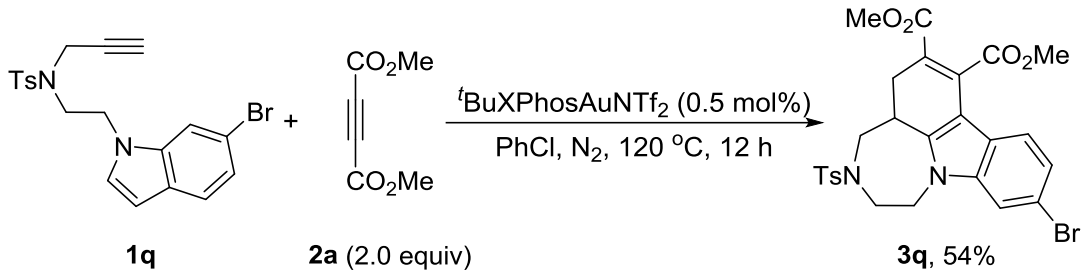
HRMS (ESI): calcd for $C_{26}H_{26}N_2BrO_6S$ $[M+H]^+$: 573.06895, found: 573.06915.

MP: 155-158 °C.


J7-3.2.fid
MeO2C
CO2Me
TsN
N
Br
1H NMR, 500 MHz, CDCl3
f1 (ppm)


J7-3.3.fid
MeO2C
CO2Me
TsN
N
Br
13C NMR, 125 MHz, CDCl3
f1 (ppm)

Dimethyl 10-bromo-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3q)



1q **2a** (2.0 equiv) **3q**, 54%

The compound **3q** (yellow solid, 31.0 mg, 54% yield) was obtained following General Procedure B from **1q** (43.0 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 12/4/1 (R_f = 0.15) as eluent.

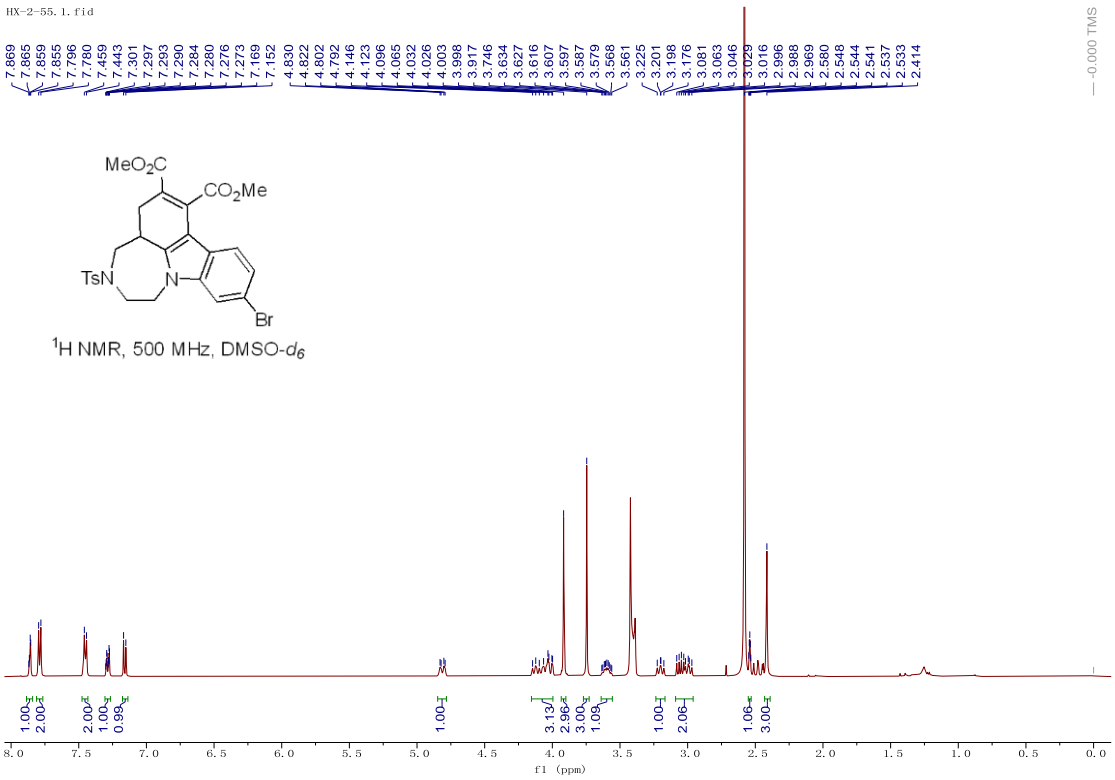
^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ 7.87-7.86 (m, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.30-7.27 (m, 1H), 7.16 (d, J = 8.5 Hz, 1H), 4.81 (dd, J = 14.0, 4.0 Hz, 1H), 4.15-4.00 (m, 3H), 3.92 (s, 3H), 3.75 (s, 3H), 3.63-3.56 (m, 1H), 3.20 (dd, J = 13.5, 12.0 Hz, 1H), 3.08-2.97 (m, 2H), 2.55-2.53 (m, 1H), 2.41 (s, 3H).

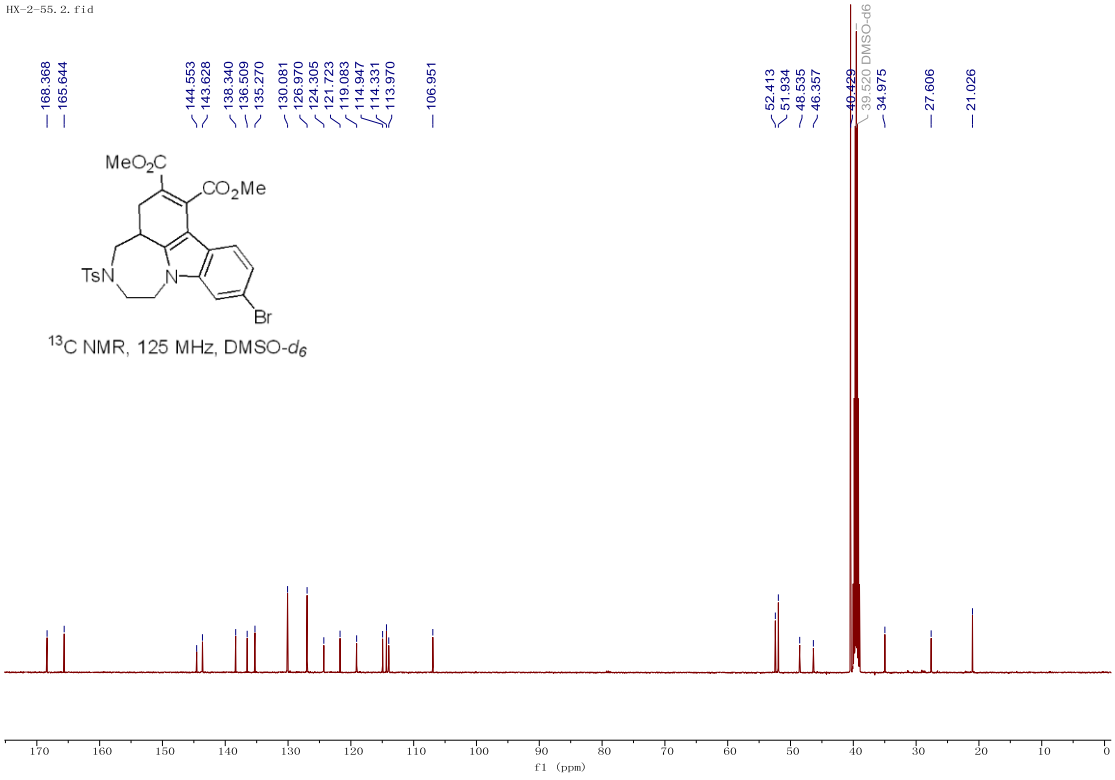
^{13}C NMR (125 MHz, DMSO-d_6) δ 168.4, 165.6, 144.6, 143.6, 138.3, 136.5, 135.3, 130.1, 127.0, 124.3, 121.7, 119.1, 114.9, 114.3, 114.0, 107.0, 52.4, 51.9, 48.5, 46.4, 40.4, 35.0, 27.6, 21.0.

IR (KBr) ν (cm^{-1}): 1731, 1696, 1257, 1238, 1206, 1158, 1106, 1027, 736 cm^{-1}.

HRMS (ESI): calcd for $C_{26}H_{26}N_2BrO_6S$ $[M+H]^+$: 573.06895, found: 573.06915.

MP: 215-218 °C.


HX-2-55.1.fid
7.869
7.865
7.859
7.855
7.796
7.780
7.459
7.443
7.301
7.297
7.293
7.290
7.284
7.280
7.276
7.273
7.169
7.152
4.830
4.822
4.802
4.792
4.146
4.123
4.096
4.065
4.032
4.026
4.003
3.998
3.917
3.746
3.634
3.627
3.616
3.607
3.597
3.587
3.579
3.568
3.561
3.225
3.201
3.198
3.176
3.081
3.063
3.046
3.029
3.016
2.996
2.988
2.969
2.580
2.548
2.544
2.541
2.537
2.533
2.414
0.000 TMS
MeO2C
CO2Me
TsN
N
Br
1H NMR, 500 MHz, DMSO-d6
1.00
2.00
2.00
1.00
0.99
1.00
3.19
2.96
3.00
1.09
1.00
2.06
1.06
3.00
f1 (ppm)


HX-2-55.2.fid
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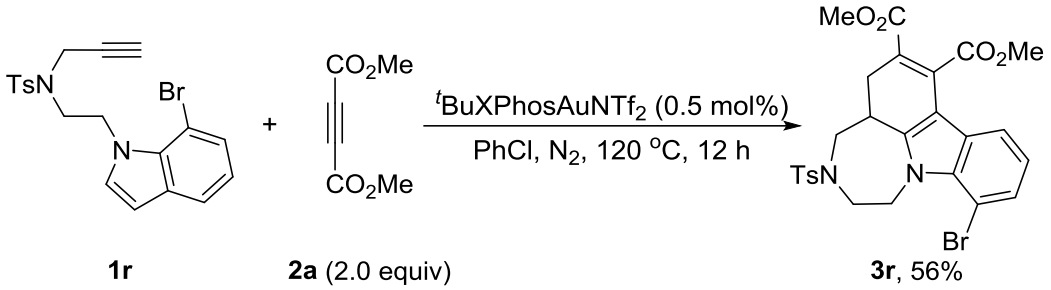
165.644
144.553
143.628
138.340
136.509
135.270
130.081
126.970
124.305
121.723
119.083
114.947
114.331
113.970
106.951
52.413
51.934
48.535
46.357
40.429
39.520 DMSO-d6
34.975
27.606
21.026
MeO2C
CO2Me
TsN
N
Br
13C NMR, 125 MHz, DMSO-d6
f1 (ppm)

Dimethyl 11-bromo-3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3r)



1r **2a** (2.0 equiv) **3r**, 56%

The compound **3r** (white solid, 32.1 mg, 56% yield) was obtained following General Procedure B from **1r** (43.0 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 12/4/1 (R_f = 0.15) as eluent.

^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.64 (d, J = 8.4 Hz, 2H), 7.34 (dd, J = 7.8, 0.6 Hz, 1H), 7.31-7.29 (m, 3H), 6.95 (t, J = 7.8 Hz, 1H), 5.92 (dd, J = 15.6, 6.0 Hz, 1H), 4.19 (dd, J = 13.8, 5.4 Hz, 1H), 4.11 (dd, J = 15.6, 9.6 Hz, 1H), 4.02-3.99 (m, 4H), 3.80 (s, 3H), 3.55-3.49 (m, 1H), 3.11 (dd, J = 17.4, 9.6 Hz, 1H), 2.88 (dd, J = 13.8, 9.6 Hz, 1H), 2.76 (dd, J = 12.6, 9.6 Hz, 1H), 2.64 (dd, J = 17.4, 10.8 Hz, 1H), 2.40 (s, 3H).

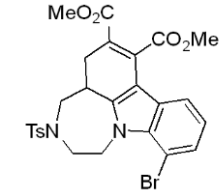
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 166.2, 145.8, 144.1, 136.7, 135.0, 134.0, 130.1, 128.7, 127.1, 127.0, 123.0, 118.0, 115.1, 108.3, 104.4, 53.0, 52.8, 52.3, 48.6, 46.9, 34.4, 28.5, 21.6.

IR (KBr) ν (cm^{-1}): 1738, 1708, 1255, 1244, 1196, 1162, 1106, 1087, 731 cm^{-1}.

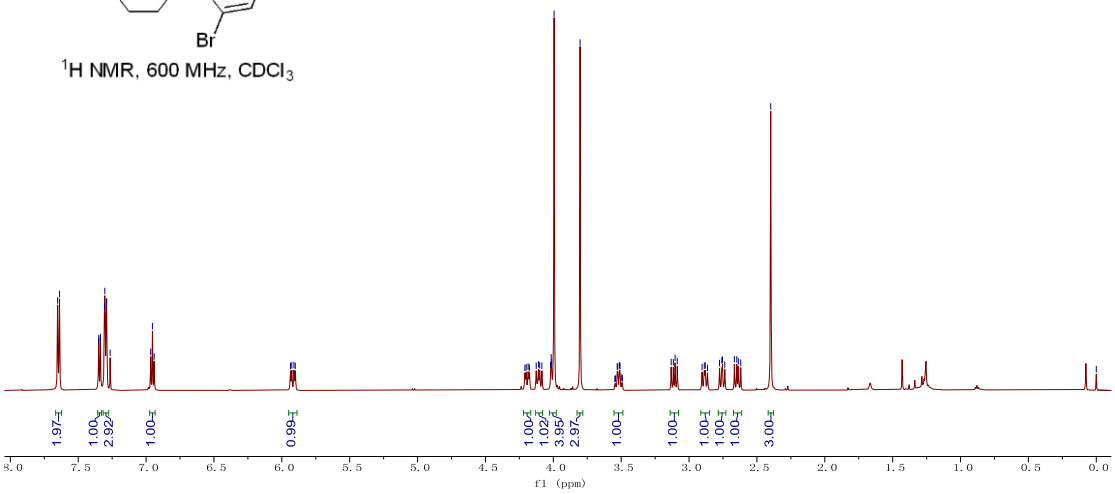
HRMS (ESI): calcd for $C_{26}H_{26}N_2BrO_6S$ $[M+H]^+$: 573.06895, found: 573.06915.

MP: 203-205 °C.

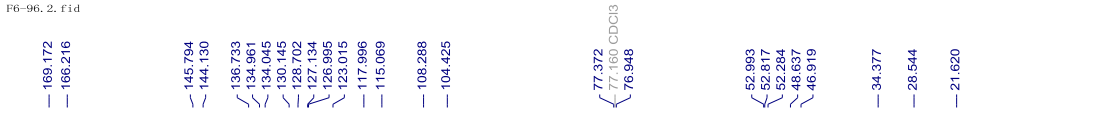
F6-96.1.fid

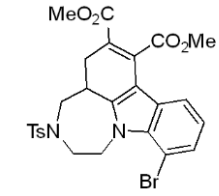


^{1}H NMR, 600 MHz, $CDCl_3$



F6-96.2.fid

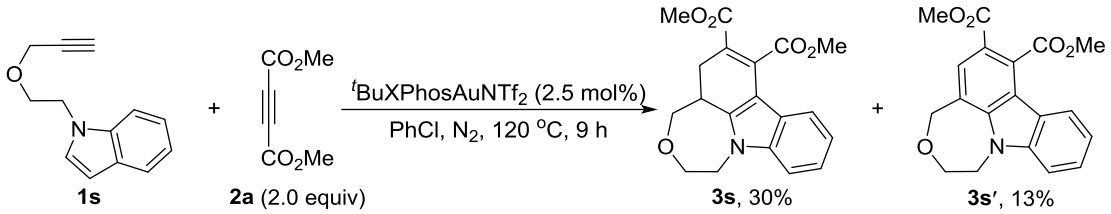




^{13}C NMR, 150 MHz, $CDCl_3$

Dimethyl 1,2,4a,5-tetrahydro-4*H*-[1,4]oxazepino[6,5,4-*jk*]carbazole-6,7-dicarboxylate (3s)

Dimethyl 1,2-dihydro-4*H*-[1,4]oxazepino[6,5,4-*jk*]carbazole-6,7-dicarboxylate (3s')



The compound **3s** (yellow solid, 20.4 mg, 30% yield) and **3s'** (white solid, 8.8 mg, 13% yield) were obtained following General Procedure B from **1s** (39.8 mg, 0.2 mmol, 1.0 equiv) and **2a** (56.8 mg, 0.4 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (4.5 mg, 2.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 ($R_{f(3s)}$ = 0.34) and petroleum ether/DCM/THF = 10/4/1 ($R_{f(3s')}$ = 0.15) as eluent.

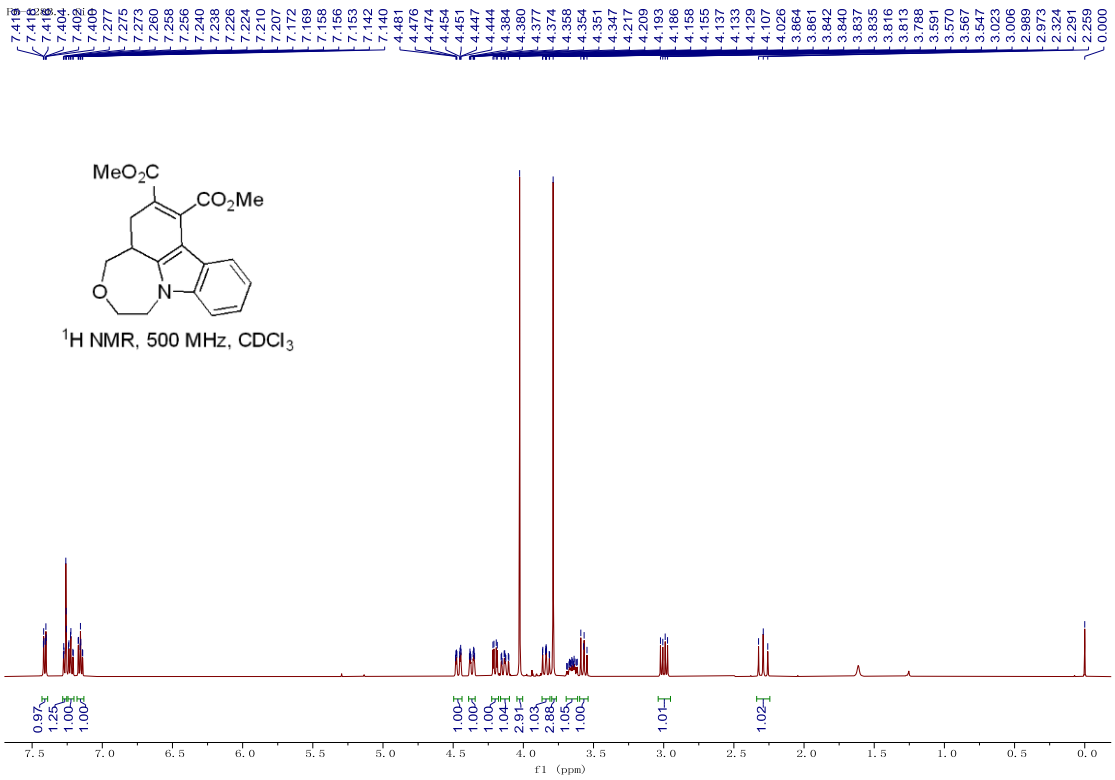
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.41 (dt, J = 8.0, 1.0 Hz, 1H), 7.28-7.26 (m, 1H), 7.22 (td, J = 7.0, 1.0 Hz, 1H), 7.17-7.14 (m, 1H), 4.46 (ddd, J = 14.5, 3.5, 1.0 Hz, 1H), 4.37 (ddd, J = 13.0, 3.5, 2.0 Hz, 1H), 4.20 (dd, J = 12.0, 4.0 Hz, 1H), 4.16-4.10 (m, 1H), 4.03 (s, 3H), 3.86-3.81 (m, 1H), 3.79 (s, 3H), 3.69-3.62 (m, 1H), 3.57 (dd, J = 12.0, 10.5 Hz, 1H), 3.00 (dd, J = 17.0, 8.5 Hz, 1H), 2.29 (t, J = 16.5 Hz, 1H).

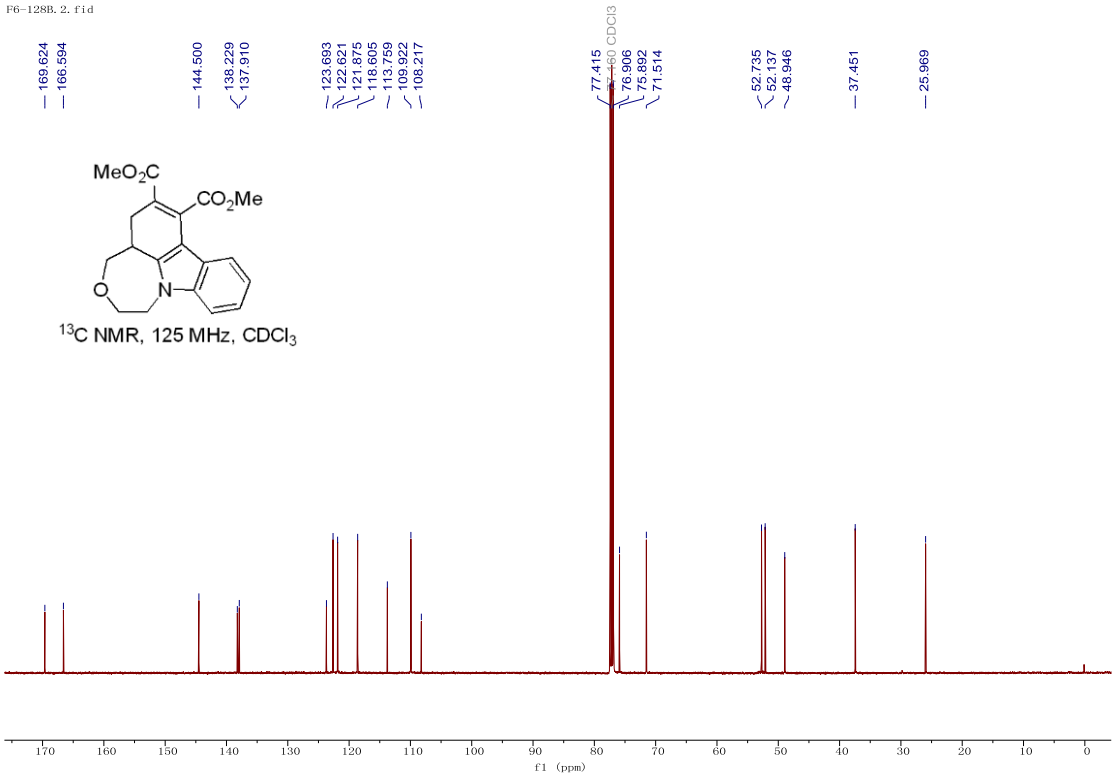
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 166.6, 144.5, 138.2, 137.9, 123.7, 122.6, 121.9, 118.6, 113.8, 109.9, 108.2, 75.9, 71.5, 52.7, 52.1, 48.9, 37.5, 26.0.

IR (KBr) ν (cm^{-1}): 1732, 1695, 1602, 1464, 1434, 1257, 1237, 1080, 744.23 cm^{-1}.

HRMS (ESI): calcd for $C_{19}H_{20}NO_5$ $[M+H]^+$: 342.13360, found: 342.13379.

MP: 131-135 °C.





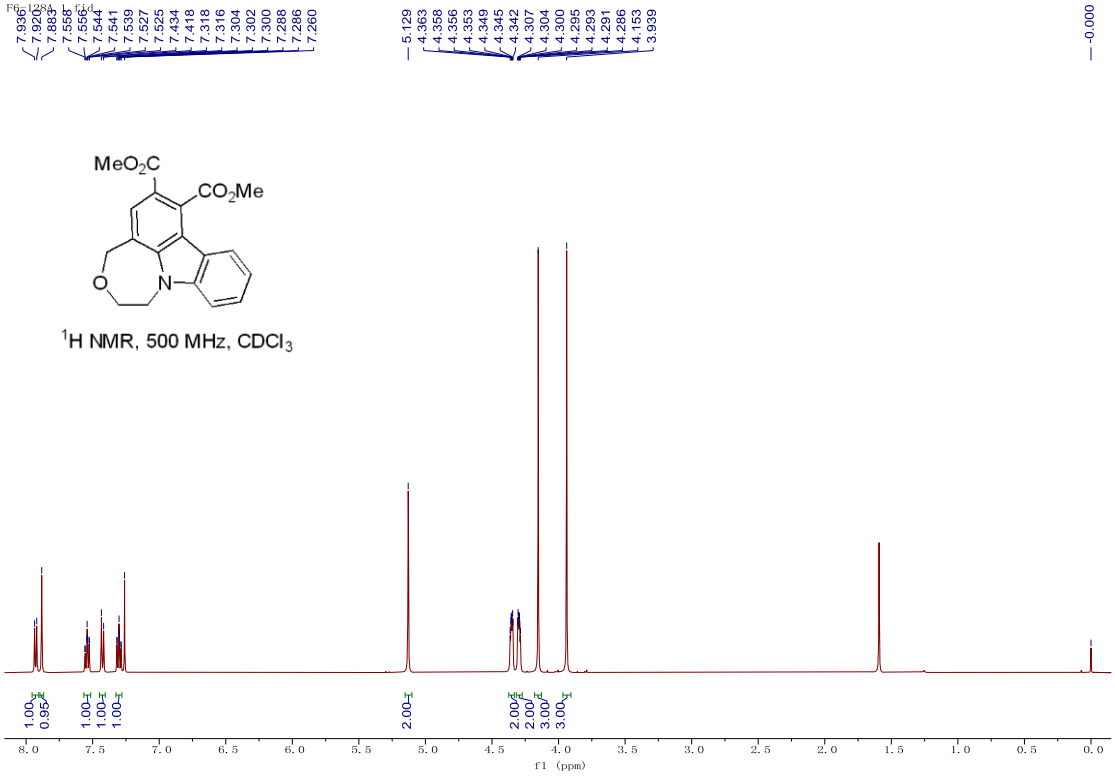
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.93 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.56-7.53 (m, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.32-7.29 (m, 1H), 5.13 (s, 2H), 4.36-4.34 (m, 2H), 4.31-4.29 (m, 2H), 4.15 (s, 3H), 3.94 (s, 3H).

