Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Synthesis of Indolines via Palladium/Norbornene-Catalyzed Reaction of Aziridines with Aryl Iodides

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1. General Information

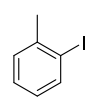
General Procedures. Unless otherwise noted, reactions were performed under a nitrogen atmosphere. Plastic syringes were used to transfer air- and moisture-sensitive reagents. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Analytical TLC was performed with silica gel GF254 plates. For column chromatography, a 200-300 mesh silica gel was employed. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Room temperature (r.t.) is 23-25 ℃.

Materials. Commercial reagents were purchased from Acros, Accela, Adamas, Alfa, Ark, Aladdin, or TCI, and used as received with the following exceptions. Tetrahydrofuran (THF), ethylene glycol dimethyl ether (DME), toluene and 1,4-dioxane were dried over Na with benzophenone-ketyl intermediate as indicator. Dichloroethane (DCE) and acetonitrile (CH_3CN) were distilled over P_2O_5. *N*,*N*-Dimethylformamide (DMF) was distilled under reduced pressure. Other commercially available reagents and solvents were used without further purification.

Instrumentation. Deuterated solvents were purchased from Cambridge Isotope Laboratories. ^{1}H NMR spectra were recorded on Bruker AVANCE III 400 ,Agilent Mercury plus 300 BB and INOVA instruments with 400, 300 and 600 MHz frequencies, and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 and Agilent Mercury plus 300 BB instruments with 100 and 75 MHz frequencies. ^{19}F NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer with a ^{19}F operating frequency of 376 MHz. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal ($CDCl_3$ δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). HRMS was obtained using a Q-TOF instrument equipped with an ESI source. Data collection for crystal structure was performed at room temperature using Mo Kα radiation on a Bruker APEXII diffractometer.

2 Substrate Structures

Aryl iodides



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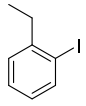

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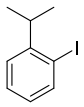

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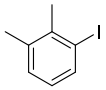

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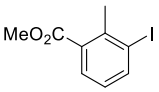

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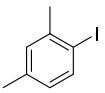

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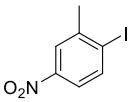

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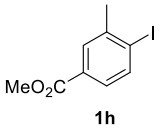

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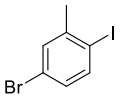

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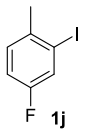

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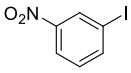

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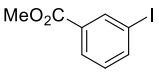

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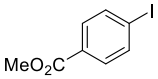

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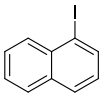

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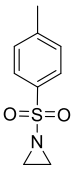
1p

1q

Aziridines



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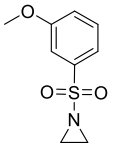

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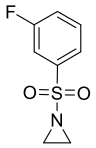

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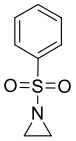

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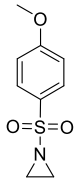

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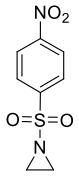

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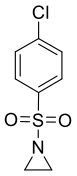

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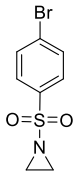

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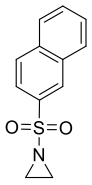

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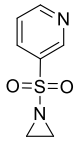

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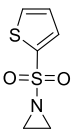

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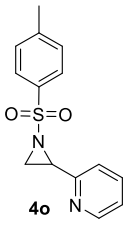

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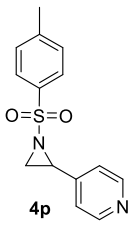

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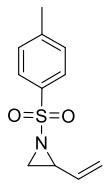

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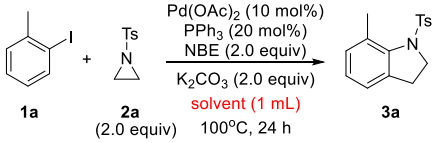
3 Experimental Section

3.1 Optimization of Reaction Conditions

3.1.1 Table S1. Solvent Screening[a]

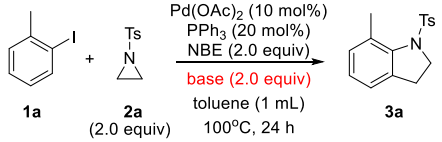


1a 2a (2.0 equiv) 3a

entry	solvent	yield (%)[b]
1	toluene	42
2	CH_3CN	trace
3	DME	trace
4	1,4-dioxane	<20
5	DCE	<20
6	THF	ND
7	DMF	trace

[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), **2a** (0.30 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), NBE (0.30 mmol, 2.0 equiv), K_2CO_3 (0.30 mmol, 2.0 equiv), solvent (1 mL), 100 ℃, 24 h. [b] Isolated yields. ND denotes not determined.

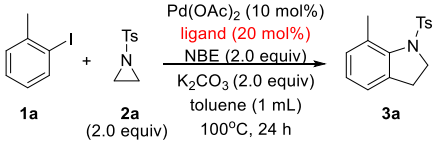
3.1.2 Table S2. Base Screening[a]



entry	base	yield (%)[b]
1	K_2CO_3	42
2	$NaOBu^t$	trace
3	$KOBu^t$	<10
4	NaOH	<10
5	KOH	<10
6	Cs_2CO_3	<10
7	$LiOBu^t$	<10
8	$KHCO_3$	34
9	KOAc	ND
10	K_3PO_4	<20
11	K_2HPO_4	trace
12	KH_2PO_4	trace
13	NEt_3	<10
14	DBU	trace
15	-	ND

[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), **2a** (0.30 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), NBE (0.30 mmol, 2.0 equiv), base (0.30 mmol, 2.0 equiv), toluene (1 mL), 100 ℃, 24 h. [b] Isolated yields. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. ND denotes not determined.

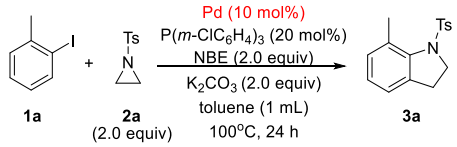
3.1.3 Table S3. Ligand Screening[a]



entry	ligand	yield (%)[b]
1	PPh_3	42
2	TFP	48
3	P(*o*-MeC_6H_4)$_3$	<20
4	P(*m*-MeC_6H_4)$_3$	64
5	P(*p*-MeC_6H_4)$_3$	45
6	P(*p*-$MeOC_6H_4$)$_3$	46
7	P(*m*-ClC_6H_4)$_3$	68
8	PCy_3	27
9	dppb[c]	trace
10	dppe[c]	ND
11	dppf[c]	28
12	X-phos	<10
13	Xantphos[c]	trace
14	bis(2-diphenylphosphinophenyl)ether[c]	34
15	tri-*tert*-butylphosphine tetrafluoroborate	ND
16	$AsPh_3$	trace
17	pyridine	ND
18	dipyridyl	ND
19	L-*α*-Alanine	ND
20	-	ND

[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), **2a** (0.30 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), ligand (20 mol%), NBE (0.30 mmol, 2.0 equiv), K_2CO_3 (0.30 mmol, 2.0 equiv), toluene (1 mL), 100 ℃, 24 h. [b] Isolated yields. [c] 10 mol%. ND denotes not determined.

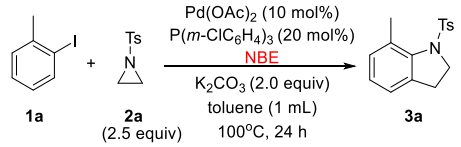
3.1.4 Table S4. Pd Source Screening[a]



entry	Pd source	yield (%)[b]
1	$Pd(OAc)_2$	68
2	$PdCl_2$	51
3	PdI_2	54
4	$Pd(CF_3COO)_2$	59
5	$PdCl_2(CH_3CN)_2$	48
6	$PdCl_2(PCy_3)_2$	trace
7	$Pd_2(dba)_3$[c,d]	21
8	$Pd(PPh_3)_4$[c]	47
9	-	ND

[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), **2a** (0.30 mmol, 2.0 equiv), Pd (10 mol%), P(*m*-ClC_6H_4) (20 mol%), NBE (0.30 mmol, 2.0 equiv), K_2CO_3 (0.30 mmol, 2.0 equiv), toluene (1 mL), 100 ℃, 24 h. [b] Isolated yields. [c] no P(*m*-ClC_6H_4). [d] $Pd_2(dba)_3$ 5 mol%. ND denotes not determined.

3.1.5 Table S5. NBE Screening[a]



entry	NBE (equiv)	yield (%)[b]
1	2.0	68[c]
2	2.0	71
3	1.0	70
4	0.6	78
5	0.5	81
6	0.4	79
7	0.25	68
8	-	ND

[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), **2a** (0.375 mmol, 2.5 equiv), $Pd(OAc)_2$ (10 mol%), P(*m*-ClC_6H_4) (20 mol%), K_2CO_3 (0.30 mmol, 2.0 equiv), toluene (1 mL), 100 ℃, 24 h. [b] Isolated yields. [c] **2a** (0.30 mmol, 2.0 equiv). ND denotes not determined.

3.2 Preparation of Aziridines

3.2.1 Preparation of aziridines **2a-k** and **4a-c** according to the procedure described in literature.[1]

A solution of aryl sulfonyl chloride (52 mmol) in pyridine (32 mL) was cooled to -15 ℃. A precooled (0 ℃) solution of aminoethanol (25 mmol) in pyridine (18 mL) was added dropwise over a period of 0.5 h. Then mixture was stirred for 7 h at 0 ℃ and placed in the fridge overnight. Ice/water was added to the reaction mixture, which was then extracted with dichloromethane (DCM) (3×20 mL) and washed with water several times. The organic layer was then dried with anhydrous $MgSO_4$, filtered, the solvent was removed under vacuum. Then the residue was dissolved in toluene (100 mL) and KOH (85 mmol) in water (25 mL) was added to it. The mixture was stirred for 2 h at room temperature. The toluene phase was separated and intensively washed with water until the aqueous phase showed a neutral pH. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under vacuum, and the residue was purified by column chromatography.

3.2.2 Preparation of aziridines **4d-k, 4m-p** according to the procedure described in literature.[2]

A r.b. flask was flame dried and charged with $TsNH_2$ (1.4 equiv), $Cu(CH_3CN)_4PF_6$ (0.1 equiv), alkene (1.0 equiv), activated 3Å molecular sieves (1.0 g/mmol alkene) and CH_3CN (2.5 mL/mmol alkene). The mixture was cooled in a 0 ℃ ice-water bath, and iodosylbenzene (1.4 equiv) was added in one portion. The mixture was allowed to warm to room temperature and stirred at room temperature overnight. The resulting mixture was filtered through a pad of Celite, and the filtrate was concentrated. The crude was purified with column chromatography.

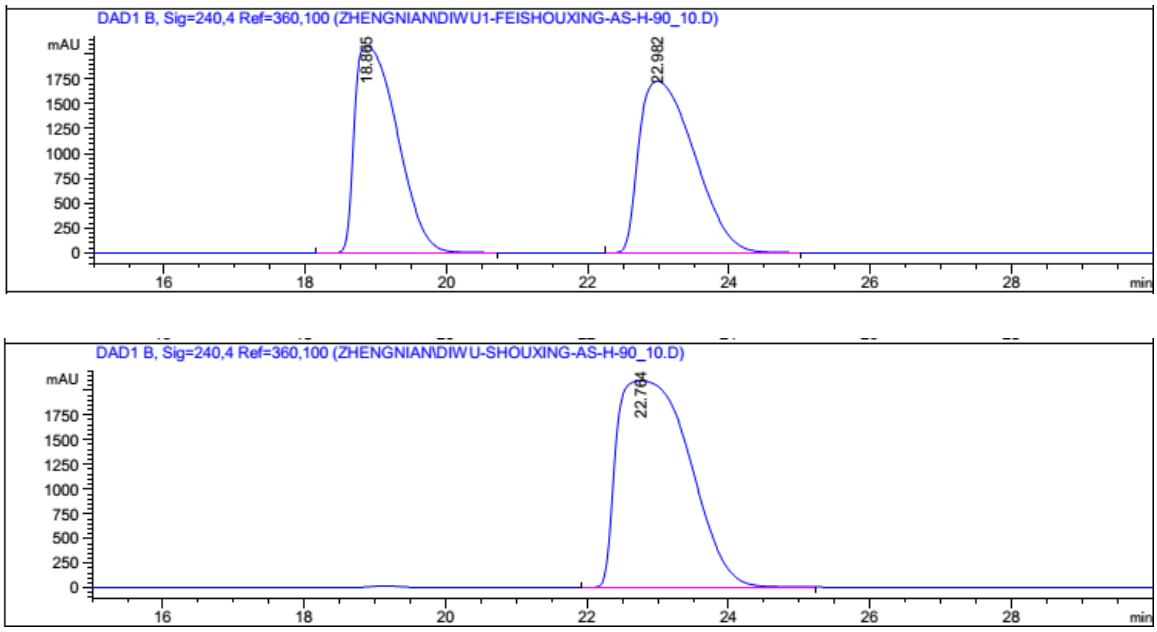
3.2.3 Preparation of aziridine **4l** according to the procedure described in literature.[2]

A r.b. flask was flame dried and charged with $Cu(OTf)_2$ (0.31 mmol, 0.1 equiv), 30 mL CH_3CN, and *α*-methylstyrene (15.38 mmol, 5.0 equiv). PhI=NTs (3.08 mmol, 1.0 equiv) was added in one portion. The mixture was stirred at room temperature under nitrogen for 1 h. The resulting yellow solution was concentrated, and the crude was purified with column chromatography to afford **4l** as a white solid.

3.2.4 Preparation of aziridine **(*S*)-4n** according to the procedure described in literature.[3]

4-Bromobenzenesulfonyl chloride (1.05 mmol) was added slowly to a solution of *(S)*-(+)-2-phenylglycinol (1.0 mmol, >99% ee) and triethylamine (4.0 mmol) in CH_2Cl_2 (10 mL) at 0 ℃. The ice bath was then removed, and the reaction was allowed to warm to room temperature and further stirred for 6 h. The reaction mixture was then washed with water and brine and dried over anhydrous Na_2SO_4. The organic layer was then concentrated to give the crude product. Then the residue was dissolved in THF (5 mL) at room temperature and triphenylphosphine (1.5 mmol) was added it. The reaction mixture was then cooled to 0 ℃ and treated slowly with diisopropyl azodicarboxylate (1.5 mmol). The ice bath was removed, and the yellow solution was stirred for 6 h. Then THF was evaporated, and the crude product was purified by column chromatography to yield the desired chiral aziridine as a white solid.

(*S*)-(+)-1-((4-bromophenyl)sulfonyl)-2-phenylaziridine ((*S*)-4n): m.p. = 88-89 ℃, $[\alpha]^{20.8}_D$ = 60.0 °(*c* 1.0, $CHCl_3$). >99% ee. The enantiomeric excess of **(*S*)-4n** was determined by HPLC (chiral column: CHIRALPAK AS-H; solvent: hexane/2-propanol = 90/10; flow rate: 1 mL/min; detection: at 240 nm) analysis in comparison with authentic racemic material: Retention time = 18.87 min (R) and 22.98 min (S). ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.84 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.17 (m, 5H), 3.81 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.01 (d, *J* = 7.2 Hz, 1H), 2.42 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 137.1, 134.6, 132.4, 129.3, 128.8, 128.6, 128.4, 126.4, 41.3, 36.1.

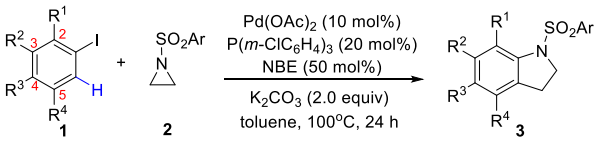


3.2.5 Preparation of aziridine **4q** according to the procedure described in literature.[4]

To a mixture of 1,3-butadiene (5 mmol, 2 mol/L in tetrahydrofuran, 2.5 mL) and anyhydrous Chloramine-T (1.248 g, 5.5 mmol) in dry MeCN (25 mL) was added pyridinium hydrobromide perbromide (0.160 g, 0.5 mmol) at 25 ℃. The pale yellow colored solution was stirred vigorously at 25 ℃ for 12h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure to give the crude product which was purified by column chromatography (silica gel, 20% EtOAc-petroleum ether as eluant).

3.3 General Procedure for Synthesis of Indolines

3.3.1 Synthesis of Indolines 3a-v



General procedure: An oven-dried Schlenk tube under a nitrogen atmosphere was charged with aryl iodide **1** (0.15 mmol, 1.0 equiv), aziridine **2** (0.375 mmol, 2.5 equiv), $Pd(OAc)_2$ (10 mol%), $P(m\text{-}ClC_6H_4)_3$ (20 mol%), NBE (50 mol%) and K_2CO_3 (0.30 mmol, 2.0 equiv) in toluene (1 mL). The mixture was stirred at room temperature for 10 minutes and then stirred in the oil bath at 100 ℃ for 24 h. The resulting mixture was cooled to room temperature and filtered through celite with EtOAc as eluents. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether 1/20-1/5) to afford pure product.

3a

7-methyl-1-tosylindoline (3a): White solid; m.p. = 94-95 ℃; yield 81%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.35 (m, 2H), 7.13 (d, *J* = 8 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 3.92 (t, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 2.36 (s, 3H), 2.11 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.9, 141.5, 137.4, 134.4, 132.3, 129.9, 129.2, 127.4, 126.4, 121.8, 52.5, 28.7, 21.4, 19.6.

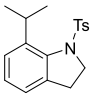
HRMS (ESI): Calcd for $C_{16}H_{17}NO_2S$ $[M+H]^+$: 288.1053, found: 288.1055.

3b

7-ethyl-1-tosylindoline (3b): Orange solid; m.p. = 126-127 ℃; yield 63%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.34 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.20 – 7.08 (m, 3H), 6.87 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.93 (t, *J* = 7.2 Hz, 2H), 3.07 (q, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 2.09 (t, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.9, 140.9, 138.5, 137.5, 134.5, 129.3, 128.0, 127.6, 126.9, 121.8, 52.6, 28.8, 25.2, 21.5, 14.3.

HRMS (ESI): Calcd for $C_{17}H_{19}NO_2S$ $[M+Na]^+$: 324.1029, found: 324.1028.

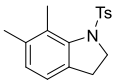


3c

7-isopropyl-1-tosylindoline (3c): Yellow solid; m.p. = 145-146 ℃; yield 48%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.09 (m, 3H), 6.85 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.95 (t, *J* = 7.2 Hz, 2H), 3.91 – 3.84 (m, 1H), 2.38 (s, 3H), 2.07 (t, *J* = 7.2 Hz, 2H), 1.28 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.9, 143.6, 140.0, 137.4, 134.4, 129.3, 127.7, 127.2, 125.5, 121.8, 52.7, 28.9, 24.0, 21.5.

HRMS (ESI): Calcd for $C_{18}H_{21}NO_2S$ $[M+H]^+$: 316.1366, found: 316.1369.

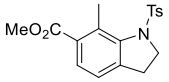


3d

6,7-dimethyl-1-tosylindoline (3d): Orange solid; m.p. = 86-87 ℃; yield 65%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 3.92 (t, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H), 2.05 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.9, 142.0, 137.0, 134.8, 134.5, 131.4, 129.2, 128.0, 127.7, 121.2, 52.7, 28.7, 21.5, 19.9, 17.1.

HRMS (ESI): Calcd for $C_{17}H_{19}NO_2S$ $[M+H]^+$: 302.1209, found: 302.1208.

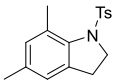


3e

methyl 7-methyl-1-tosylindoline-6-carboxylate (3e): Light yellow solid; m.p. = 144-145 ℃; yield 43%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8 Hz, 1H), 7.38 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8 Hz, 1H), 3.98 (t, *J* = 7.2 Hz, 2H), 3.95 (s, 3H), 2.75 (s, 3H), 2.39 (s, 3H), 2.17 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.9, 144.2, 143.3, 141.8, 134.8, 134.4, 130.7, 129.5, 129.4, 127.7, 121.4, 52.6, 51.9, 29.2, 21.5, 18.9.

HRMS (ESI): Calcd for $C_{18}H_{19}NO_4S$ $[M+NH_4]^+$: 363.1373, found: 363.1372.

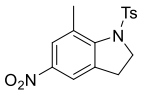


3f

5,7-dimethyl-1-tosylindoline (3f): Orange solid; m.p. = 100-101 ℃; yield 63%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.38 (m, 2H), 7.15 (d, *J* = 8 Hz, 2H), 6.91 (d, *J* = 1.6 Hz, 1H), 6.68 (s, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 2.53 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H), 2.06 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.8, 139.2, 137.5, 136.3, 134.7, 131.9, 130.7, 129.3, 127.6, 122.6, 52.7, 28.8, 21.5, 21.0, 19.6.

HRMS (ESI): Calcd for $C_{17}H_{19}NO_2S$ $[M+Na]^+$: 324.1029, found: 324.1031.

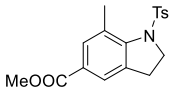


3g

7-methyl-5-nitro-1-tosylindoline (3g): Yellow solid; m.p. = 116-117 ℃; yield 87%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.75 (s, 1H), 7.43 (dd, *J* = 8, 1.6 Hz, 2H), 7.22 (d, *J* = 8 Hz, 2H), 4.05 (t, *J* = 7.2 Hz, 2H), 2.65 (s, 3H), 2.42 (s, 3H), 2.29 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.4, 145.9, 144.7, 139.0, 134.3, 133.3, 129.7, 127.3, 126.0, 117.3, 53.0, 28.6, 21.5, 20.2.

HRMS (ESI): Calcd for $C_{16}H_{16}N_2O_4S$ $[M+Na]^+$: 355.0723, found: 355.0722.

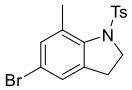


3h

methyl 7-methyl-1-tosylindoline-5-carboxylate (3h): Orange liquid; yield 77%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.55 (s, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8 Hz, 2H), 3.99 (t, J = 7.2 Hz, 2H), 3.89 (s, 3H), 2.61 (s, 3H), 2.39 (s, 3H), 2.18 (t, J = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.5, 145.7, 144.2, 137.8, 134.4, 132.2, 132.0, 129.4, 128.1, 127.3, 123.1, 52.7, 52.0, 28.5, 21.4, 19.8.

HRMS (ESI): Calcd for $C_{18}H_{19}NO_4S$ $[M+H]^+$: 346.1108, found: 346.1109.

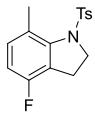


3i

5-bromo-7-methyl-1-tosylindoline (3i): Light orange liquid; yield 60%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.39 (m, 2H), 7.25 (s, 1H), 7.19 (d, J = 8 Hz, 2H), 7.01 (s, 1H), 3.93 (t, J = 7.2 Hz, 2H), 2.54 (s, 3H), 2.40 (s, 3H), 2.11 (t, J = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.2, 140.9, 139.6, 134.5, 134.3, 132.8, 129.5, 127.5, 125.0, 119.6, 52.7, 28.7, 21.5, 19.7.

HRMS (ESI): Calcd for $C_{16}H_{16}BrNO_2S$ $[M+H]^+$: 366.0158, found: 366.0159.



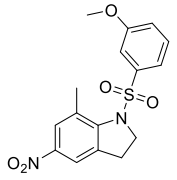
3j

4-fluoro-7-methyl-1-tosylindoline (3j): Light orange liquid; yield 56%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8 Hz, 2H), 7.08 (dd, J =8.4, 5.6 Hz, 1H), 6.78 (t, J = 8.4 Hz, 1H), 3.98 (t, J = 7.2 Hz, 2H), 2.53 (s, 3H), 2.40 (s, 3H), 2.17 (t, J = 7.2 Hz, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -121.24 (t, J = 6.8 Hz).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.8 (d, J = 243.3 Hz), 144.3, 143.5 (d, J = 6.5 Hz), 134.4, 131.4 (d, J = 7.2 Hz), 129.5, 128.1 (d, J = 3.7 Hz), 127.6, 123.4 (d, J = 20.1 Hz), 113.5 (d, J = 20.2 Hz), 53.0, 25.3, 21.5, 19.2.

HRMS (ESI): Calcd for $C_{16}H_{16}FNO_2S$ $[M+H]^+$: 306.0959, found: 306.0958.



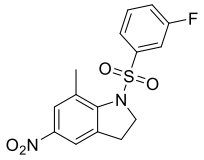
3k

1-((3-methoxyphenyl)sulfonyl)-7-methyl-5-nitroindoline (3k): Yellow solid; m.p. = 127-129 ℃; yield 89%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.77 (s, 1H), 7.34 (t, J = 8 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.02 (t, J = 2 Hz, 1H), 4.07 (t, J = 7.2 Hz, 2H), 3.70 (s, 3H), 2.65 (s, 3H), 2.33 (t, J = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.7, 147.3, 146.0, 139.1, 138.3, 133.3, 130.2, 126.0, 119.9, 119.5,

117.3, 112.1, 55.5, 53.2, 28.7, 20.2.

HRMS (ESI): Calcd for $C_{16}H_{16}N_2O_5S$ $[M+H]^+$: 349.0853, found: 349.0856.



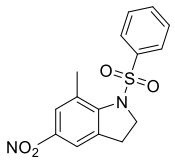
3l

1-((3-fluorophenyl)sulfonyl)-7-methyl-5-nitroindoline (3l): Orange solid; m.p. = 100-101 ℃; yield 86%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.79 (s, 1H), 7.47 – 7.41 (m, 1H), 7.35 – 7.31 (m, 3H), 4.10 (t, *J* = 7.2 Hz, 2H), 2.64 (s, 3H), 2.39 (t, *J* = 7.2 Hz, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -121.24 (t, *J* = 6.8 Hz).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.2 (d, *J* = 251.5 Hz), 146.9, 146.2, 139.4 (d, *J* = 6.6 Hz), 138.8, 133.3, 131.0 (d, *J* = 7.6 Hz), 126.2, 123.2 (d, *J* = 3.4 Hz), 120.9 (d, *J* = 21.1 Hz), 117.5, 114.8 (d, *J* = 24.3 Hz), 53.2, 28.8, 20.3.

HRMS (ESI): Calcd for $C_{15}H_{13}FN_2O_4S$ $[M+H]^+$: 337.0653, found: 337.0650.

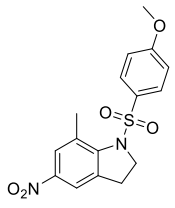


3m

7-methyl-5-nitro-1-(phenylsulfonyl)indoline (3m): Yellow solid; m.p. = 128-130 ℃; yield 87%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.75 (s, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.07 (t, *J* = 7.6 Hz, 2H), 2.66 (s, 3H), 2.29 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3, 146.0, 139.0, 137.3, 133.7, 133.4, 129.2, 127.4, 126.1, 117.3, 53.1, 28.7, 20.3.

HRMS (ESI): Calcd for $C_{15}H_{14}N_2O_4S$ $[M+H]^+$: 319.0747, found: 319.0745.

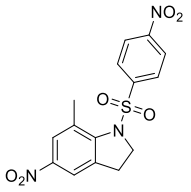


3n

1-((4-methoxyphenyl)sulfonyl)-7-methyl-5-nitroindoline (3n): Orange liquid; yield 93%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 2.4 Hz, 1H), 7.75 (s, 1H), 7.49 – 7.45 (m, 2H), 6.90 – 6.86 (m, 2H), 4.04 (t, *J* = 7.6 Hz, 2H), 3.85 (s, 3H), 2.65 (s, 3H), 2.32 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.6, 147.5, 145.9, 139.1, 133.5, 129.5, 128.7, 126.0, 117.3, 114.3, 114.3, 55.6, 53.0, 28.7, 20.2.

HRMS (ESI): Calcd for $C_{16}H_{16}N_2O_5S$ $[M+H]^+$: 349.0853, found: 349.0851.

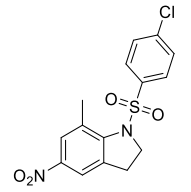


3o

7-methyl-5-nitro-1-((4-nitrophenyl)sulfonyl)indoline (3o): Light yellow liquid; yield 49%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.08 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 3H), 4.14 (t, *J* = 7.5 Hz, 2H), 2.65 (s, 3H), 2.42 (t, *J* = 7.5 Hz, 4H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.60, 146.36, 143.26, 138.45, 133.41, 128.71, 124.37, 117.71, 53.28, 28.84, 20.37.

HRMS (ESI): Calcd for $C_{15}H_{13}N_3O_6S$ $[M+H]^+$: 364.0598, found: 364.0597.

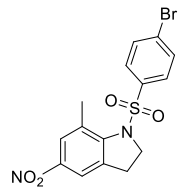


3p

1-((4-chlorophenyl)sulfonyl)-7-methyl-5-nitroindoline (3p): Light yellow solid; m.p. = 134-135 ℃; yield 88%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 2.4 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 4.08 (t, *J* = 7.2 Hz, 2H), 2.64 (s, 3H), 2.38 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.9, 146.1, 140.4, 138.8, 135.9, 133.4, 129.5, 128.7, 126.2, 117.5, 53.1, 28.7, 20.2.

HRMS (ESI): Calcd for $C_{15}H_{13}ClN_2O_4S$ $[M+H]^+$: 353.0357, found: 353.0352.

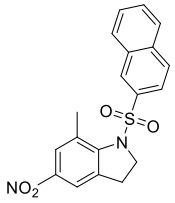


3q

1-((4-bromophenyl)sulfonyl)-7-methyl-5-nitroindoline (3q): Light yellow solid; m.p. = 150-151 ℃; yield 79%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.79 (s, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 4.07 (t, *J* = 7.6 Hz, 2H), 2.64 (s, 3H), 2.38 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.9, 146.1, 138.8, 136.4, 133.4, 132.5, 128.9, 128.8, 126.2, 117.5, 53.1, 28.7, 20.3.

HRMS (ESI): Calcd for $C_{15}H_{13}BrN_2O_4S$ $[M+H]^+$: 396.9852, found: 396.9854.

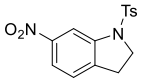


3r

7-methyl-1-(naphthalen-2-ylsulfonyl)-5-nitroindoline (3r): Orange liquid; yield 69%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 2.0 Hz, 1H), 8.06 (d, *J* = 2.0 Hz, 1H), 7.89 (t, *J* = 7.2 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.58 (m, 3H), 7.43 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.12 (t, *J* = 7.6 Hz, 2H), 2.70 (s, 3H), 2.25 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 146.0, 138.9, 135.0, 134.5, 133.4, 131.9, 129.4, 129.3, 129.2, 129.0, 128.0, 127.9, 126.1, 122.2, 117.3, 53.2, 28.8, 20.4.

HRMS (ESI): Calcd for $C_{19}H_{16}N_2O_4S$ $[M+H]^+$: 369.0904, found: 369.0902.

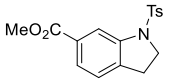


3s

6-nitro-1-tosylindoline (3s): Light yellow solid; m.p. = 182-184 ℃; yield 58%; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.40 (d, *J* = 2 Hz, 1H), 7.84 (dd, *J* = 8, 2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 4.02 (t, *J* = 8.4 Hz, 2H), 3.06 (t, *J* = 8.6 Hz, 2H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 148.2, 144.8, 143.2, 138.8, 133.4, 130.0, 127.3, 125.3, 119.0, 109.1, 50.3, 27.7, 21.5.

HRMS (ESI): Calcd for $C_{15}H_{14}N_2O_4S$ $[M+H]^+$: 319.0747, found: 319.0749.

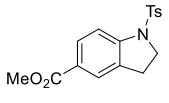


3t

methyl 1-tosylindoline-6-carboxylate (3t): White solid; m.p. = 150-151 ℃; yield 61%; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.24 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 3H), 7.23 (d, *J* = 8 Hz, 2H), 7.13 (d, *J* = 8 Hz, 1H), 3.97 – 3.93 (m, 5H), 2.94 (t, *J* = 8.4 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 166.6, 144.2, 142.3, 137.0, 133.6, 130.0, 129.7, 127.2, 125.4, 124.9, 115.3, 52.1, 50.0, 27.8, 21.4.

HRMS (ESI): Calcd for $C_{17}H_{17}NO_4S$ $[M+H]^+$: 332.0951, found: 332.0954.



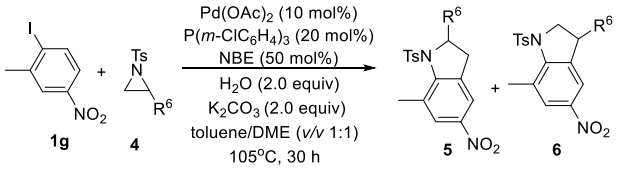
3u

methyl 1-tosylindoline-5-carboxylate (3u): Light yellow solid; m.p. = 134-135 ℃; yield 16%; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.94 – 7.86 (m, 1H), 7.80 – 7.60 (m, 4H), 7.31 – 7.20 (m, 2H), 3.96 (t, *J* = 8.7 Hz, 2H), 3.87 (s, 3H), 2.98 (t, *J* = 8.7 Hz, 2H), 2.37 (s, 3H).

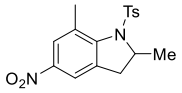
^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.5, 146.0, 144.5, 133.7, 131.6, 130.1, 129.8, 127.1, 126.5, 125.2, 113.5, 51.9, 50.1, 27.2, 21.5.

HRMS (ESI): Calcd for $C_{17}H_{17}NO_4S$ $[M+H]^+$: 332.0951, found: 332.0946.

3.3.2 Synthesis of Indolines 5a-j and 6a-k



General procedure: An oven-dried Schlenk tube under a nitrogen atmosphere was charged with aryl iodide **1g** (0.15 mmol, 1.0 equiv), aziridine **4** (0.30 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), P(*m*-$ClC_6H_4)_3$ (20 mol%), NBE (50 mol%), H_2O (0.3 mmol, 2.0 equiv) and K_2CO_3 (0.30 mmol, 2.0 equiv) in toluene/DME (1 mL, *v/v* 1:1). The mixture was stirred at room temperature for 10 minutes and then stirred in the oil bath at 105 ℃ for 30 h. The resulting mixture was cooled to room temperature and filtered through celite with EtOAc as eluents. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (dichloromethane/ petroleum ether or ethyl acetate/petroleum ether) to afford pure product.

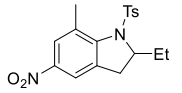


5a

2,7-dimethyl-5-nitro-1-tosylindoline (5a): Yellow liquid; yield 71%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 2.4 Hz, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8 Hz, 2H), 4.54 – 4.47 (m, 1H), 2.66 (s, 3H), 2.41 (s, 3H), 2.30 (dd, *J* = 16, 7.6 Hz, 1H), 2.15 (d, *J* = 16 Hz, 1H), 1.22 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.0, 145.9, 144.6, 138.0, 134.5, 134.0, 129.7, 127.3, 126.2, 117.9, 60.7, 35.4, 21.5, 21.4, 20.4.

HRMS (ESI): Calcd for $C_{17}H_{18}N_2O_4S$ $[M+H]^+$: 347.1060, found: 347.1054.

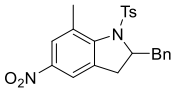


5b

2-ethyl-7-methyl-5-nitro-1-tosylindoline (5b): Yellow solid; m.p. = 129-130 ℃; yield 61%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, *J* = 2.4 Hz, 1H), 7.73 (d, *J* = 2 Hz, 1H), 7.40 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8 Hz, 2H), 4.28 – 4.22 (m, 1H), 2.67 (s, 3H), 2.40 (s, 3H), 2.23 – 2.20 (m, 2H), 1.55 – 1.37 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.4, 146.0, 144.5, 138.5, 134.6, 134.0, 129.7, 127.4, 126.1, 117.6, 66.2, 33.8, 28.1, 21.6, 20.4, 10.1.

HRMS (ESI): Calcd for $C_{18}H_{20}N_2O_4S$ $[M+H]^+$: 361.1217, found: 361.1215.

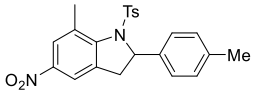


5c

2-benzyl-7-methyl-5-nitro-1-tosylindoline (5c): Yellow liquid; yield 41%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 2.4 Hz, 1H), 7.72 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.15 (d, *J* = 8 Hz, 2H), 7.10 – 7.08 (m, 2H), 4.61 – 4.55 (m, 1H), 2.93 (dd, *J* = 13.6, 6 Hz, 1H), 2.66 – 2.60 (m, 4H), 2.38 – 2.24 (m, 5H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.3, 146.1, 144.5, 138.0, 136.3, 134.6, 133.8, 129.7, 129.4, 128.4, 127.4, 126.8, 126.2, 117.7, 65.6, 41.0, 33.0, 21.6, 20.4.

HRMS (ESI): Calcd for $C_{23}H_{22}N_2O_4S$ $[M+H]^+$: 423.1373, found: 423.1367.

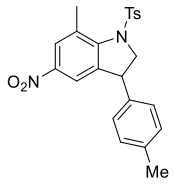


5d

7-methyl-5-nitro-2-(*p*-tolyl)-1-tosylindoline (5d): Yellow liquid; yield 15%; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 1.5 Hz, 1H), 7.74 (s, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.20 (m, 3H), 7.13 – 7.01 (m, 4H), 5.46 (dd, *J* = 6.3, 2.7 Hz, 1H), 2.74 – 2.64 (m, 5H), 2.43 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 146.7, 146.2, 144.8, 137.8, 137.7, 137.1, 134.7, 133.5, 129.8, 129.4, 127.4, 126.4, 125.6, 117.6, 66.4, 36.3, 21.7, 21.0, 20.5.

HRMS (ESI): Calcd for $C_{23}H_{22}N_2O_4S$ $[M+H]^+$: 423.1373, found: 423.1364.

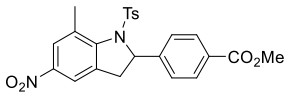


6d

7-methyl-5-nitro-3-(*p*-tolyl)-1-tosylindoline (6d)： Yellow liquid; yield 60%; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.41 (s, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.78 (d, *J* = 7.8 Hz, 2H), 4.45 (dd, *J* = 12.9, 8.1 Hz, 1H), 3.86 (t, *J* = 12.0 Hz, 1H), 3.56 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.69 (s, 3H), 2.46 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 147.7, 146.4, 144.9, 143.0, 137.7, 135.7, 134.7, 133.1, 129.9, 129.7, 128.0, 127.5, 126.4, 117.7, 61.8, 46.9, 21.7, 21.0, 20.4.

HRMS (ESI): Calcd for $C_{23}H_{22}N_2O_4S$ $[M+H]^+$: 423.1373, found: 423.1366.

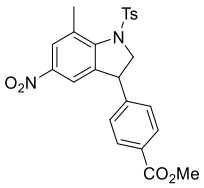


5e

methyl 4-(7-methyl-5-nitro-1-tosylindolin-2-yl)benzoate (5e): Light yellow liquid; yield 29%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 2.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.23 (m, 4H), 5.54 (dd, *J* = 6.4, 3.6 Hz, 1H), 3.88 (s, 3H), 2.79 – 2.66 (m, 5H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.5, 146.5, 146.3, 145.0, 137.2, 134.4, 133.6, 130.1, 130.0, 129.8, 127.4, 126.6, 125.7, 117.7, 66.2, 52.2, 36.3, 21.7, 20.6.

HRMS (ESI): Calcd for $C_{24}H_{22}N_2O_6S$ $[M+H]^+$: 467.1271, found: 467.1266.

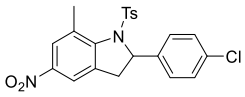


6e

methyl 4-(7-methyl-5-nitro-1-tosylindolin-3-yl)benzoate (6e): Light yellow liquid; yield 37%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 2 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.41 (s, 1H), 7.28 (d, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 4.51 (dd, *J* = 12.8, 7.6 Hz, 1H), 3.93 – 3.87 (m, 1H), 3.90 (s, 3H), 3.75 (dd, *J* = 11.2, 8 Hz, 1H), 2.70 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.4, 147.7, 146.4, 145.1, 144.2, 141.8, 134.6, 133.3, 130.3, 130.0, 129.9, 128.2, 127.5, 126.8, 117.7, 61.5, 52.2, 47.3, 21.7, 20.4.

HRMS (ESI): Calcd for $C_{24}H_{22}N_2O_6S$ $[M+H]^+$: 467.1271, found: 467.1268.

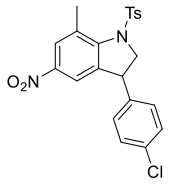


5f

2-(4-chlorophenyl)-7-methyl-5-nitro-1-tosylindoline (5f): Yellow liquid; yield 25%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 2 Hz, 1H), 7.74 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.22 (m, 4H), 7.15 (d, *J* = 8.8 Hz, 2H), 5.46 (dd, *J* = 6.4, 3.2 Hz, 1H), 2.70 – 2.68 (m, 5H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.4, 146.3, 145.0, 138.6, 137.4, 134.5, 133.8, 133.5, 129.9, 128.9, 127.4, 127.1, 126.5, 117.6, 65.9, 36.2, 21.6, 20.5.

HRMS (ESI): Calcd for $C_{22}H_{19}ClN_2O_4S$ $[M+H]^+$: 443.0827, found: 443.0820.

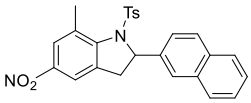


6f

3-(4-chlorophenyl)-7-methyl-5-nitro-1-tosylindoline (6f): Yellow solid; m.p. = 178-180 ℃; yield 49%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 2 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 1H), 7.28 – 7.23 (m, 4H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.48 (dd, *J* = 12.8, 7.6 Hz, 1H), 3.85 (dd, *J* = 12.4, 11.2 Hz, 1H), 3.69 – 3.64 (m, 1H), 2.69 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.7, 146.3, 145.0, 142.0, 137.5, 134.6, 133.7, 133.2, 129.9, 129.4, 129.2, 127.4, 126.6, 117.6, 61.6, 46.7, 21.6, 20.3.

HRMS (ESI): Calcd for $C_{22}H_{19}ClN_2O_4S$ $[M+H]^+$: 443.0827, found: 443.0823.



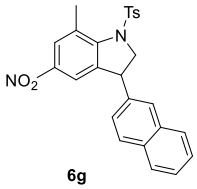
5g

7-methyl-2-(naphthalen-2-yl)-5-nitro-1-tosylindoline (5g): Light yellow solid; m.p. = 76-78 ℃ yield 20%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 2.4 Hz, 1H), 7.79 – 7.70 (m, 4H), 7.65 (s, 1H), 7.55 – 7.50

(m, 2H), 7.47 – 7.42 (m, 2H), 7.30 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.27 – 7.23 (m, 3H), 5.66 (d, *J* = 7.6 Hz, 1H), 2.84 (d, *J* = 16.0 Hz, 1H), 2.81 – 2.72 (m, 4H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.7, 146.3, 144.9, 137.7, 137.2, 134.7, 133.6, 133.0, 132.9, 129.9, 128.8, 128.0, 127.6, 127.5, 126.5, 126.4, 126.3, 124.6, 123.8, 117.6, 66.7, 36.1, 21.7, 20.6.

HRMS (ESI): Calcd for $C_{26}H_{22}N_2O_4S$ $[M+H]^+$: 459.1373, found: 459.1368.

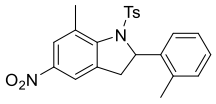


6g

7-methyl-3-(naphthalen-2-yl)-5-nitro-1-tosylindoline (6g): Yellow solid; m.p. = 66-68 ℃ yield 58%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 2.0 Hz, 1H), 7.83 – 7.68 (m, 3H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.38 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.55 (dd, *J* = 12.8, 8.0 Hz, 1H), 4.01 (dd, *J* = 12.8, 10.8 Hz, 1H), 3.84 (dd, *J* = 11.2, 8.0 Hz, 1H), 2.72 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.7, 146.4, 145.0, 142.5, 136.2, 134.7, 133.3, 133.2, 132.8, 129.9, 129.1, 127.7, 127.6, 127.5, 126.6, 126.3, 125.2, 117.9, 61.5, 47.5, 21.6, 20.4.

HRMS (ESI): Calcd for $C_{26}H_{22}N_2O_4S$ $[M+H]^+$: 459.1373, found: 459.1369.

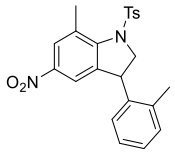


5h

7-methyl-5-nitro-2-(*o*-tolyl)-1-tosylindoline (5h)： Yellow solid; m.p. = 56-58 ℃ yield 23%; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.10 (d, *J* = 2 Hz, 1H), 7.69 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.16 – 7.11 (m, 2H), 7.04 – 7.019 (m, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.64 (d, *J* = 8.4 Hz, 1H), 2.82 – 2.75 (m, 4H), 2.47 – 2.43 (m, 4H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 147.4, 146.3, 144.8, 138.9, 137.3, 134.6, 133.7, 133.2, 130.9, 129.9, 127.8, 127.4, 126.5, 126.3, 124.5, 117.9, 64.1, 37.0, 21.6, 20.7, 19.4.

HRMS (ESI): Calcd for $C_{23}H_{22}N_2O_4S$ $[M+Na]^+$: 445.1192, found: 445.1186.

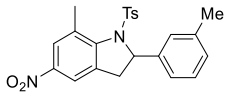


6h

7-methyl-5-nitro-3-(*o*-tolyl)-1-tosylindoline (6h): Yellow solid; m.p. = 140-141 ℃ yield 38%; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.09 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 8 Hz, 2H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.14 – 7.12 (m, 2H), 7.09 – 7.05 (m, 1H), 6.76 – 6.74 (m, 1H), 4.43 (dd, *J* = 10, 4.8 Hz, 1H), 3.83 – 3.73 (m, 2H), 2.72 (s, 3H), 2.44 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 148.0, 146.4, 145.0, 142.8, 136.8, 136.5, 134.6, 133.5, 130.7, 129.9, 127.6, 127.5, 126.9, 126.8, 126.4, 117.6, 60.9, 43.1, 21.6, 20.3, 19.3.

HRMS (ESI): Calcd for $C_{23}H_{22}N_2O_4S$ $[M+Na]^+$: 445.1192, found: 445.1187.

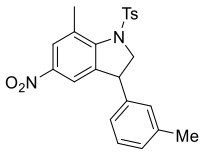


5i

7-methyl-5-nitro-2-(*m*-tolyl)-1-tosylindoline (5i): Yellow liquid; yield 23%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 2 Hz, 1H), 7.73 (s, 1H), 7.49 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.46 (dd, *J* = 6.4, 2.8 Hz, 1H), 2.72 – 2.69 (m, 5H), 2.42 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.8, 146.2, 144.8, 140.1, 138.4, 137.8, 134.7, 133.4, 129.8, 128.7, 128.6, 127.4, 126.5, 126.4, 122.6, 117.6, 66.5, 36.4, 21.6, 21.4, 20.5.

HRMS (ESI): Calcd for $C_{23}H_{22}N_2O_4S$ $[M+H]^+$: 423.1373, found: 423.1368.

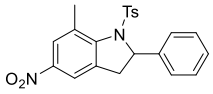


6i

7-methyl-5-nitro-3-(*m*-tolyl)-1-tosylindoline (6i): Yellow liquid; yield 43%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.32 – 7.25 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.2 Hz, 2H), 4.46 (dd, *J* = 13.2, 8.0 Hz, 1H), 3.88 (t, *J* = 12.0 Hz,1H), 3.55 (dd, *J* = 11.6, 8.0 Hz, 1H), 2.70 (s, 3H), 2.47 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.6, 146.3, 144.9, 142.9, 138.7, 138.7, 134.5, 133.1, 129.9, 128.9, 128.8, 128.6, 127.5, 126.4, 125.2, 117.7, 61.7, 47.2, 21.7, 21.3, 20.3.

HRMS (ESI): Calcd for $C_{23}H_{22}N_2O_4S$ $[M+H]^+$: 423.1373, found: 423.1368.

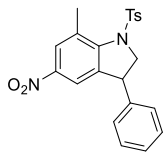


5j

7-methyl-5-nitro-2-phenyl-1-tosylindoline (5j): Yellow liquid; yield 20%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 2.4 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.19 (m, 7H), 5.50 (t, *J* = 4.4 Hz, 1H), 2.72 (s, 5H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.8, 146.3, 144.8, 140.2, 137.7, 134.7, 133.5, 129.9, 128.7, 127.9, 127.4, 126.4, 125.7, 117.6, 66.5, 36.4, 21.6, 20.6.

HRMS (ESI): Calcd for $C_{22}H_{20}N_2O_4S$ $[M+H]^+$: 409.1217, found: 409.1220.

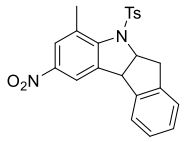


6j

7-methyl-5-nitro-3-phenyl-1-tosylindoline (6j): Yellow liquid; yield 55%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 2.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 1H), 7.29 – 7.26 (m, 5H), 6.92 – 6.89 (m, 2H), 4.48 (dd, *J* = 13.2, 8 Hz, 1H), 3.88 (dd, *J* = 12.8, 11.2 Hz, 1H), 3.62 (dd, *J* = 11.2, 8 Hz, 1H), 2.70 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.7, 146.4, 144.9, 142.7, 138.8, 134.7, 133.1, 129.9, 129.1, 128.2, 127.9, 127.5, 126.5, 117.7, 61.8, 47.4, 21.7, 20.4.

HRMS (ESI): Calcd for $C_{22}H_{20}N_2O_4S$ $[M+H]^+$: 409.1217, found: 409.1221.

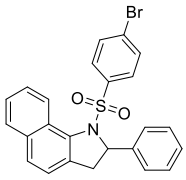


6k

4-methyl-2-nitro-5-tosyl-5,5*a*,6,10*b*-tetrahydroindeno[2,1-*b*]indole (6k): Yellow solid; m.p. = 88-89 ℃; yield 66%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 2 Hz, 1H) 7.73 (s, 1H), 7.42 – 7.40 (m, 2H), 7.33 – 7.31 (m, 1H), 7.26 – 7.11 (m, 5H), 5.23 – 5.17 (m, 1H), 3.73 (d, *J* = 7.6 Hz, 1H), 3.57 (dd, *J* = 16.8, 9.2 Hz, 1H), 2.94 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.69 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.5, 145.8, 144.8, 140.4, 140.1, 139.5, 134.4, 133.4, 129.8, 128.1, 127.8, 127.7, 126.4, 124.8, 124.5, 117.4, 68.8, 50.4, 38.9, 21.6, 20.5.

HRMS (ESI): Calcd for $C_{23}H_{20}N_2O_4S$ $[M+H]^+$: 421.1217, found: 421.1211.

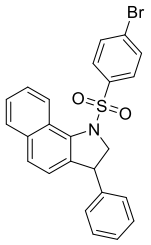


5n

1-((4-bromophenyl)sulfonyl)-2-phenyl-2,3-dihydro-1*H*-benzo[*g*]indole (5n): Light yellow solid; m.p. = 138-139 ℃; yield 9%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.54 – 7.46 (m, 3H), 7.31 – 7.14 (m, 8H), 5.55 (dd, *J* = 7.6, 1.6 Hz, 1H), 2.85 – 2.69 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.0, 137.3, 135.9, 134.1, 132.6, 132.1, 129.1, 128.6, 128.4, 128.4, 127.9, 127.6, 127.2, 126.5, 126.1, 125.8, 125.7, 122.3, 66.7, 37.4.

HRMS (ESI): Calcd for $C_{24}H_{18}BrNO_2S$ $[M+H]^+$: 464.0314, found: 464.0313.



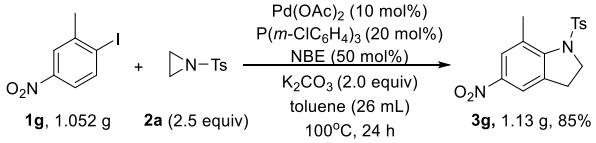
6n

1-((4-bromophenyl)sulfonyl)-3-phenyl-2,3-dihydro-1*H*-benzo[*g*]indole (6n): Light yellow solid; m.p. = 184-185 ℃; yield 43%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.56 – 7.50 (m, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.30 – 7.20 (m, 5H), 6.92 – 6.84 (m, 3H), 4.60 (dd, *J* = 12.8, 7.6 Hz, 1H), 3.98 (dd, *J* = 13.2, 11.2 Hz, 1H), 3.72 (dd, *J* = 10.8, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.4, 137.0, 135.9, 134.1, 132.1, 129.2, 128.8, 128.5, 128.2, 127.9, 127.4, 126.5, 126.3, 125.9, 122.2, 62.3, 47.9.

HRMS (ESI): Calcd for $C_{24}H_{18}BrNO_2S$ $[M+H]^+$: 464.0314, found: 464.0312.