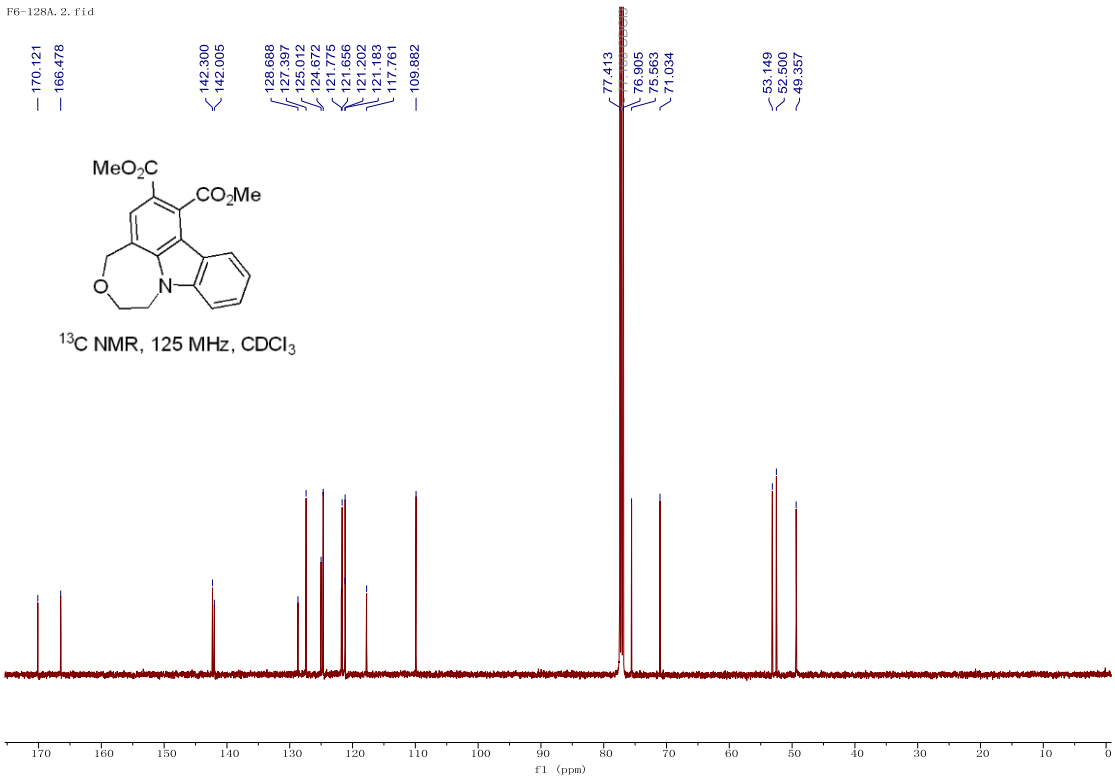
^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 166.5, 142.3, 142.0, 128.7, 127.4, 125.0, 124.7, 121.8, 121.7, 121.20, 121.18, 117.8, 109.9, 75.6, 71.0, 53.1, 52.5, 49.4.

IR (KBr) ν (cm^{-1}): 1732, 1574, 1433, 1418, 1326, 1267, 1233, 1144, 1099, 749 cm^{-1}.

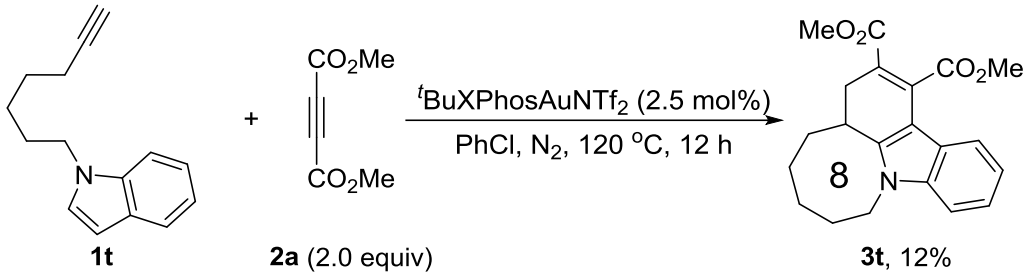
HRMS (ESI): calcd for $C_{19}H_{17}NNaO_5$ $[M+Na]^+$: 362.09989, found: 362.09995.

MP: 160-162 ºC.





Dimethyl 3a,4,5,6,7,8-hexahydro-3*H*-azocino[3,2,1-*jk*]carbazole-1,2-dicarboxylate (3t)

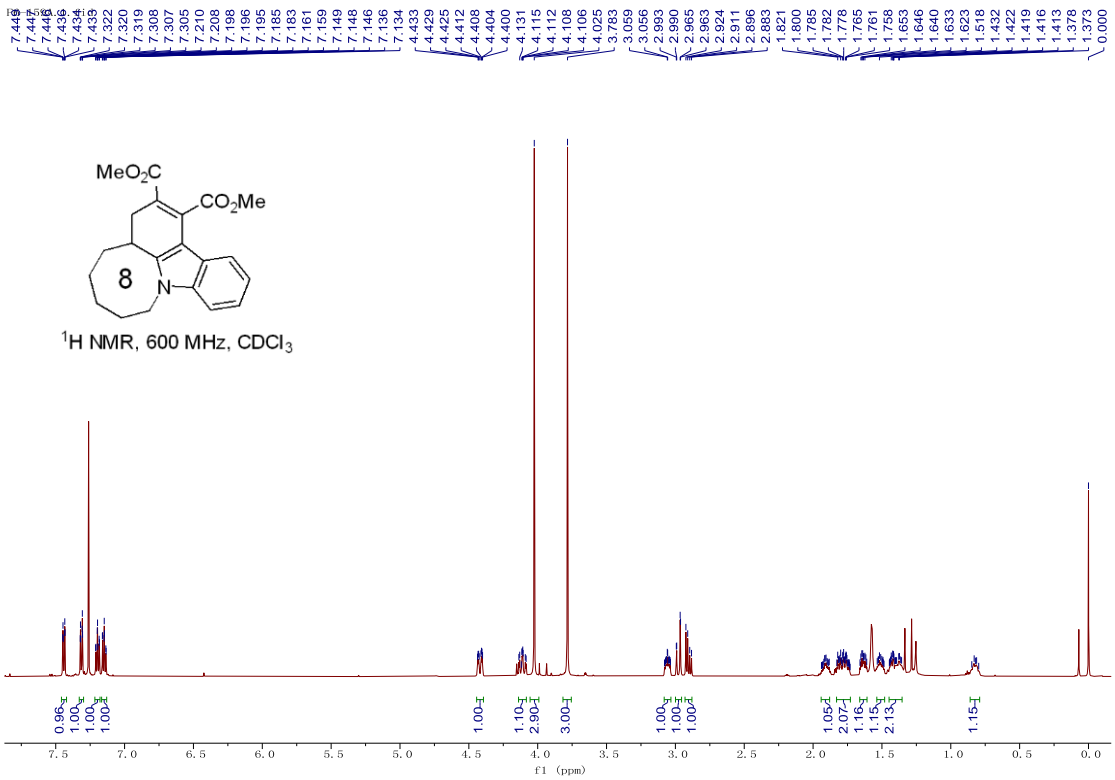


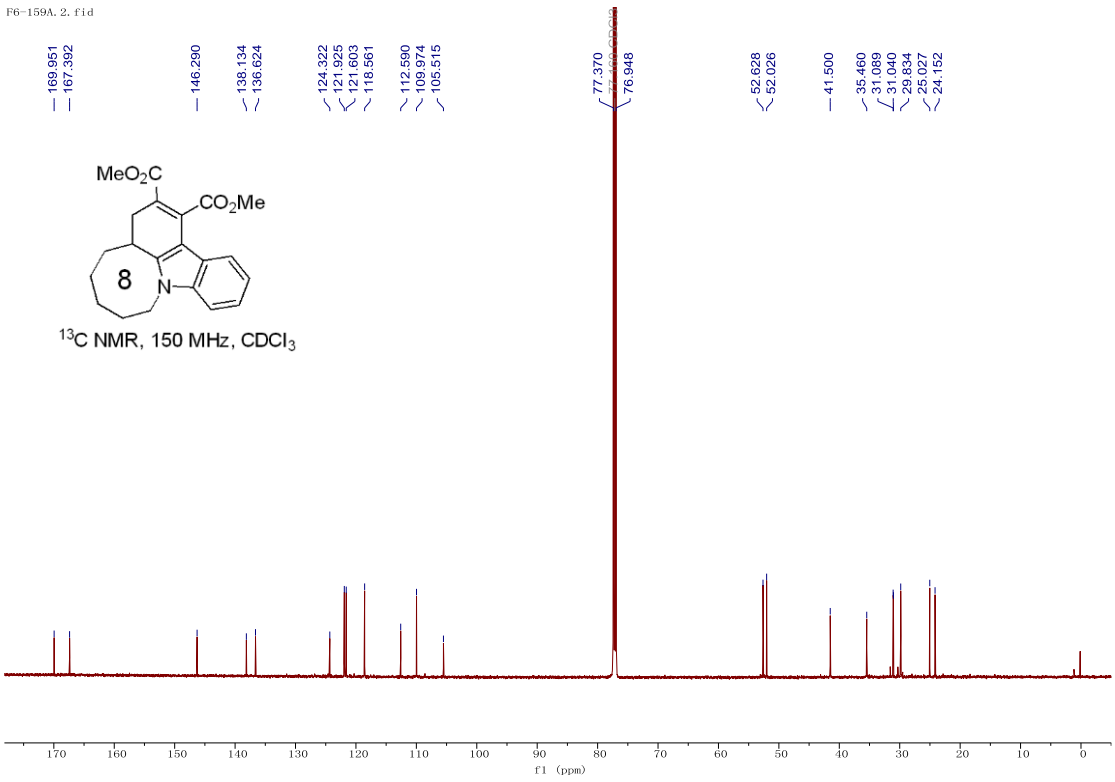
The compound **3t** (yellow oil, 4.1 mg, 12% yield) was obtained following General Procedure B from **1t** (21.1 mg, 0.1 mmol, 1.0 equiv) and **2a** (28.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (2.25 mg, 2.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 10/4/1 (R_f = 0.27) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$, TMS) δ 7.44 (dt, J = 7.8, 1.2 Hz, 1H), 7.31 (dt, J = 7.8, 1.2 Hz, 1H), 7.21-7.18 (m, 1H), 7.16-7.13 (m, 1H), 4.44-4.40 (m, 1H), 4.14-4.08 (m, 1H), 4.03 (s, 3H), 3.78 (s, 3H), 3.08-3.04 (m, 1H), 2.98 (dd, J = 16.8, 1.8 Hz, 1H), 2.90 (dd, J = 16.8, 7.8 Hz, 1H), 1.94-1.88 (m, 1H), 1.84-1.73 (m, 2H), 1.66-1.61 (m, 1H), 1.53-1.49 (m, 1H), 1.45-1.36 (m, 2H), 0.85-0.80 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 167.4, 146.3, 138.1, 136.6, 124.3, 121.9, 121.6, 118.6, 112.6, 110.0, 105.5, 52.6, 52.0, 41.5, 35.5, 31.1, 31.0, 29.8, 25.0, 24.2.

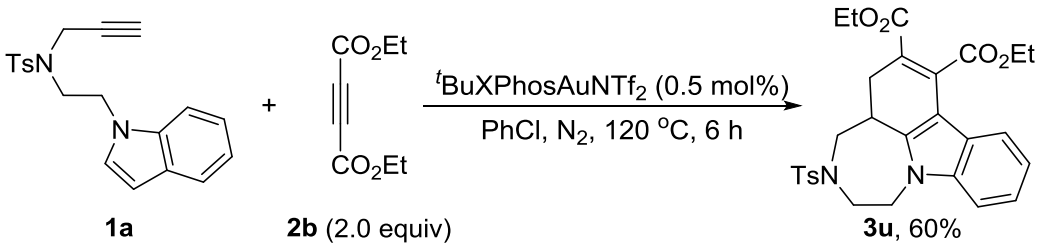
IR (KBr) ν (cm^{-1}): 1737, 1698, 1594, 1474, 1459, 1296, 1275, 1154, 744 cm^{-1}.

HRMS (ESI): calcd for $C_{21}H_{24}NO_4$ $[M+H]^+$: 354.16998, found: 354.17014.





Diethyl 3-tosyl-1,2,3,4,4a,5-hexahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (3u)



1a **2b** (2.0 equiv) **3u**, 60%

The compound **3u** (white solid, 31.4 mg, 60% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **2b** (34.0 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 10/4/1 (R_f = 0.10) as eluent.

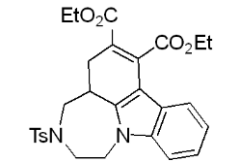
^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.69 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.24-7.19 (m, 2H), 7.14-7.11 (m, 1H), 4.53-4.47 (m, 3H), 4.29-4.22 (m, 3H), 4.13-4.08 (m, 2H), 3.61-3.54 (m, 1H), 3.12 (dd, J = 16.8, 9.0 Hz, 1H), 3.05 (dd, J = 14.4, 10.8 Hz, 1H), 2.76 (dd, J = 13.8, 10.8 Hz, 1H), 2.44-2.39 (m, 4H), 1.39 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 165.9, 144.2, 143.2, 137.85, 137.75, 135.5, 130.2, 127.1, 123.6, 122.7, 121.8, 118.8, 114.1, 109.8, 108.5, 61.8, 61.0, 53.8, 49.3, 46.9, 35.8, 28.4, 21.6, 14.4, 14.2.

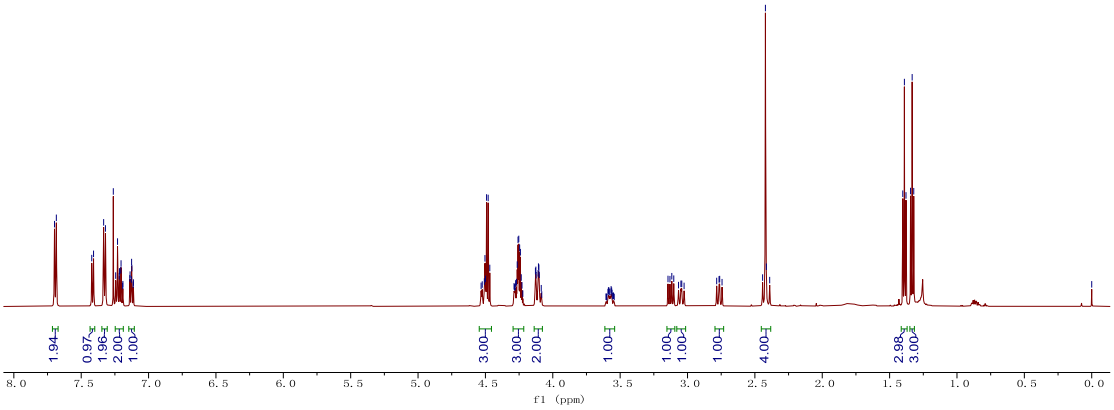
IR (KBr) ν (cm^{-1}): 1729, 1693, 1461, 1255, 1236, 1201, 1162, 1106, 744 cm^{-1}.

HRMS (ESI): calcd for $C_{28}H_{31}N_2O_6S$ $[M+H]^+$: 523.18973, found: 523.19019.

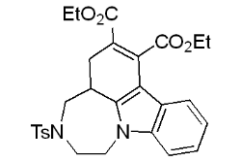
MP: 87-90 °C.



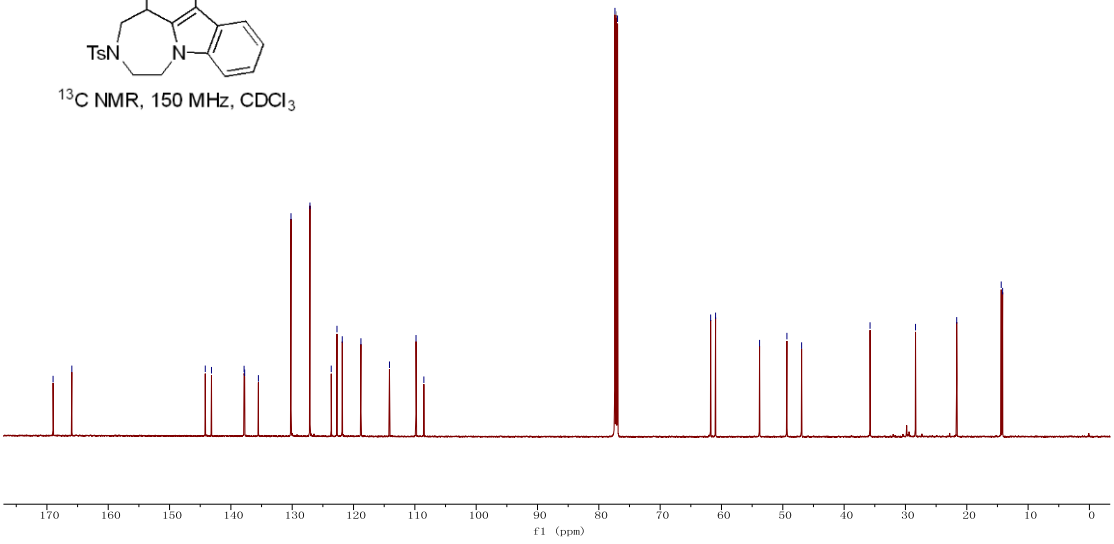
^{1}H NMR, 600 MHz, $CDCl_3$



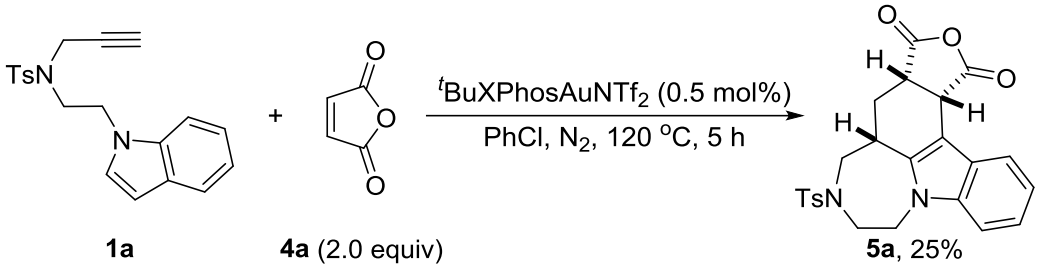
HX-2-49R.2.fid



^{13}C NMR, 150 MHz, $CDCl_3$



6-tosyl-3a,4,4a,5,6,7,8,13c-octahydro-[1,4]diazepino[1,7,6-*lm*]furo[3,4-*c*]carbazole-1,3-dione (5a)



1a **4a** (2.0 equiv) **5a**, 25%

The compound **5a** (yellow solid, 11.3 mg, 25% yield) was obtained following General Procedure B from **1a** (35.4 mg, 0.1 mmol, 1.0 equiv) and **4a** (19.6 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using EtOAc (R_f = 0.10) as eluent.

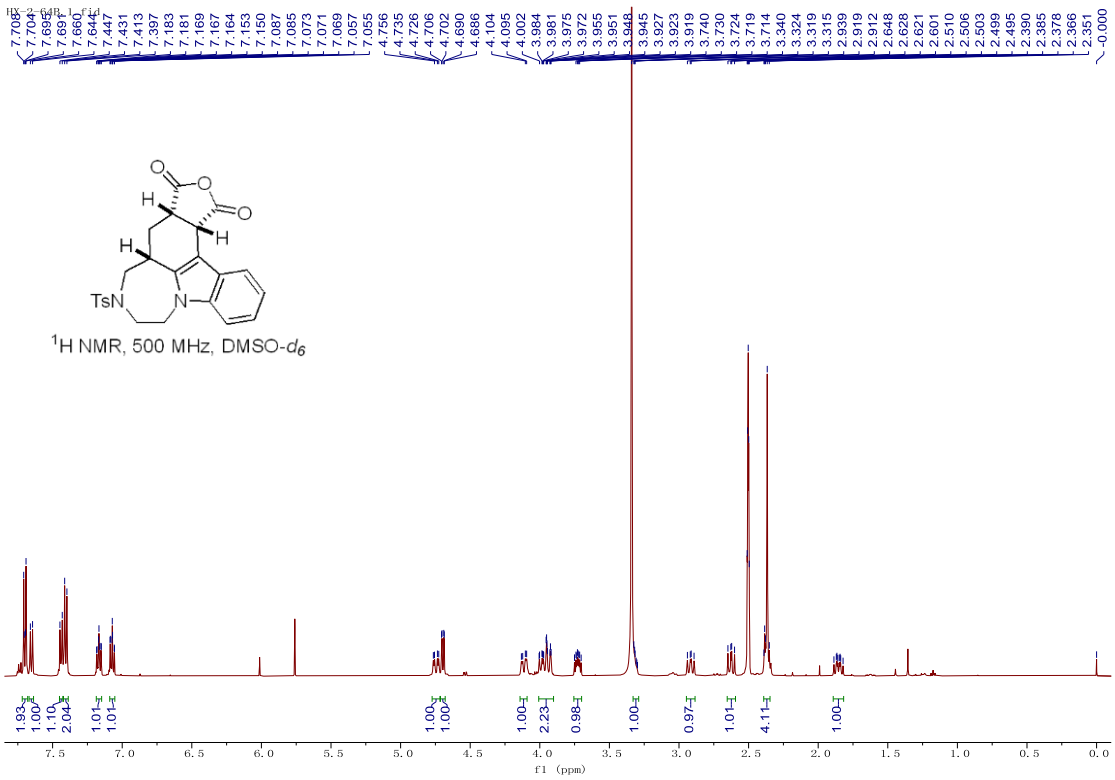
^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ 7.70 (dt, J = 8.5, 2.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.18-7.15 (m, 1H), 7.09-7.06 (m, 1H), 4.75 (dd, J = 15.0, 4.5 Hz,, 1H), 4.70 (dd, J = 8.0, 2.0 Hz, 1H), 4.11 (dd, J = 14.0, 4.5 Hz, 1H), 4.01-3.92 (m, 2H), 3.75-3.70 (m, 1H), 3.32-3.30 (m, 1H), 2.92 (dd, J = 13.5, 10.0 Hz, 1H), 2.62 (dd, J = 13.5, 10.0 Hz, 1H), 2.39-2.35 (m, 4H), 1.89-1.82 (m, 1H).

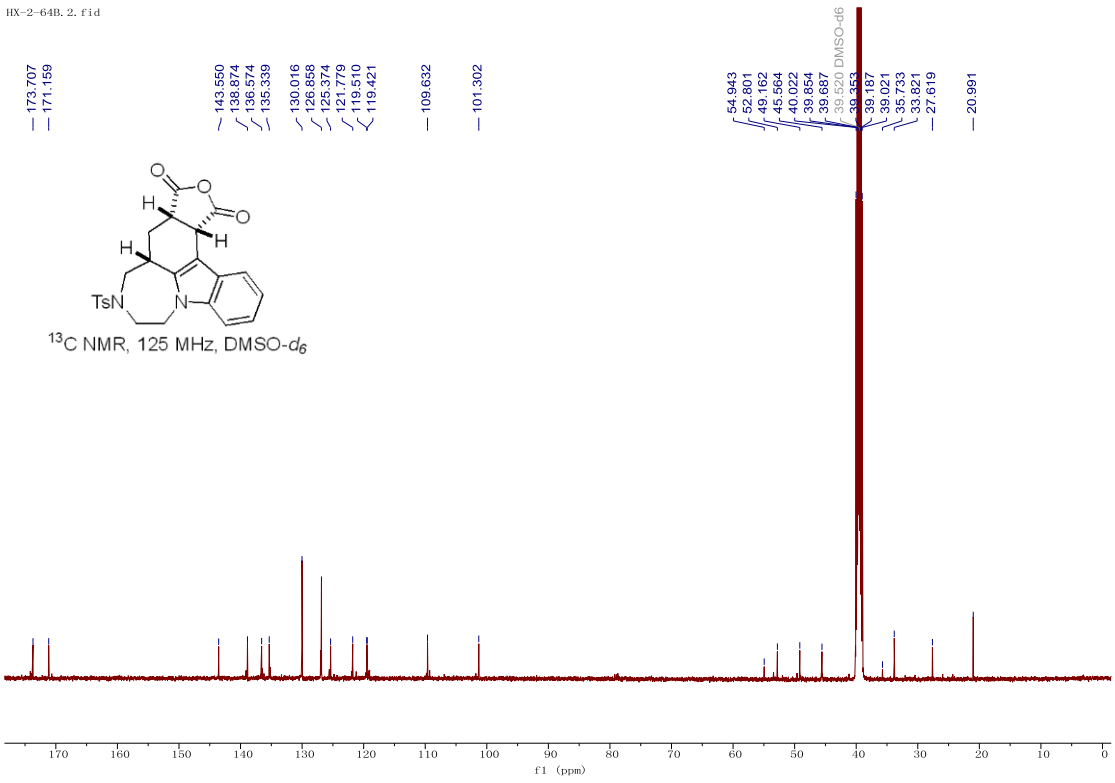
^{13}C NMR (125 MHz, DMSO-d_6) δ 173.7, 171.2, 143.6, 138.9, 136.6, 135.3, 130.0, 126.9, 125.4, 121.8, 119.5, 119.4, 109.6, 101.3, 54.9, 52.8, 49.2, 45.6, 35.7, 33.8, 27.6, 21.0.

IR (KBr) ν (cm^{-1}): 1782, 1467, 1387, 1327, 1156, 1107, 1012, 905, 740 cm^{-1}.

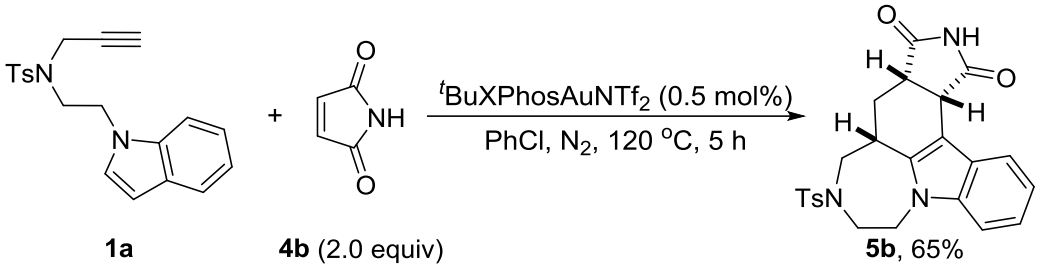
HRMS (ESI): calcd for $C_{24}H_{23}N_2O_5S$ $[M+H]^+$: 451.13222, found: 451.13239.

MP: 136-140 °C.


HX-2-64B. 1. fid
TsN
^{1}H NMR, 500 MHz, DMSO-d_6
f1 (ppm)


HX-2-64B. 2. fid
DMSO-d6
TsN
^{13}C NMR, 125 MHz, DMSO-d_6
f1 (ppm)

6-tosyl-3a,4,4a,5,6,7,8,13c-octahydro-1*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (5b)



1a **4b** (2.0 equiv) **5b**, 65%

The compound **5b** (yellow solid, 29.2 mg, 65% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **4b** (19.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.23) as eluent.