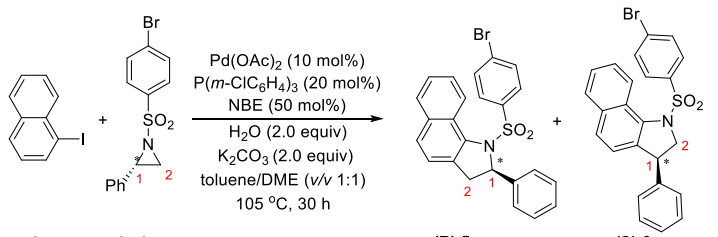
3.4 Procedure for Gram-scale reaction



1g, 1.052 g **2a** (2.5 equiv) **3g,** 1.13 g, 85%

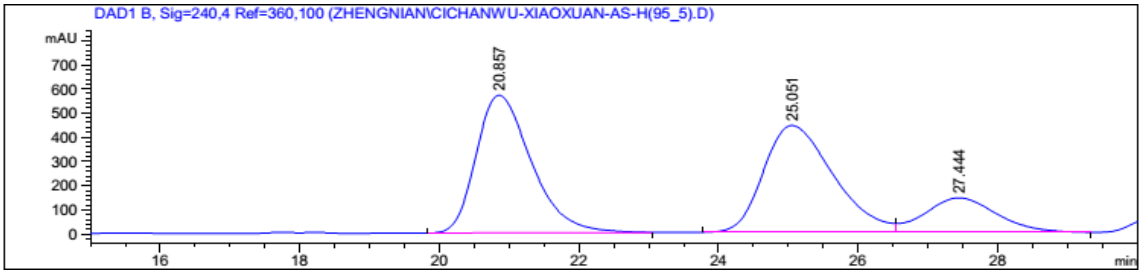
An oven-dried Schlenk tube under a nitrogen atmosphere was charged with aryl iodide **1g** (1.052 g, 4.0 mmol), aziridine **2a** (1.97 g, 10.0 mmol), $Pd(OAc)_2$ (90.6 mg, 0.4 mmol), P(*m*-$ClC_6H_4)_3$ (293 mg, 0.8 mmol), NBE (190 mg, 2.0 mmol) and K_2CO_3 (1.11 g, 8.0 mmol) in toluene (26 mL). The mixture was stirred at room temperature for 10 minutes and then stirred in the oil bath at 100 ℃ for 24 h. The resulting mixture was cooled to room temperature and filtered through celite with EtOAc as eluents. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether 1/10) to give the product **3g** as yellow solid (1.13 g, 85% yield).

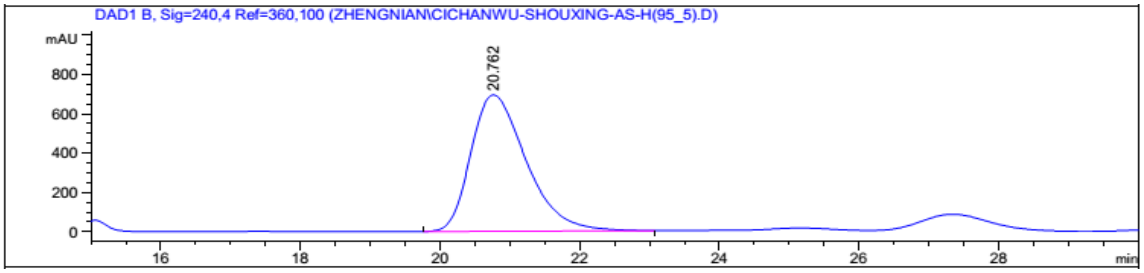
3.5 Coupling Reaction Using 1-Iodonaphthalene and Chiral Aziridine *(S)*-4n



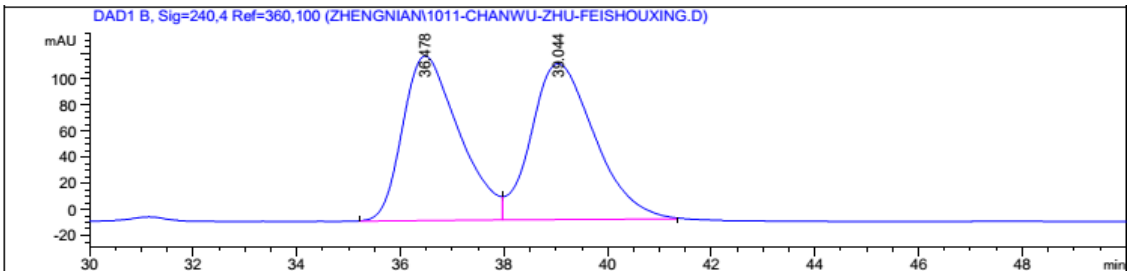
1o **(*S*)-4n** >99% ee **(*R*)-5n** 9% yield, >99% ee **(*S*)-6n** 43% yield, >99% ee

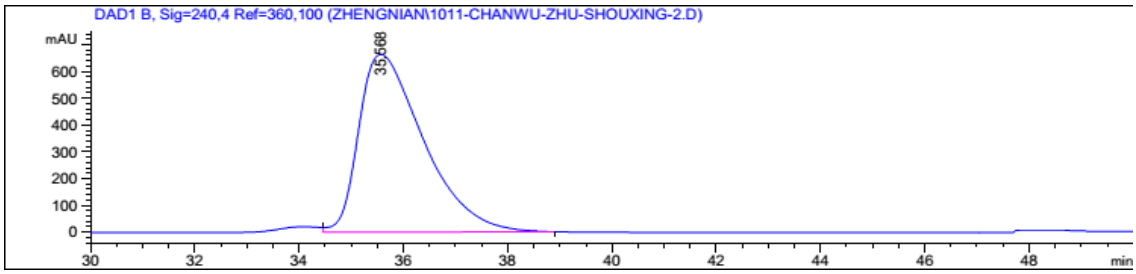
The enantiomeric excess of **(*R*)-5n** was determined by HPLC (chiral column: CHIRALPAK AS-H; solvent: hexane/2-propanol = 95/5; flow rate: 1 mL/min; detection: at 240 nm) analysis in comparison with authentic racemic material: Retention time = 20.86 min (R) and 25.05 min (S). $[\alpha]^{22.1}_{D}$ = - 124.0 ° (*c* 0.5, $CHCl_3$). >99% ee.



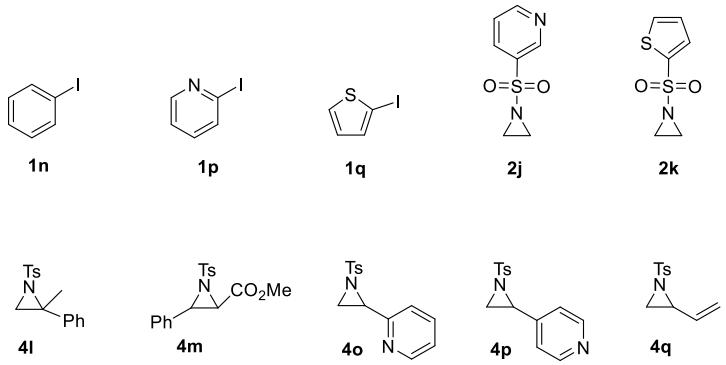


The enantiomeric excess of **(*S*)-6n** was determined by HPLC (chiral column: CHIRALPAK AD-H; solvent: hexane/2-propanol = 98/2; flow rate: 1 mL/min; detection: at 240 nm) analysis in comparison with authentic racemic material: Retention time = 36.48 min (S) and 39.05 min (R). $[\alpha]^{19.8}_{D}$ = - 184.0 ° (*c* 1.0, $CHCl_3$). >99% ee.



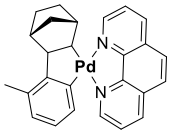


3.6 The further study of the reaction



1) The iodobenzene **1n** without any substituent groups was unable to give the corresponding product **3v** (trace, Determined by GC-MS).
2) We tried some heterocyclic substrates, such as (i) 2-iodopyridine **1p**, 2-iodothiophene **1q**; (ii) 3-(aziridin-1-ylsulfonyl)pyridine **2j,** 1-(thiophen-2-ylsulfonyl)aziridine **2k**; (iii) 2-(1-tosylaziridin-2-yl)pyridine **4o**, 4-(1-tosylaziridin-2-yl)pyridine **4p**. Nevertheless, none of them can be transformed to desired heterocyclic products (Determined by GC-MS or FID-MS).
3) Poly-substituted aziridines, like *gem*-disubstituted **4l** and 1,2-disubstituted **4m** aziridines were incompatible with aryl iodide **1g** (Determined by GC-MS or FID-MS).
4) No desired products were tested when unsaturated aziridine 1-tosyl-2-vinylaziridine **4q** was combined with aryl iodide **1g** (Determined by GC-MS).

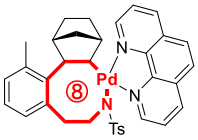
4 Preparation of X-ray Structures of Intermediates B, D and F



B

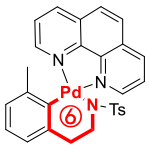
(a) intermediate **B**: Orange solid complex **B** was prepared as described previously.[5] Low-temperature liquid diffusion-controlled crystallization ($CHCl_3$/n-hexane) of intermediate **B** was carried out at about 0 ℃. About two weeks, orange crystal was isolated from solution, which was fully characterized by ^{1}H NMR spectroscopy and single crystal X-ray analysis.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.55 (dd, *J* = 4.8, 1.2 Hz, 1H), 9.22 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.46 – 8.44 (m, 2H), 7.92 (s, 2H), 7.90 – 7.88 (m, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 3.42 (dd, *J* = 7.2, 2.4 Hz, 1H), 3.07 (d, *J* = 6.6 Hz, 1H), 2.63 (d, *J* = 4.2 Hz, 1H), 2.41 (d, *J* = 3.6 Hz, 1H), 2.38 (s, 3H), 2.26 (d, *J* = 9.0 Hz, 1H), 1.76 – 1.74 (m, 1H), 1.64 – 1.62 (m, 1H), 1.54 – 1.50 (m, 1H), 1.46 – 1.43 (m, 1H), 1.08 (d, *J* = 9.0 Hz, 1H).



E

(b) intermediate **E**: The reaction between **B** (0.03 mmol, 1.0 equiv) and **2a** (0.15 mmol, 5.0 equiv) was carried out in CH_2Cl_2 (0.6 mL) under nitrogen at room temperature. 20 minutes later, removal of most of solution and addition of ether led to the formation of an orange powder. Then low-temperature gas diffusion-controlled crystallization (DMF/EtOAc) of the orange powder was carried out below -20 ℃. About one year, yellow crystal was isolated from solution, which was characterized by single crystal X-ray analysis.



F

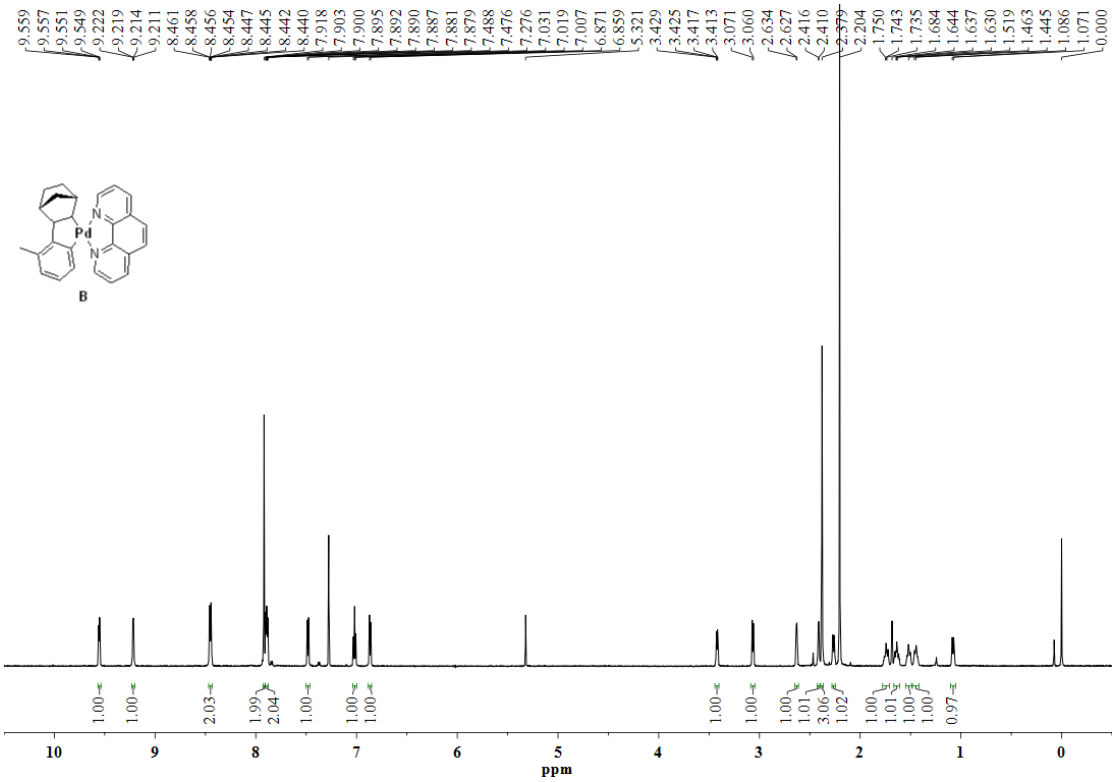
(c) intermediate **F**: The reaction between **B** (0.03 mmol, 1.0 equiv) and **2a** (0.15 mmol, 5.0 equiv) was carried out in CH_2Cl_2 (0.6 mL) under nitrogen at room temperature. 20 minutes later, most of CH_2Cl_2 was removed. Then low-temperature liquid diffusion-controlled crystallization (CH_2Cl_2/MeOH) was carried out at about 0 ℃. About three weeks, yellow crystal was isolated from solution, which was fully characterized by ^{1}H NMR spectroscopy (273 K) and single crystal X-ray analysis.

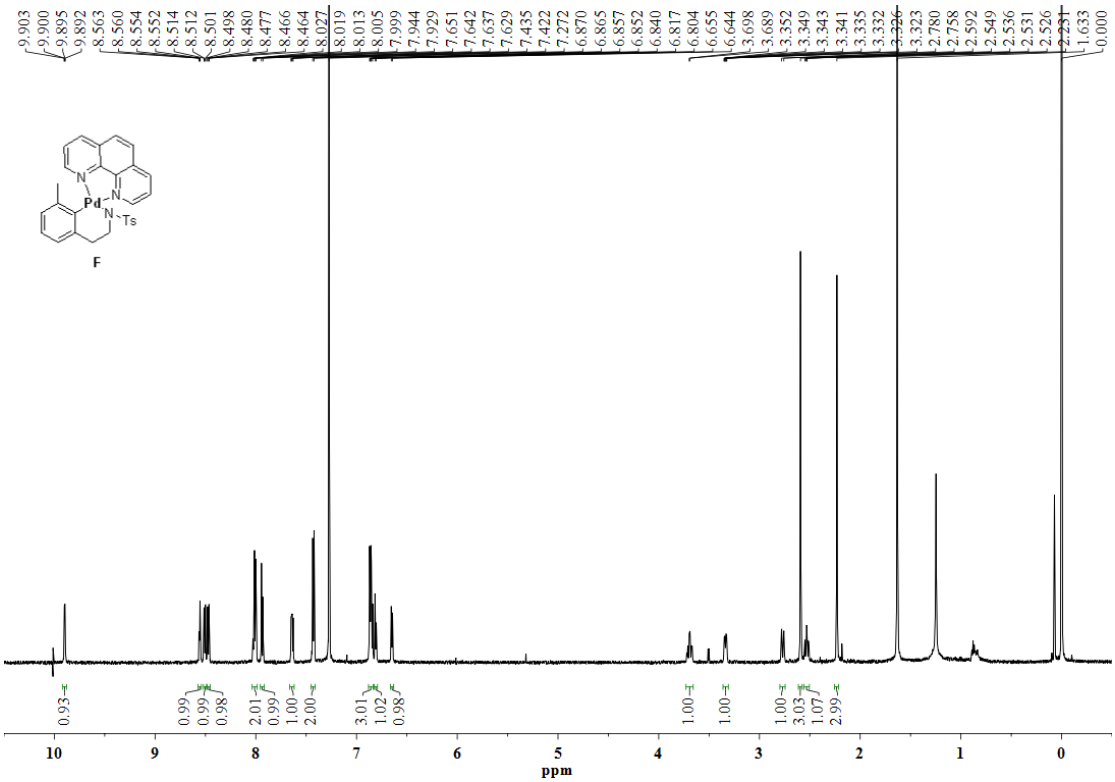
^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.90 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.56 (dd, *J* = 5.4, 1.8 Hz, 1H), 8.51 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.47 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.03 – 8.00 (m, 2H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.64 (dd, *J* = 8.4, 5.4 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 6.87 – 6.84 (m, 3H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 6.6 Hz, 1H), 3.69 (td, *J* = 13.2, 5.4 Hz, 1H), 3.35 – 3.32 (m, 1H), 2.77 (d, *J* = 13.2 Hz, 1H), 2.59 (s, 3H), 2.55 – 2.51 (m, 1H), 2.23 (s, 3H).

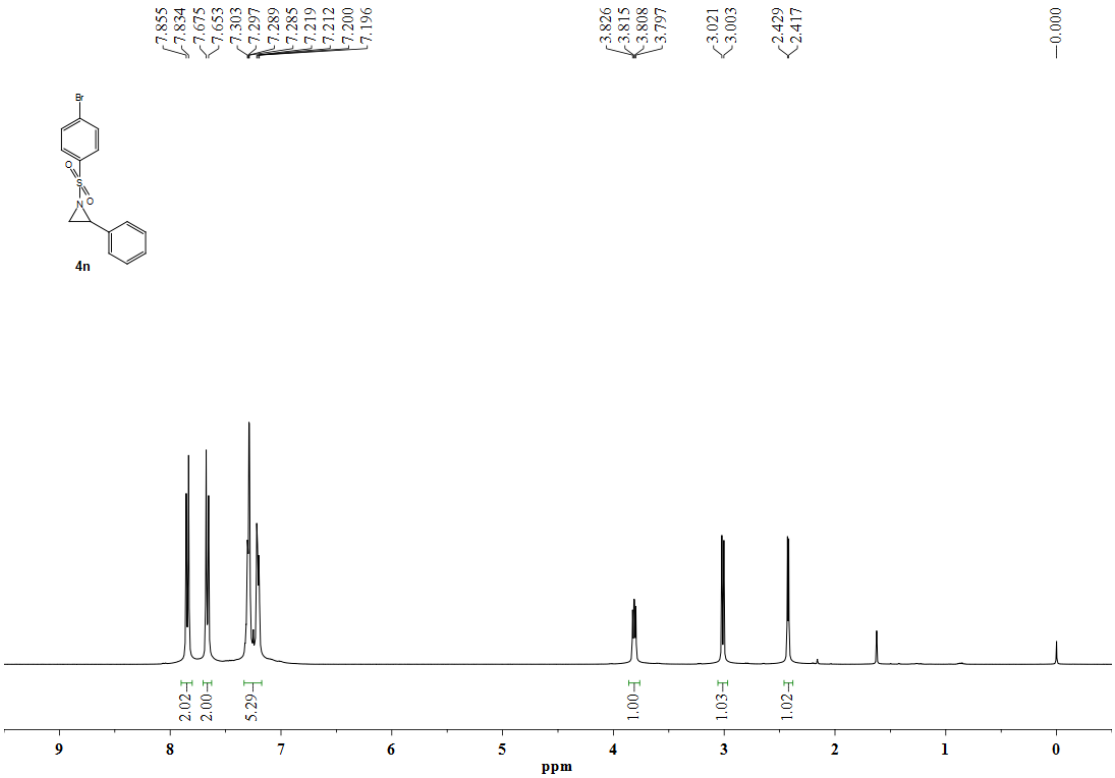
5 References

1. (a) A. E. Martin, T. M. Ford and J. E. Bulkowski, *J. Org. Chem.*, 1982, **47**, 412; (b) R. Shintani, K. Ikehata and T. Hayashi, *J. Org. Chem.*, 2011, **76**, 4776.
2. C.-Y. Huang and A. G. Doyle, *J. Am. Chem. Soc.*, 2012, **134**, 9541.
3. S. Gandhi, A. Bisai, B. A. B. Prasad and V. K. Singh, *J. Org. Chem.*, 2007, **72**, 2133.
4. S. I. Ali, M. D. Nikalje and A. Sudalai, *Org. Lett.*, 1999, **1**, 705.
5. M. Catellani and G. P. Chiusoli, *J. Organomet. Chem.*, 1988, **346**, C27.

6 NMR Spectra



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3.815
3.808
3.797
3.021
3.003
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2.417
0.000
Br
O
S
N
O
4n
2.02
2.00
5.29
1.00
1.03
1.02
9
8
7
6
5
4
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2
1
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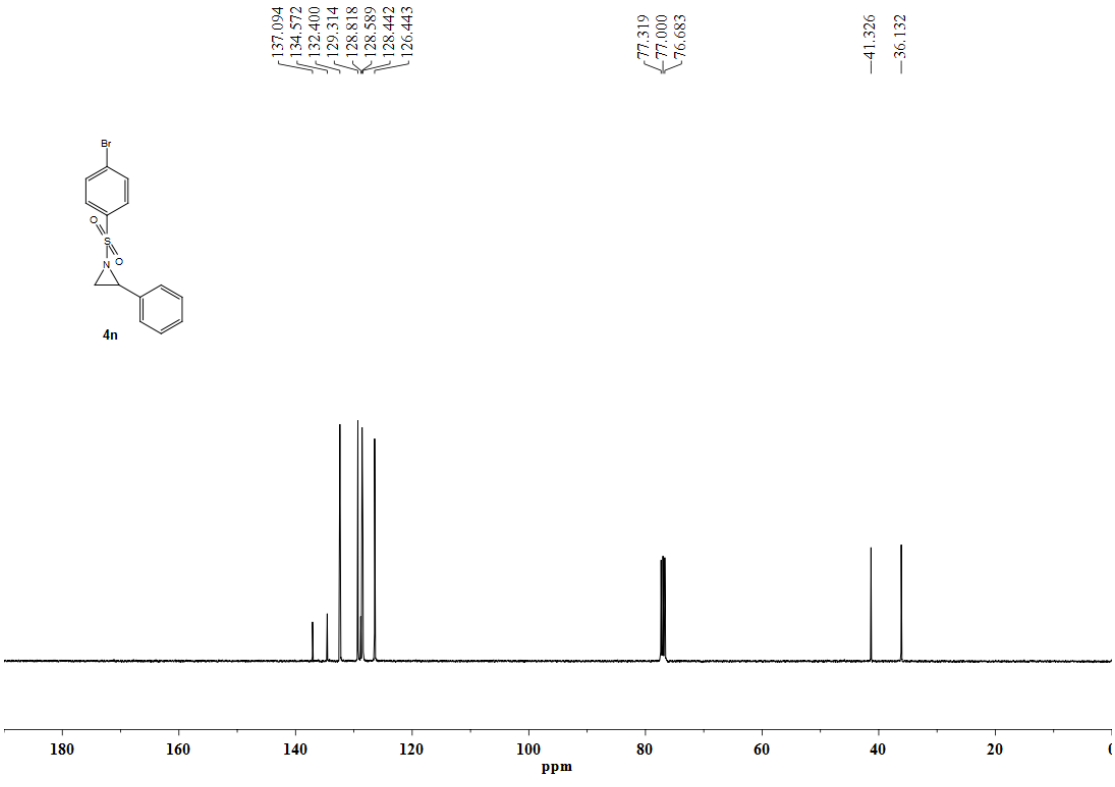
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134.572
132.400
129.314
128.818
128.589
128.442
126.443
77.319
77.000
76.683
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Br
O
S
N
O
4n
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140
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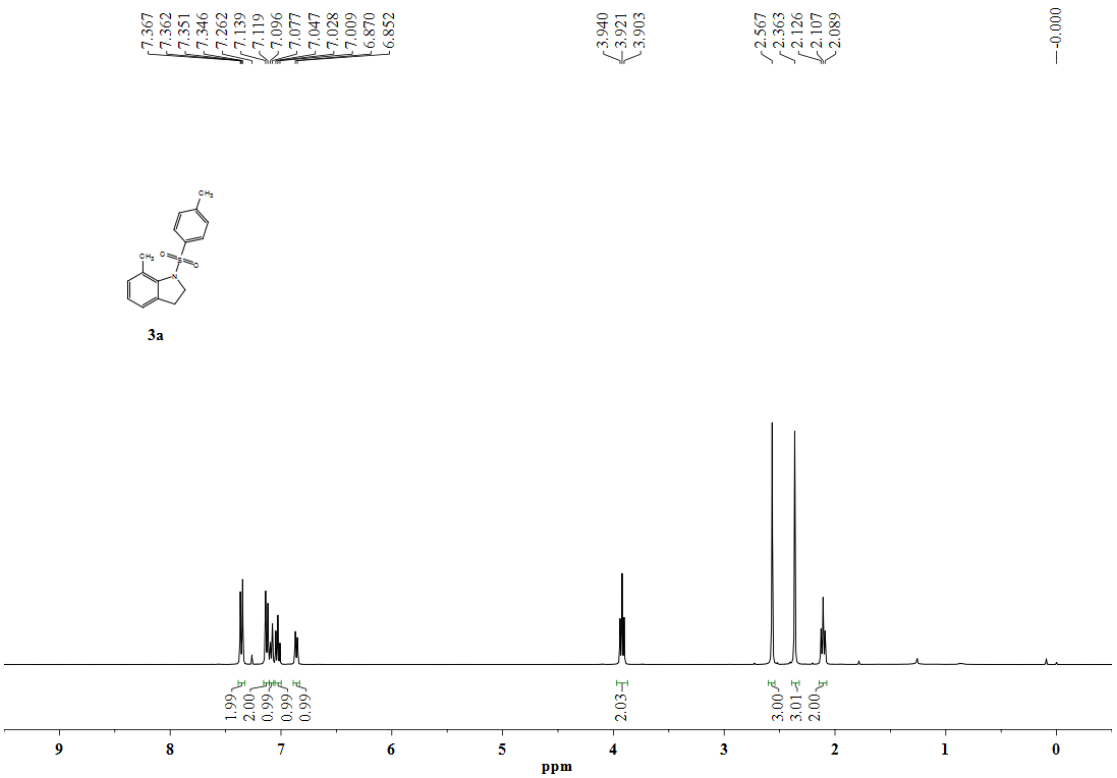
60
40
20
ppm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7.351
7.346
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7.139
7.119
7.096
7.077
7.047
7.028
7.009
6.870
6.852
3.940
3.921
3.903
2.567
2.363
2.126
2.107
2.089
0.000
3a
1.99
2.00
0.99
0.99
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3.00
3.01
2.00
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8
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6
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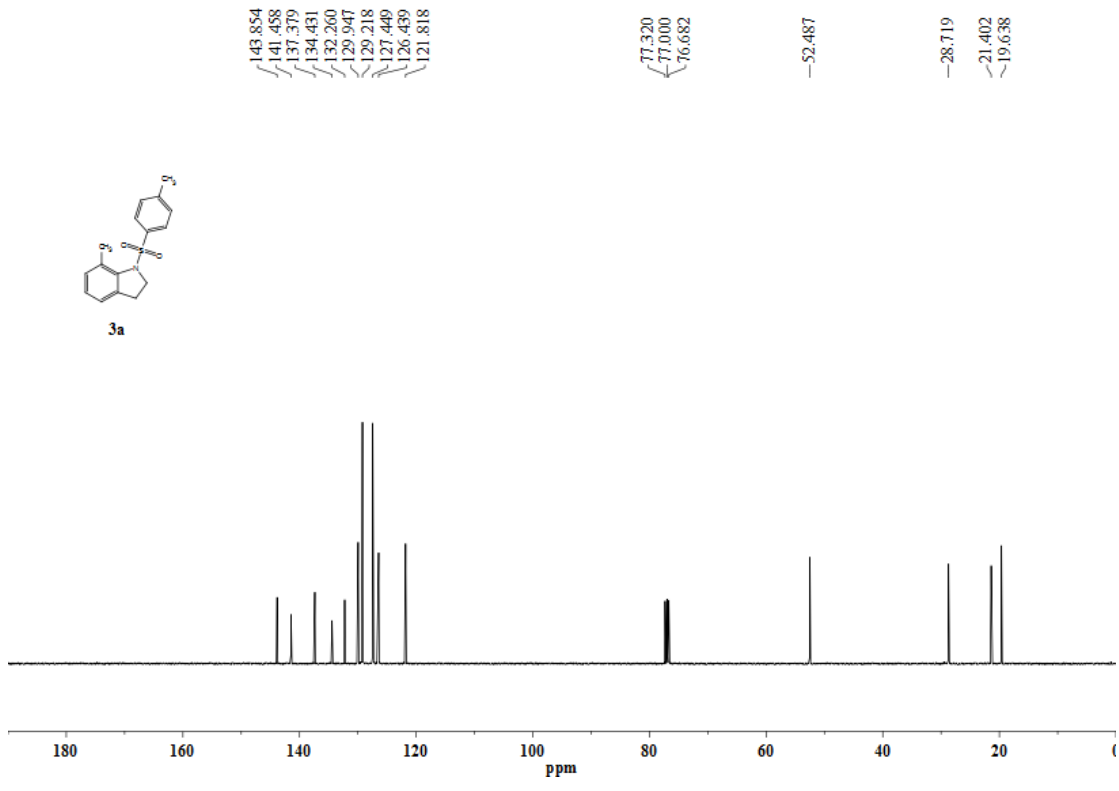
0
ppm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141.458
137.379
134.431
132.260
129.947
129.218
127.449
126.439
121.818
77.320
77.000
76.682
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28.719
21.402
19.638
3a
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140
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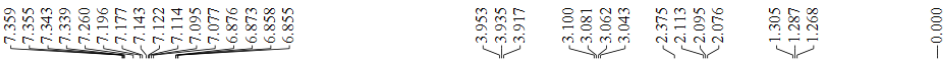
60
40
20
ppm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7.343
7.339
7.260
7.196
7.177
7.143
7.122
7.114
7.095
7.077
6.876
6.873
6.858
6.855
3.953
3.935
3.917
3.100
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3.062
3.043
2.375
2.113
2.095
2.076
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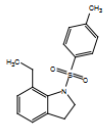
1.287
1.268
0.000



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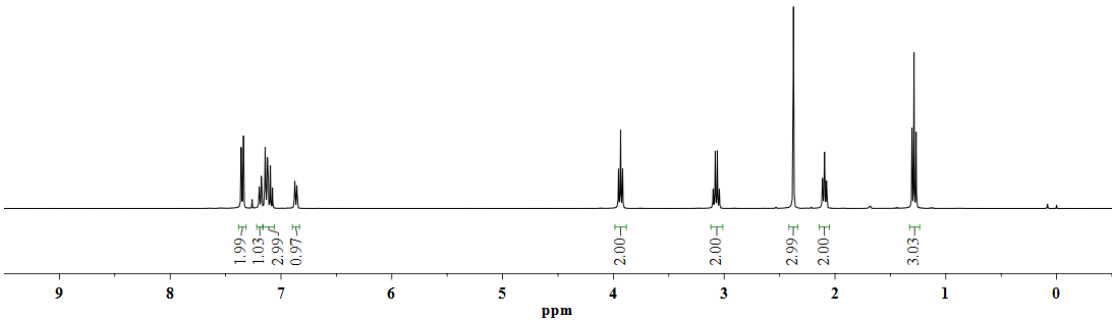
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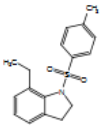
2.99
0.97
2.00
2.00
2.99
2.00
3.03
9
8
7
6
5
4
3
2
1
0
ppm


143.894
140.898
138.501
137.477
134.513
129.271
128.000
127.606
126.873
121.832
77.319
77.000
76.683
52.637
28.804
25.174
21.495
14.299



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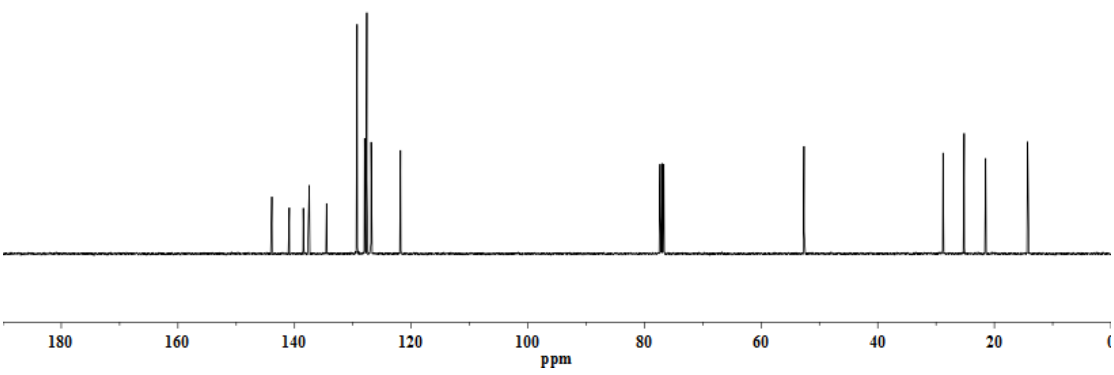
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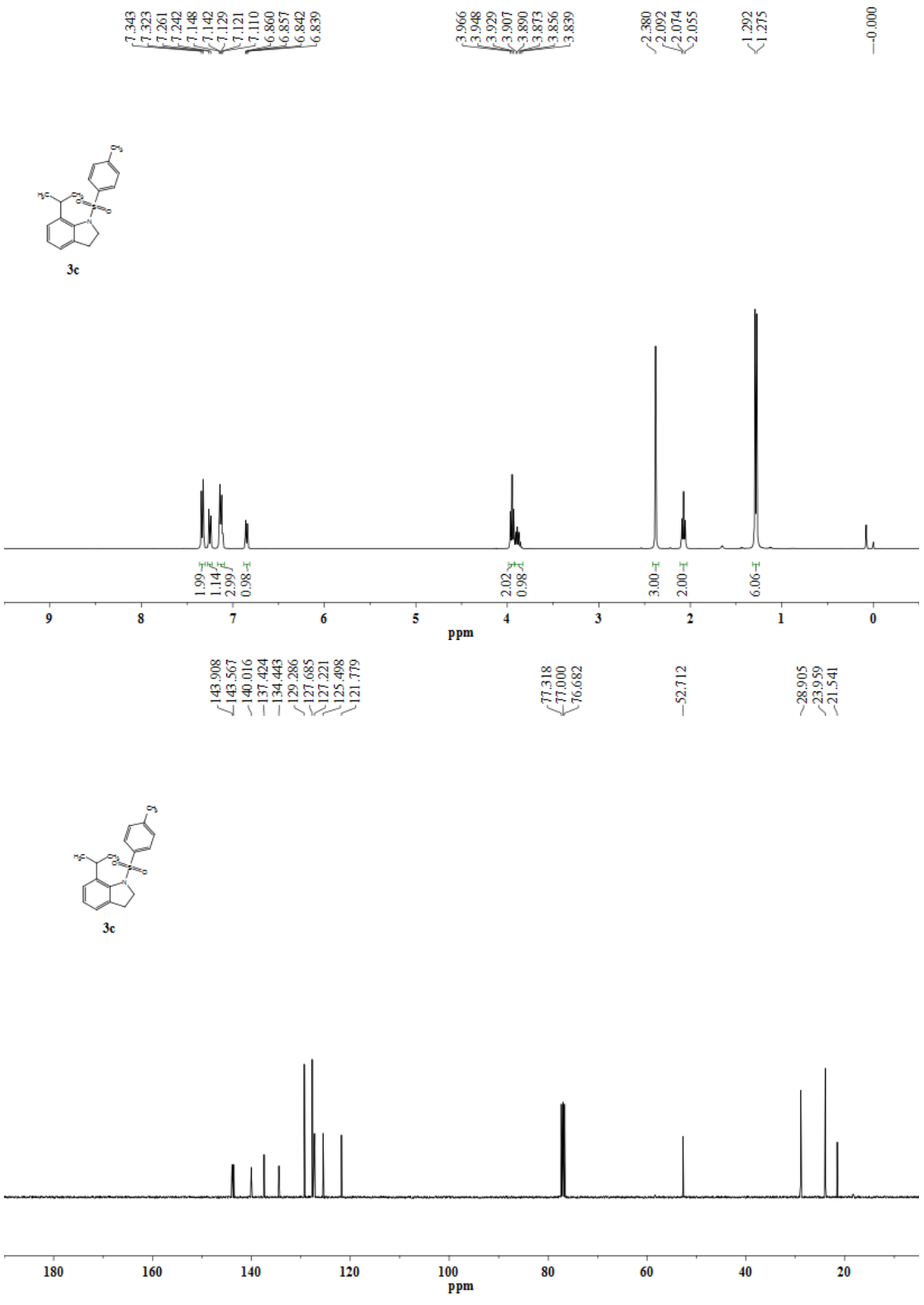
160
140
120
100
80
60
40
20
ppm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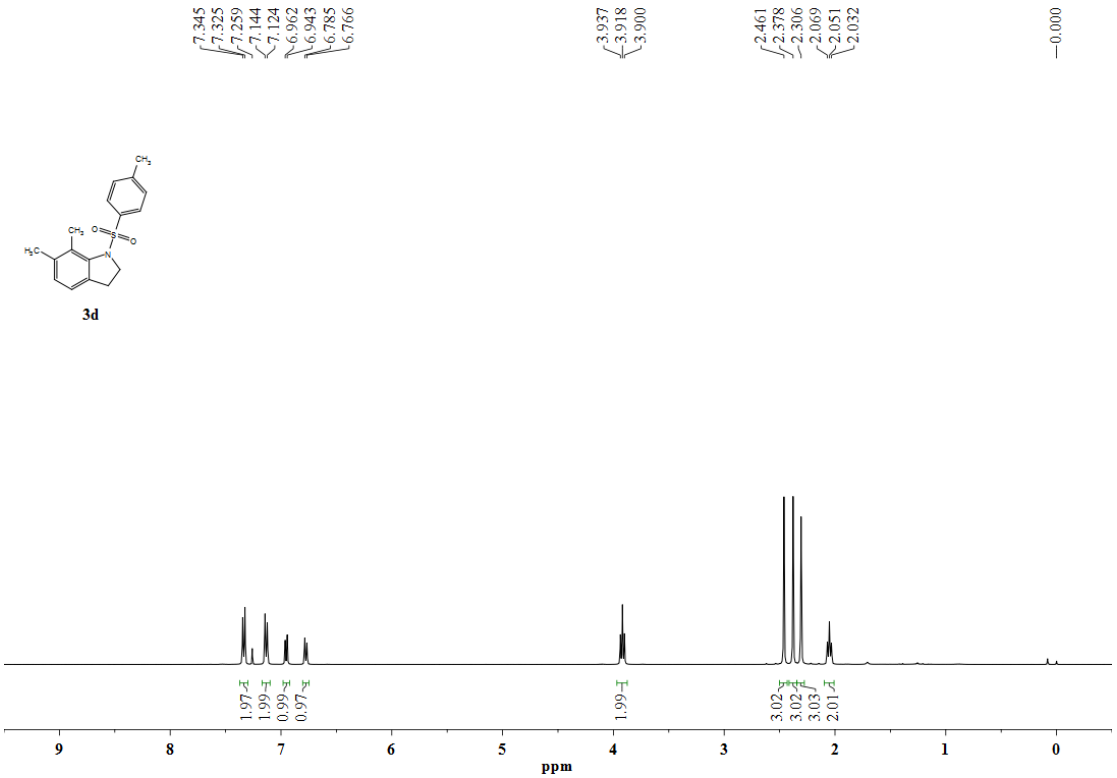
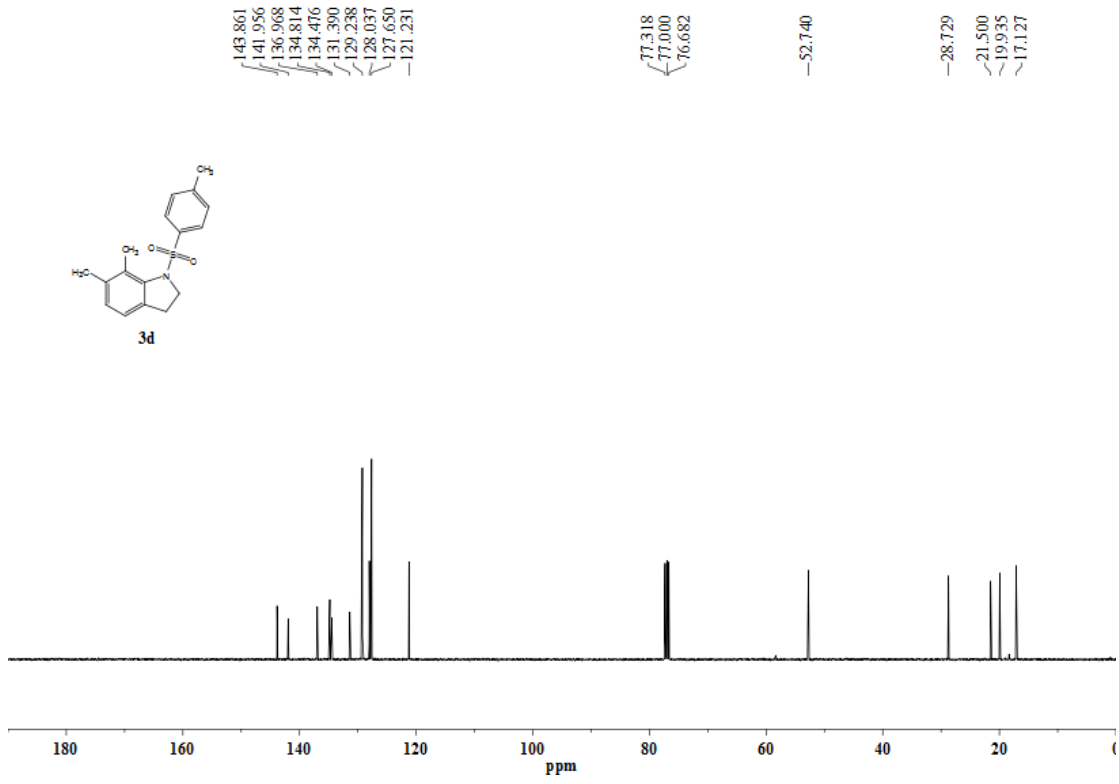
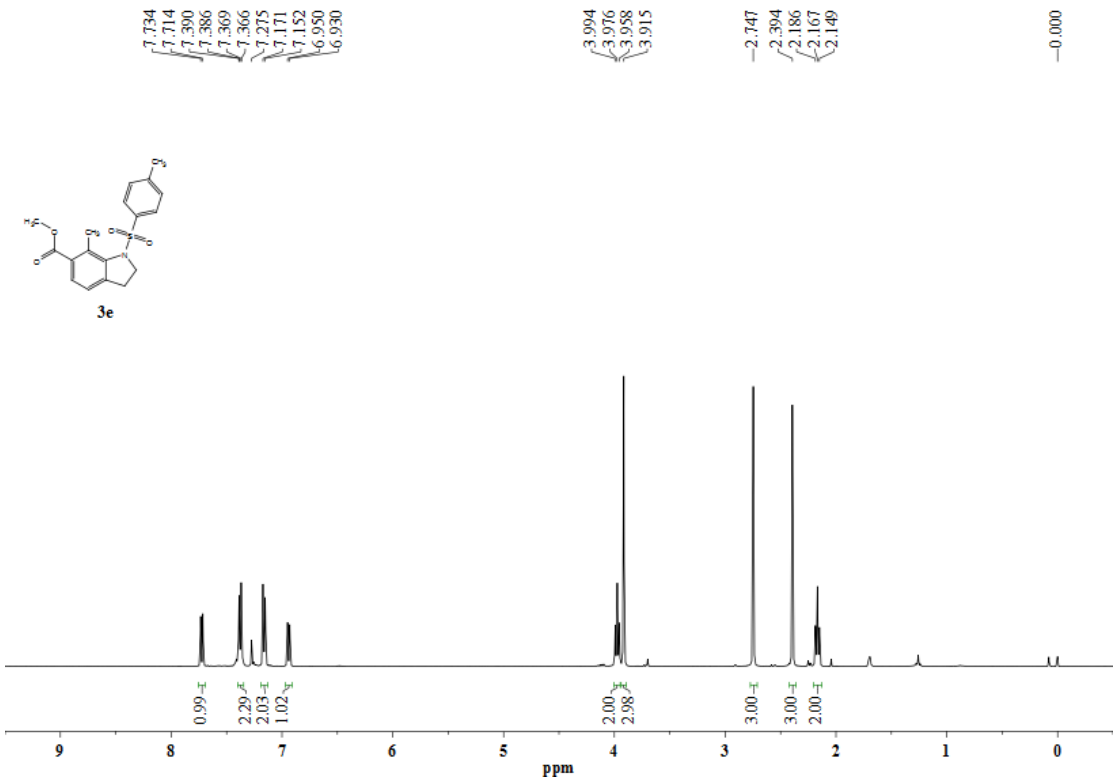
7.323
7.261
7.242
7.148
7.142
7.129
7.121
7.110
6.860
6.857
6.842
6.839
3.966
3.948
3.929
3.907
3.890
3.873
3.856
3.839
2.380
2.092
2.074
2.055
1.292
1.275
0.000
3c
1.99
1.14
2.99
0.98
2.02
0.98
3.00
2.00
6.06
9
8
7
6
5
4
3
2
1
0
ppm
143.908
143.567
140.016
137.424
134.443
129.286
127.685
127.221
125.498
121.779
77.318
77.000
76.682
52.712
28.905
23.959
21.541
3c
180
160
140
120
100
80
60
40
20
ppm


7.345
7.325
7.259
7.144
7.124
6.962
6.943
6.785
6.766
3.937
3.918
3.900
2.461
2.378
2.306
2.069
2.051
2.032
0.000
3d
1.97
1.99
0.99
0.97
1.99
3.02
3.02
3.03
2.01
9
8
7
6
5
4
3
2
1
0
ppm


143.861
141.956
136.968
134.814
134.476
131.390
129.238
128.037
127.650
121.231
77.318
77.000
76.682
52.740
28.729
21.500
19.935
17.127
3d
180
160
140
120
100
80
60
40
20
ppm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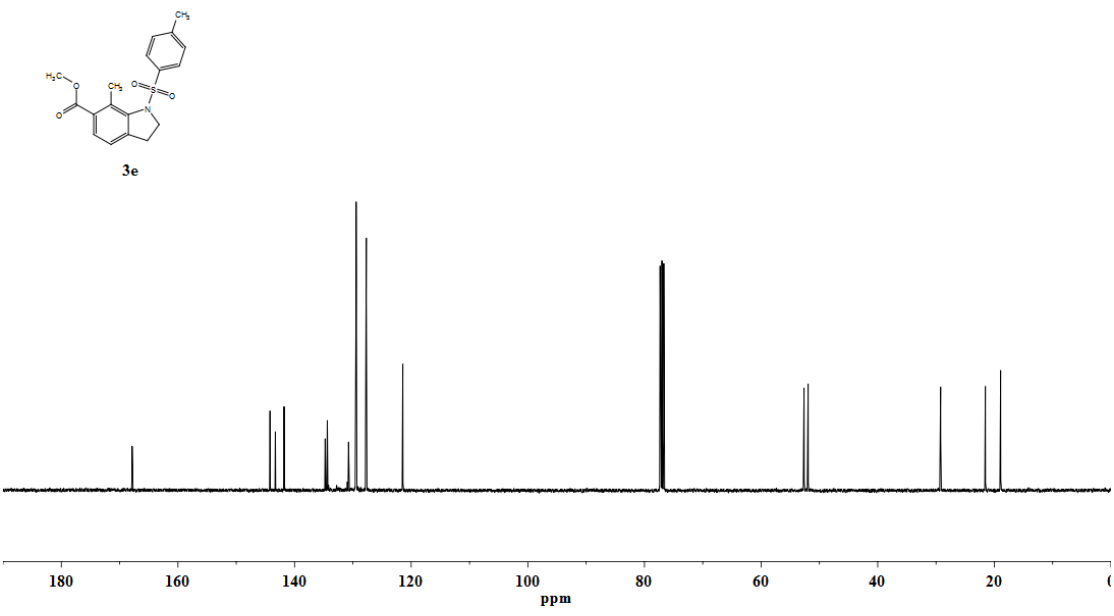
7.714
7.390
7.386
7.369
7.366
7.275
7.171
7.152
6.950
6.930
3.994
3.976
3.958
3.915
2.747
2.394
2.186
2.167
2.149
0.000
0.99
2.29
2.03
1.02
2.00
2.98
3.00
3.00
2.00
ppm

3e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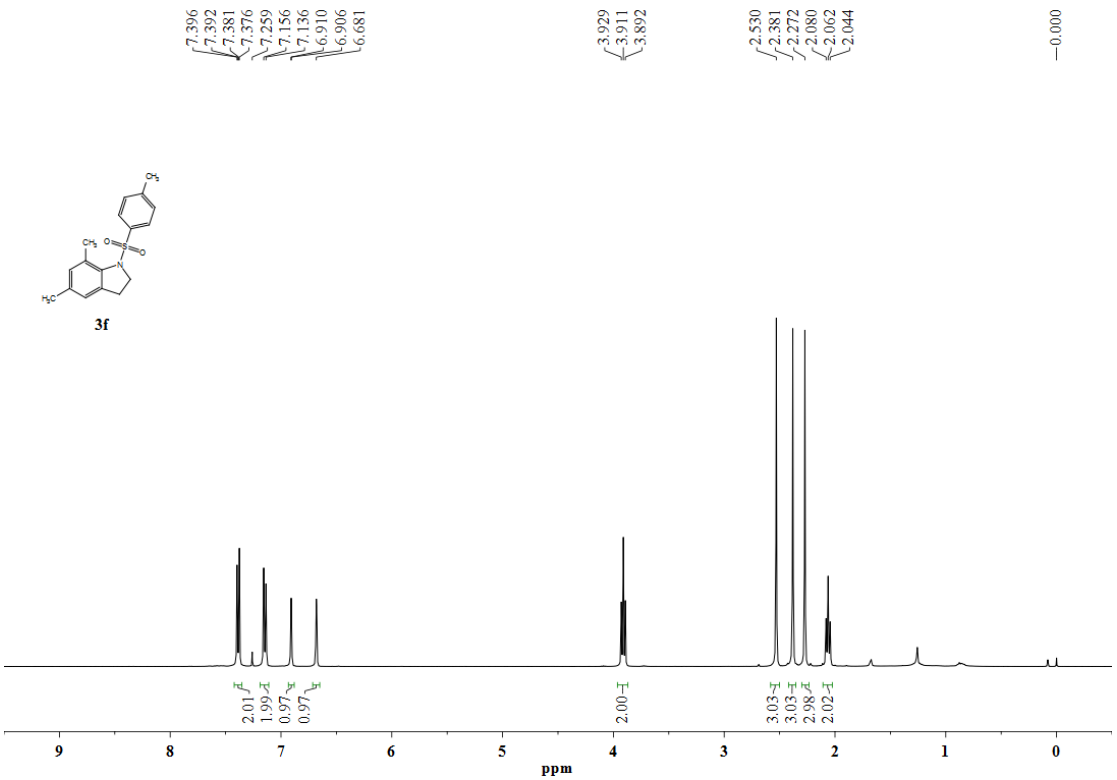
144.213
143.293
141.797
134.753
134.385
130.742
129.506
129.440
127.700
121.440
77.318
76.999
76.682
52.635
51.934
29.211
21.546
18.925
ppm