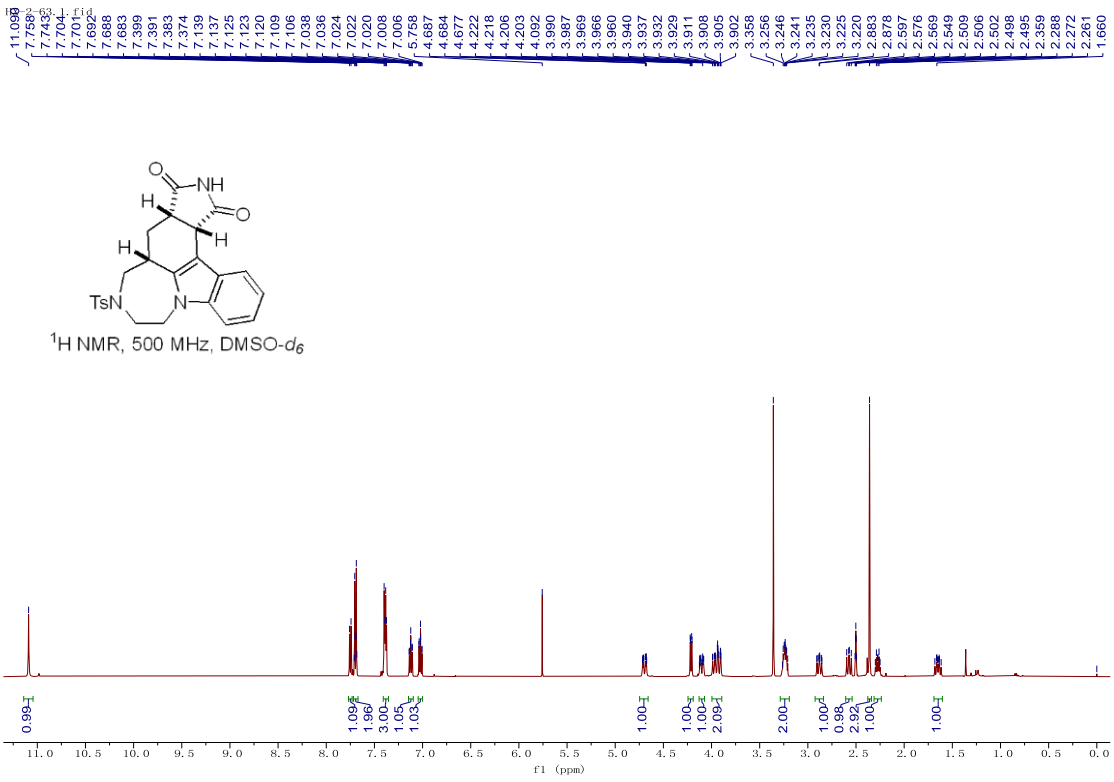
^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ 11.09 (s, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.70 (dt, J = 8.0, 1.5 Hz, 2H), 7.40-7.37 (m, 3H), 7.14-7.11 (m, 1H), 7.04-7.01 (m, 1H), 4.72-4.67 (m, 1H), 4.21 (dd, J = 8.0, 2.0 Hz, 1H), 4.13-4.08 (m, 1H), 3.99-3.90 (m, 2H), 3.26-3.21 (m, 2H), 2.91-2.85 (m, 1H), 2.57 (dd, J = 14.0, 10.5 Hz, 1H), 2.36 (s, 3H), 2.27 (dt, J = 13.5, 5.5 Hz, 1H), 1.68-1.62 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 180.4, 177.9, 143.5, 138.6, 136.5, 135.4, 130.0, 126.9, 126.1, 121.4, 120.4, 119.1, 109.3, 103.8, 53.1, 49.2, 45.3, 40.6, 40.4, 33.9, 28.6, 21.0.

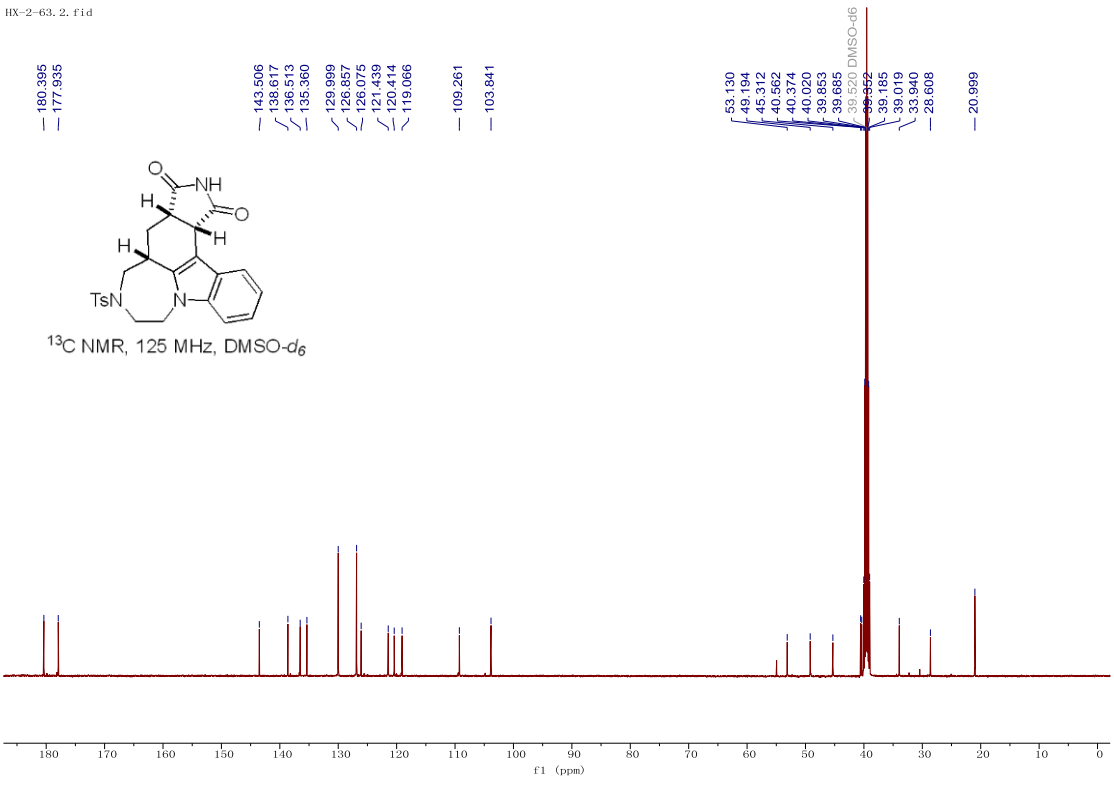
IR (KBr) ν (cm^{-1}): 1717, 1632, 1597, 1465, 1384, 1261, 1184, 1161, 726, 548 cm^{-1}.

HRMS (ESI): calcd for $C_{24}H_{23}N_3NaO_4S$ [M+Na]$^+$: 472.13015, found: 472.13046.

MP: 207-209 °C.

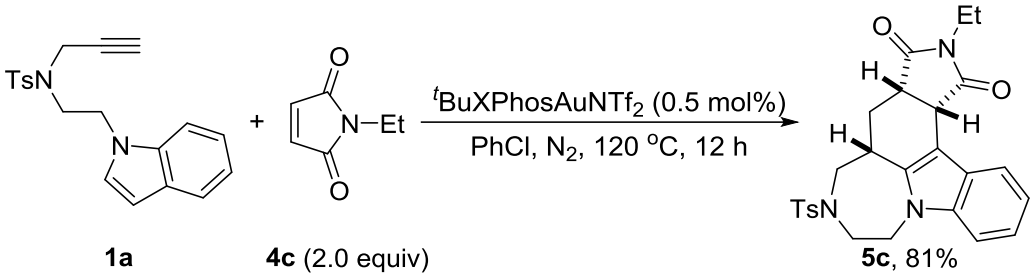


^{1}H NMR, 500 MHz, DMSO-d_6



^{13}C NMR, 125 MHz, DMSO-d_6

2-ethyl-6-tosyl-3a,4,4a,5,6,7,8,13c-octahydro-1*H*-[1,4]diazpino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (5c)



1a **4c** (2.0 equiv) **5c**, 81%

The compound **5c** (white solid, 38.7 mg, 81% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **4c** (25.0 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.16) as eluent.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.96 (d, J = 8.0 Hz, 1H), 7.66 (dt, J = 8.0, 1.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.22-7.19 (m, 2H), 7.16-7.13 (m, 1H), 4.53-4.50 (m, 1H), 4.30-4.25 (m, 1H), 4.14 (dd, J = 7.5, 1.5 Hz, 1H), 4.12-4.04 (m, 2H), 3.51 (q, J = 7.0 Hz, 2H), 3.37-3.31 (m, 1H), 3.24-3.19 (m, 1H), 2.76 (dd, J = 14.0, 10.0 Hz, 1H), 2.46 (dt, J = 14.0, 5.5 Hz, 1H), 2.42-2.39 (m, 4H), 1.73-1.66 (m, 1H), 1.10 (t, J = 7.0 Hz, 3H).

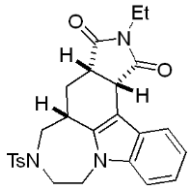
^{13}C NMR (125 MHz, $CDCl_3$) δ 178.7, 176.3, 144.0, 138.5, 137.0, 135.4, 130.0, 127.1, 126.4, 122.5, 120.8, 120.3, 108.8, 104.0, 54.3, 49.9, 46.4, 39.81, 39.78, 34.9, 33.7, 29.2, 21.6, 13.0.

IR (KBr) ν (cm^{-1}): 1699, 1464, 1401, 1378, 1327, 1221, 1163, 1103, 733, 549 cm^{-1}.

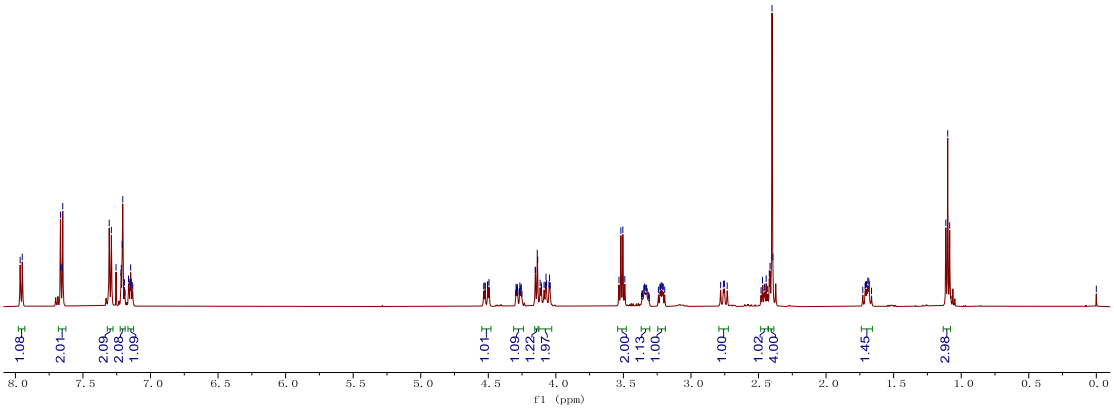
HRMS (ESI): calcd for $C_{26}H_{27}N_3NaO_4S$ $[M+Na]^+$: 500.16145, found: 500.16183.

MP: 169-172 °C.

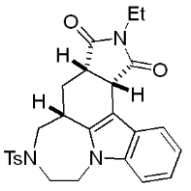
F6-172T-1.fid



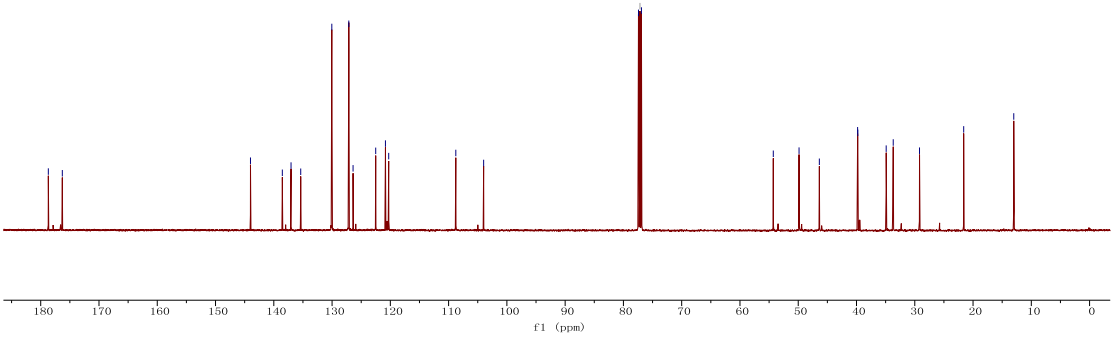
^{1}H NMR, 500 MHz, $CDCl_3$



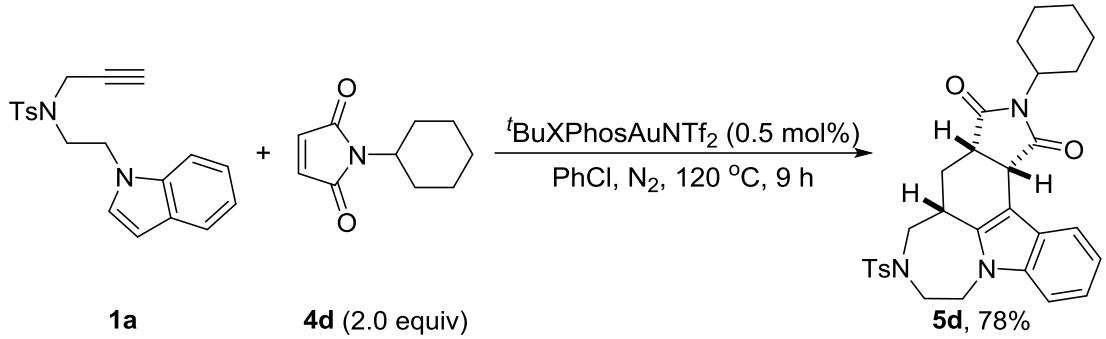
F6-172T.2.fid



^{13}C NMR, 125 MHz, $CDCl_3$



2-cyclohexyl-6-tosyl-3a,4,4a,5,6,7,8,13c-octahydro-1*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (5d)



1a **4d** (2.0 equiv) **5d**, 78%

The compound **5d** (yellow solid, 41.5 mg, 78% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **4d** (35.8 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.22) as eluent.

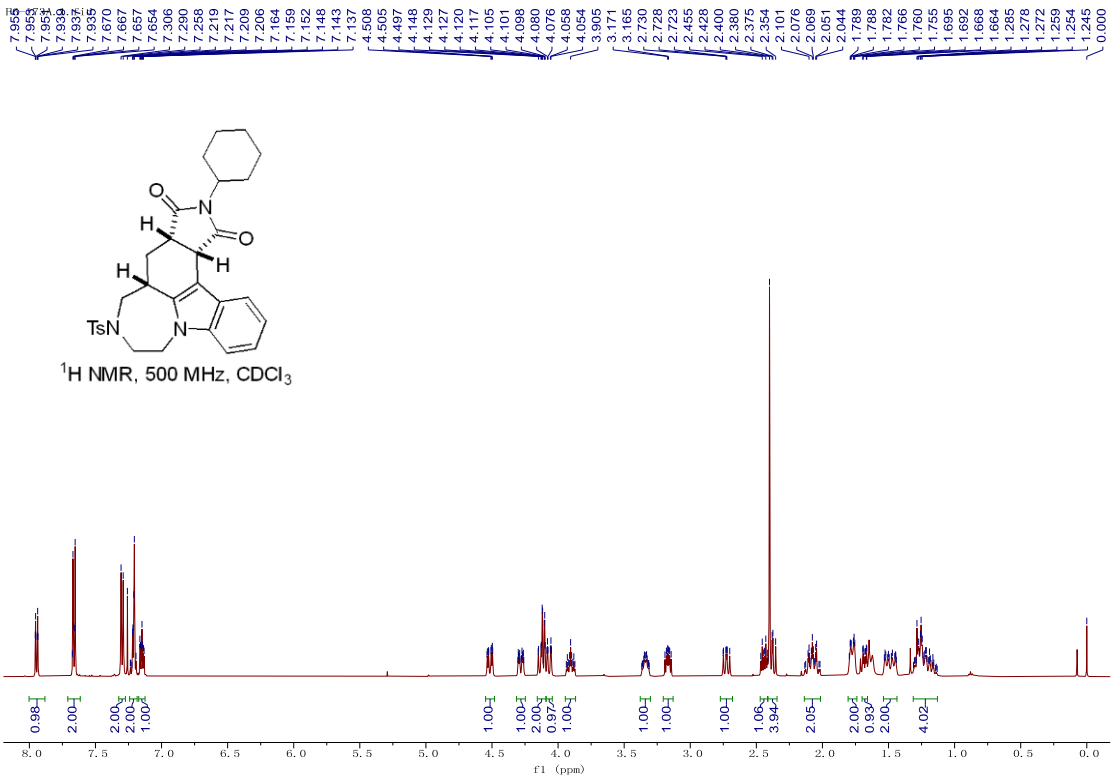
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.94 (dt, J = 8.0, 1.0 Hz, 1H), 7.66 (dt, J = 8.0, 1.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.24-7.19 (m, 2H), 7.16-7.13 (m, 1H), 4.52 (ddd, J = 14.5, 5.0, 1.0 Hz, 1H), 4.30-4.26 (m, 1H), 4.15-4.10 (m, 2H), 4.07 (dt, J = 13.0, 2.5 Hz, 1H), 3.91 (tt, J = 12.5, 4.0 Hz, 1H), 3.37-3.31 (m, 1H), 3.19-3.15 (m, 1H), 2.75-2.70 (m, 1H), 2.44 (dt, J = 13.5, 5.5 Hz, 1H), 2.41-2.35 (m, 4H), 2.13-2.02 (m, 2H), 1.80-1.76 (m, 2H), 1.70-1.66 (m, 1H), 1.53-1.44 (m, 2H), 1.31-1.13 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.0, 176.7, 144.0, 138.6, 137.1, 135.3, 130.0, 127.2, 126.5, 122.5, 120.9, 120.3, 108.8, 104.2, 54.4, 51.6, 50.0, 46.4, 39.58, 39.56, 34.9, 29.4, 29.1, 28.6, 25.93, 25.89, 25.1, 21.6.

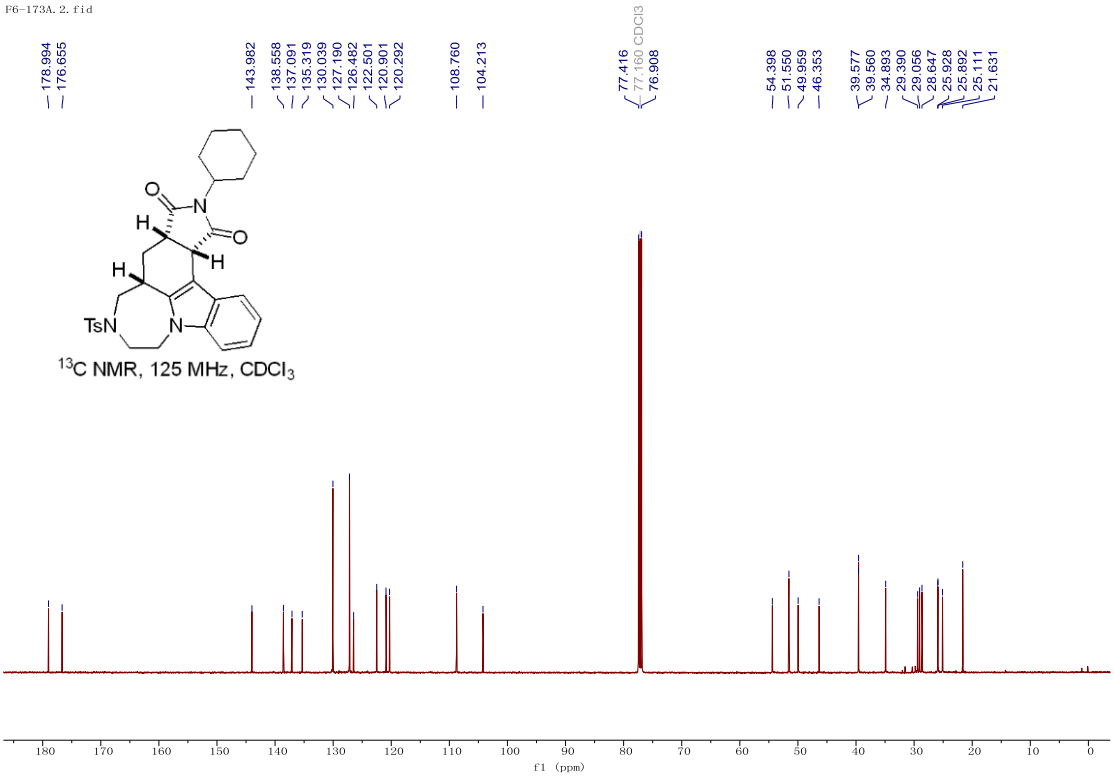
IR (KBr) ν (cm^{-1}): 1707, 1597, 1463, 1374, 1343, 1184, 1159, 747, 548 cm^{-1}.

HRMS (ESI): calcd for $C_{30}H_{33}N_3NaO_4S$ $[M+Na]^+$: 554.20840, found: 554.20880.

MP: 202-205 °C.

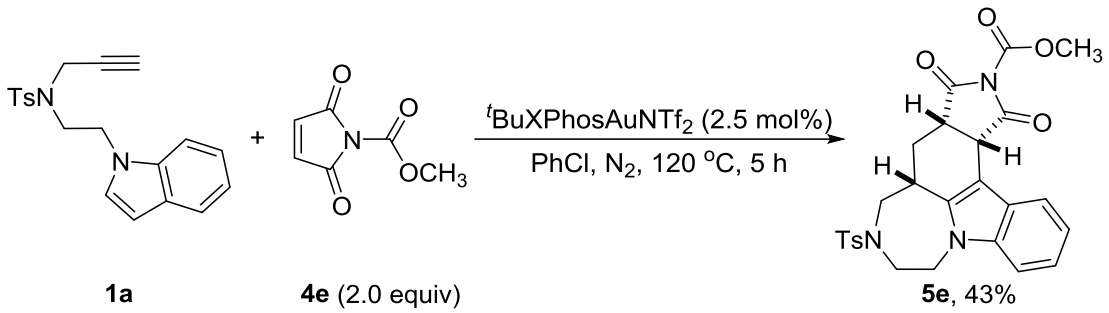


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

methyl 1,3-dioxo-6-tosyl-1,3,3a,4,4a,5,6,7,8,13c-decahydro-2*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-2-carboxylate (5e)



1a **4e** (2.0 equiv) **5e**, 43%

The compound **5e** (yellow solid, 21.8 mg, 43% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **4e** (31.0 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (2.25 mg, 2.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.22) as eluent.

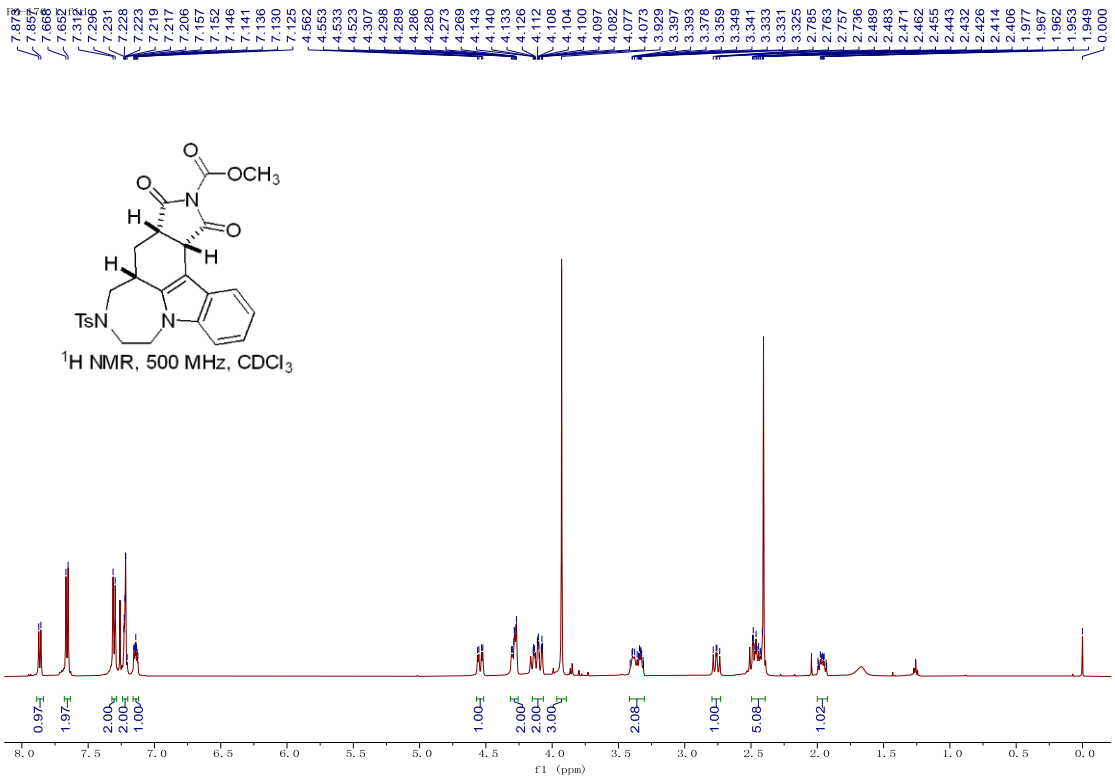
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.86 (d, J = 8.0 Hz, 1H), 7.66 (dt, J = 8.5, 1.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.23-7.21 (m, 2H), 7.16-7.13 (m, 1H), 4.54 (dd, J = 14.5, 4.5 Hz, 1H), 4.31-4.27 (m, 2H), 4.14-4.07 (m, 2H), 3.93 (s, 3H), 3.41-3.31 (m, 2H), 2.76 (dd, J = 14.0, 10.5 Hz, 1H), 2.49-2.41 (m, 5H), 2.00-1.93 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 171.6, 148.9, 144.1, 138.5, 136.9, 135.5, 130.1, 127.1, 126.1, 122.7, 120.6, 120.5, 108.8, 102.5, 54.9, 54.3, 49.8, 46.5, 40.5, 34.9, 28.0, 21.6.

IR (KBr) ν (cm^{-1}): 1772, 1650, 1598, 1464, 1385, 1322, 1252, 1161, 746, 547 cm^{-1}.

HRMS (ESI): calcd for $C_{26}H_{26}N_3O_6S$ $[M+H]^+$: 508.15368, found: 508.15433.