3e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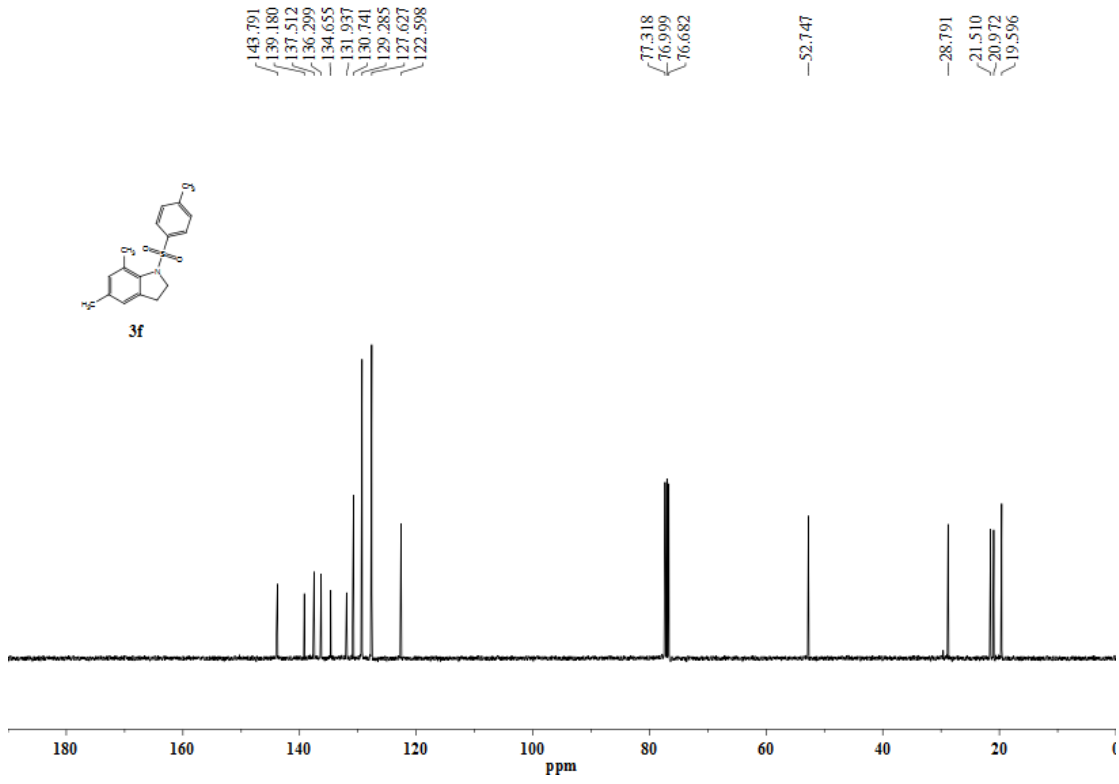
7.392
7.381
7.376
7.259
7.156
7.136
6.910
6.906
6.681
3.929
3.911
3.892
2.530
2.381
2.272
2.080
2.062
2.044
0.000
3f
2.01
1.99
0.97
0.97
2.00
3.03
3.03
2.98
2.02
ppm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137.512
136.299
134.655
131.937
130.741
129.285
127.627
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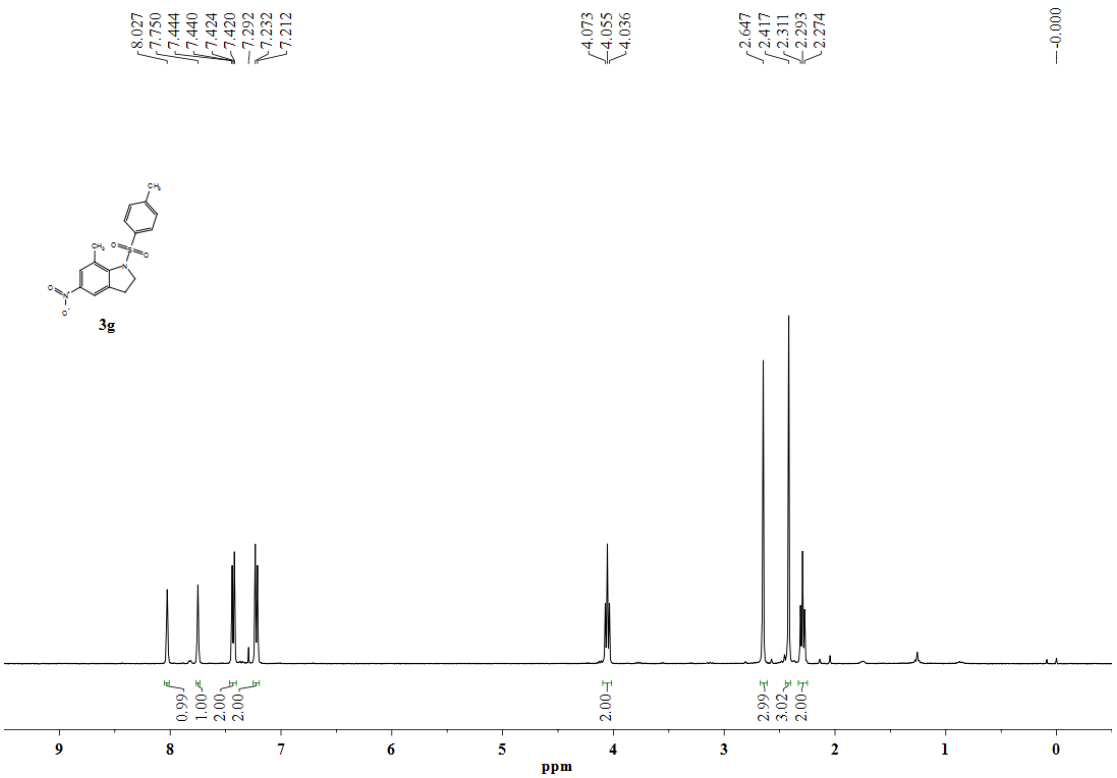
77.318
76.999
76.682
52.747
28.791
21.510
20.972
19.596
3f
ppm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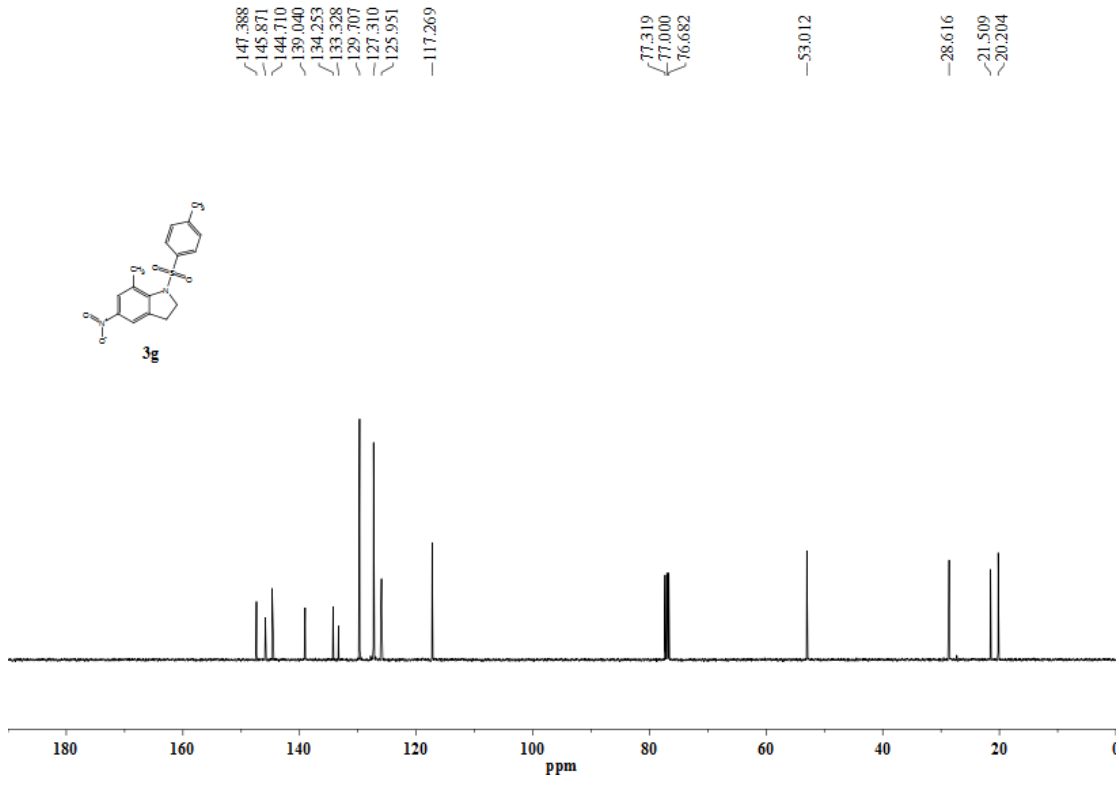
7.444
7.440
7.424
7.420
7.292
7.232
7.212
4.073
4.055
4.036
2.647
2.417
2.311
2.293
2.274
0.000
3g
0.99
1.00
2.00
2.00
2.00
2.99
3.02
2.00
9
8
7
6
5
4
3
2
1
0
ppm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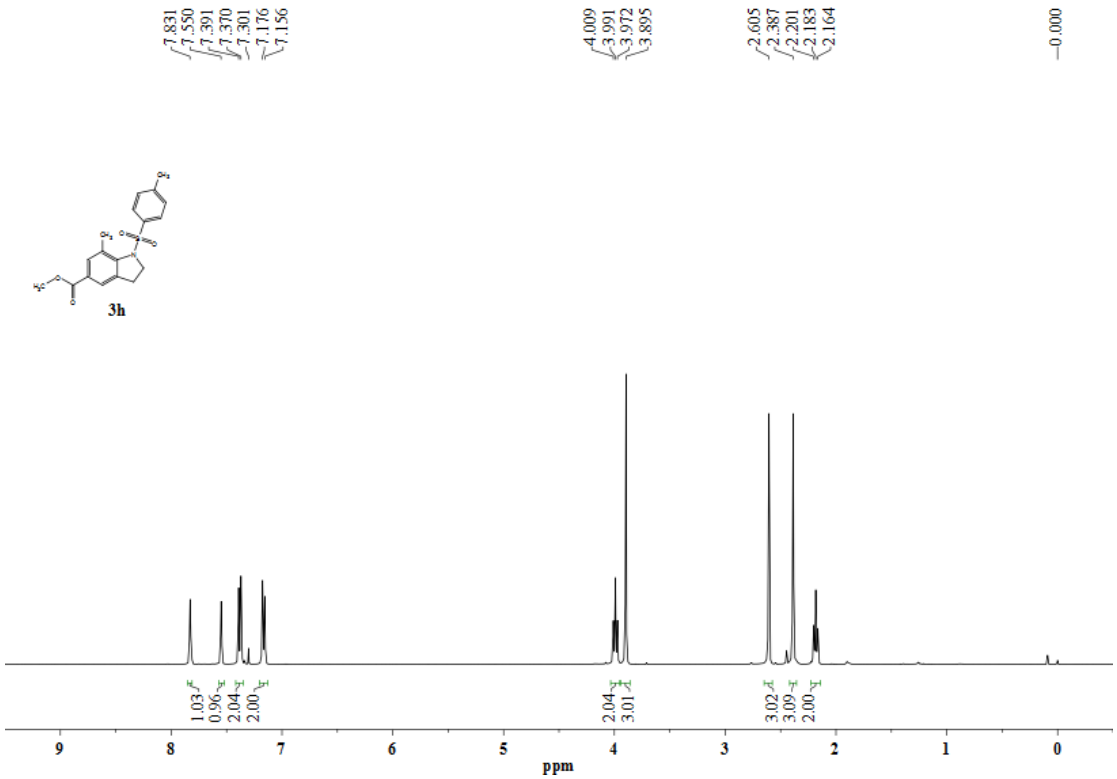
145.871
144.710
139.040
134.253
133.328
129.707
127.310
125.951
117.269
77.319
77.000
76.682
53.012
28.616
21.509
20.204
3g
180
160
140
120
100
80
60
40
20
ppm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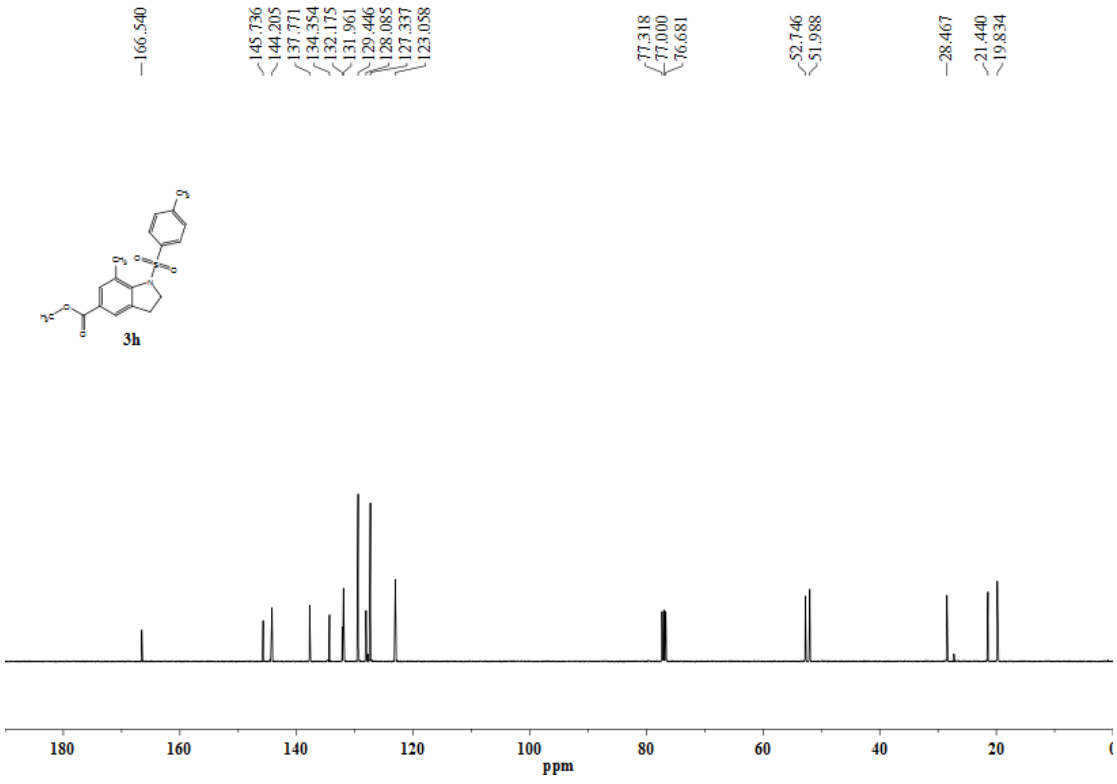
7.550
7.391
7.370
7.301
7.176
7.156
4.009
3.991
3.972
3.895
2.605
2.387
2.201
2.183
2.164
0.000
3h
1.03
0.96
2.04
2.00
2.04
3.01
3.02
3.09
2.00
ppm


166.540
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144.205
137.771
134.354
132.175
131.961
129.446
128.085
127.337
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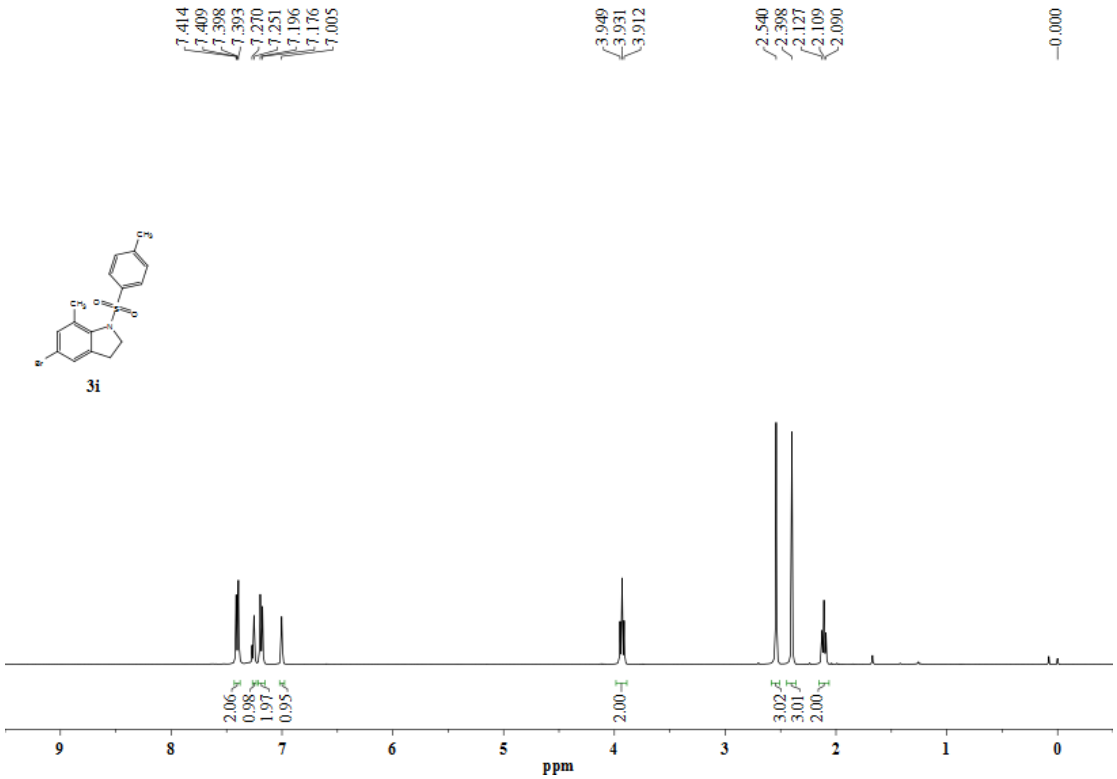
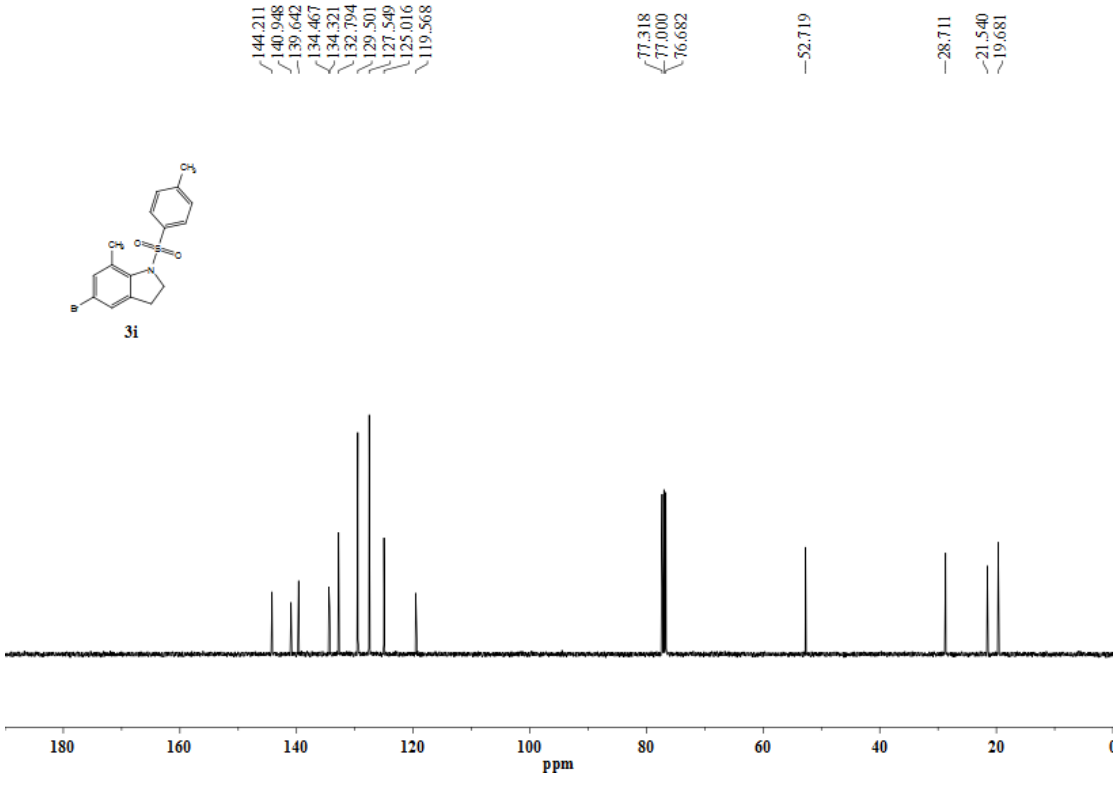
77.318
77.000
76.681
52.746
51.988
28.467
21.440
19.834
3h
ppm


7.414
7.409
7.398
7.393
7.270
7.251
7.196
7.176
7.005
3.949
3.931
3.912
2.540
2.398
2.127
2.109
2.090
0.000
3i
2.06
0.98
1.97
0.95
2.00
3.02
3.01
2.00
9
8
7
6
5
4
3
2
1
0
ppm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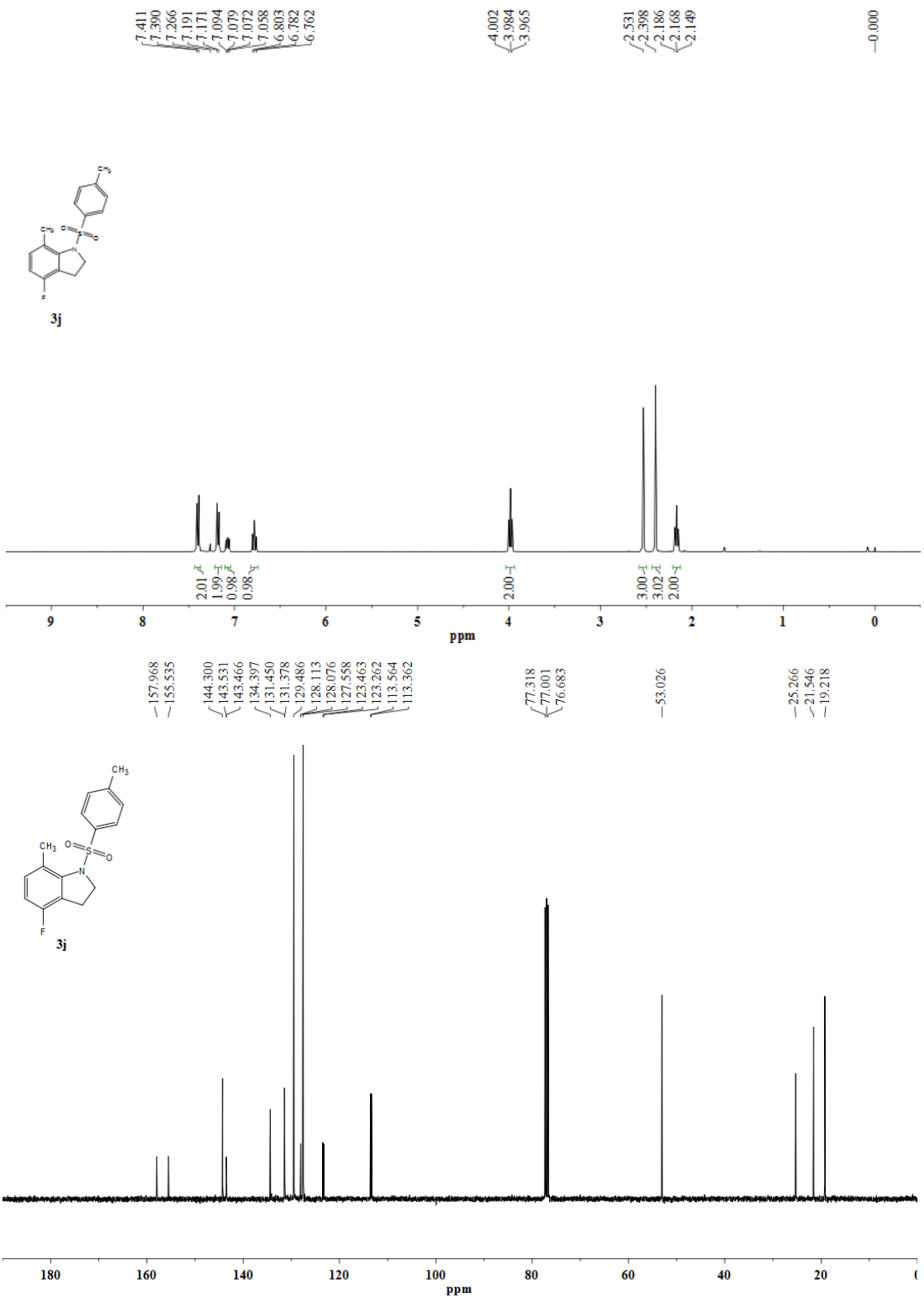
140.948
139.642
134.467
134.321
132.794
129.501
127.549
125.016
119.568
77.318
77.000
76.682
52.719
28.711
21.540
19.681
3i
180
160
140
120
100
80
60
40
20
ppm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7.191
7.171
7.094
7.079
7.072
7.058
6.803
6.782
6.762
4.002
3.984
3.965
2.531
2.398
2.186
2.168
2.149
0.000
3j
2.01
1.99
0.98
0.98
2.00
3.00
3.02
2.00
ppm
157.968
155.535
144.300
143.531
143.466
134.397
131.450
131.378
129.486
128.113
128.076
127.558
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123.262
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113.362
77.318
77.001
76.683
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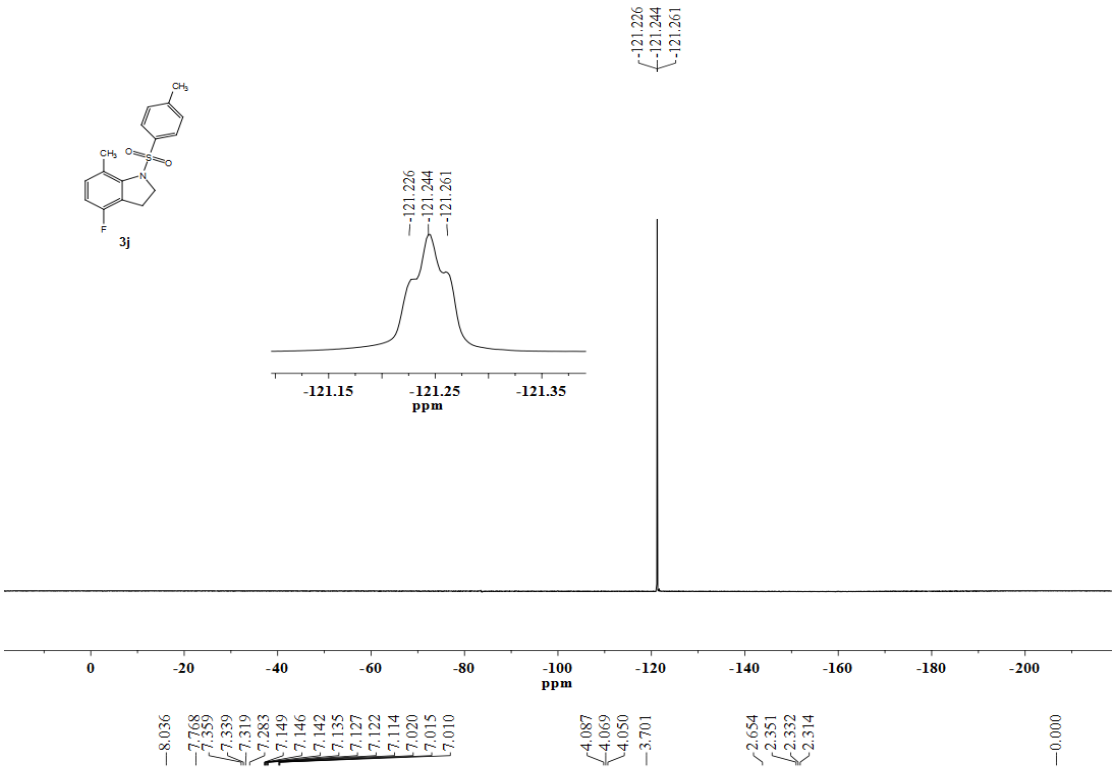
25.266
21.546
19.218
3j
ppm


3j
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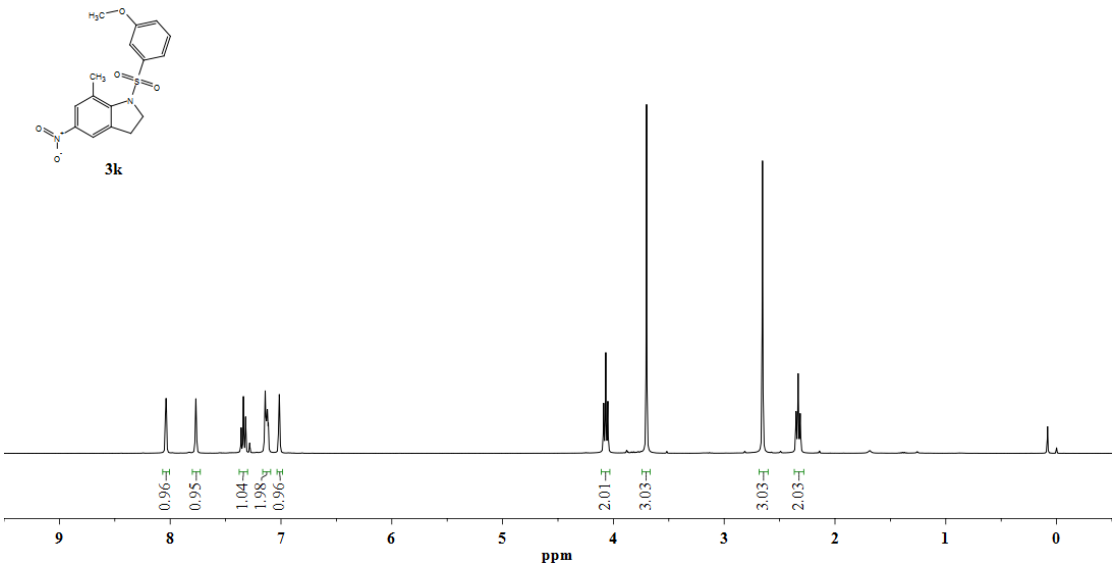
-121.244
-121.261
-121.15
-121.25
-121.35
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
8.036
7.768
7.359
7.339
7.319
7.283
7.149
7.146
7.142
7.135
7.127
7.122
7.114
7.020
7.015
7.010
4.087
4.069
4.050
3.701
2.654
2.351
2.332
2.314
0.000


3k
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0.95
1.04
1.98
0.96
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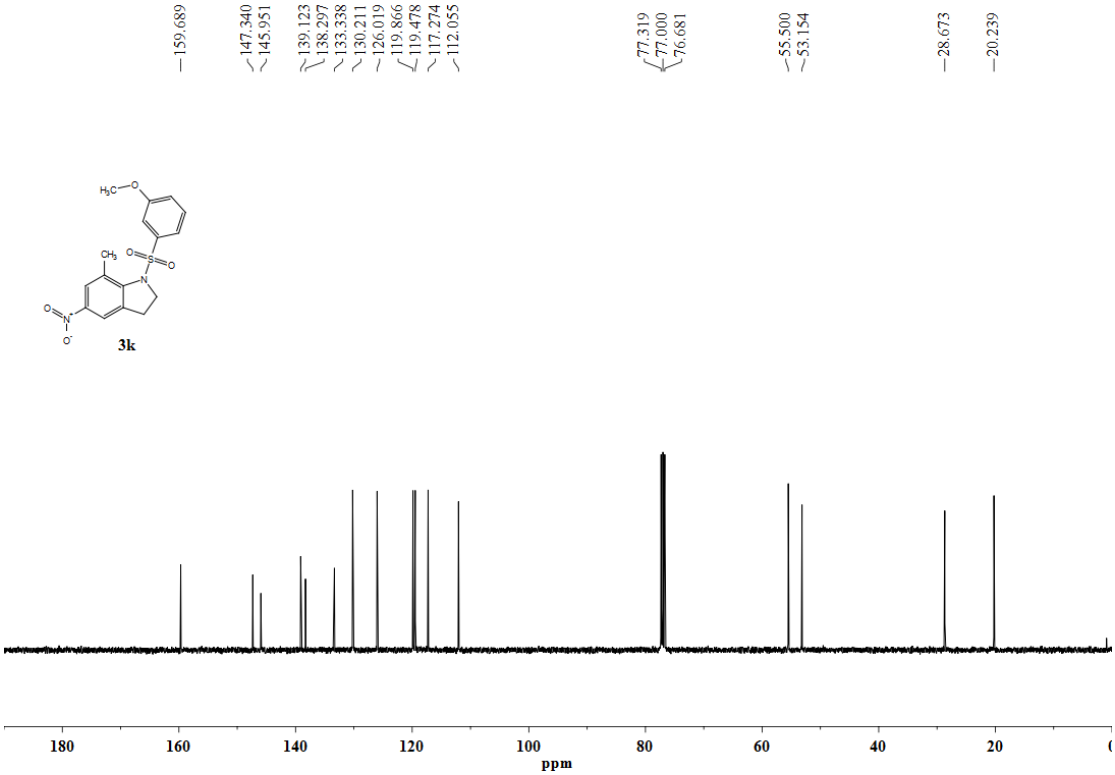
3.03
3.03
2.03
9
8
7
6
5
4
3
2
1
0
ppm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138.297
133.338
130.211
126.019
119.866
119.478
117.274
112.055
77.319
77.000
76.681
55.500
53.154
28.673
20.239
3k
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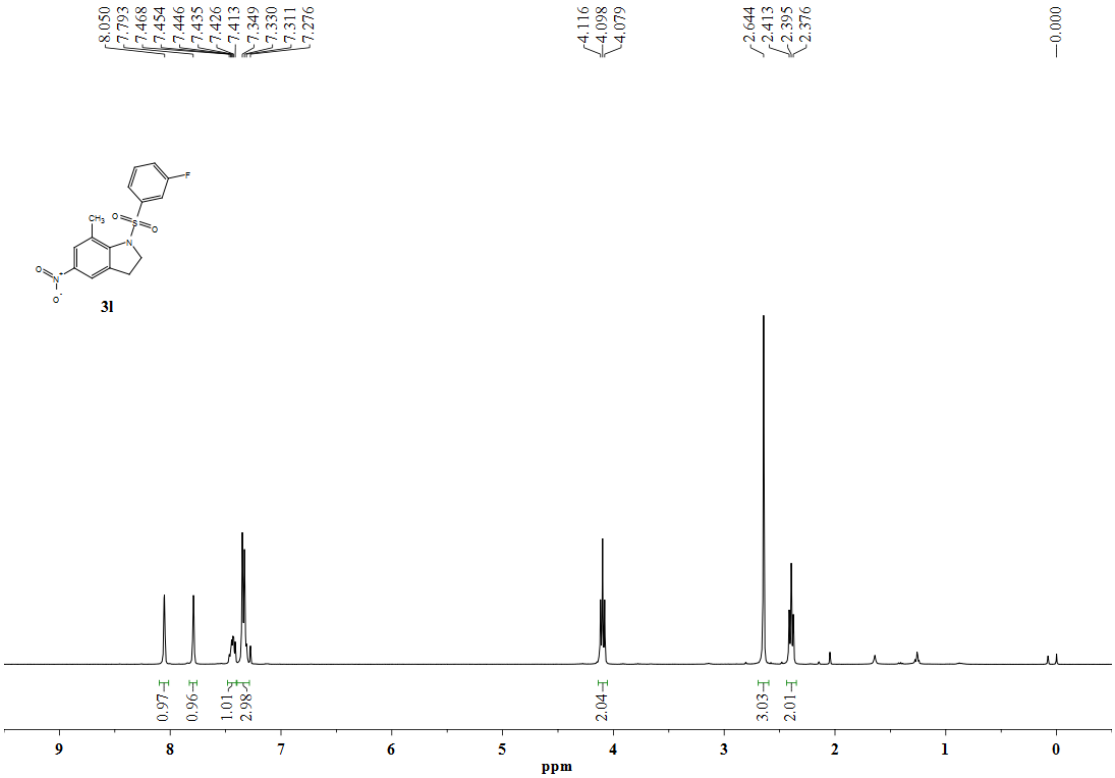
160
140
120
100
80
60
40
20
ppm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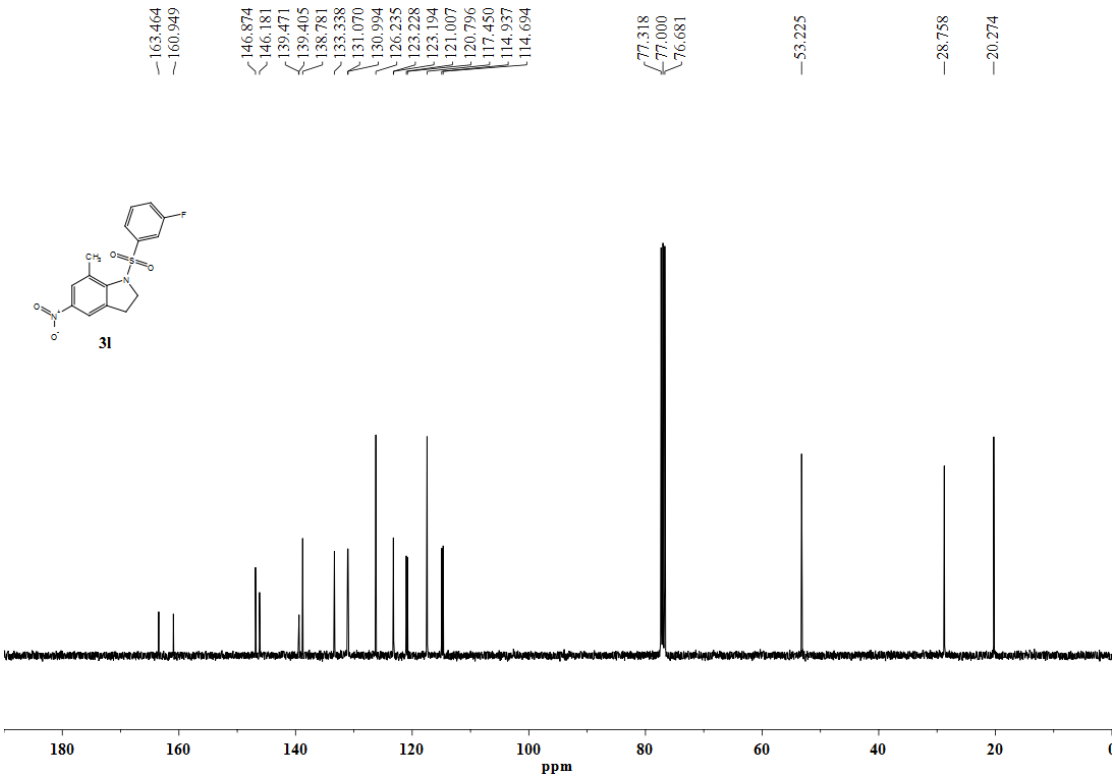
7.454
7.446
7.435
7.426
7.413
7.349
7.330
7.311
7.276
4.116
4.098
4.079
2.644
2.413
2.395
2.376
0.000
3l
0.97
0.96
1.01
2.98
2.04
3.03
2.01
9
8
7
6
5
4
3
2
1
0
ppm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160.949
146.874
146.181
139.471
139.405
138.781
133.338
131.070
130.994
126.235
123.228
123.194
121.007
120.796
117.450
114.937
114.694
77.318
77.000
76.681
53.225
28.758
20.274
3l
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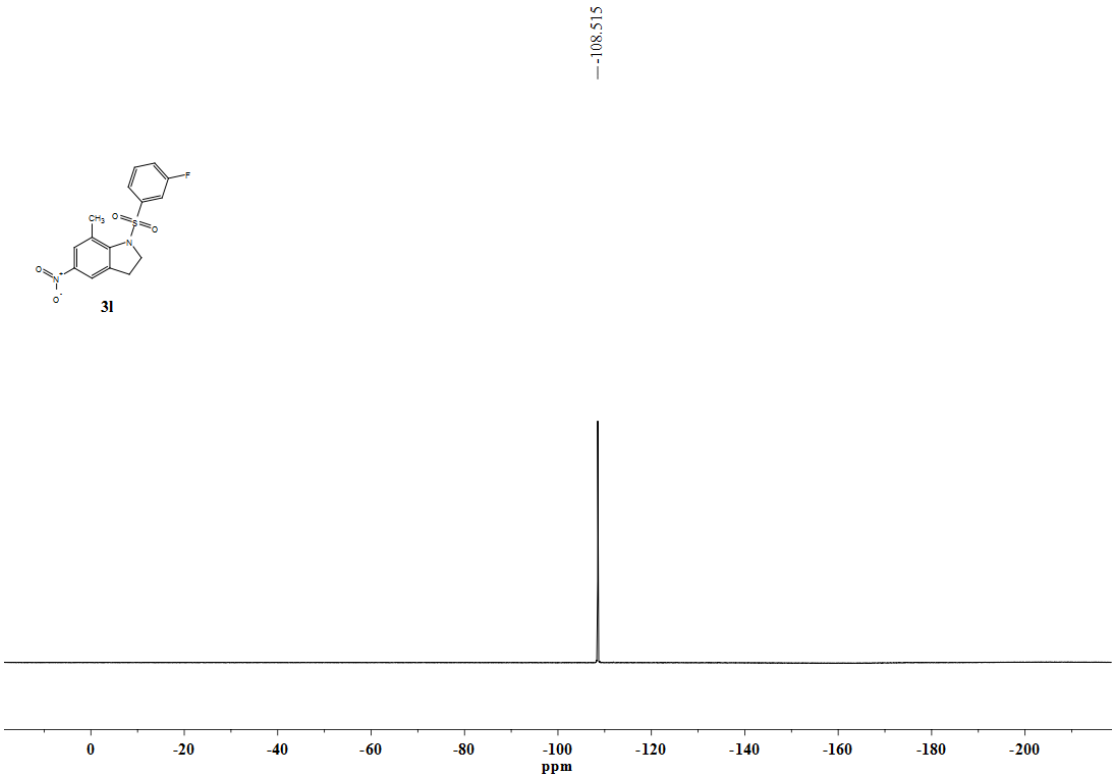
160
140
120
100
80
60
40
20
ppm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3l
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-20
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-60
-80
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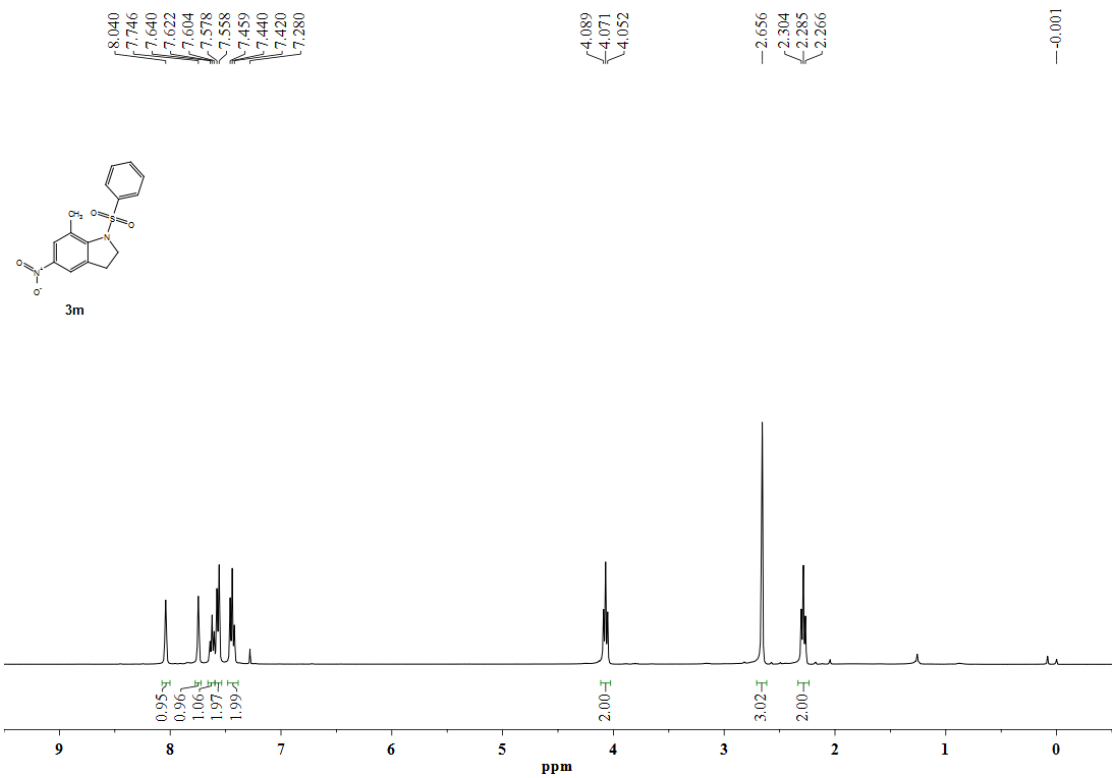
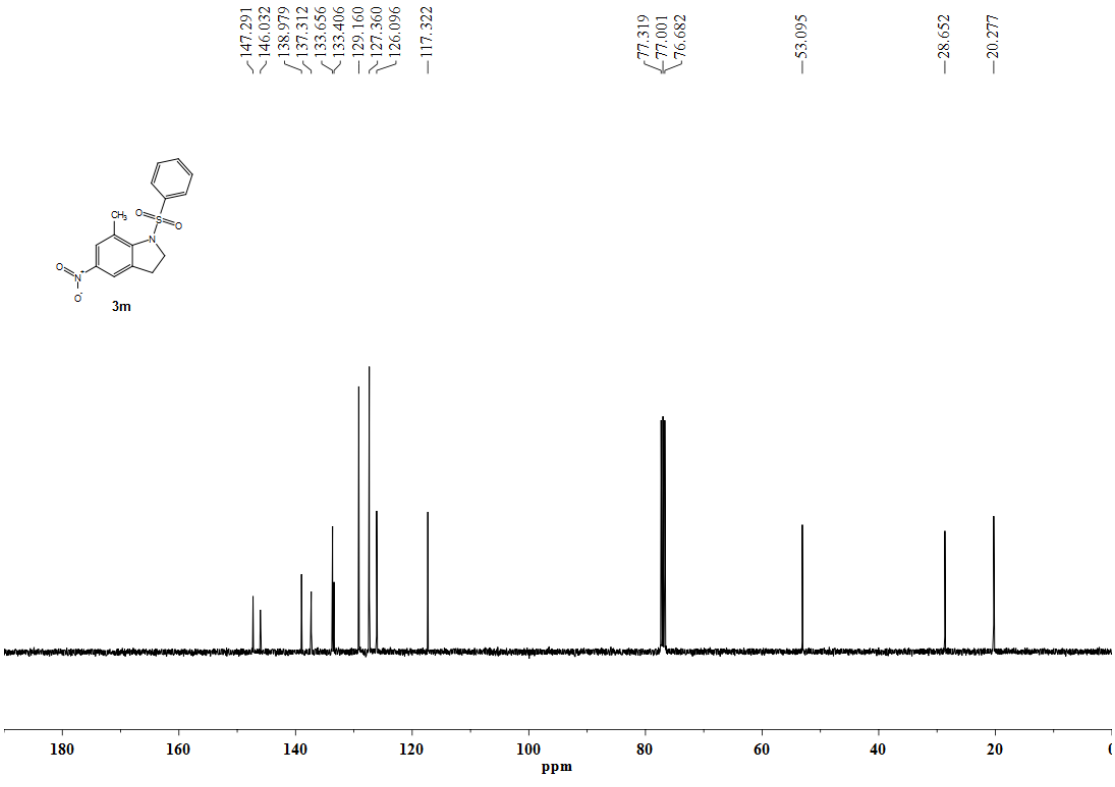
-120
-140
-160
-180
-200
ppm