MP: 130-133 °C.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7.668
7.652
7.312
7.296
7.231
7.228
7.223
7.219
7.217
7.206
7.157
7.152
7.146
7.141
7.136
7.130
7.125
4.562
4.553
4.533
4.523
4.307
4.298
4.289
4.286
4.280
4.273
4.269
4.143
4.140
4.133
4.126
4.112
4.108
4.104
4.100
4.097
4.082
4.077
4.073
3.929
3.397
3.393
3.378
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3.349
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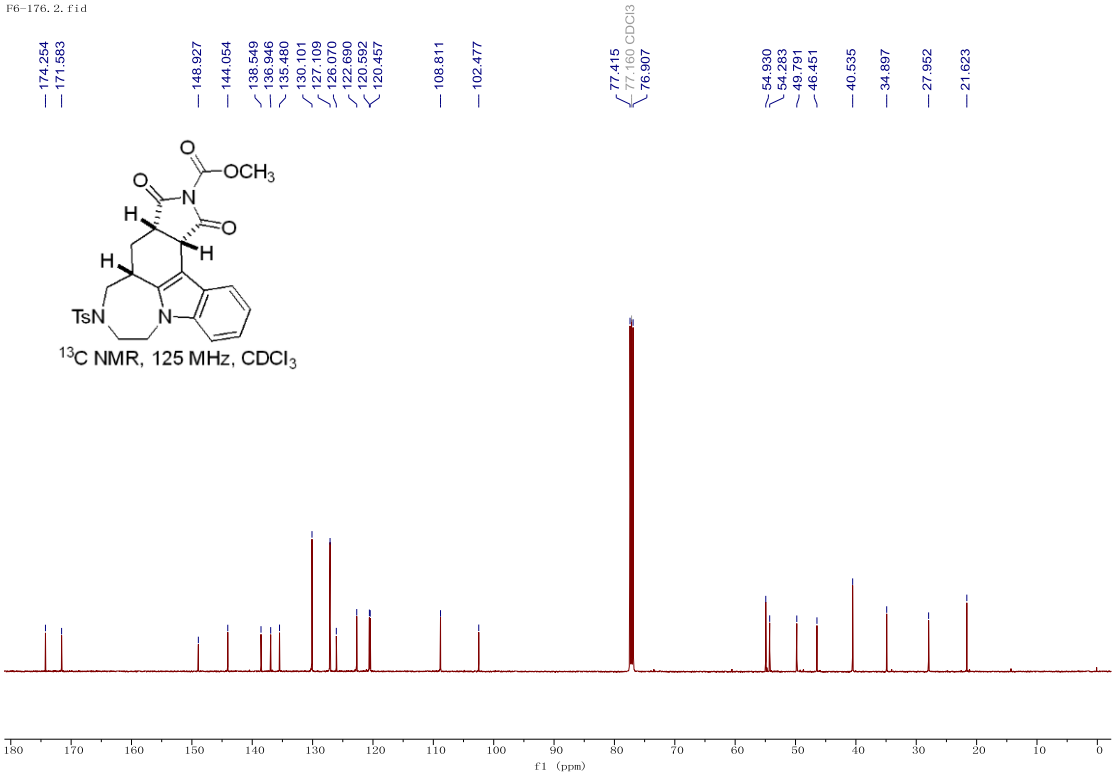
2.471
2.462
2.455
2.443
2.432
2.426
2.414
2.406
1.977
1.967
1.962
1.953
1.949
0.000
OCH3
TsN
1H NMR, 500 MHz, CDCl3
0.97
1.97
2.00
2.00
1.00
1.00
2.00
2.00
3.00
2.08
1.00
5.08
1.02
f1 (ppm)


F6-176.2.fid
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144.054
138.549
136.946
135.480
130.101
127.109
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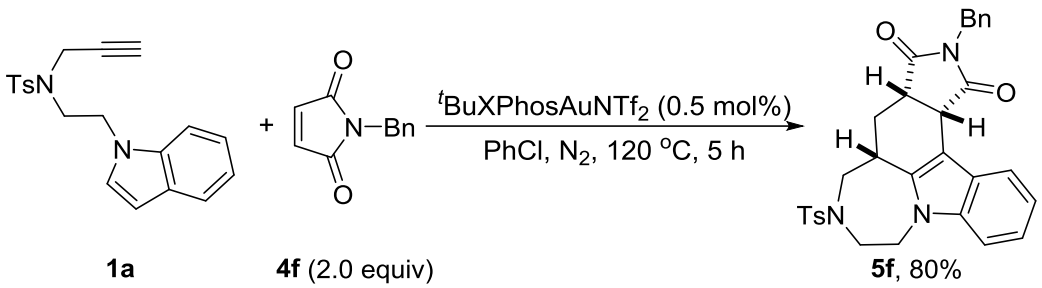
122.690
120.592
120.457
108.811
102.477
77.415
77.160 CDCl3
76.907
54.930
54.283
49.791
46.451
40.535
34.897
27.952
21.623
OCH3
TsN
13C NMR, 125 MHz, CDCl3
f1 (ppm)

2-benzyl-6-tosyl-3a,4,4a,5,6,7,8,13c-octahydro-1*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (5f)



1a **4f** (2.0 equiv) **5f**, 80%

The compound **5f** (yellow solid, 44.7 mg, 80% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **4f** (37.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.20) as eluent.

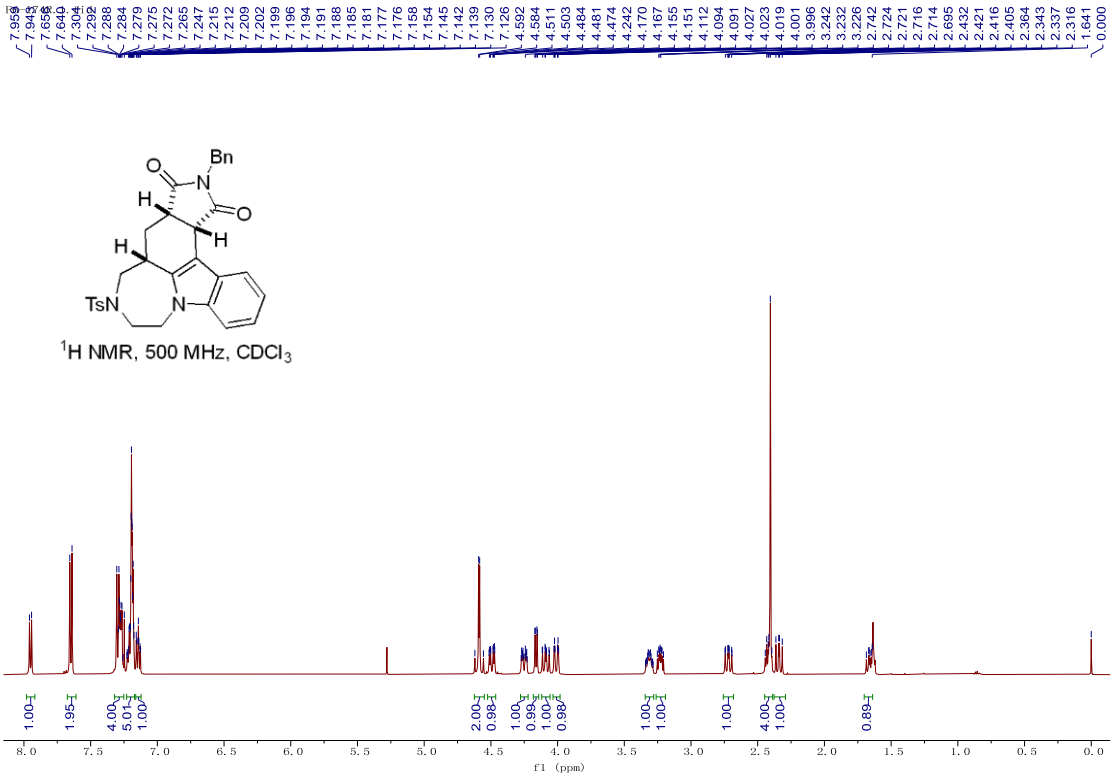
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.95 (dt, J = 8.0, 1.5 Hz, 1H), 7.65 (dt, J = 8.0, 2.0 Hz, 2H), 7.30-7.26 (m, 4H), 7.23-7.18 (m, 5H), 7.16-7.13 (m, 1H), 4.61 (d, J = 14.0 Hz, 1H), 4.57 (d, J = 14.0 Hz, 1H), 4.49 (ddd, J = 14.5, 5.0, 1.0 Hz, 1H), 4.27-4.23 (m, 1H), 4.16 (dd, J = 7.5, 1.5 Hz, 1H), 4.09 (ddd, J = 15.0, 10.5, 1.5 Hz, 1H), 4.01 (dt, J = 13.0, 2.0 Hz, 1H), 3.34-3.28 (m, 1H), 3.25-3.21 (m, 1H), 2.72 (ddd, J = 14.5, 10.5, 1.5 Hz, 1H), 2.44-2.39 (m, 4H), 2.34 (dd, J = 13.5, 10.5 Hz, 1H), 1.69-1.64 (m, 1H).

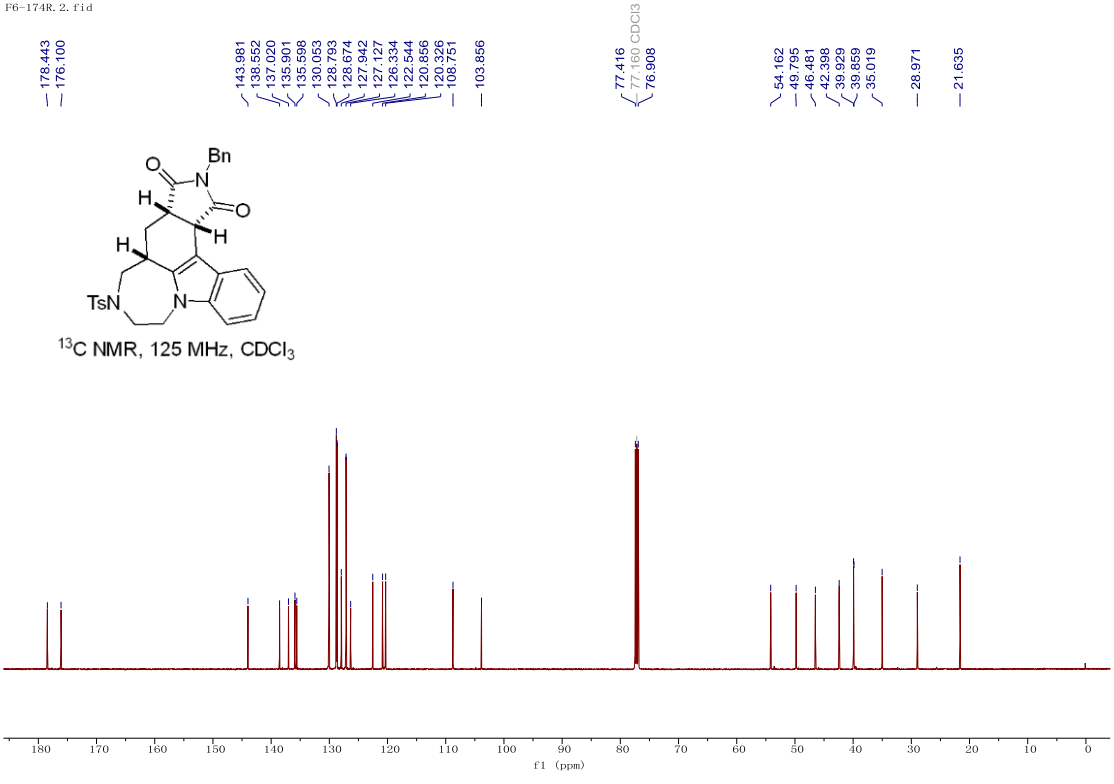
^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 176.1, 144.0, 138.6, 137.0, 135.9, 135.6, 130.1, 128.8, 128.7, 127.9, 127.1, 126.3, 122.5, 120.9, 120.3, 108.8, 103.9, 54.2, 49.8, 46.5, 42.4, 39.93, 39.86, 35.0, 29.0, 21.6.

IR (KBr) ν (cm^{-1}): 1703, 1465, 1429, 1394, 1325, 1159, 1105, 1009, 735 cm^{-1}.

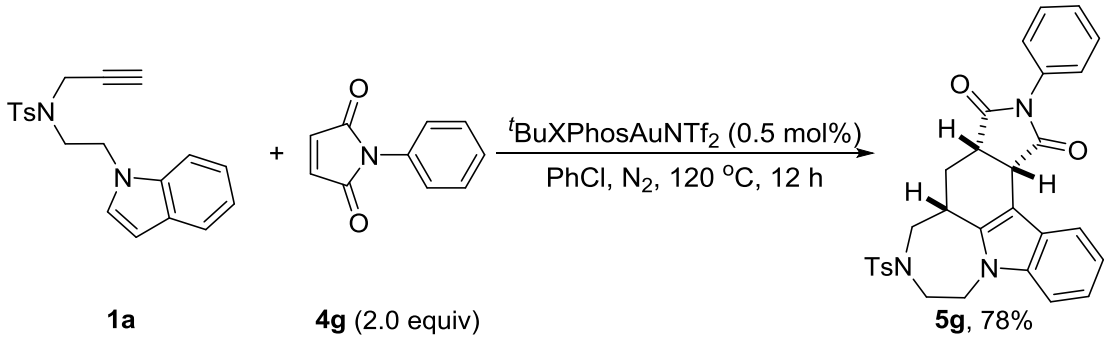
HRMS (ESI): calcd for $C_{31}H_{30}N_3O_4S$ $[M+H]^+$: 540.19515, found: 540.19543.

MP: 202-205 °C.


Bn
O
N
H
O
H
H
TsN
N
1H NMR, 500 MHz, CDCl3
f1 (ppm)


F6-174R.2.fid
CDCl3
Bn
O
N
H
O
H
H
TsN
N
13C NMR, 125 MHz, CDCl3
f1 (ppm)

2-phenyl-6-tosyl-3a,4,4a,5,6,7,8,13c-octahydro-1*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (5g)



1a **4g** (2.0 equiv) **5g**, 78%

The compound **5g** (yellow solid, 41.0 mg, 78% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **4g** (34.6 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.34) as eluent.

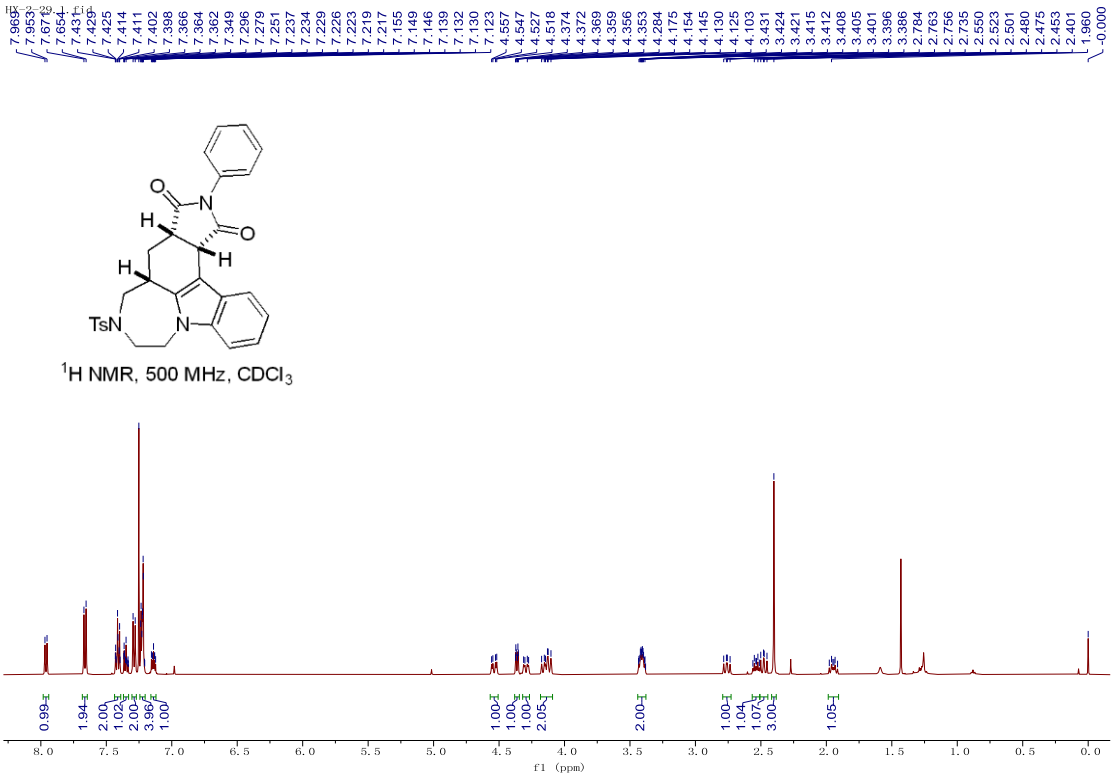
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.96 (dt, J = 8.0, 1.5 Hz, 1H), 7.66 (dt, J = 8.5, 1.5 Hz, 2H), 7.43-7.40 (m, 2H), 7.35 (tt, J = 7.5, 1.0 Hz, 1H), 7.29 (d, J = 8.5 Hz, 2H), 7.24-7.21 (m, 4H), 7.16-7.12 (m, 1H), 4.54 (dd, J = 15.0, 5.0 Hz, 1H), 4.36 (dt, J = 8.0, 1.5 Hz, 1H), 4.29 (dd, J = 14.0, 4.5 Hz, 1H), 4.18-4.10 (m, 2H), 3.43-3.38 (m, 2H), 2.76 (dd, J = 14.0, 10.5 Hz, 1H), 2.56-2.51 (m, 1H), 2.48 (dd, J = 13.0, 10.5 Hz, 1H), 2.40 (s, 3H), 1.98-1.92 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8, 175.3, 144.0, 138.6, 137.1, 135.4, 131.9, 130.1, 129.1, 128.5, 127.2, 126.4, 126.3, 122.6, 120.9, 120.4, 108.8, 103.7, 54.5, 49.9, 46.4, 40.1, 40.0, 34.9, 29.0, 21.7.

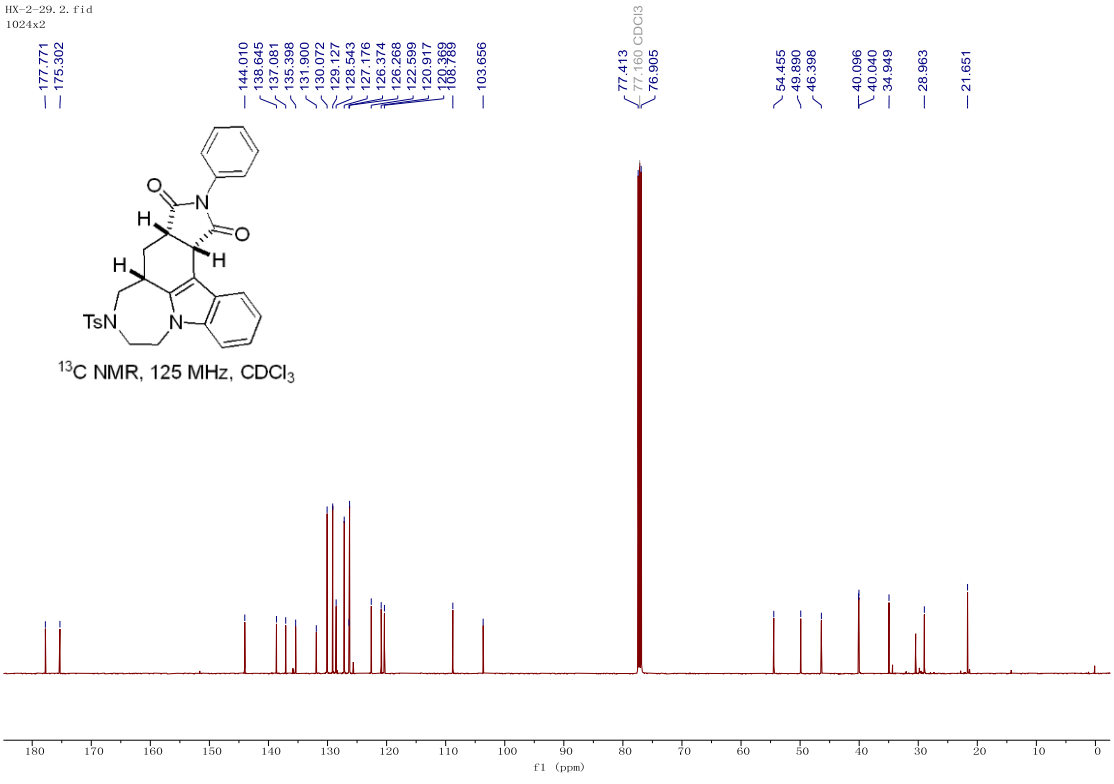
IR (KBr) ν (cm^{-1}): 1715, 1498, 1464, 1378, 1325, 1160, 1102, 1020, 734 cm^{-1}.

HRMS (ESI): calcd for $C_{30}H_{27}N_3NaO_4S$ $[M+Na]^+$: 548.16145, found: 548.16187.

MP: 141-145 °C.

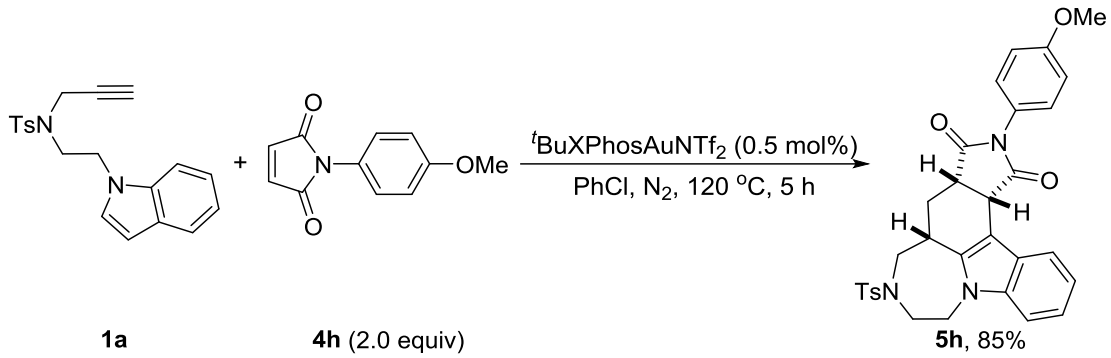


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

2-(4-methoxyphenyl)-6-tosyl-3a,4,4a,5,6,7,8,13c-octahydro-1*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (5h)



The compound **5h** (yellow solid, 47.2 mg, 85% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **4h** (40.6 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 10/4/1 (R_f = 0.12) as eluent.

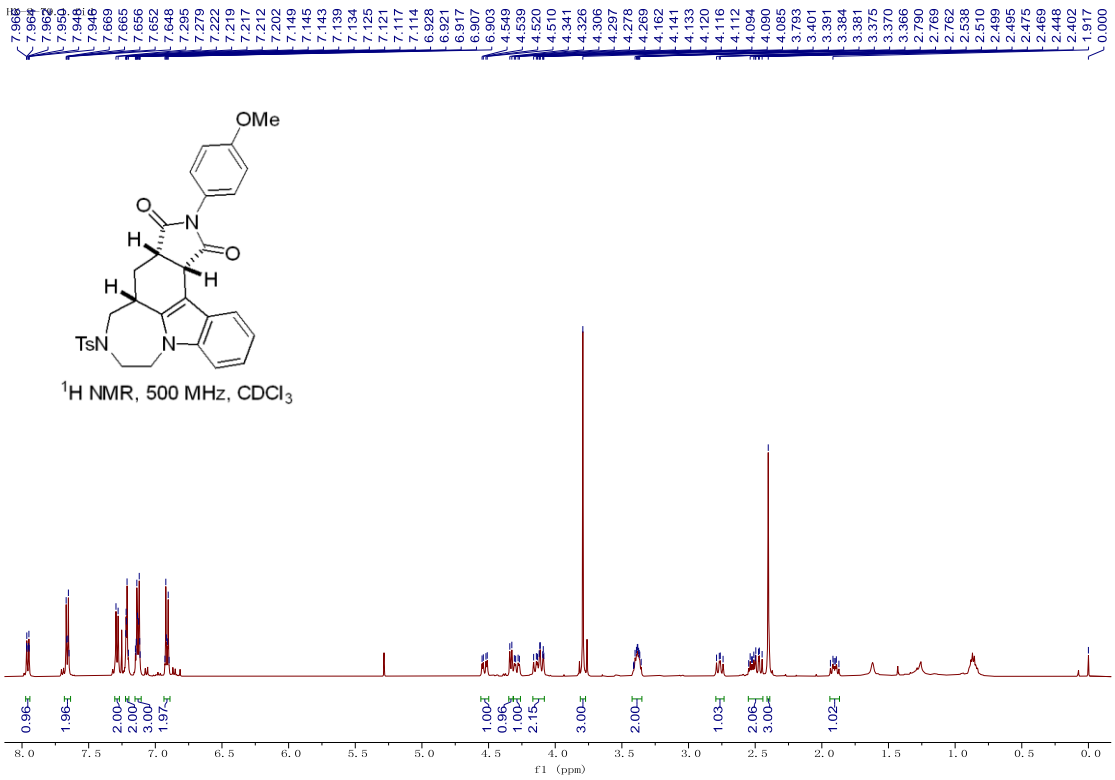
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.96 (dt, J = 8.0, 1.0 Hz, 1H), 7.66 (dt, J = 8.5, 2.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.22-7.20 (m, 2H), 7.15-7.11 (m, 3H), 6.91 (dt, J = 9.0, 2.0 Hz, 2H), 4.53 (dd, J = 14.5, 5.0 Hz, 1H), 4.33 (d, J = 7.5 Hz, 1H), 4.29 (dd, J = 14.0, 4.5 Hz, 1H), 4.16-4.09 (m, 2H), 3.79 (s, 3H), 3.41-3.36 (m, 2H), 2.77 (dd, J = 14.0, 10.5 Hz, 1H), 2.55-2.45 (m, 2H), 2.40 (s, 3H), 1.94-1.87 (m, 1H).

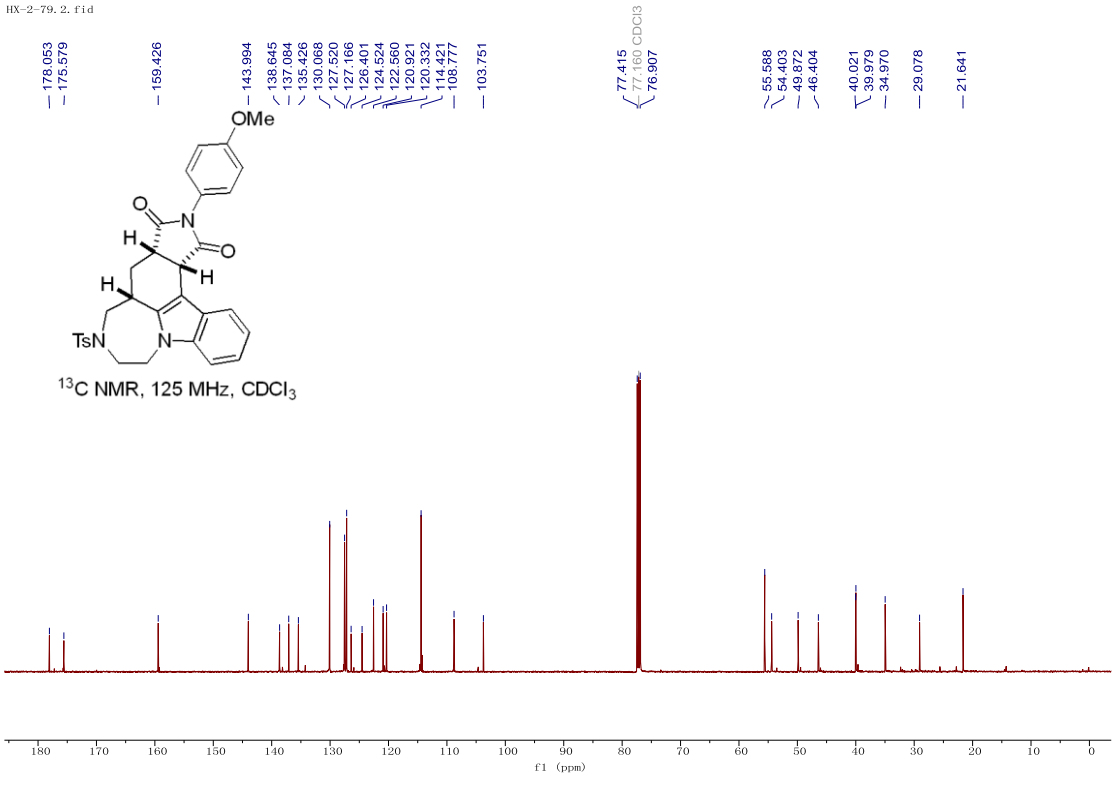
^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 175.6, 159.4, 144.0, 138.6, 137.1, 135.4, 130.1, 127.5, 127.2, 126.4, 124.5, 122.6, 120.9, 120.3, 114.4, 108.8, 103.8, 55.6, 54.4, 49.9, 46.4, 40.02, 39.98, 35.0, 29.1, 21.6.

IR (KBr) ν (cm^{-1}): 1713, 1597, 1513, 1385, 1327, 1250, 1161, 736, 548 cm^{-1}.

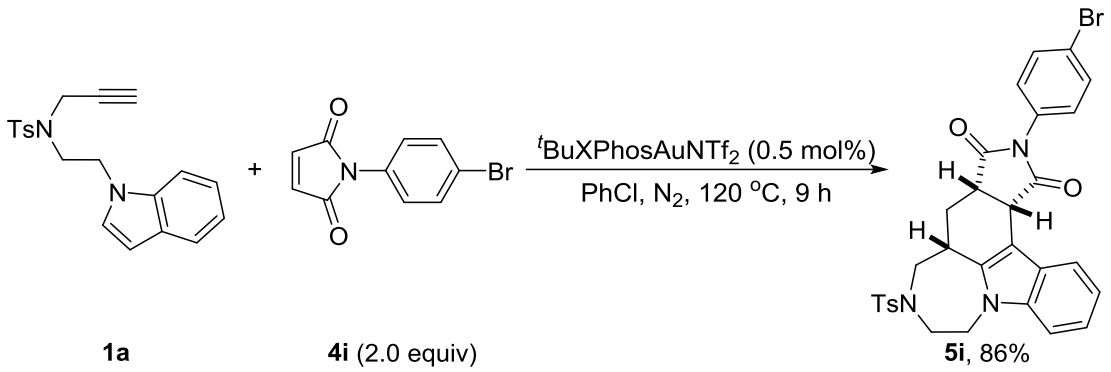
HRMS (ESI): calcd for $C_{31}H_{30}N_3O_5S$ $[M+H]^+$: 556.19007, found: 556.19025.

MP: 124-126 °C.


OMe
TsN
^{1}H NMR, 500 MHz, $CDCl_3$


OMe
TsN
^{13}C NMR, 125 MHz, $CDCl_3$

2-(4-bromophenyl)-6-tosyl-3a,4,4a,5,6,7,8,13c-octahydro-1*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (5i)



1a **4i** (2.0 equiv) **5i**, 86%

The compound **5i** (white solid, 51.9 mg, 86% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **4i** (50.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.30) as eluent.

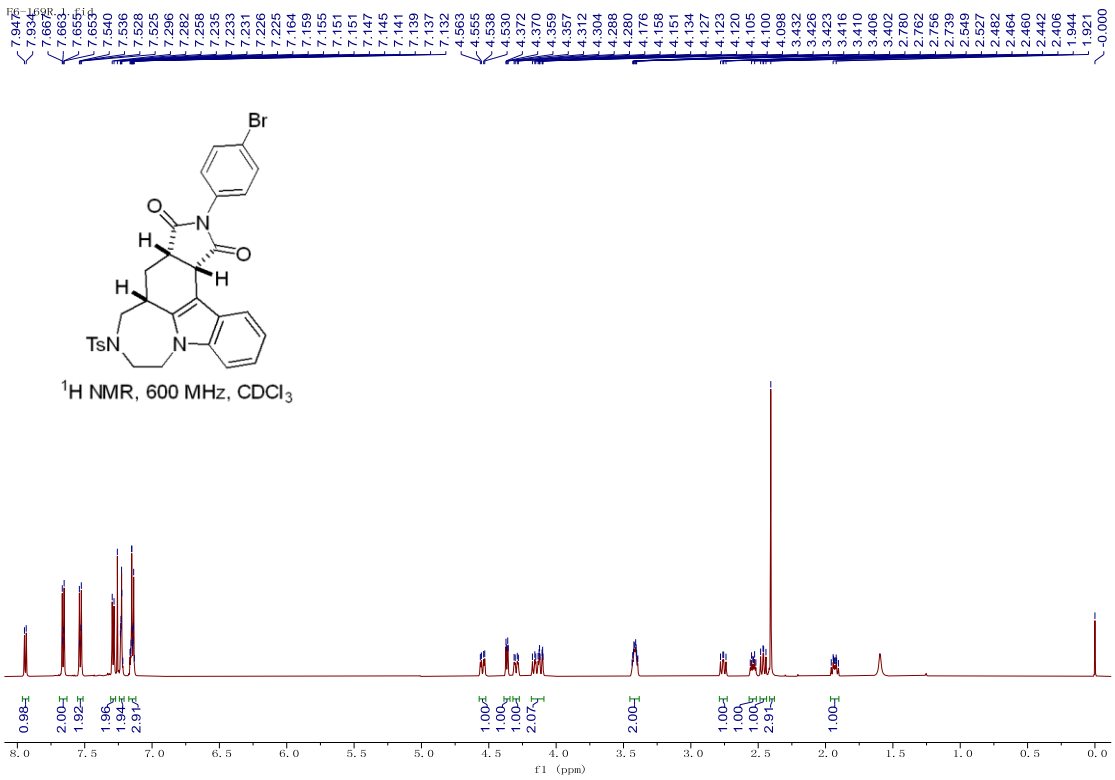
^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.94 (d, J = 7.8 Hz, 1H), 7.66 (dt, J = 8.4, 2.4 Hz, 2H), 7.53 (dt, J = 9.0, 2.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.24-7.22 (m, 2H), 7.16-7.13 (m, 3H), 4.55 (dd, J = 15.0, 4.8 Hz, 1H), 4.37 (dd, J = 7.8, 1.2 Hz, 1H), 4.30 (dd, J = 14.4, 4.8 Hz, 1H), 4.18-4.10 (m, 2H), 3.44-3.39 (m, 2H), 2.76 (dd, J = 14.4, 10.8 Hz, 1H), 2.54 (dt, J = 13.2, 5.4 Hz, 1H), 2.46 (dd, J = 13.2, 10.8 Hz, 1H), 2.41 (s, 3H), 1.96-1.90 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 175.0, 144.1, 138.7, 137.1, 135.4, 132.3, 130.9, 130.1, 127.7, 127.2, 126.3, 122.7, 122.3, 120.8, 120.4, 108.8, 103.4, 54.4, 49.9, 46.4, 40.1, 40.0, 34.9, 28.9, 21.7.

IR (KBr) ν (cm^{-1}): 1716, 1490, 1464, 1378, 1326, 1160, 1102, 1013, 738, 548 cm^{-1}.

HRMS (ESI): calcd for $C_{30}H_{27}BrN_3O_4S$ $[M+H]^+$: 604.09002, found: 604.08985.

MP: 202-205 °C.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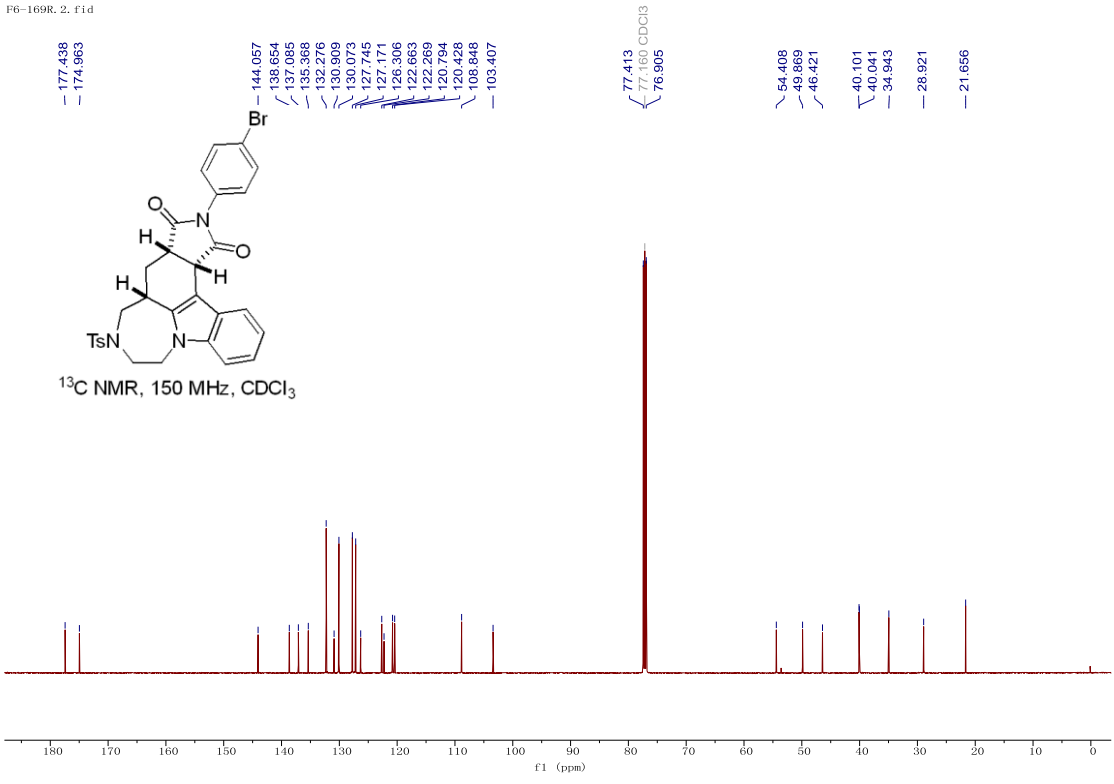
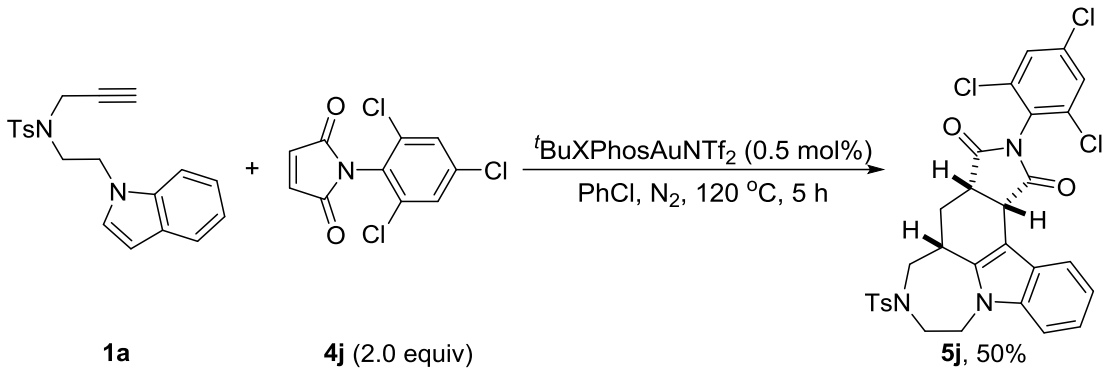
Br
TsN
^{1}H NMR, 600 MHz, CDCl$_3$
f1 (ppm)


F6-169R.2.fid
77.160 CDCl3
Br
TsN
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)

6-tosyl-2-(2,4,6-trichlorophenyl)-3a,4,4a,5,6,7,8,13c-octahydro-1*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (5j)



1a **4j** (2.0 equiv) **5j**, 50%

The compound **5j** (yellow solid, 31.5 mg, 50% yield) was obtained following General Procedure B from **1a** (35.2 mg, 0.1 mmol, 1.0 equiv) and **4j** (55.3 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 10/4/1 (R_f = 0.27) as eluent.

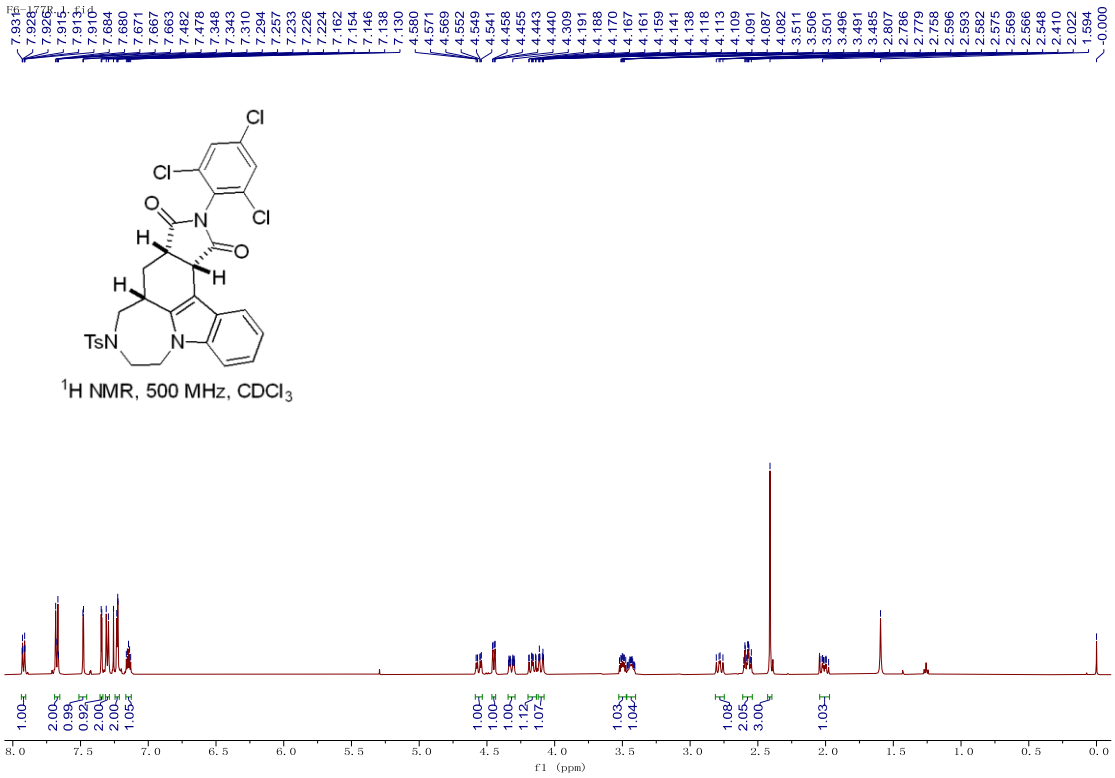
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.92 (dt, J = 7.5, 1.0 Hz, 1H), 7.67 (dt, J = 8.5, 2.0 Hz, 2H), 7.48 (d, J = 2.0 Hz, 1H), 7.35 (d, J = 2.5 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.23-7.22 (m, 2H), 7.16-7.13 (m, 1H), 4.58-4.54 (m, 1H), 4.45 (dd, J = 7.5, 1.5 Hz, 1H), 4.34-4.30 (m, 1H), 4.16 (ddd, J = 15.0, 10.5, 1.5 Hz, 1H), 4.10 (dt, J = 13.0, 2.5 Hz, 1H), 3.52-3.48 (m, 1H), 3.47-3.41 (m, 1H), 2.78 (dd, J = 14.0, 10.5 Hz, 1H), 2.60-2.55 (m, 2H), 2.41 (s, 3H), 2.04-1.98 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 173.5, 144.0, 138.7, 137.1, 136.6, 135.5, 135.4, 135.2, 130.1, 129.0, 128.8, 127.2, 126.9, 126.3, 122.7, 120.8, 120.5, 108.8, 103.4, 54.1, 50.0, 46.7, 40.8, 40.6, 35.2, 29.2, 21.7.

IR (KBr) ν (cm^{-1}): 1720, 1631, 1598, 1468, 1384, 1325, 1165, 814, 740, 549 cm^{-1}.

HRMS (ESI): calcd for $C_{30}H_{25}Cl_3N_3O_4S$ $[M+H]^+$: 628.06259, found: 628.06293.

MP: 196-198 °C.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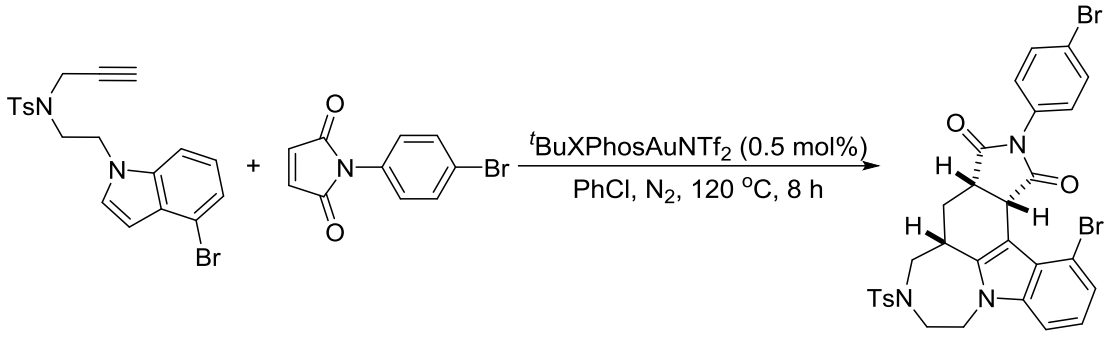
7.931 7.928 7.926 7.915 7.913 7.910 7.684 7.680 7.671 7.667 7.663 7.482 7.478 7.348 7.343 7.310 7.294 7.257 7.233 7.226 7.224 7.162 7.154 7.146 7.138 7.130 4.580 4.571 4.569 4.552 4.549 4.541 4.458 4.455 4.443 4.440 4.309 4.191 4.188 4.170 4.167 4.161 4.159 4.141 4.138 4.118 4.113 4.109 4.091 4.087 4.082 3.511 3.506 3.501 3.496 3.491 3.485 2.807 2.786 2.779 2.758 2.596 2.593 2.582 2.575 2.569 2.566 2.548 2.410 2.022 1.594 -0.000
Cl
Cl
Cl
O
N
H
O
H
H
TsN
N
1H NMR, 500 MHz, CDCl3
1.00 2.00 0.99 0.92 2.00 2.00 1.05 1.00 1.00 1.12 1.07 1.03 1.04 1.08 2.05 3.00 1.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
F6-177R.2.fid
175.903 173.473 144.025 138.699 137.074 136.614 135.514 135.374 135.190 130.099 128.977 128.830 127.175 126.941 126.293 122.687 120.761 120.454 108.837 103.365 77.412 77.166 CDCl3 76.904 54.112 50.015 46.663 40.787 40.638 35.206 29.175 21.662
Cl
Cl
Cl
O
N
H
O
H
H
TsN
N
13C NMR, 125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

13-bromo-2-(4-bromophenyl)-6-tosyl-3a,4,4a,5,6,7,8,13c-octahydro-1*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (5k)



1o **4i** (2.0 equiv) **5k**, 56%

The compound **5k** (white solid, 38.2 mg, 56% yield) was obtained following General Procedure B from **1o** (43.1 mg, 0.1 mmol, 1.0 equiv) and **4i** (50.4 mg, 0.2 mmol, 2.0 equiv) using [^{t}BuXPhosAuNTf$_2$] (0.45 mg, 0.5 mol%) after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.20) as eluent.

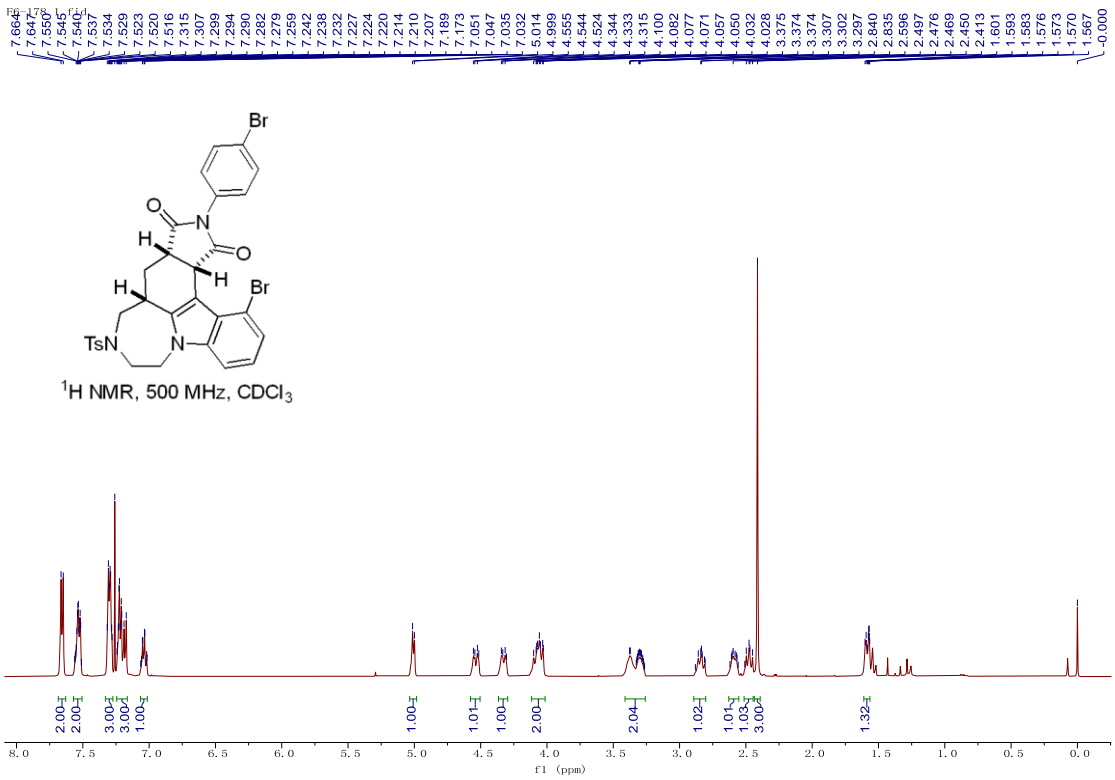
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.66 (d, J = 8.5 Hz, 2H), 7.56-7.51 (m, 2H), 7.32-7.28 (m, 3H), 7.24-7.17 (m, 3H), 7.06-7.02 (m, 1H), 5.01 (d, J = 7.5 Hz, 1H), 4.53 (dd, J = 15.5, 5.5 Hz, 1H), 4.34-4.31 (m, 1H), 4.10-4.03 (m, 2H), 3.38-3.26 (m, 2H), 2.88-2.81 (m, 1H), 2.62-2.56 (m, 1H), 2.51-2.45 (m, 1H), 2.41 (s, 3H), 1.60-1.57 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 174.9, 144.2, 139.7, 138.3, 135.2, 132.3, 131.1, 130.2, 127.7, 127.2, 125.4, 124.9, 123.2, 122.1, 114.3, 108.4, 103.6, 53.7, 49.7, 47.0, 41.2, 40.4, 35.5, 30.3, 21.7.

IR (KBr) ν (cm^{-1}): 1716, 1632, 1596, 1491, 1382, 1324, 1163, 740, 549 cm^{-1}.

HRMS (ESI): calcd for $C_{30}H_{25}Br_2N_3NaO_4S$ $[M+Na]^+$: 703.98247, found: 703.98285.

MP: 245-247 °C.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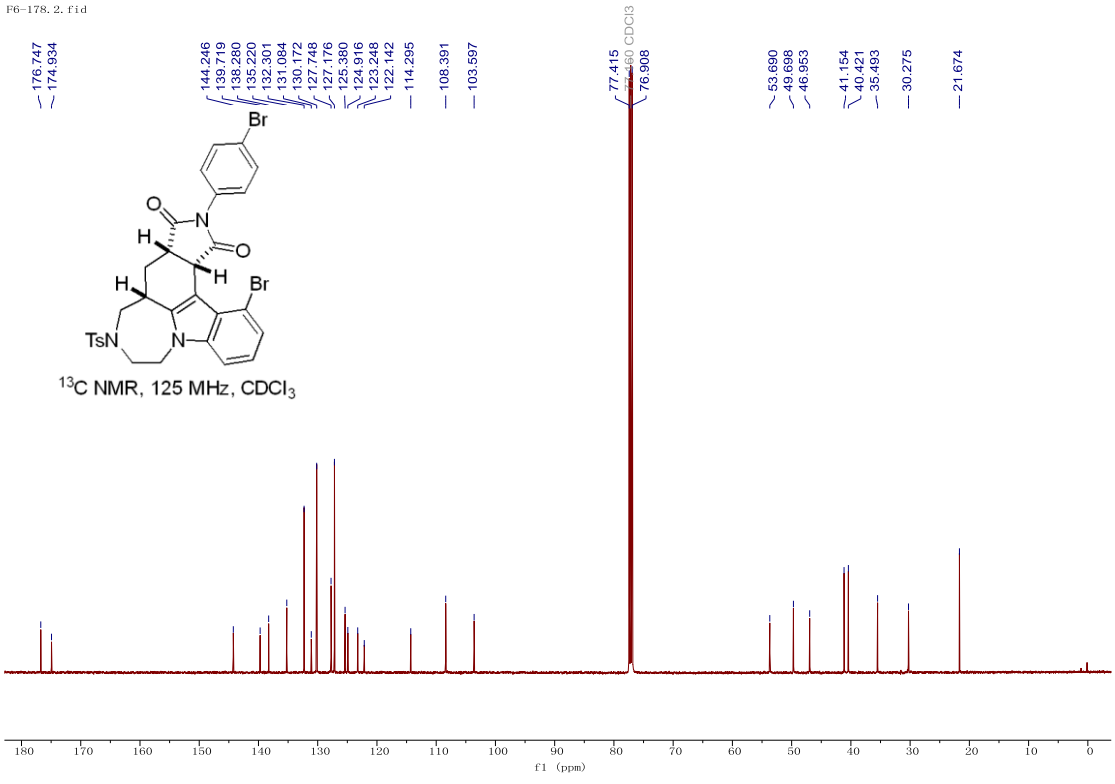
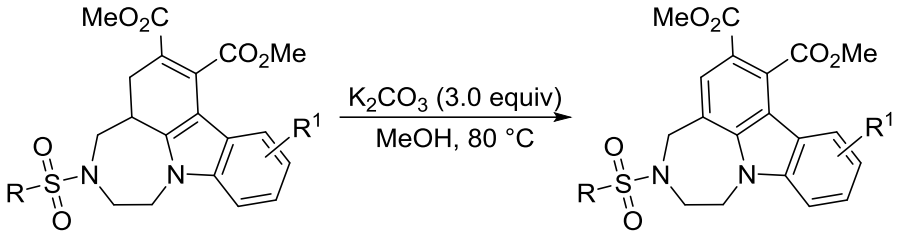
O
N
H
O
H
H
Br
TsN
N
1H NMR, 500 MHz, CDCl3
f1 (ppm)


F6-178.2.fid
CDCl3
Br
O
N
H
O
H
H
Br
TsN
N
13C NMR, 125 MHz, CDCl3
f1 (ppm)

5. General Procedure for the Synthesis of 6

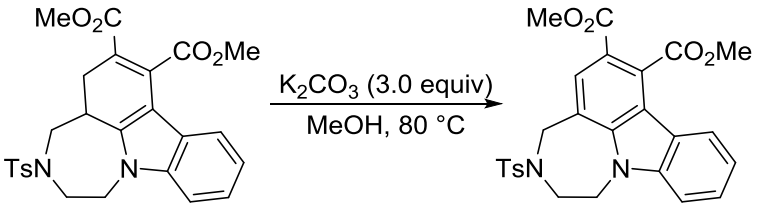
5.1 General Procedure C for 6a-f



3 **6a-f**

MeOH (1.0 mL) was added to a mixture of **3** (0.02-0.05 mmol, 1.0 equiv) and K_2CO_3 (3.0 equiv). Then the reaction was stirred at 80 °C and was complete as monitored by TLC. The mixture was concentrated under vacuum and purified by flash column chromatography using petroleum ether/DCM/THF as eluent to give the desired product **6a-f**.