8.040
7.746
7.640
7.622
7.604
7.578
7.558
7.459
7.440
7.420
7.280
4.089
4.071
4.052
2.656
2.304
2.285
2.266
-0.001
3m
0.95
0.96
1.06
1.97
1.99
2.00
3.02
2.00
9
8
7
6
5
4
3
2
1
0
ppm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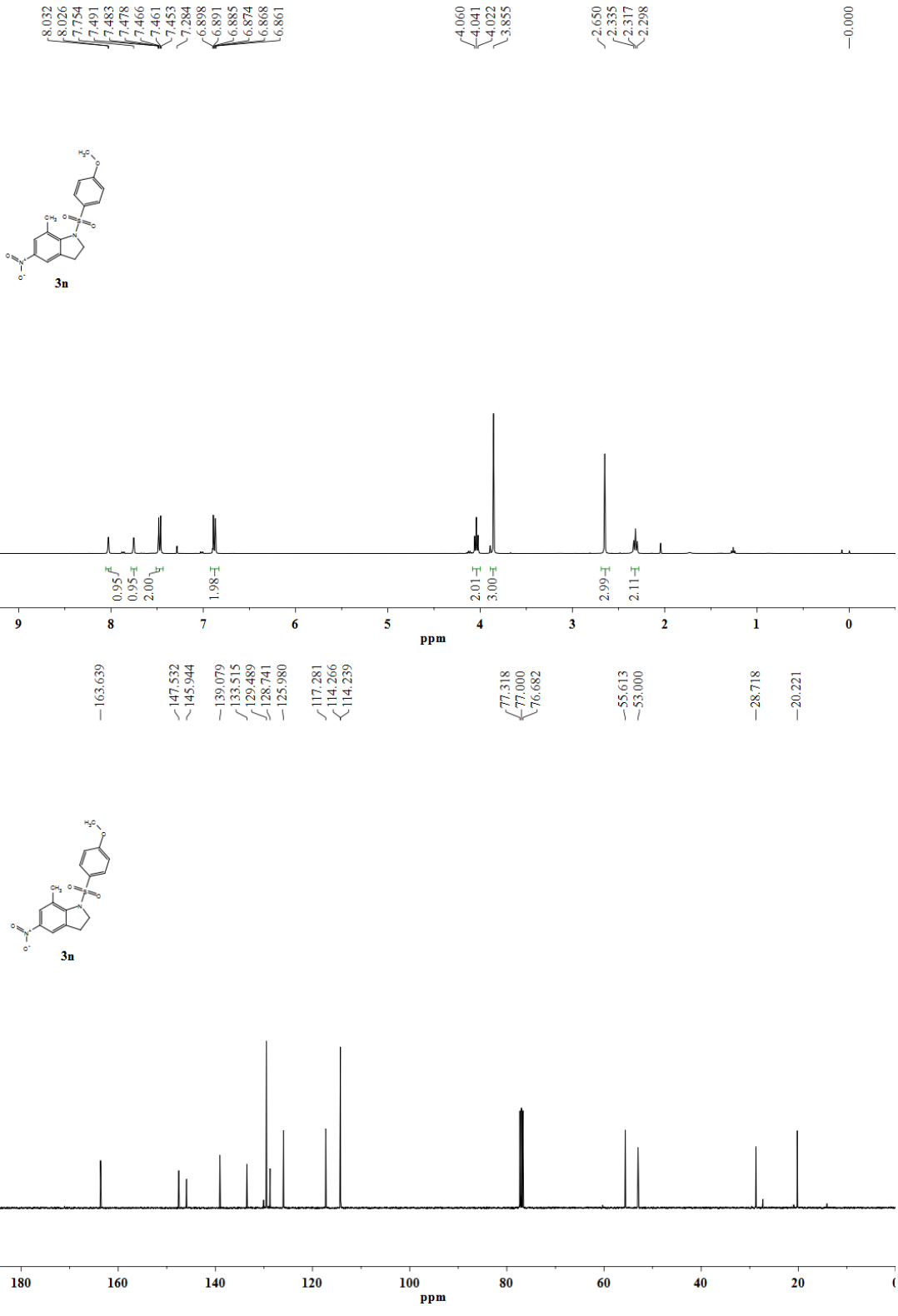
137.312
133.656
133.406
129.160
127.360
126.096
117.322
77.319
77.001
76.682
53.095
28.652
20.277
3m
180
160
140
120
100
80
60
40
20
ppm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6.874
6.868
6.861
4.060
4.041
4.022
3.855
2.650
2.335
2.317
2.298
0.000
3n
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0.95
2.00
1.98
2.01
3.00
2.99
2.11
ppm
163.639
147.532
145.944
139.079
133.515
129.489
128.741
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114.239
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53.000
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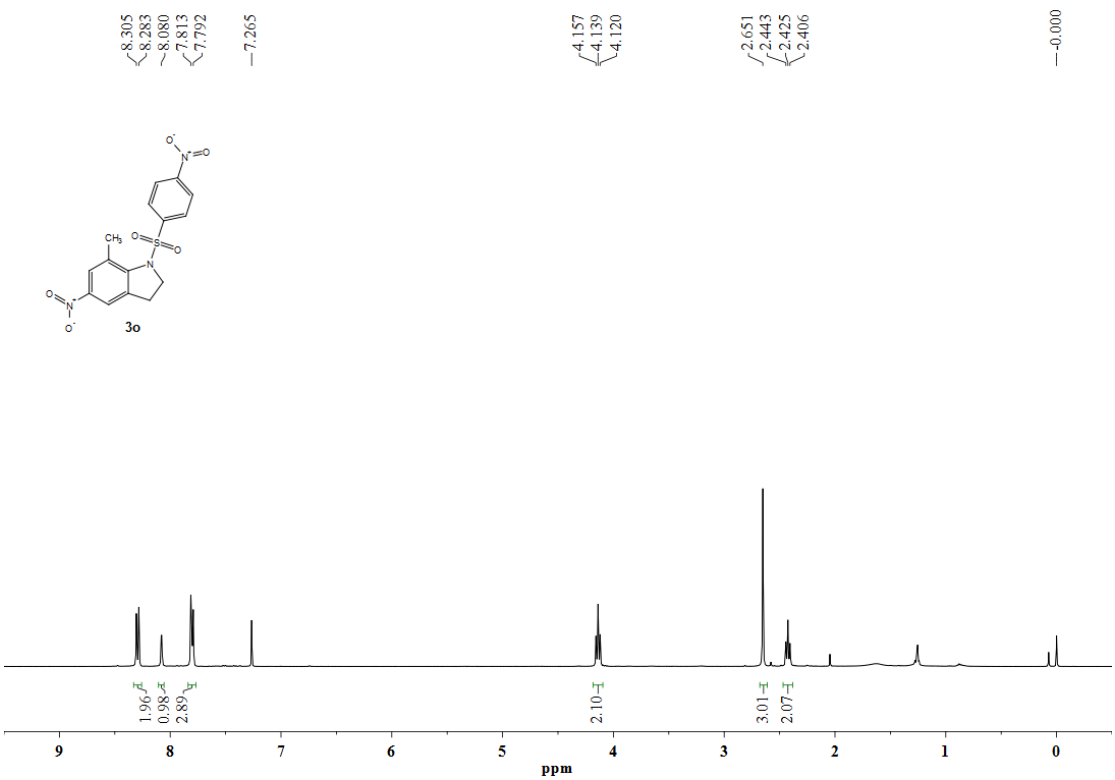
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4.139
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2.406
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2.07
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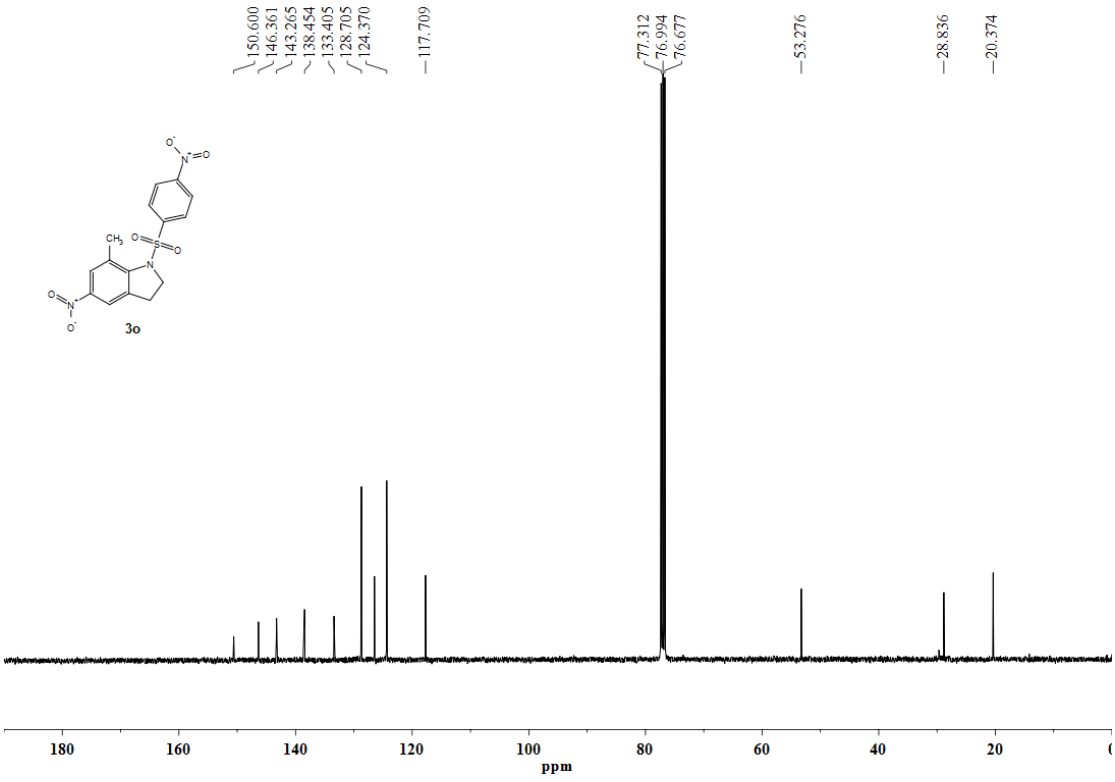
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53.276
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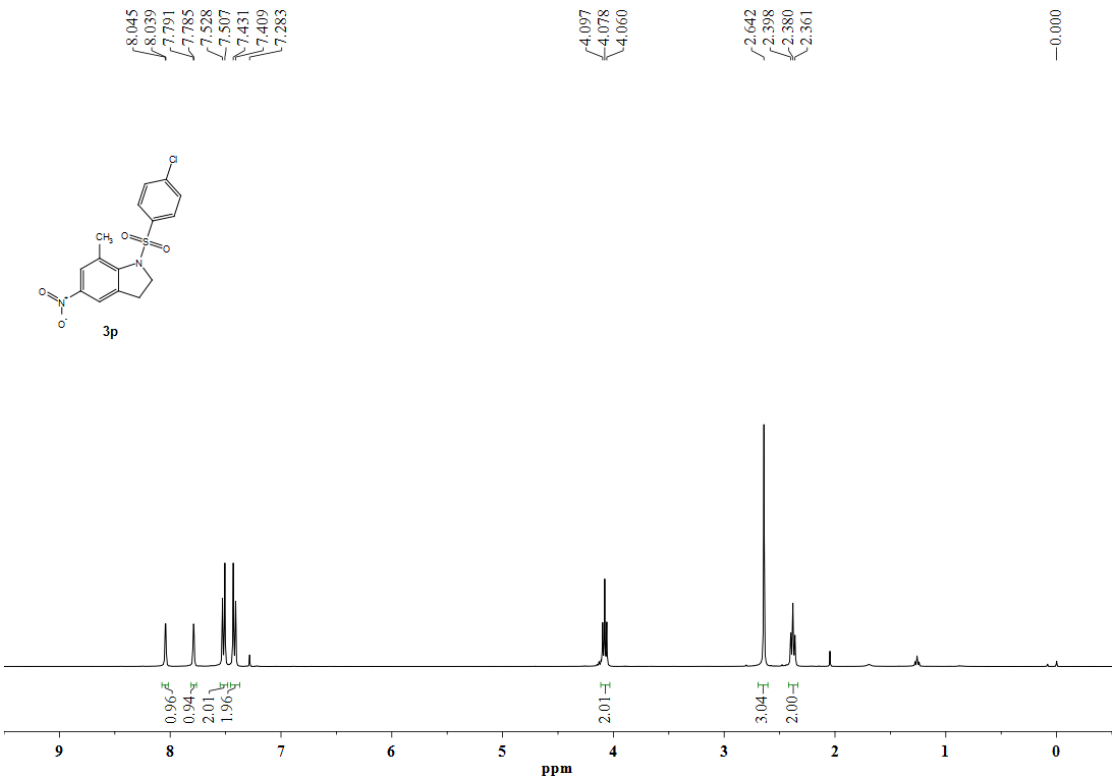
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7.431
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4.078
4.060
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1.96
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2.00
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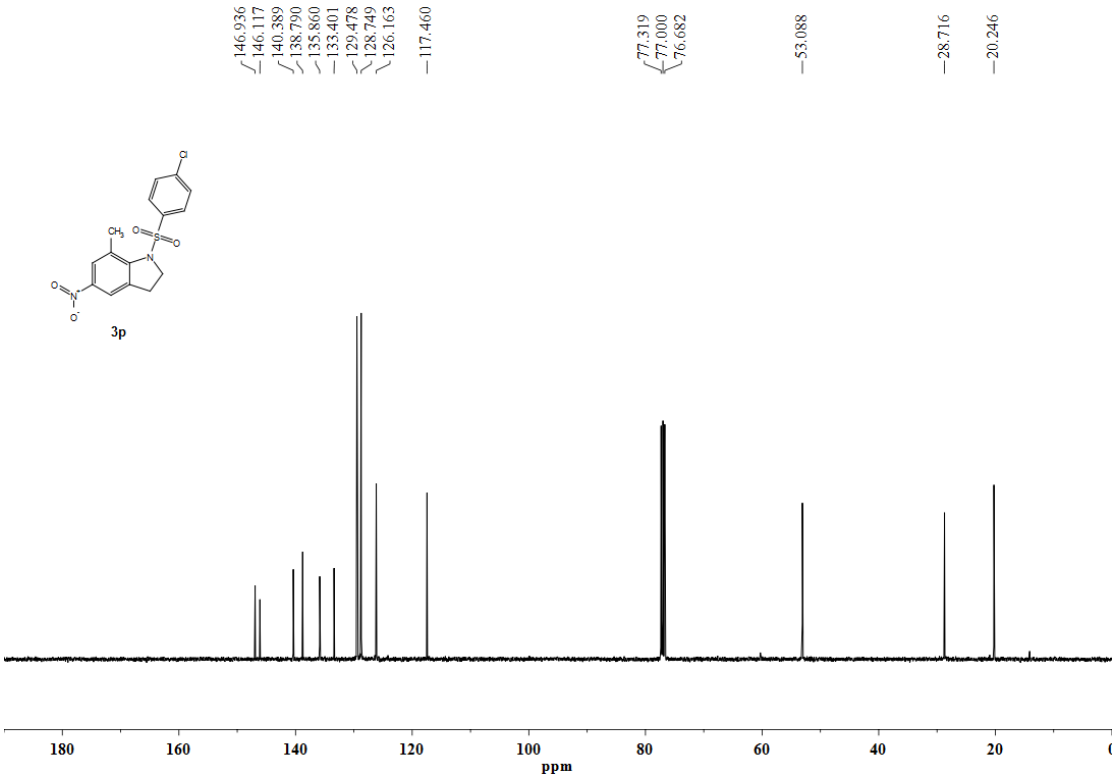
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53.088
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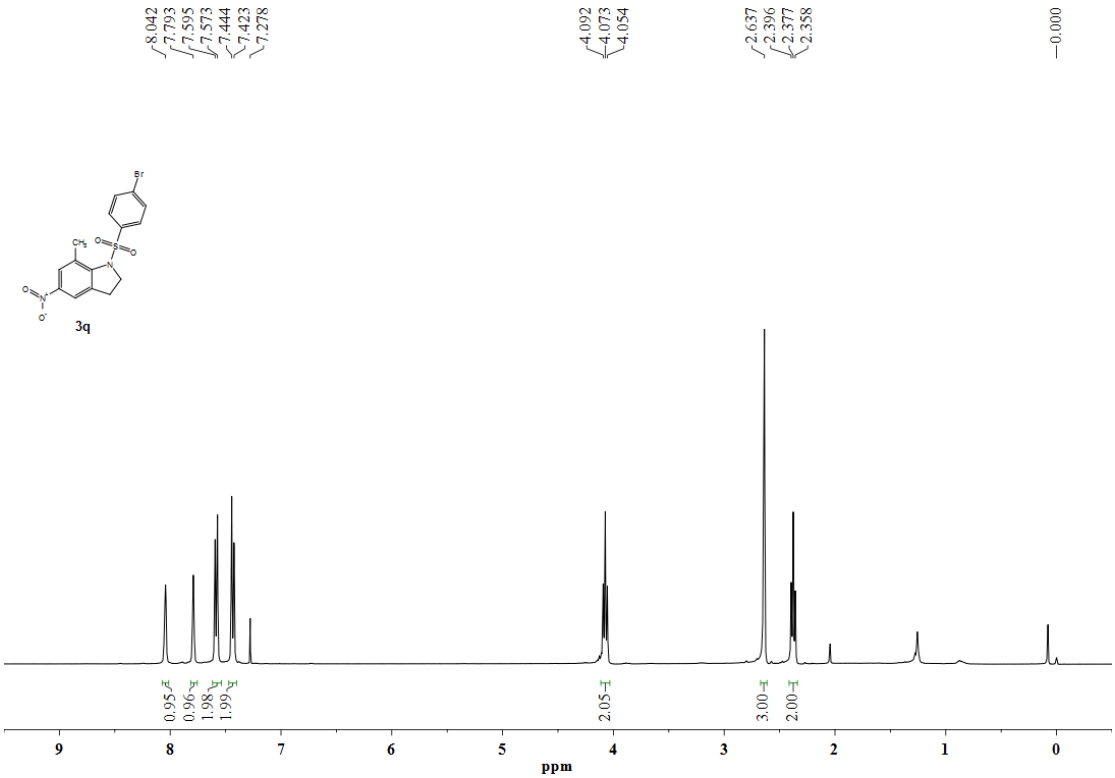
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7.423
7.278
4.092
4.073
4.054
2.637
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0.000
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2.00
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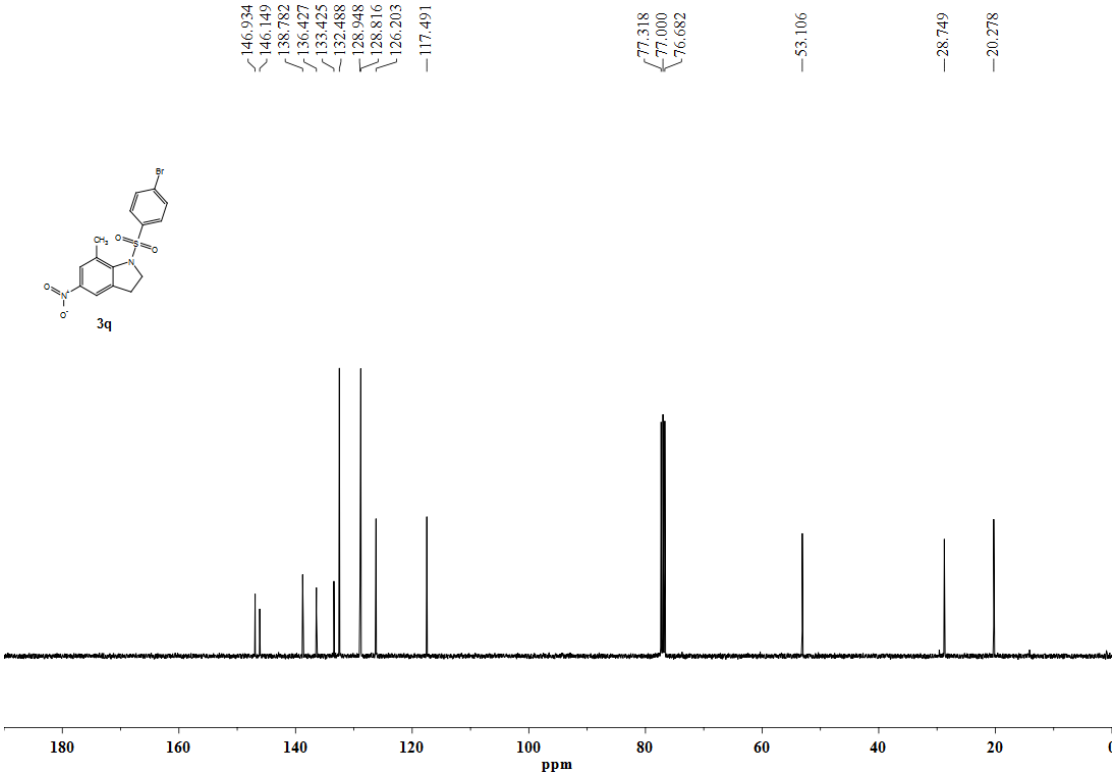
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3q
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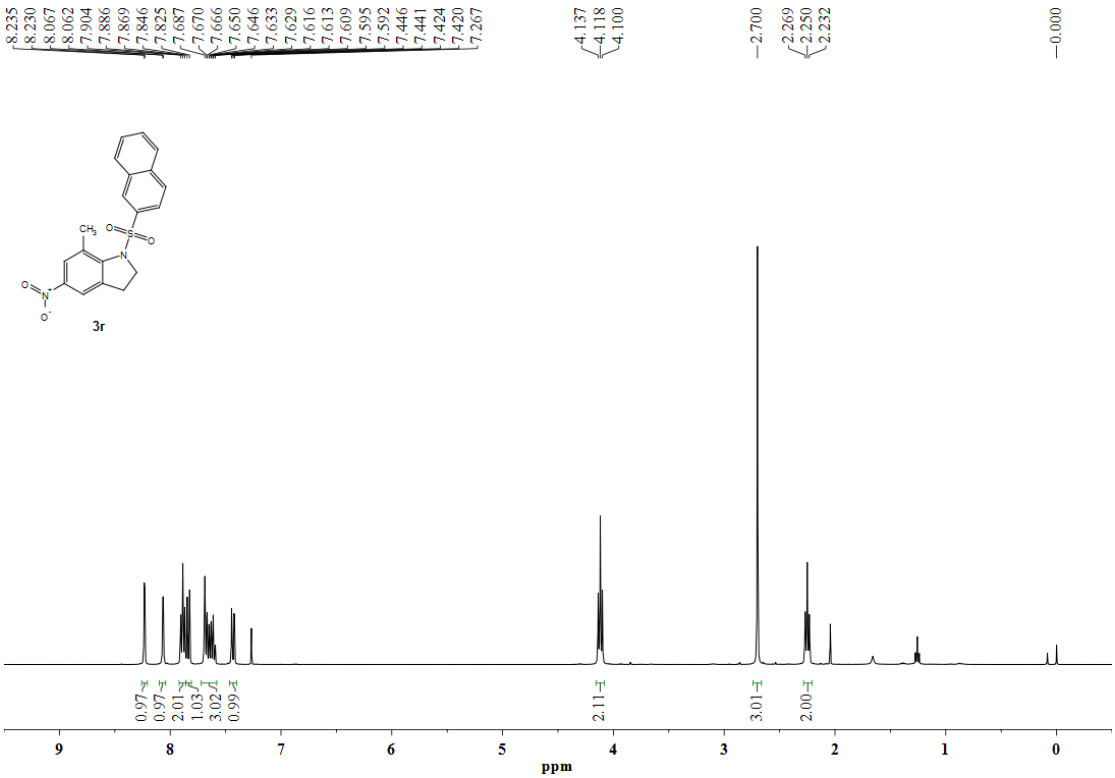
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7.846
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7.687
7.670
7.666
7.650
7.646
7.633
7.629
7.616
7.613
7.609
7.595
7.592
7.446
7.441
7.424
7.420
7.267
4.137
4.118
4.100
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2.269
2.250
2.232
0.000
3r
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0.97
2.01
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2.11
3.01
2.00
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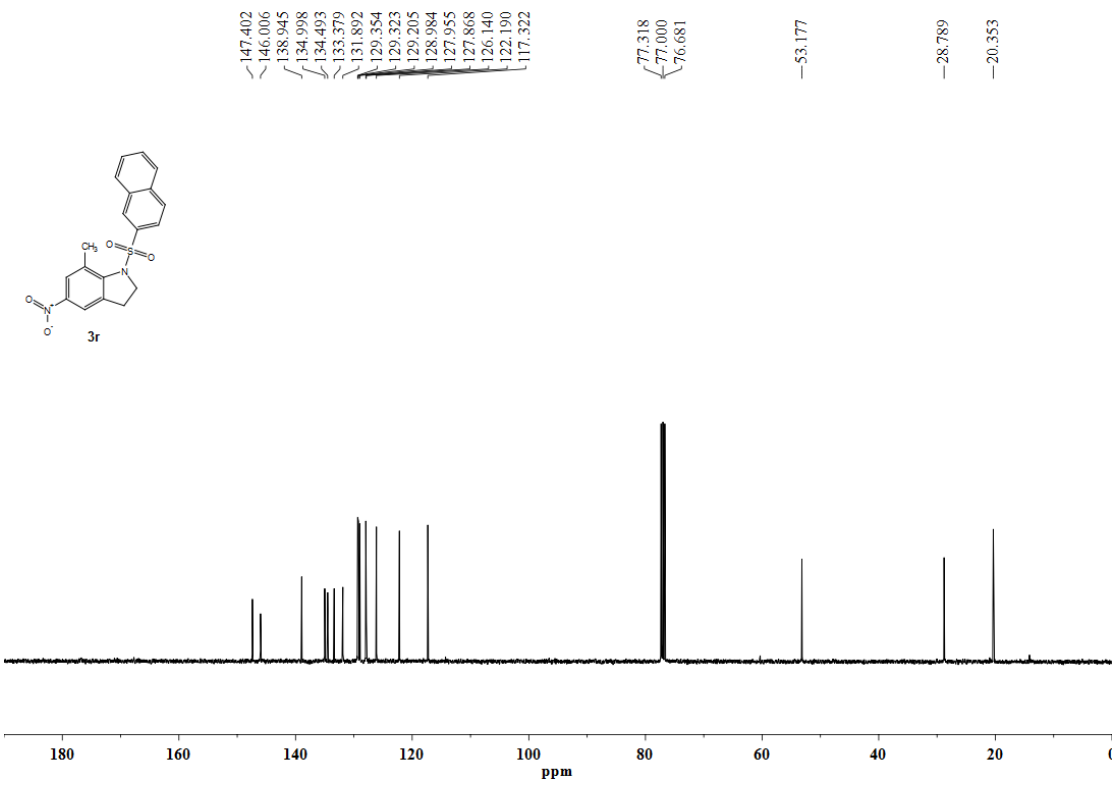
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129.205
128.984
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122.190
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77.318
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140
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80
60
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20
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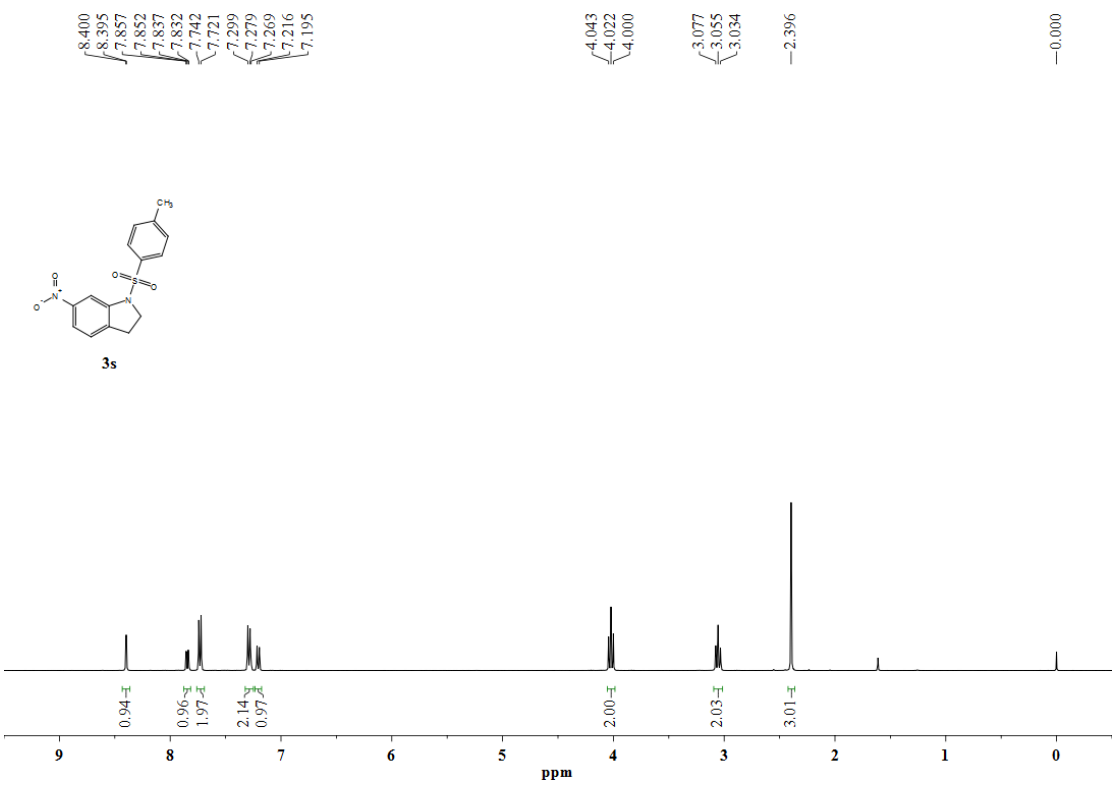
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7.721
7.299
7.279
7.269
7.216
7.195
4.043
4.022
4.000
3.077
3.055
3.034
2.396
0.000
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0.96
1.97
2.14
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2.00
2.03
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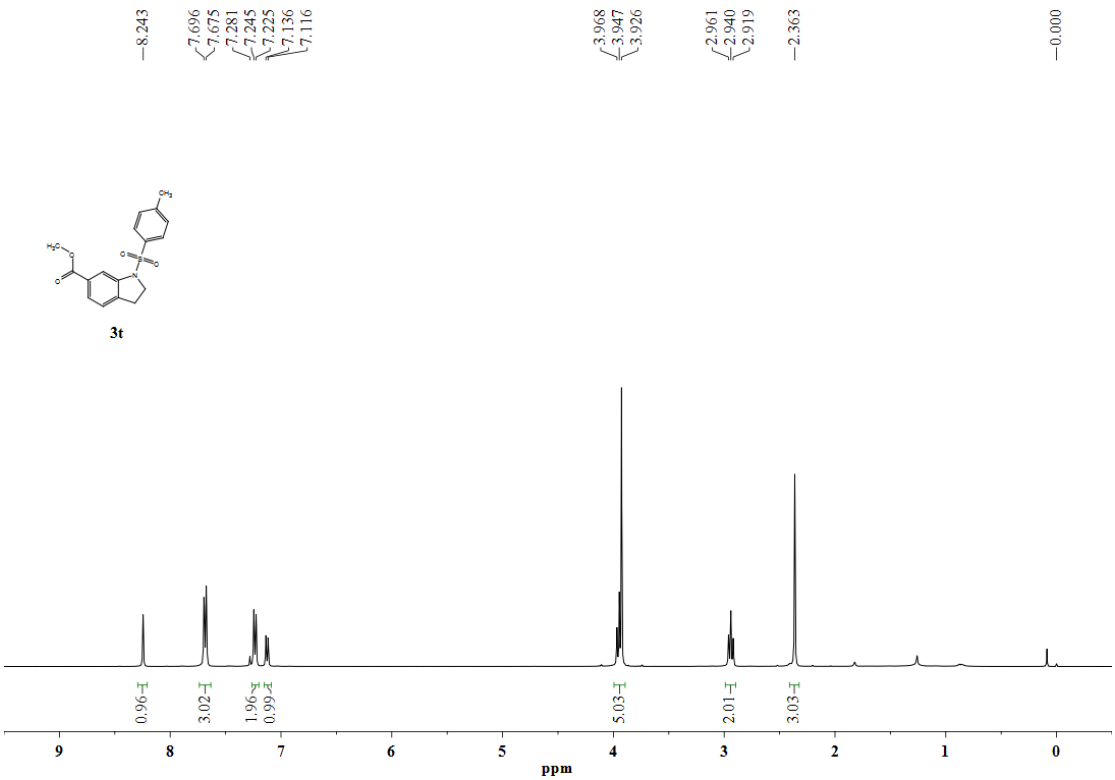
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7.116
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3.947
3.926
2.961
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0.99
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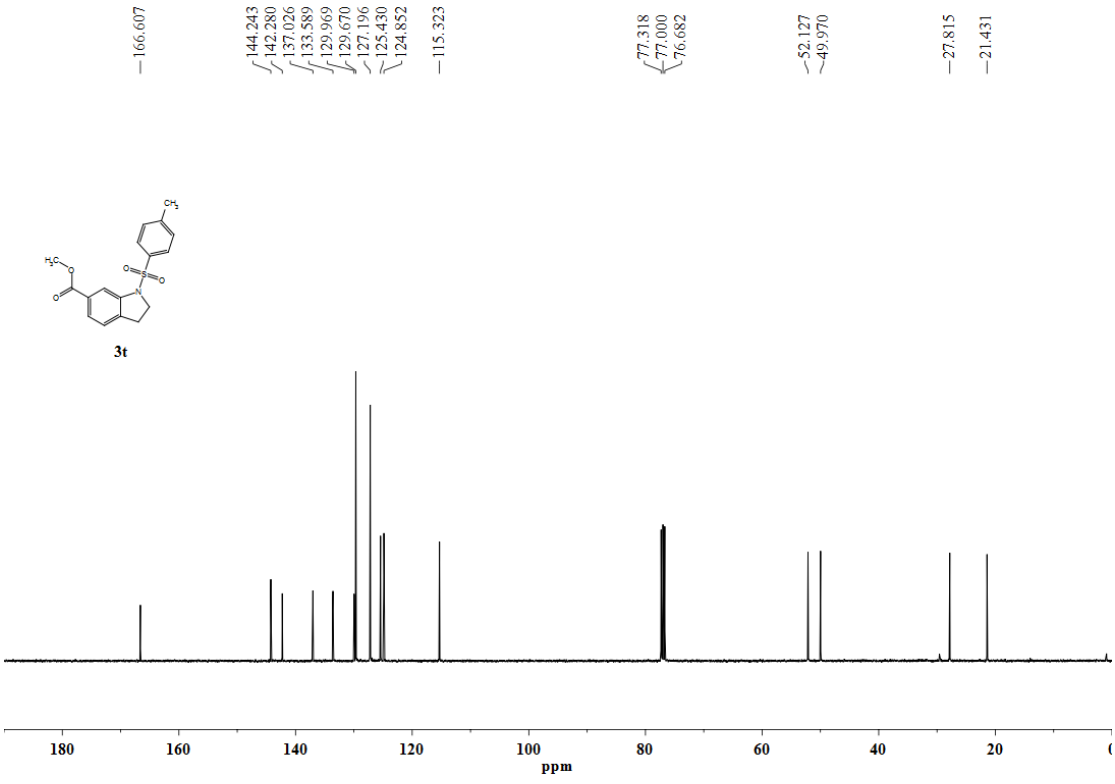
2.01
3.03
ppm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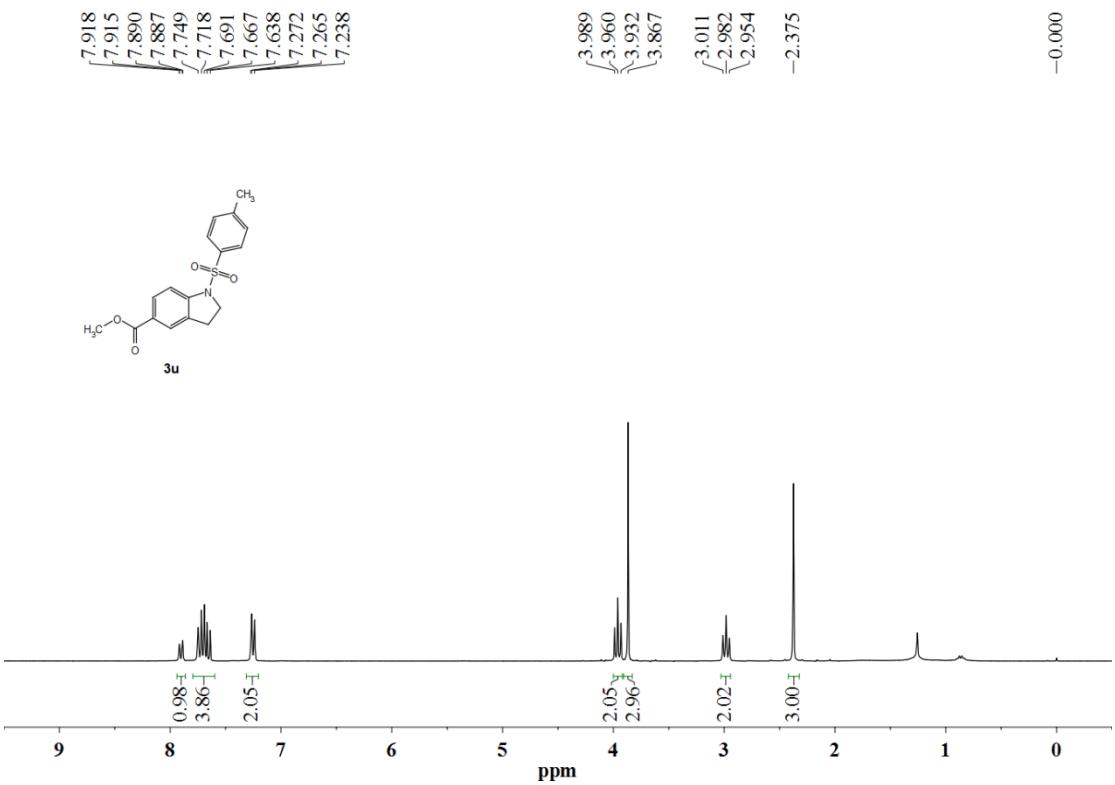
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7.667
7.638
7.272
7.265
7.238
3.989
3.960
3.932
3.867
3.011
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2.05
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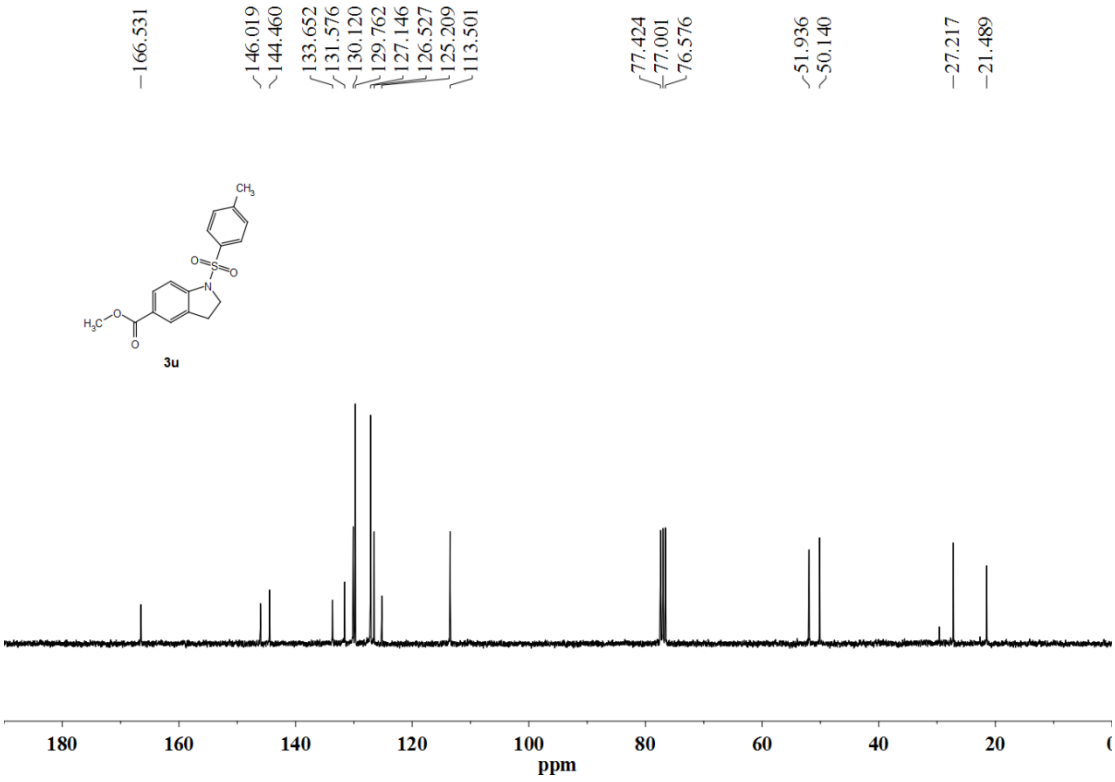
3.00
ppm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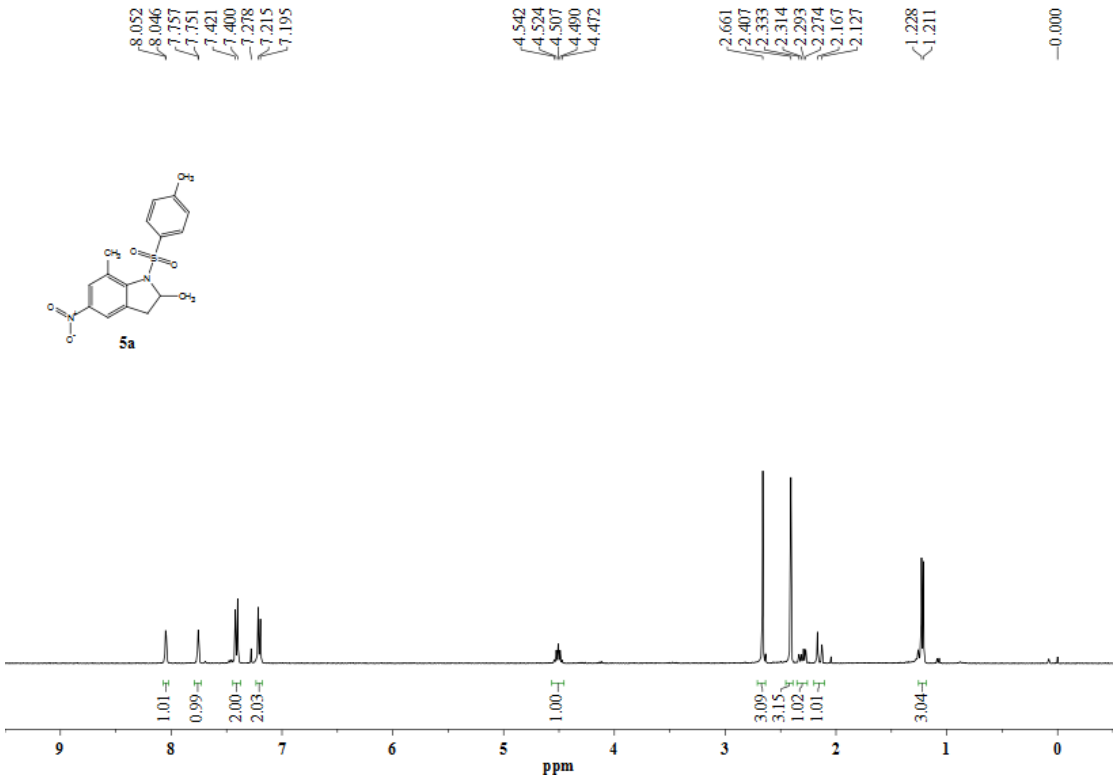
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4.524
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2.407
2.333
2.314
2.293
2.274
2.167
2.127
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1.211
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1.00
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3.15
1.02
1.01
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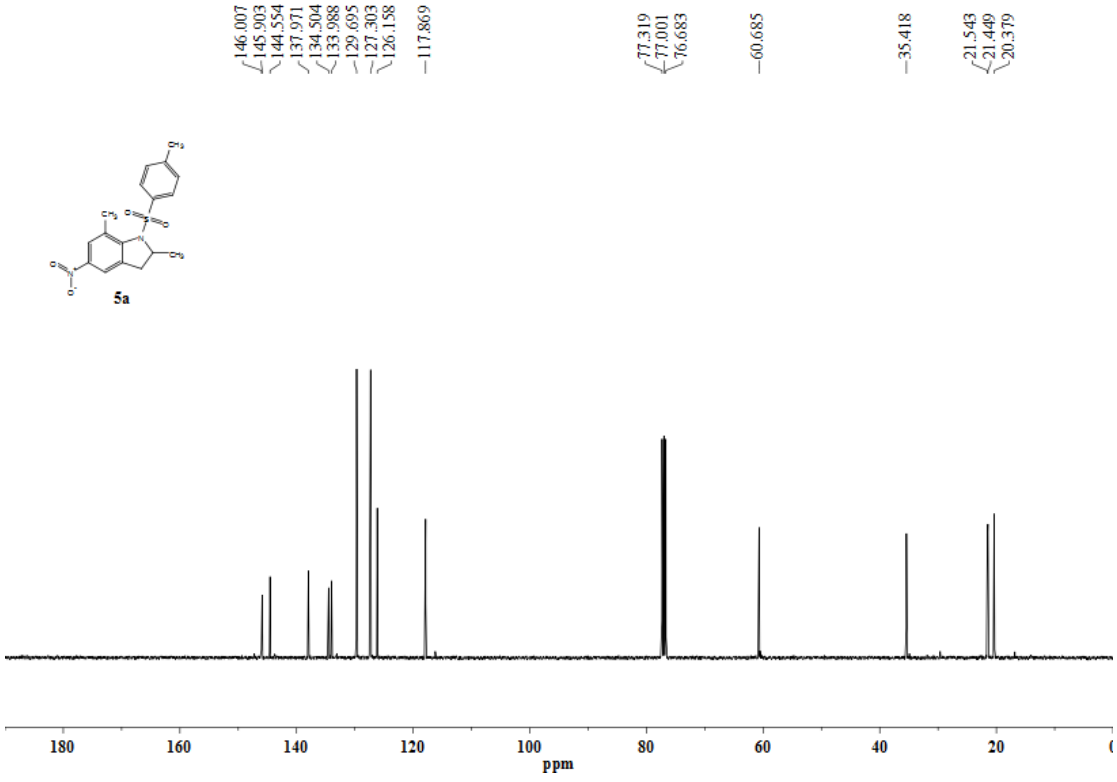
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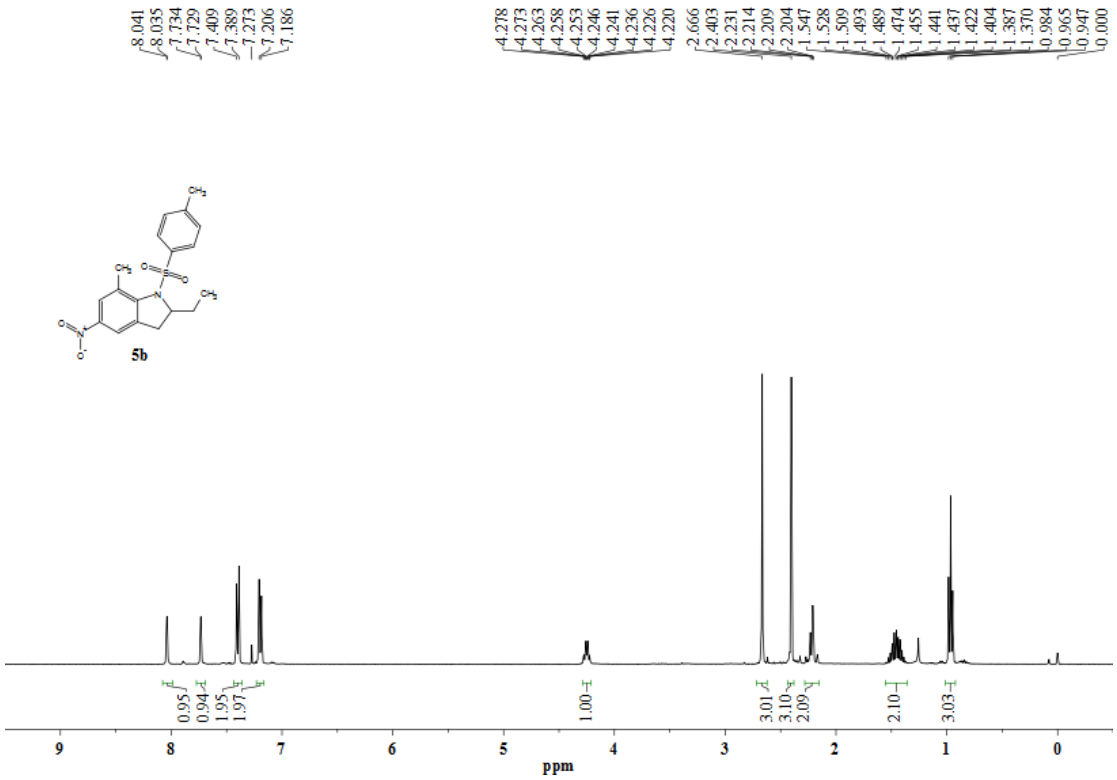
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4.246
4.241
4.236
4.226
4.220
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2.403
2.231
2.214
2.209
2.204
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1.528
1.509
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1.474
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1.441
1.437
1.422
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1.387
1.370
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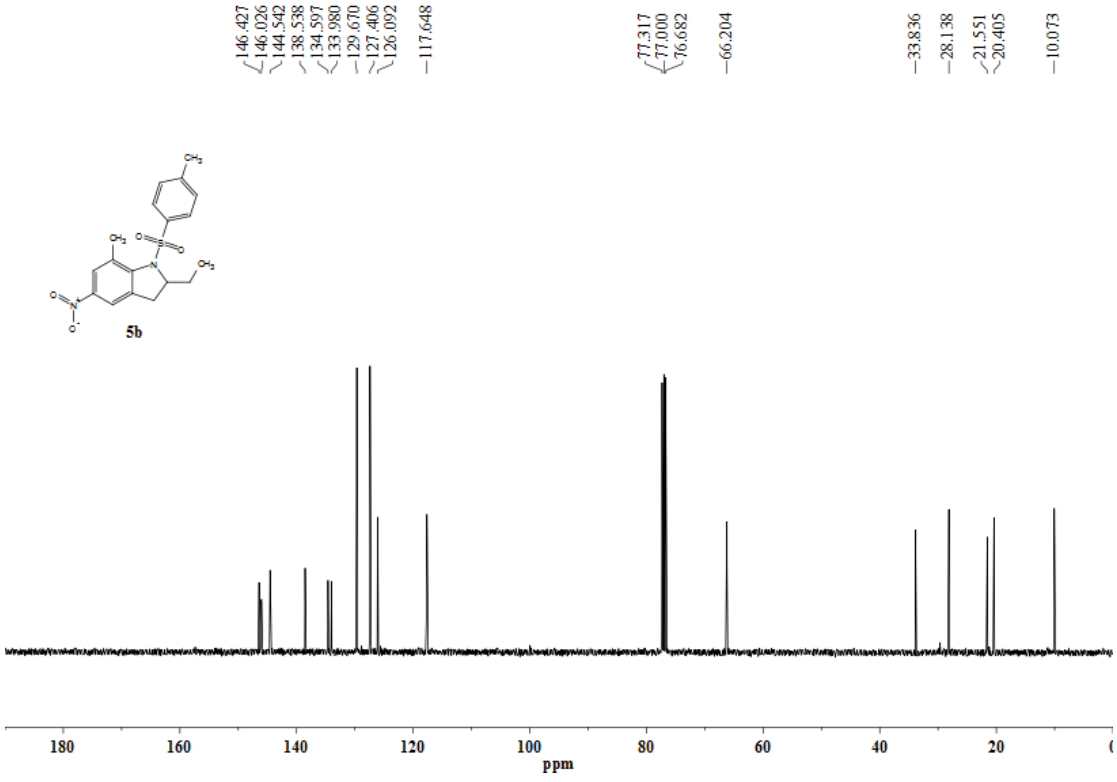
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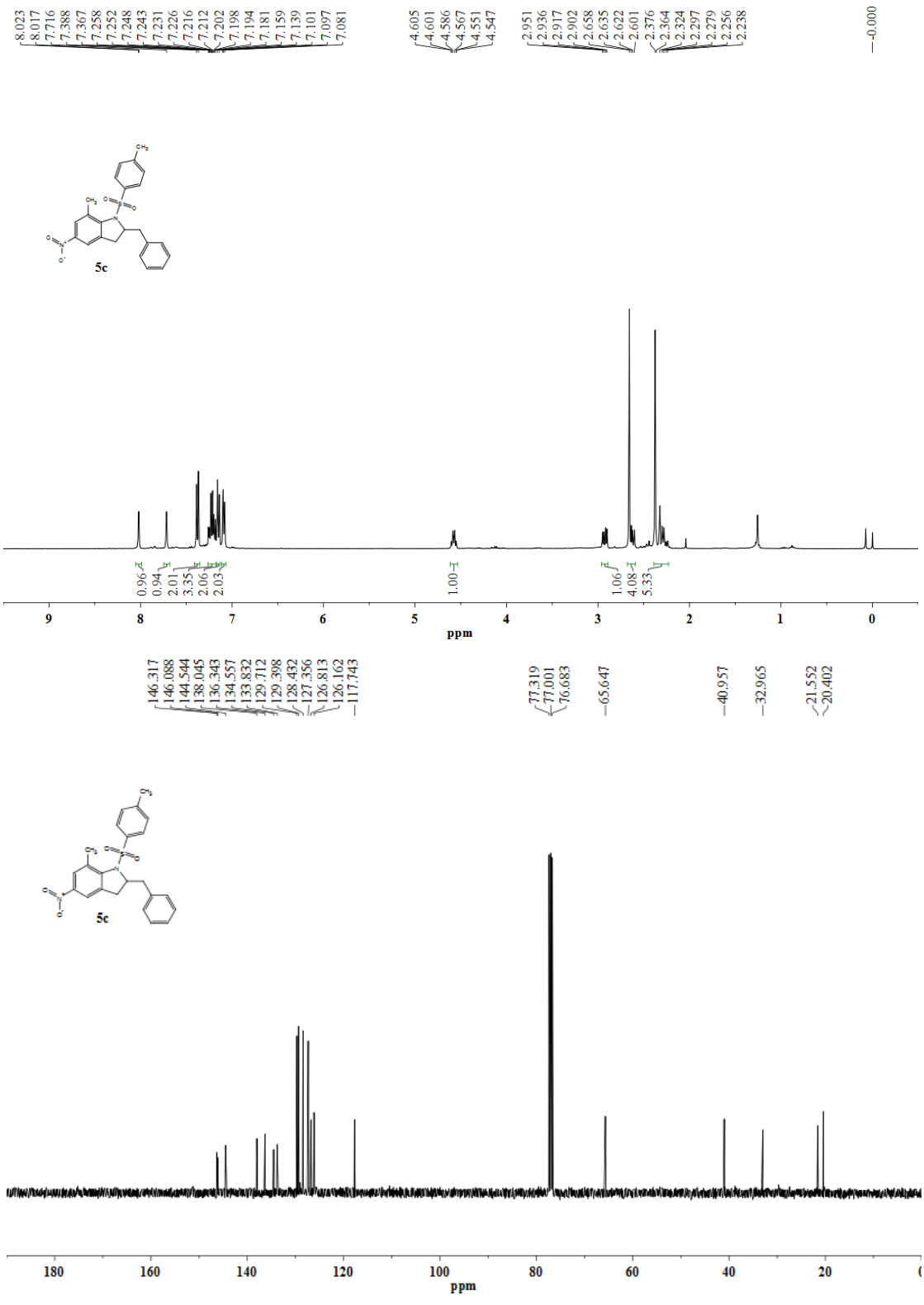
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7.198
7.194
7.181
7.159
7.139
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7.097
7.081
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4.567
4.551
4.547
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2.03
1.00
1.06
4.08
5.33
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133.832
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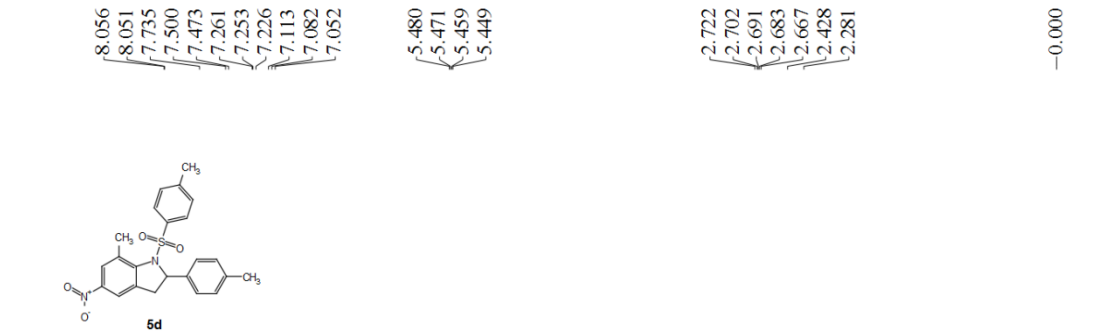
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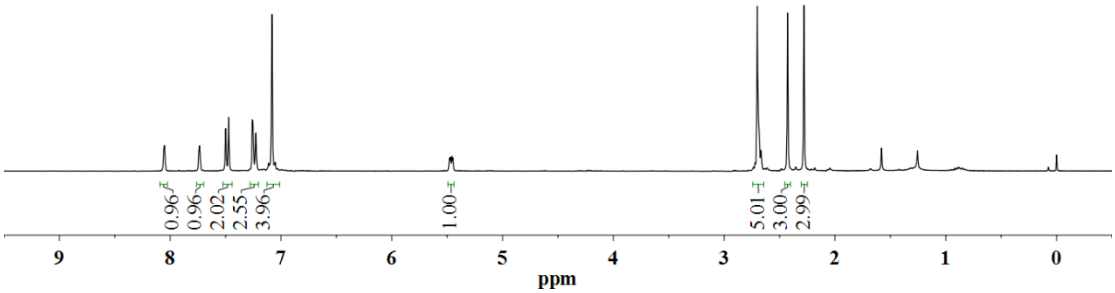
5d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6
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2
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0
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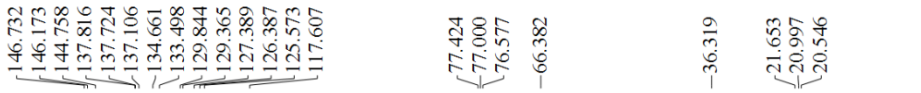
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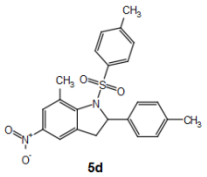
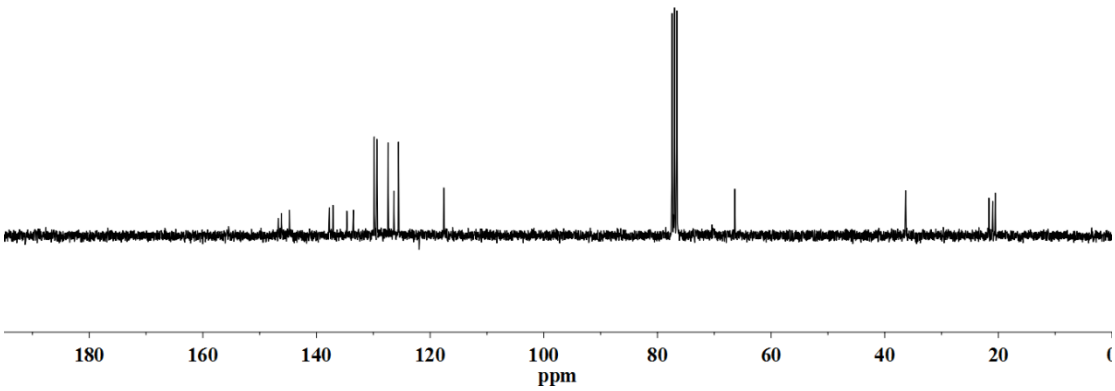