Dimethyl 3-tosyl-1,2,3,4-tetrahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicaboxylate (6a)



3a **6a**, 78%

The compound **6a** (white solid, 19.2 mg, 78% yield) was obtained following General Procedure C from **3a** (24.7 mg, 0.05 mmol, 1.0 equiv), after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.20) as eluent.

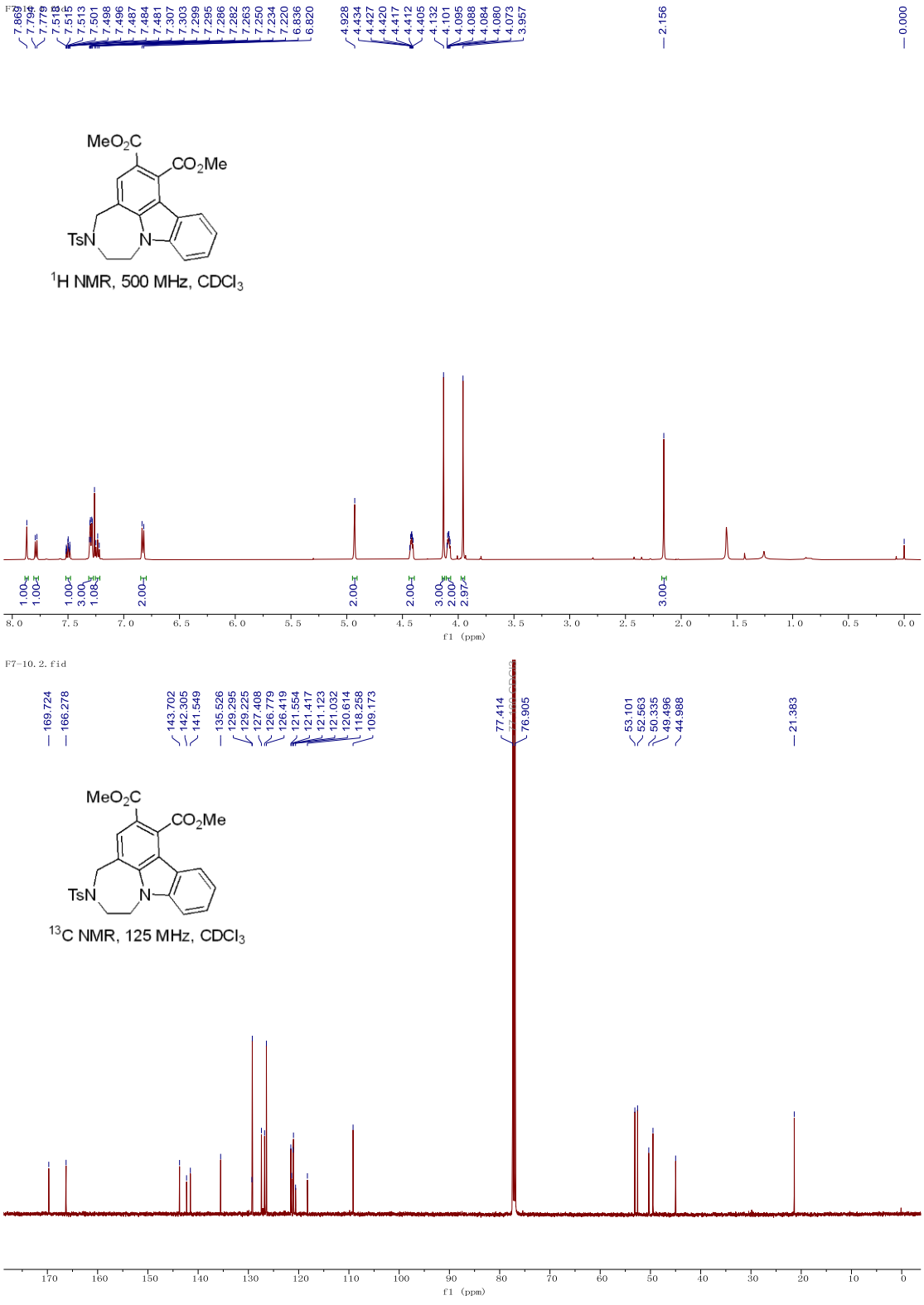
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.87 (s, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.52-7.48 (m, 1H), 7.31-7.28 (m, 3H), 7.23 (t, J = 8.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 4.93 (s, 2H), 4.43-4.41 (m, 2H), 4.13 (s, 3H), 4.10-4.07 (m, 2H), 3.96 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 166.3, 143.7, 142.3, 141.5, 135.5, 129.3, 129.2, 127.4, 126.8, 126.4, 121.6, 121.4, 121.1, 121.0, 120.6, 118.3, 109.2, 53.1, 52.6, 50.3, 49.5, 45.0, 21.4.

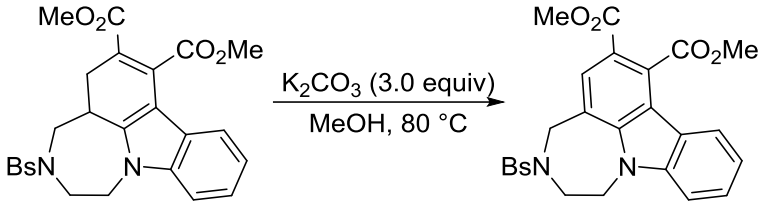
IR (KBr) ν (cm^{-1}): 1732, 1717, 1443, 1339, 1269, 1231, 1157, 1138, 745 cm^{-1}.

HRMS (ESI): calcd for $C_{26}H_{24}N_2NaO_6S$ $[M+Na]^+$: 515.12473, found: 515.12482.

MP: 195-198 ºC.



Dimethyl 3-((4-bromophenyl)sulfonyl)-1,2,3,4-tetrahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (6b)



The compound **6b** (white solid, 12.4 mg, 43% yield) was obtained following General Procedure C from **3e** (28.0 mg, 0.05 mmol, 1.0 equiv), after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.19) as eluent.

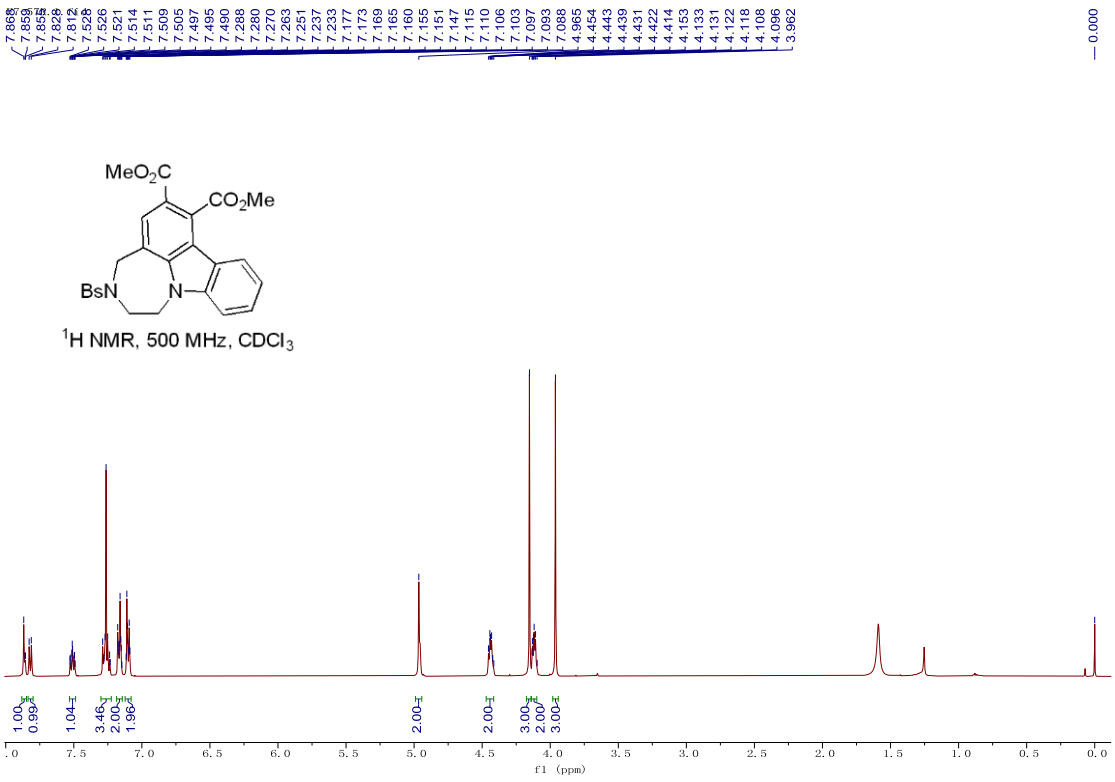
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.87-7.86 (m, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.53-7.49 (m, 1H), 7.29-7.23 (m, 2H), 7.18-7.15 (m, 2H), 7.12-7.09 (m, 2H), 4.97 (s, 2H), 4.45-4.41 (m, 2H), 4.15 (s, 3H), 4.13-4.10 (m, 2H), 3.96 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 166.2, 142.3, 141.3, 137.7, 131.7, 129.4, 127.73, 127.66, 127.57, 126.8, 122.0, 121.3, 121.2, 120.9, 120.6, 118.5, 108.9, 53.2, 52.6, 49.9, 49.7, 44.4.

IR (KBr) ν (cm^{-1}): 1732, 1713, 1339, 1273, 1234, 1227, 1165, 752 cm^{-1}.

HRMS (ESI): calcd for $C_{25}H_{21}BrN_2NaO_6S$ $[M+Na]^+$: 579.01959, found: 579.01990.

MP: 197-200 °C.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7.514
7.511
7.509
7.505
7.497
7.495
7.490
7.288
7.280
7.270
7.263
7.251
7.237
7.233
7.177
7.173
7.169
7.165
7.160
7.155
7.151
7.147
7.115
7.110
7.106
7.103
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7.093
7.088
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4.439
4.431
4.422
4.414
4.153
4.133
4.131
4.122
4.118
4.108
4.096
3.962
0.000
MeO2C
CO2Me
BsN
N
1H NMR, 500 MHz, CDCl3
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0.99
1.04
3.46
2.00
1.96
2.00
2.00
3.00
2.00
3.00
f1 (ppm)
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142.296
141.334
137.666
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129.443
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127.659
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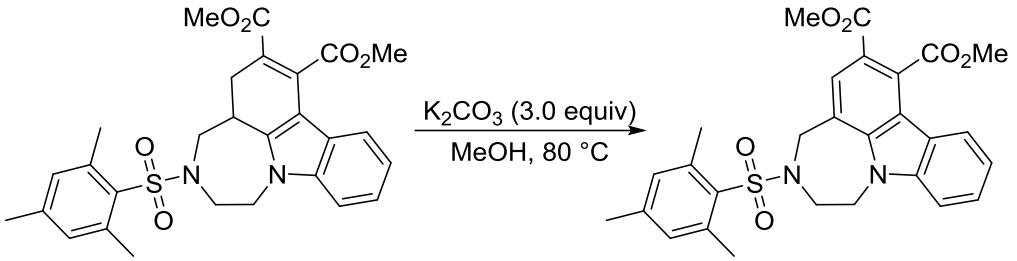
126.759
121.963
121.334
121.247
120.677
120.585
118.495
108.868
77.414
76.906
53.164
52.626
49.881
49.695
44.434
MeO2C
CO2Me
BsN
N
13C NMR, 125 MHz, CDCl3
f1 (ppm)

dimethyl 3-(mesitylsulfonyl)-1,2,3,4-tetrahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (6c)



3c **6c**, 52%

The compound **6c** (white solid, 13.6 mg, 52% yield) was obtained following General Procedure C from **3c** (26.1 mg, 0.05 mmol, 1.0 equiv), after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.30) as eluent.

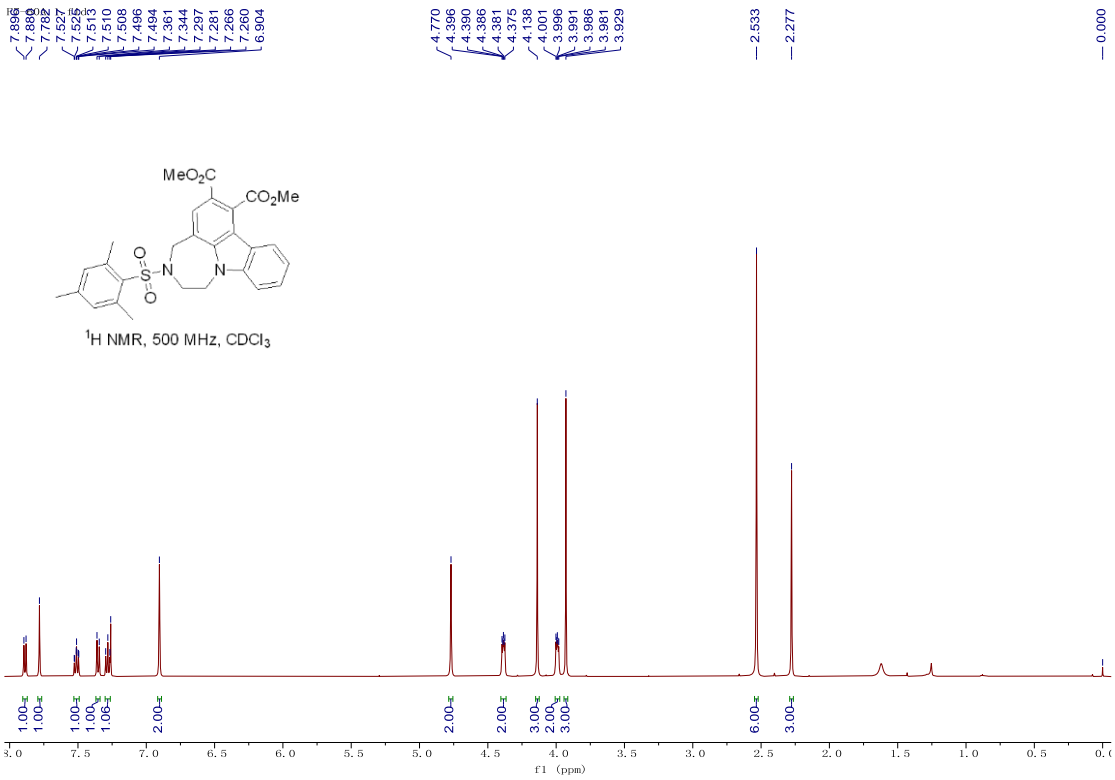
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.89 (d, J = 8.0 Hz, 1H), 7.78 (s, 1H), 7.53-7.49 (m, 1H), 7.35 (d, J = 8.5 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 6.90 (s, 2H), 4.77 (s, 2H), 4.40-4.38 (m, 2H), 4.14 (s, 3H), 4.00-3.98 (m, 2H), 3.93 (s, 3H), 2.53 (s, 6H), 2.28 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 166.3, 143.2, 142.3, 142.2, 140.5, 132.3, 131.9, 129.1, 127.4, 126.3, 122.2, 121.7, 121.6, 121.3, 121.1, 118.1, 109.7, 53.1, 52.5, 50.7, 48.0, 46.6, 23.0, 21.1.

IR (KBr) ν (cm^{-1}): 1732, 1721, 1327, 1315, 1269, 1227, 1146, 741 cm^{-1}.

HRMS (ESI): calcd for $C_{28}H_{28}N_2NaO_6S$ $[M+Na]^+$: 543.15603, found: 543.15637.

MP: 210-212 °C.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7.527
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7.508
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7.297
7.281
7.266
7.260
6.904
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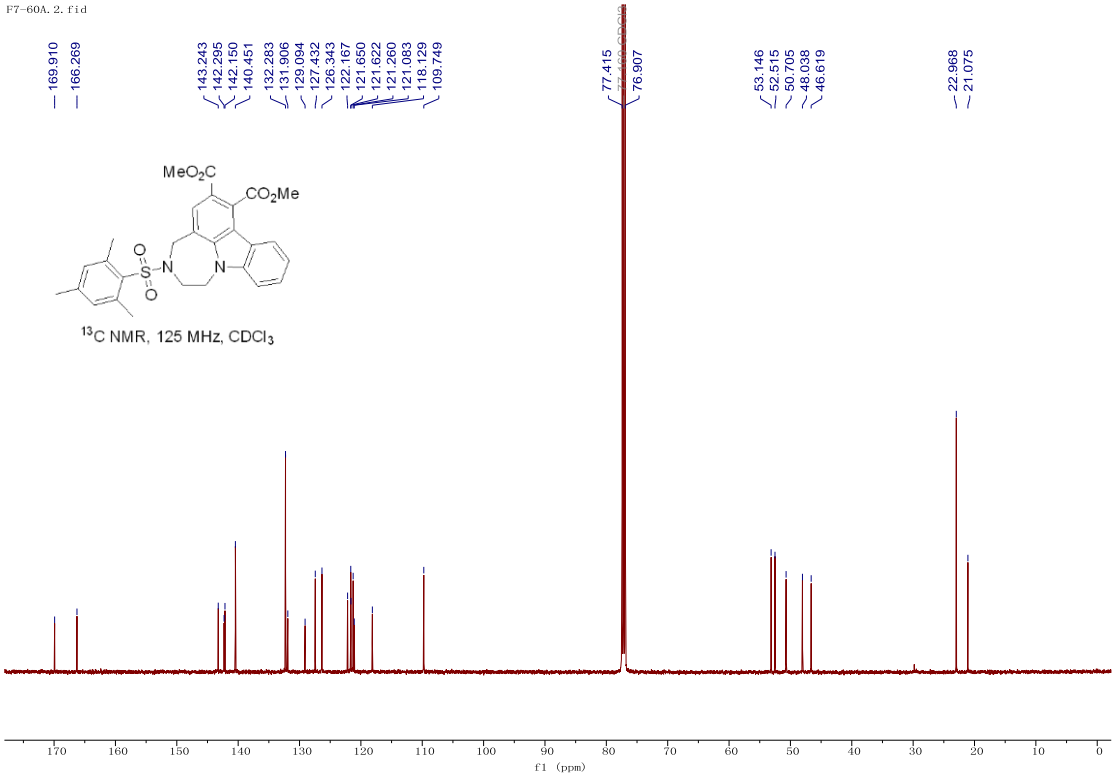
4.396
4.390
4.386
4.381
4.375
4.138
4.001
3.996
3.991
3.986
3.981
3.929
2.533
2.277
0.000
MeO2C
CO2Me
1H NMR, 500 MHz, CDCl3
1.00
1.00
1.00
1.00
1.06
2.00
2.00
2.00
3.00
2.00
3.00
6.00
3.00
f1 (ppm)


F7-60A. 2. fid
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143.243
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142.150
140.451
132.283
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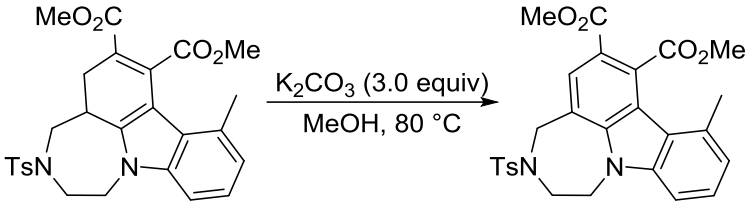
126.343
122.167
121.650
121.622
121.260
121.083
118.129
109.749
77.415
76.907
53.146
52.515
50.705
48.038
46.619
22.968
21.075
MeO2C
CO2Me
13C NMR, 125 MHz, CDCl3
f1 (ppm)

dimethyl 8-methyl-3-tosyl-1,2,3,4-tetrahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (6d)



The compound **6d** (white solid, 14.3 mg, 70% yield) was obtained following General Procedure C from **3g** (21.8 mg, 0.04 mmol, 1.0 equiv), after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.27) as eluent.

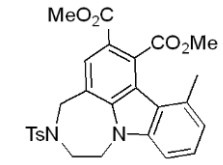
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.86 (d, J = 1.5 Hz, 1H), 7.37-7.34 (m, 1H), 7.11-7.07 (m, 3H), 7.00 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 8.0 Hz, 2H), 4.98 (d, J = 2.5 Hz, 2H), 4.42-4.39 (m, 2H), 4.09-4.06 (m, 2H), 4.04 (s, 3H), 3.94 (s, 3H), 2.64 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 166.6, 143.3, 143.0, 141.9, 135.3, 134.6, 130.8, 128.8, 127.4, 127.1, 126.1, 124.0, 121.0, 120.7, 120.0, 118.7, 106.3, 52.9, 52.5, 49.3, 48.6, 43.3, 22.0, 21.2.

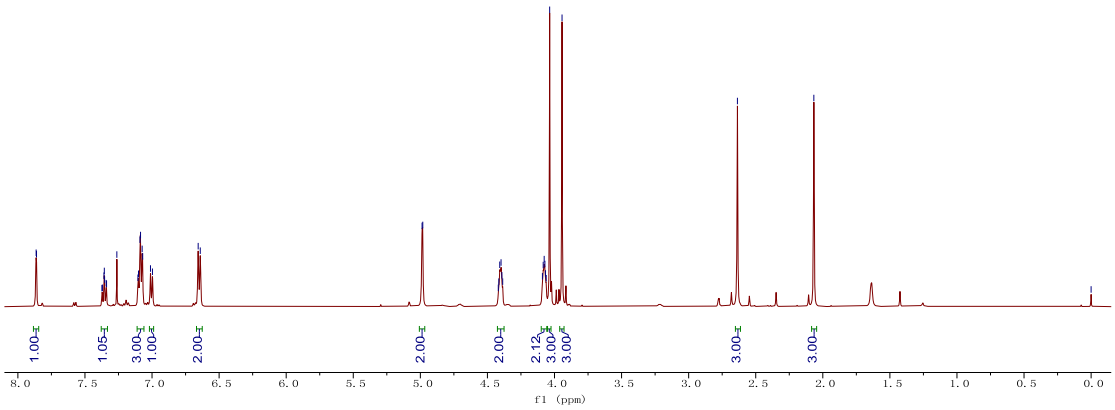
IR (KBr) ν (cm^{-1}): 1724, 1562, 1342, 1277, 1250, 1207, 1157, 787 cm^{-1}.

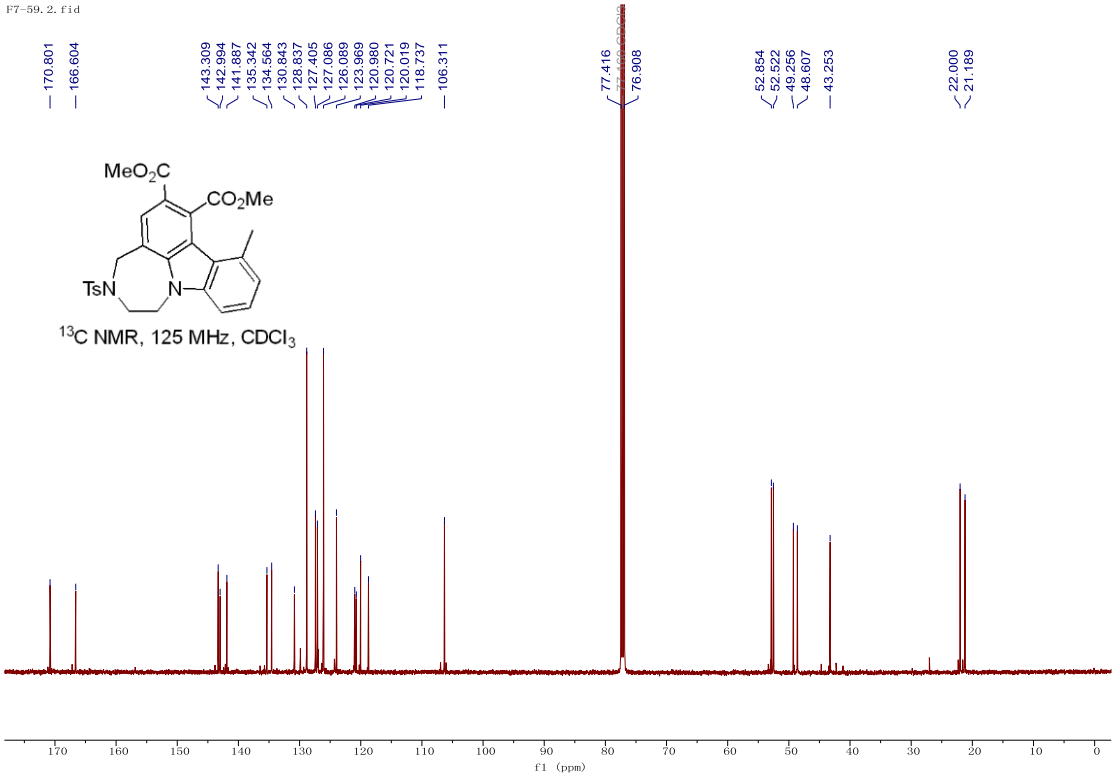
HRMS (ESI): calcd for $C_{27}H_{26}N_2NaO_6S$ $[M+Na]^+$: 529.14038, found: 529.14014.

MP: 157-160 °C.



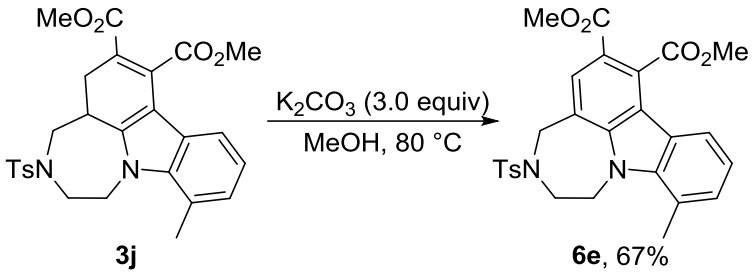
^{1}H NMR, 500 MHz, $CDCl_3$





^{13}C NMR, 125 MHz, $CDCl_3$

dimethyl 11-methyl-3-tosyl-1,2,3,4-tetrahydro-[1,4]diazepino[6,7,1-*jk*]carbazole-6,7-dicarboxylate (6e)



3j **6e**, 67%

The compound **6e** (white solid, 10.2 mg, 67% yield) was obtained following General Procedure C from **3j** (15.2 mg, 0.03 mmol, 1.0 equiv), after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.22) as eluent.

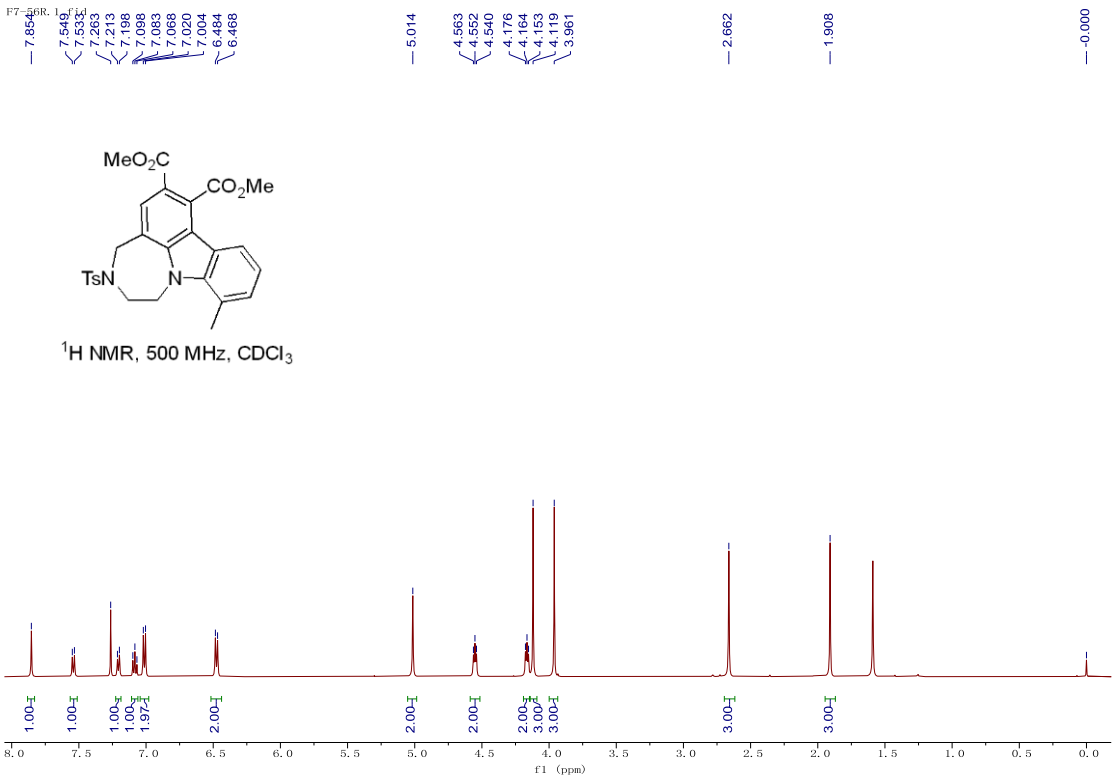
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.85 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.48 (d, J = 8.0 Hz, 2H), 5.01 (s, 2H), 4.55 (t, J = 5.5 Hz, 2H), 4.16 (t, J = 5.5 Hz, 2H), 4.12 (s, 3H), 3.96 (s, 3H), 2.66 (s, 3H), 1.91 (s, 3H).

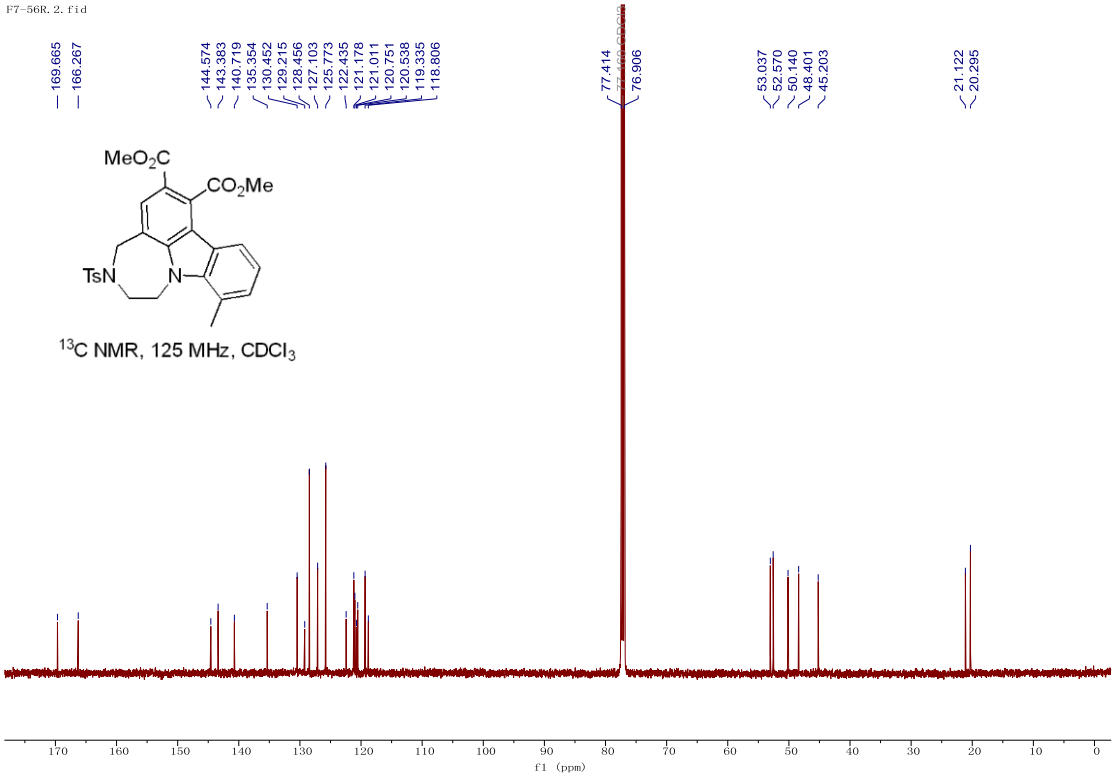
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 166.3, 144.6, 143.4, 140.7, 135.4, 130.5, 129.2, 128.5, 127.1, 125.8, 122.4, 121.2, 121.0, 120.8, 120.5, 119.3, 118.8, 53.0, 52.6, 50.1, 48.4, 45.2, 21.1, 20.3.

IR (KBr) ν (cm^{-1}): 1732, 1701, 1339, 1273, 1231, 1227, 1157, 798 cm^{-1}.

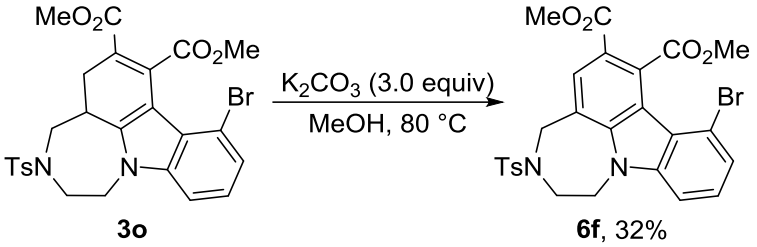
HRMS (ESI): calcd for $C_{27}H_{26}N_2NaO_6S$ $[M+Na]^+$: 529.14038, found: 529.14050.

MP: 192-195 °C.


F7-56R. 1. fid
7.854
7.549
7.533
7.263
7.213
7.198
7.098
7.083
7.068
7.020
7.004
6.484
6.468
5.014
4.563
4.552
4.540
4.176
4.164
4.153
4.119
3.961
2.662
1.908
-0.000
MeO2C
CO2Me
TsN
N
1H NMR, 500 MHz, CDCl3
1.00
1.00
1.00
1.00
1.97
2.00
2.00
2.00
2.00
3.00
3.00
3.00
f1 (ppm)


F7-56R. 2. fid
169.665
166.267
144.574
143.383
140.719
135.354
130.452
129.215
128.456
127.103
125.773
122.435
121.178
121.011
120.751
120.538
119.335
118.806
77.414
76.906
53.037
52.570
50.140
48.401
45.203
21.122
20.295
MeO2C
CO2Me
TsN
N
13C NMR, 125 MHz, CDCl3
f1 (ppm)

dimethyl 8-bromo-3-tosyl-1,2,3,4-tetrahydro-[1,4]diazepino[6,7,1-jk]carbazole-6,7-dicarboxylate (6f)



3o **6f**, 32%

The compound **6f** (yellow solid, 9.1 mg, 32% yield) was obtained following General Procedure C from **3o** (28.7 mg, 0.05 mmol, 1.0 equiv), after purification by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.18) as eluent.

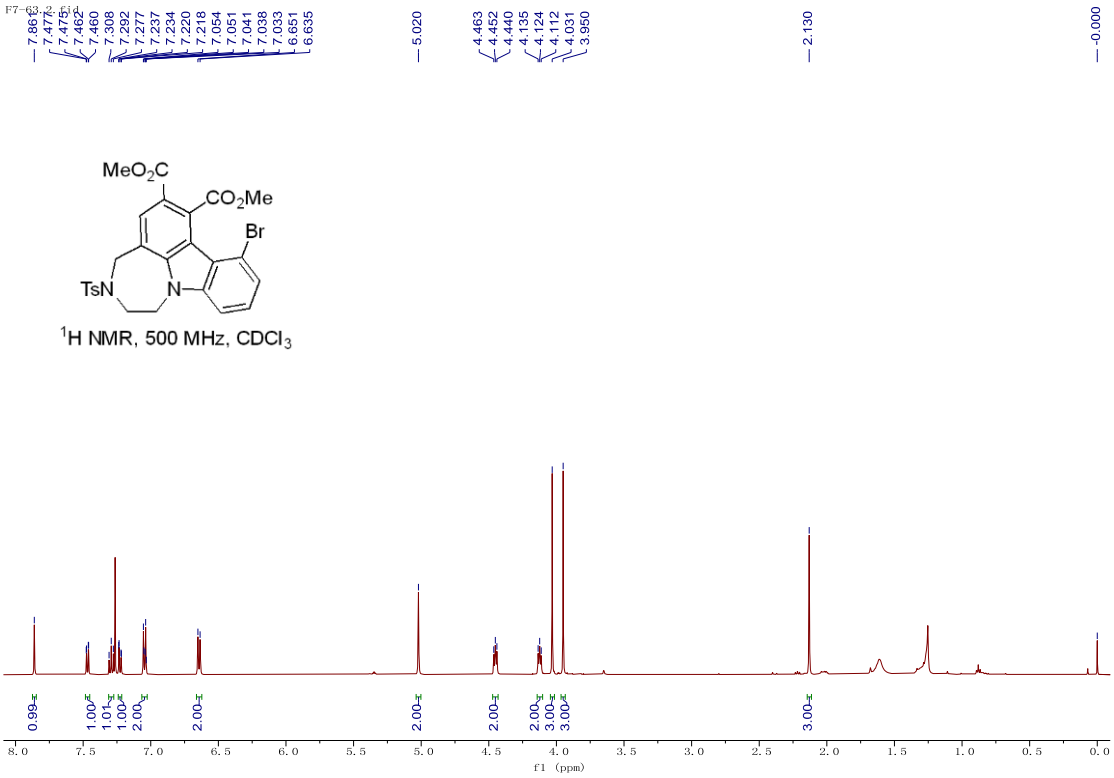
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.86 (s, 1H), 7.47 (dd, J = 7.5, 1.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.23 (dd, J = 8.5, 1.5 Hz, 1H), 7.05 (dt, J = 8.0, 1.5 Hz, 2H), 6.64 (d, J = 8.0 Hz, 2H), 5.02 (s, 2H), 4.45 (t, J = 6.0 Hz, 2H), 4.12 (t, J = 6.0 Hz, 2H), 4.03 (s, 3H), 3.95 (s, 3H), 2.13 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 166.8, 143.8, 142.85, 142.78, 135.3, 131.0, 128.9, 128.3, 127.6, 127.0, 126.0, 121.6, 120.5, 120.4, 119.0, 116.9, 107.7, 52.9, 52.7, 49.1, 48.4, 43.5, 21.4.

IR (KBr) ν (cm^{-1}): 1732, 1574, 1431, 1342, 1277, 1219, 1157, 914, 783 cm^{-1}.

HRMS (ESI): calcd for $C_{26}H_{23}BrN_2NaO_6S$ $[M+Na]^+$: 593.03524, found: 593.03552.

MP: 187-190 ºC.


F7-63.2.fid
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7.475
7.462
7.460
7.308
7.292
7.277
7.237
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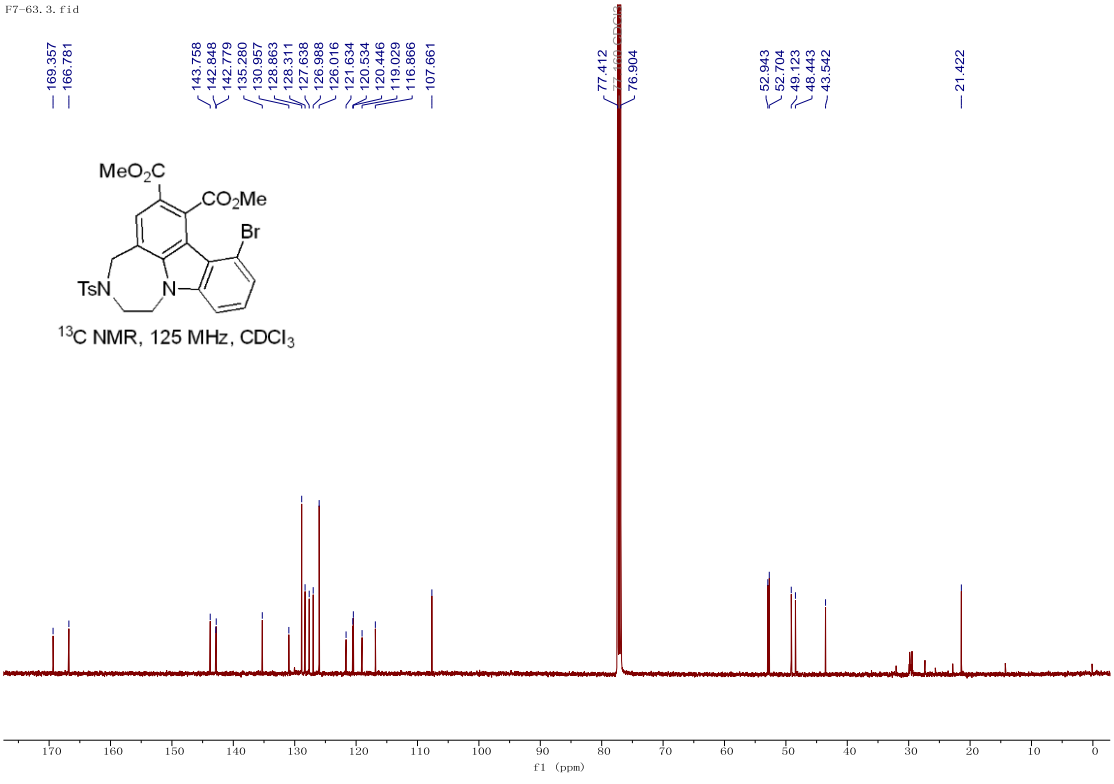
7.220
7.218
7.054
7.051
7.041
7.038
7.033
6.651
6.635
5.020
4.463
4.452
4.440
4.135
4.124
4.112
4.031
3.950
2.130
-0.000
MeO2C
CO2Me
Br
TsN
N
1H NMR, 500 MHz, CDCl3
0.99
1.00
1.01
1.00
2.00
2.00
2.00
2.00
2.00
3.00
3.00
3.00
f1 (ppm)


F7-63.3.fid
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143.758
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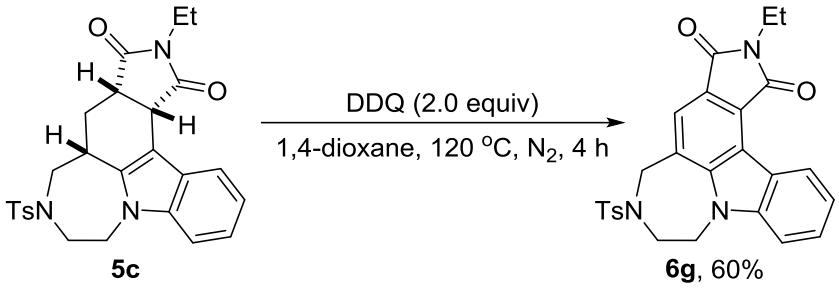
142.779
135.280
130.957
128.863
128.311
127.638
126.988
126.016
121.634
120.534
120.446
119.029
116.866
107.661
77.412
77.094
76.904
52.943
52.704
49.123
48.443
43.542
21.422
MeO2C
CO2Me
Br
TsN
N
13C NMR, 125 MHz, CDCl3
f1 (ppm)

5.2 The Synthesis of 6g-h

2-ethyl-6-tosyl-5,6,7,8-tetrahydro-1*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (6g)



5c **6g**, 60%

Under nitrogen atmosphere, 1,4-dioxane (1.0 mL) was added to a mixture of **5c** (37.7 mg, 0.08 mmol, 1.0 equiv) and DDQ (35.9 mg, 0.16 mmol, 2.0 equiv). Then the reaction was stirred at 120 °C for 4 h. The mixture was concentrated under vacuum and purified by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.25) as eluent to give the desired product **6g** (yellow solid, 22.6 mg, 60% yield).

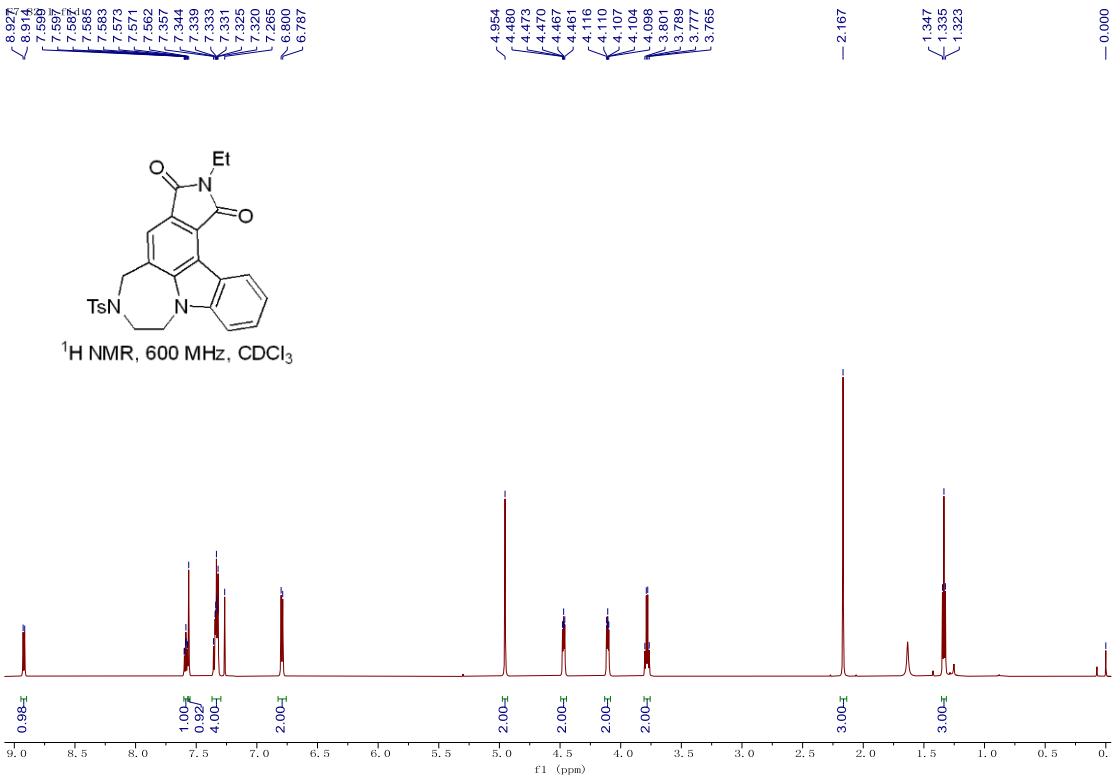
^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 8.92 (d, J = 7.8 Hz, 1H), 7.60-7.57 (m, 1H), 7.56 (s, 1H), 7.36-7.32 (m, 4H), 6.79 (d, J = 7.8 Hz, 2H), 4.95 (s, 2H), 4.48-4.46 (m, 2H), 4.12-4.10 (m, 2H), 3.78 (q, J = 7.2 Hz, 2H), 2.17 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 168.8, 143.8, 143.7, 142.4, 135.7, 129.1, 128.7, 126.5, 125.9, 125.6, 125.1, 124.3, 121.4, 121.0, 120.7, 119.5, 108.9, 50.3, 49.6, 44.9, 33.0, 21.4, 14.3.

IR (KBr) ν (cm^{-1}): 1759, 1705, 1447, 1396, 1350, 1165, 748 cm^{-1}.

HRMS (ESI): calcd for $C_{26}H_{23}N_3NaO_4S$ $[M+Na]^+$: 496.13015, found: 496.13007.

MP: 214-216 °C.


8.927
8.914
7.599
7.597
7.587
7.585
7.583
7.573
7.571
7.562
7.357
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7.339
7.333
7.331
7.325
7.320
7.265
6.800
6.787
4.954
4.480
4.473
4.470
4.467
4.461
4.116
4.110
4.107
4.104
4.098
3.801
3.789
3.777
3.765
2.167
1.347
1.335
1.323
0.000
Et
N
O
O
TsN
N
1H NMR, 600 MHz, CDCl3
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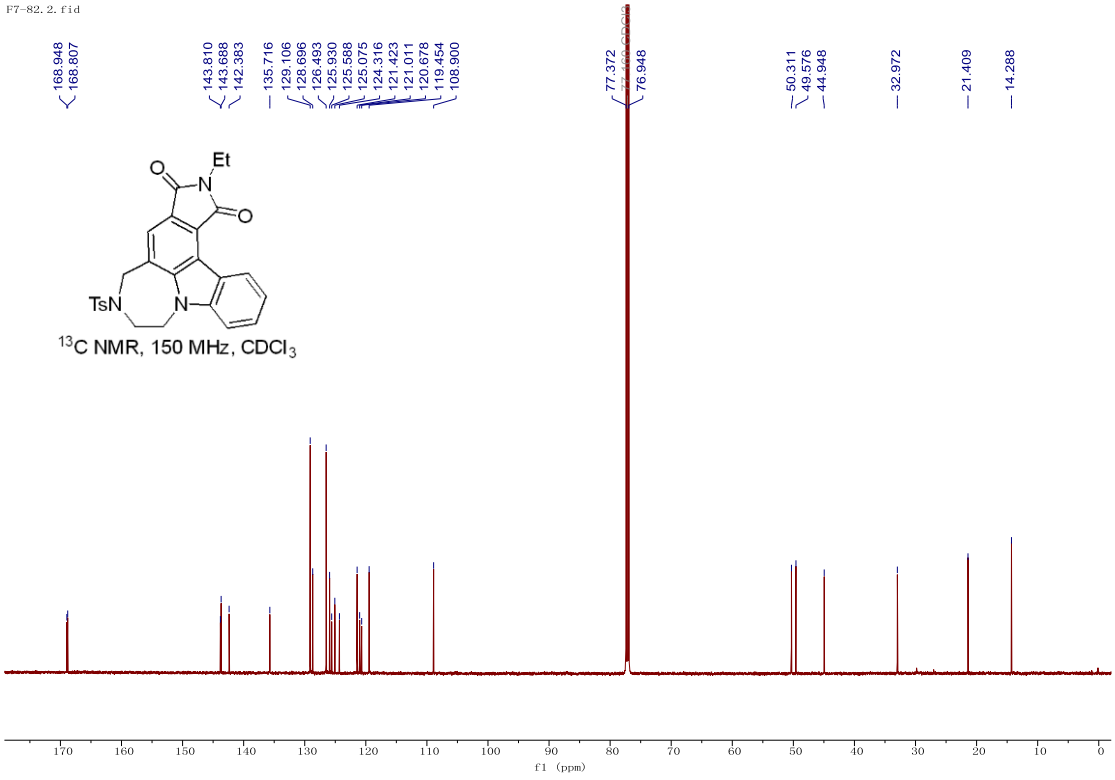
1.00
0.92
4.00
2.00
2.00
2.00
2.00
3.00
3.00
f1 (ppm)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135.716
129.106
128.696
126.493
125.930
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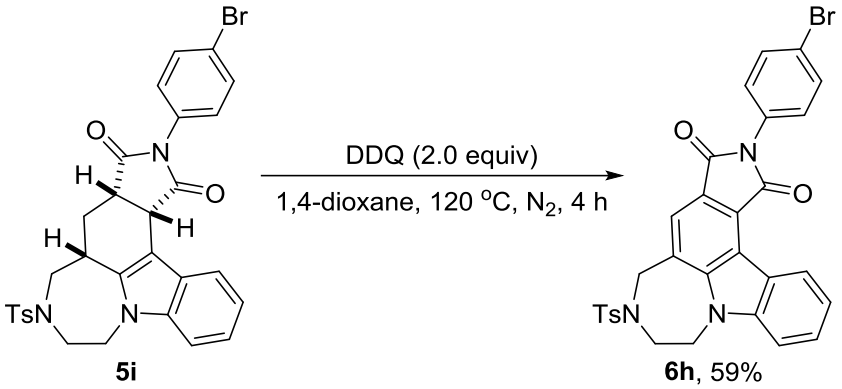
125.075
124.316
121.423
121.011
120.678
119.454
108.900
77.372
76.948
50.311
49.576
44.948
32.972
21.409
14.288
Et
N
O
O
TsN
N
13C NMR, 150 MHz, CDCl3
f1 (ppm)

2-(4-bromophenyl)-6-tosyl-5,6,7,8-tetrahydro-1*H*-[1,4]diazepino[1,7,6-*lm*]pyrrolo[3,4-*c*]carbazole-1,3(2*H*)-dione (6h)



5i **6h**, 59%

Under nitrogen atmosphere, 1,4-dioxane (1.0 mL) was added to a mixture of **5i** (30.0 mg, 0.05 mmol, 1.0 equiv) and DDQ (22.7 mg, 0.10 mmol, 2.0 equiv). Then the reaction was stirred at 120 °C for 4 h. The mixture was concentrated under vacuum and purified by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.25) as eluent to give the desired product **6h** (yellow solid, 17.6 mg, 59% yield).

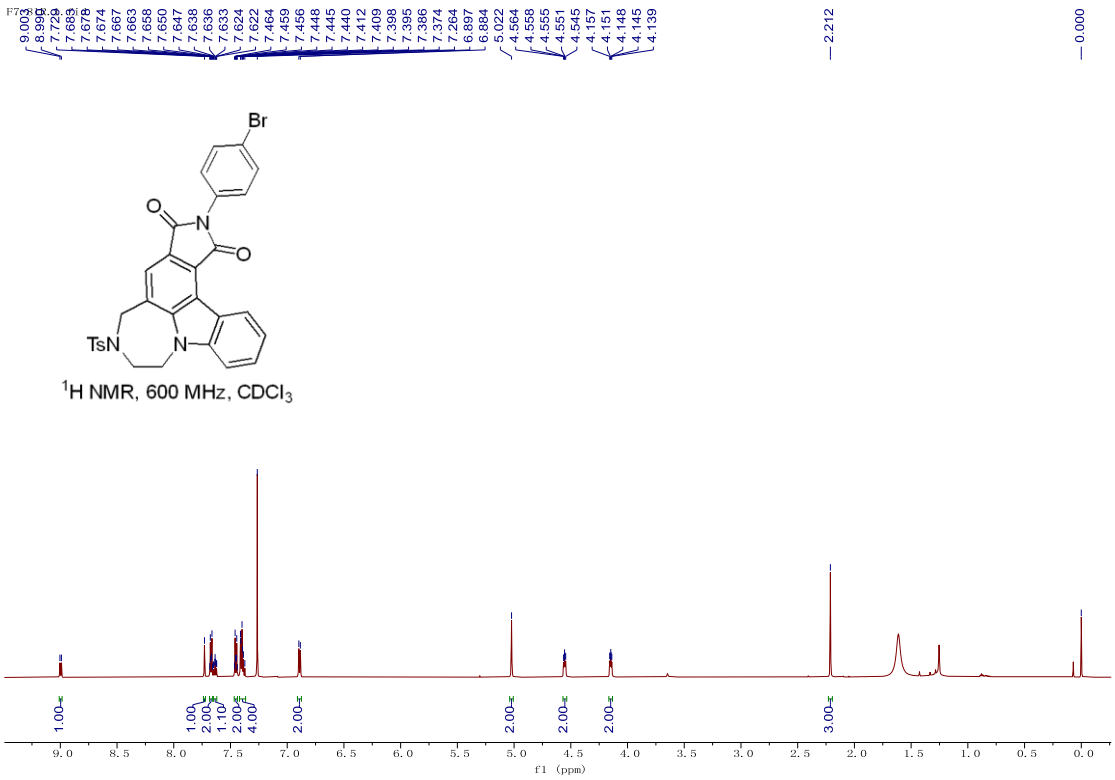
^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 9.00 (d, J = 7.8 Hz, 1H), 7.73 (s, 1H), 7.67 (dt, J = 9.0, 3.0 Hz, 2H), 7.65-7.62 (m, 1H), 7.45 (dt, J = 8.4, 3.0 Hz, 2H), 7.41-7.37 (m, 4H), 6.89 (d, J = 7.8 Hz, 2H), 5.02 (s, 2H), 4.56-4.55 (m, 2H), 4.16-4.14 (m, 2H), 2.21 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.64, 167.58, 144.3, 143.9, 142.6, 135.7, 132.4, 131.2, 129.3, 129.1, 128.1, 126.7, 126.2, 126.1, 125.0, 123.7, 121.8, 121.6, 121.2, 121.0, 120.0, 109.1, 50.5, 49.5, 45.2, 21.5.

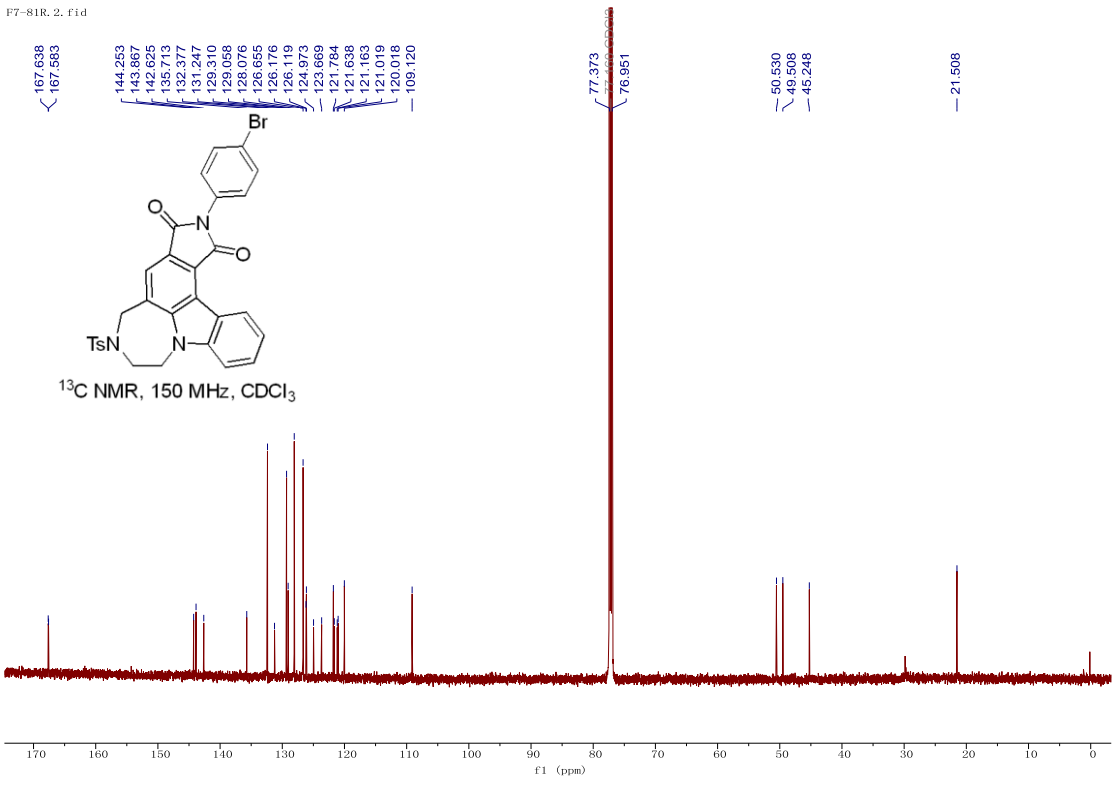
IR (KBr) ν (cm^{-1}): 1767, 1709, 1489, 1366, 1350, 1342, 1161, 748 cm^{-1}.

HRMS (ESI): calcd for $C_{30}H_{23}BrN_3O_4S$ $[M+H]^+$: 600.05872, found: 600.05908.

MP: 260-264 °C.

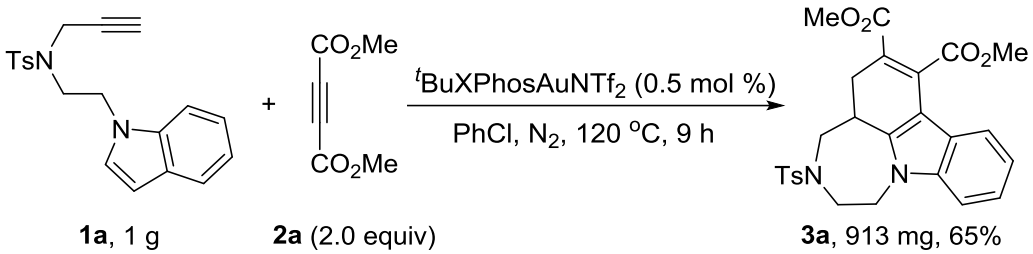


^{1}H NMR, 600 MHz, $CDCl_3$



^{13}C NMR, 150 MHz, $CDCl_3$

6. Scale-up Reaction Procedure

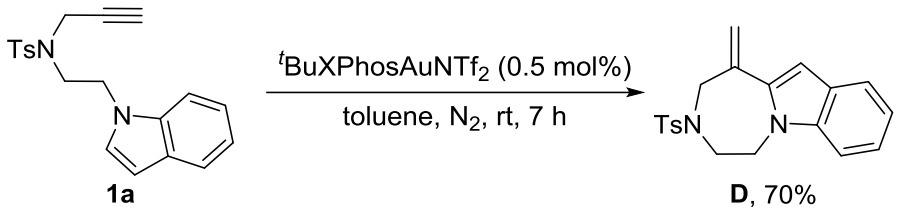


1a, 1 g **2a** (2.0 equiv) **3a**, 913 mg, 65%

Under nitrogen atmosphere, anhydrous PhCl (30.0 mL) was added to a sealed tube which equipped with **1a** (1 g, 2.8 mmol, 1.0 equiv), **2a** (795.8 mg, 5.6 mmol, 2.0 equiv) and [^{t}BuXPhosAuNTf$_2$] (12.6 mg, 0.5 mol%). The mixture was stirred at 120 ^{o}C and was complete as monitored by TLC. The mixture was concentrated under vacuum and purified by flash column chromatography using petroleum ether/DCM/THF = 8/4/1 (R_f = 0.20) as eluent to afford **3a** (yellow solid, 913 mg, 65% yield).

7. Control Experiments

1-methylene-3-tosyl-2,3,4,5-tetrahydro-1*H*-[1,4]diazepino[1,7-*a*]indole (D)



Under nitrogen atmosphere, anhydrous toluene (3.0 mL) was added to a sealed tube which equipped with the **1a** (176.2 mg, 0.5 mmol, 1.0 equiv) and [^{t}BuXPhosAuNTf$_2$] (2.25 mg, 0.5 mol%). The mixture was stirred at room temperature for 7 h. The mixture was concentrated under vacuum and purified by flash column chromatography using petroleum ether/EtOAc = 8/1 (R_f = 0.20) as eluent to afford **D** (yellow solid, 121.0 mg, 70% yield).

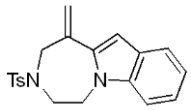
^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.56 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 7.8 Hz, 1H), 7.12-7.09 (m, 4H), 7.01-6.97 (m, 1H), 6.37 (s, 1H), 5.50 (s, 1H), 5.29 (s, 1H), 4.11-4.10 (m, 2H), 4.07 (s, 2H), 3.63-3.62 (m, 2H), 2.28 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 143.7, 140.9, 137.7, 136.3, 135.9, 129.8, 127.8, 127.2, 122.2, 120.8, 120.1, 119.5, 109.0, 102.0, 52.8, 48.7, 44.9, 21.6.

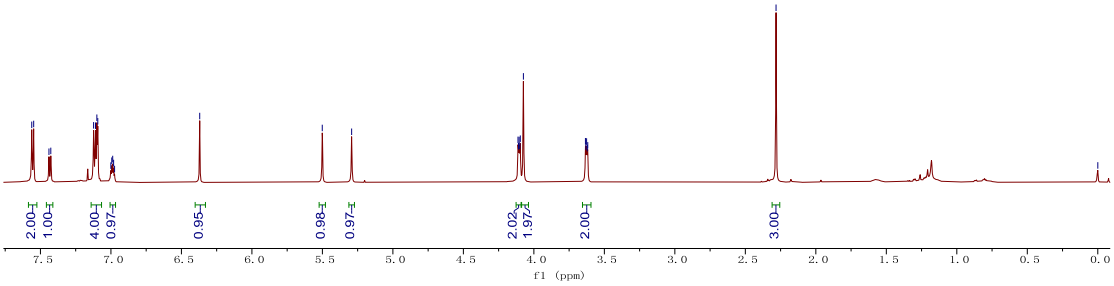
IR (KBr) ν (cm^{-1}): 1631, 1621, 1596, 1352, 1339, 1326, 1163, 1111, 794, 775, 740 cm^{-1}.

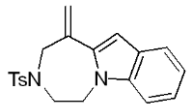
HRMS (ESI): calcd for $C_{20}H_{21}N_2O_2S$ $[M+H]^+$: 353.13183, found: 353.13174.

MP: 143-145 ^{o}C.

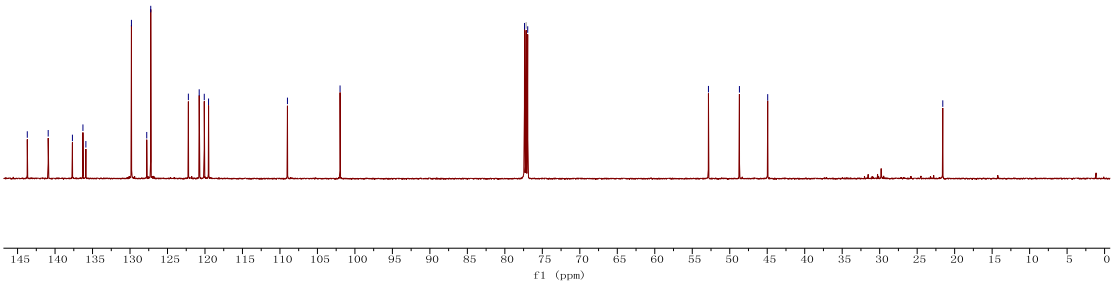


^{1}H NMR, 600 MHz, $CDCl_3$

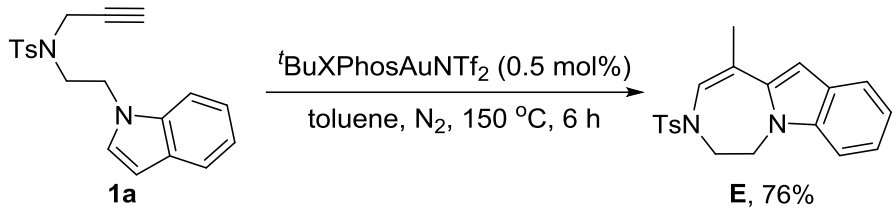




^{13}C NMR, 150 MHz, $CDCl_3$



1-methyl-3-tosyl-4,5-dihydro-3*H*-[1,4]diazepino[1,7-*a*]indole (E)



Under nitrogen atmosphere, anhydrous toluene (3.0 mL) was added to a sealed tube which equipped with the **1a** (176.2 mg, 0.5 mmol, 1.0 equiv) and [^{t}BuXPhosAuNTf$_2$] (2.25 mg, 0.5 mol%). The mixture was stirred at 150 ^{o}C for 6 h. The mixture was concentrated under vacuum and purified by flash column chromatography using petroleum ether/EtOAc = 15/1 (R_f = 0.26) as eluent to afford **E** (red solid, 133.4 mg, 76% yield).

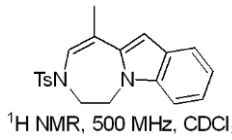
^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.71 (dt, J = 8.5, 2.0 Hz, 2H), 7.54 (dt, J = 8.0, 1.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.18-7.14 (m, 2H), 7.07-7.04 (m, 1H), 6.80 (d, J = 1.0 Hz, 1H), 6.47 (s, 1H), 4.15-4.13 (m, 2H), 3.92-3.91 (m, 2H), 2.40 (s, 3H), 2.18 (d, J = 1.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 137.5, 135.8, 130.2, 127.5, 127.0, 122.1, 121.4, 120.7, 119.9, 108.7, 108.4, 102.1, 47.4, 44.9, 22.2, 21.7.

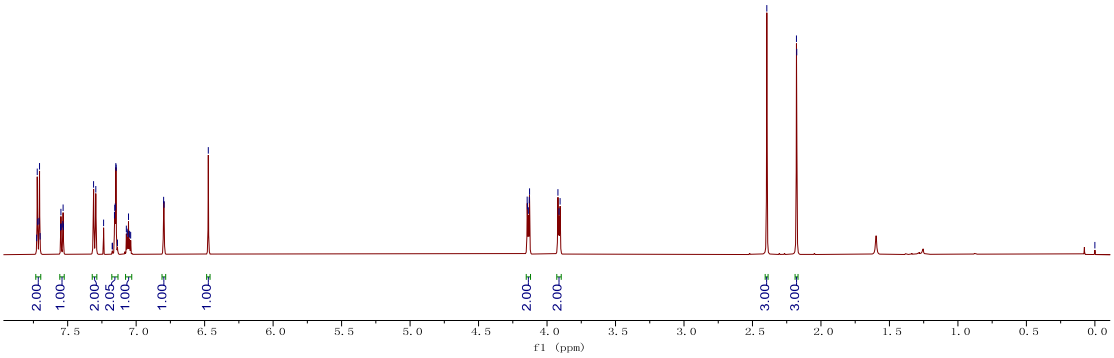
IR (KBr) ν (cm^{-1}): 1636, 1366, 1335,1165, 1107,1053, 918, 664 cm^{-1}.

HRMS (ESI): calcd for $C_{20}H_{21}N_2O_2S$ $[M+H]^+$: 353.13183, found: 353.13162.

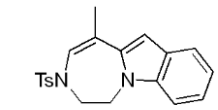
MP: 65-68 ^{o}C.



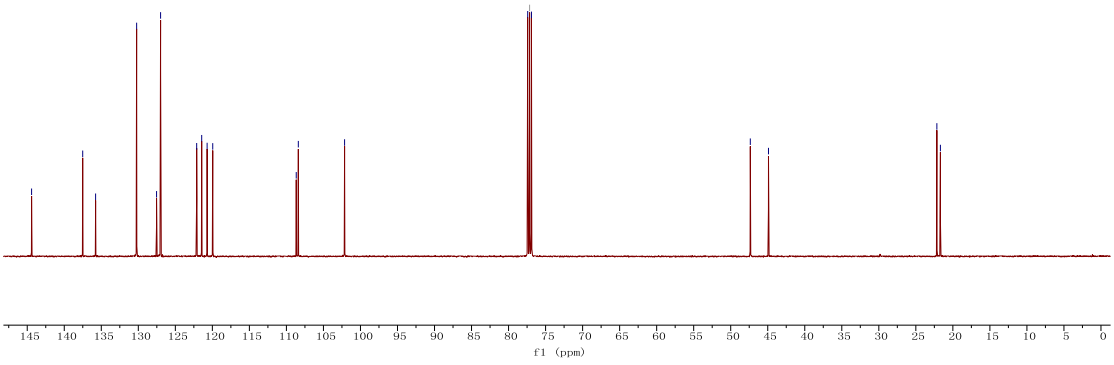
^{1}H NMR, 500 MHz, $CDCl_3$

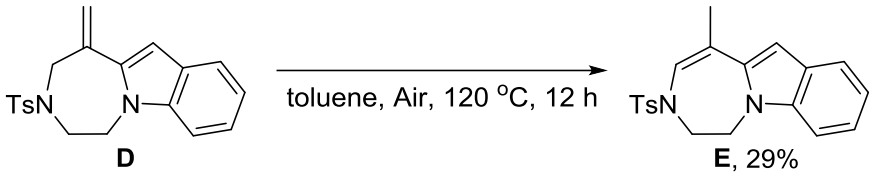


F7-100.2.fid

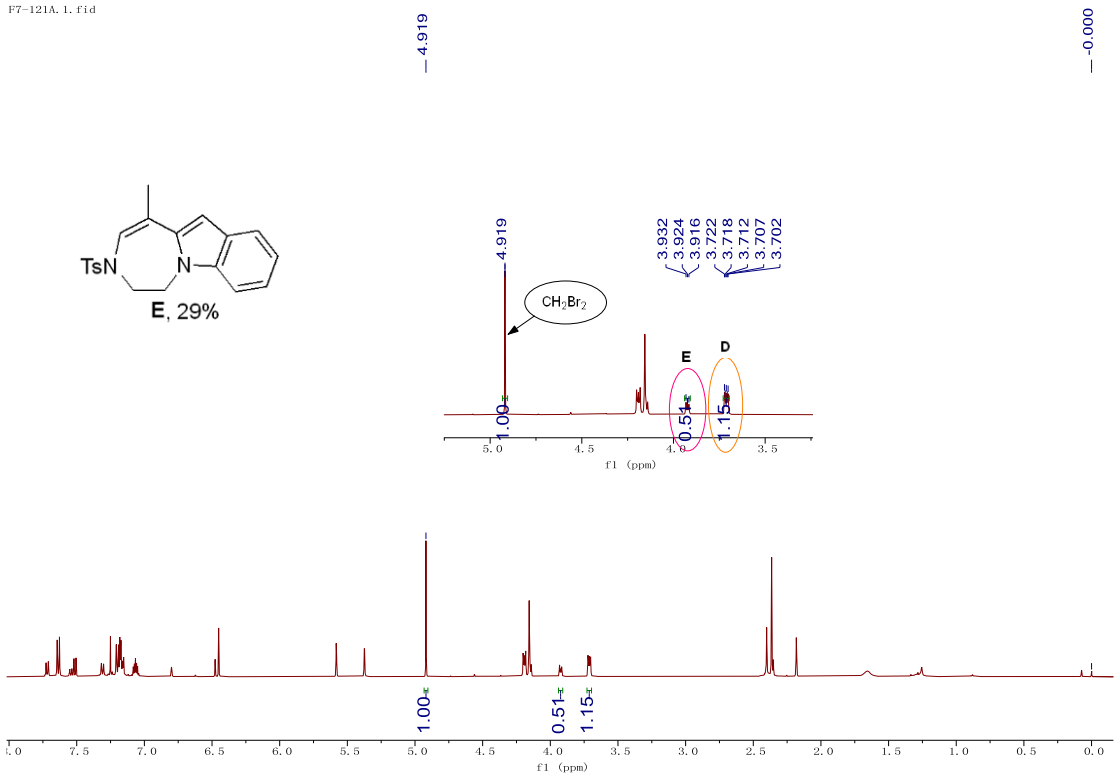


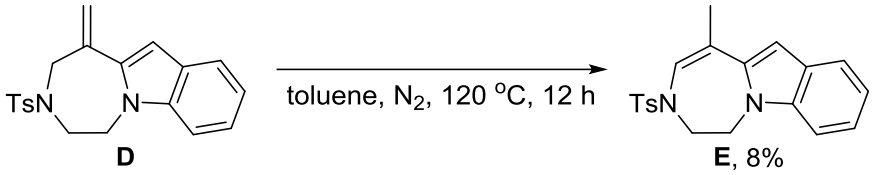
^{13}C NMR, 125 MHz, $CDCl_3$



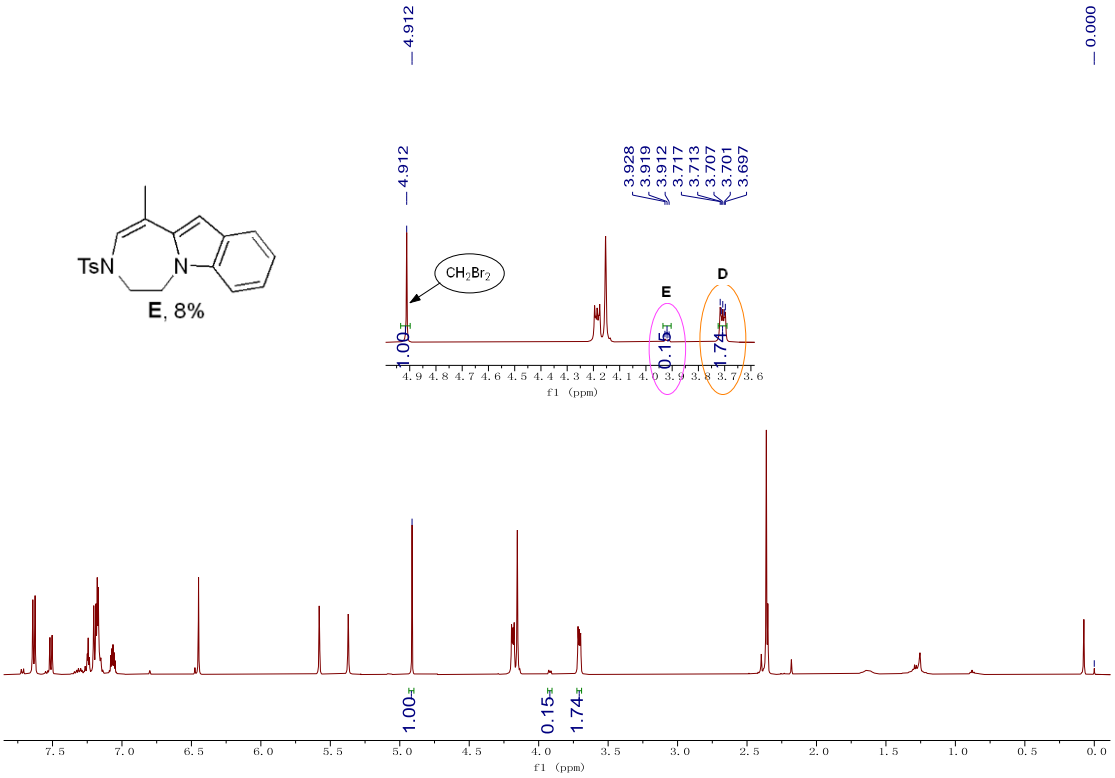


Under air atmosphere, a sealed tube was equipped with **D** (17.6 mg, 0.05 mmol, 1.0 equiv) and anhydrous toluene (1.0 mL). The mixture was stirred at 120 °C for 12 h. Then the mixture was concentrated under vacuum. The *in-situ* yield of product **E** was determined by ^{1}H NMR analysis by using CH_2Br_2 as an internal standard.

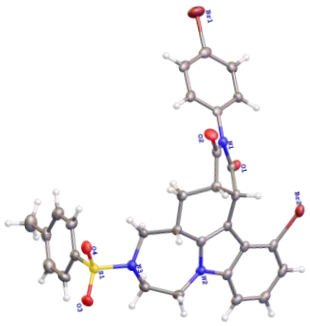




Under nitrogen atmosphere, anhydrous toluene (1.0 mL) was added to a sealed tube which equipped with **D** (17.6 mg, 0.05 mmol, 1.0 equiv). The mixture was stirred at 120 °C for 12 h. Then the mixture was concentrated under vacuum. The *in-situ* yield of product **E** was determined by ^{1}H NMR analysis by using CH_2Br_2 as an internal standard.


4.912
0.000
TsN
N
E, 8%
4.912
3.928
3.919
3.912
3.717
3.713
3.707
3.701
3.697
CH2Br2
E
D
1.00
0.15
1.74
f1 (ppm)
1.00
0.15
1.74
f1 (ppm)

8. X-ray Crystal Data of Compound 5k.



The crystal data of **5k** have been deposited in CCDC with number 2281024.

Table 1 Crystal data and structure refinement for 5k.

Empirical formula	$C_{30}H_{25}Br_2N_3O_4S$
Formula weight	683.41
Temperature/K	170.00(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	20.8975(8)
b/Å	9.0370(2)
c/Å	31.2449(14)
α/°	90
β/°	108.922(5)
γ/°	90
Volume/Å^3	5581.8(4)
Z	8
ρ_{calc}g/cm^3	1.626
μ/mm^{-1}	4.732
F(000)	2752.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.98 to 147.768
Index ranges	-25 ≤ h ≤ 25, -6 ≤ k ≤ 11, -36 ≤ l ≤ 38
Reflections collected	18816
Independent reflections	5534 [R_{int} = 0.1078, R_{sigma} = 0.1047]
Data/restraints/parameters	5534/0/362
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0558, wR_2 = 0.1267
Final R indexes [all data]	R_1 = 0.0889, wR_2 = 0.1434
Largest diff. peak/hole / e Å^{-3}	0.79/-0.82

Crystal Data for **5k**: $C_{30}H_{25}Br_2N_3O_4S$ (M =683.41 g/mol): monoclinic, space group I2/a (no. 15), a = 20.8975(8) Å, b = 9.0370(2) Å, c = 31.2449(14) Å, β = 108.922(5) , V = 5581.8(4) Å^3, Z = 8, T = 170.00(10) K, μ(Cu Kα) = 4.732 mm^{-1}, *Dcalc* = 1.626 g/cm^3, 18816 reflections measured ($5.98 \leq 2\Theta \leq 147.768$), 5534 unique ($R_{int}$ = 0.1078, R_{sigma} = 0.1047) which were used in all calculations. The final R_1 was 0.0558 ($I > 2\sigma(I)$) and wR_2 was 0.1434 (all data).

9. References

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