5d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60
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20
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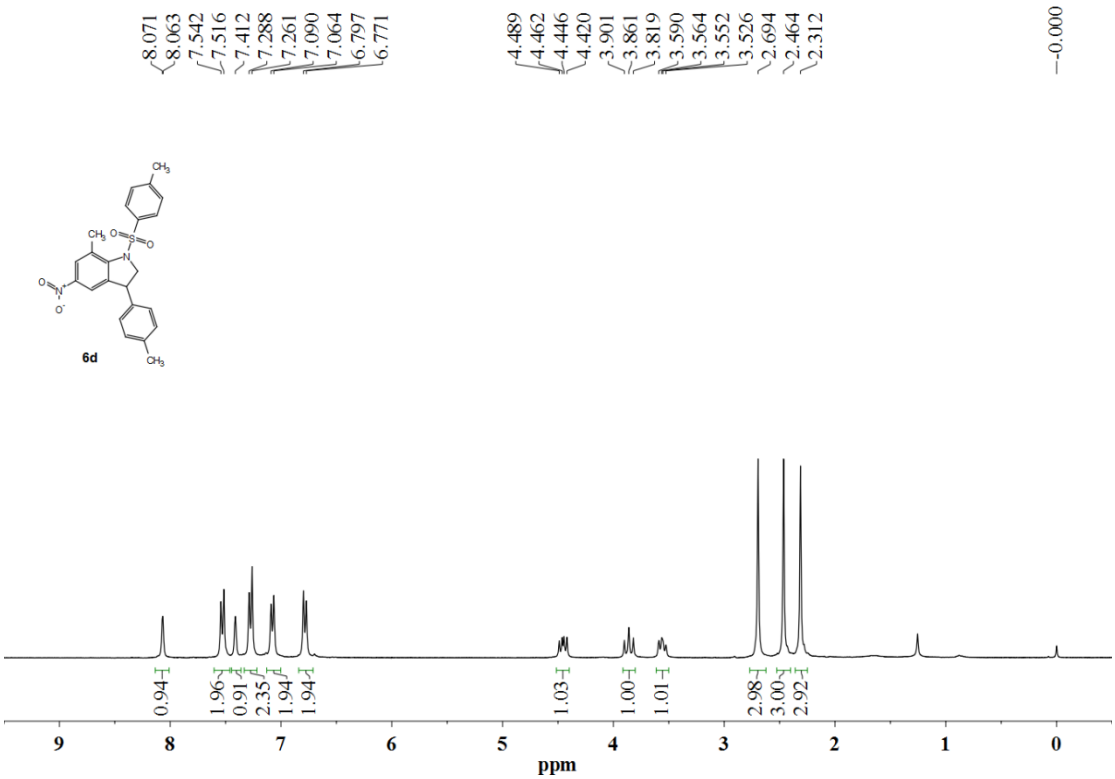
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4.446
4.420
3.901
3.861
3.819
3.590
3.564
3.552
3.526
2.694
2.464
2.312
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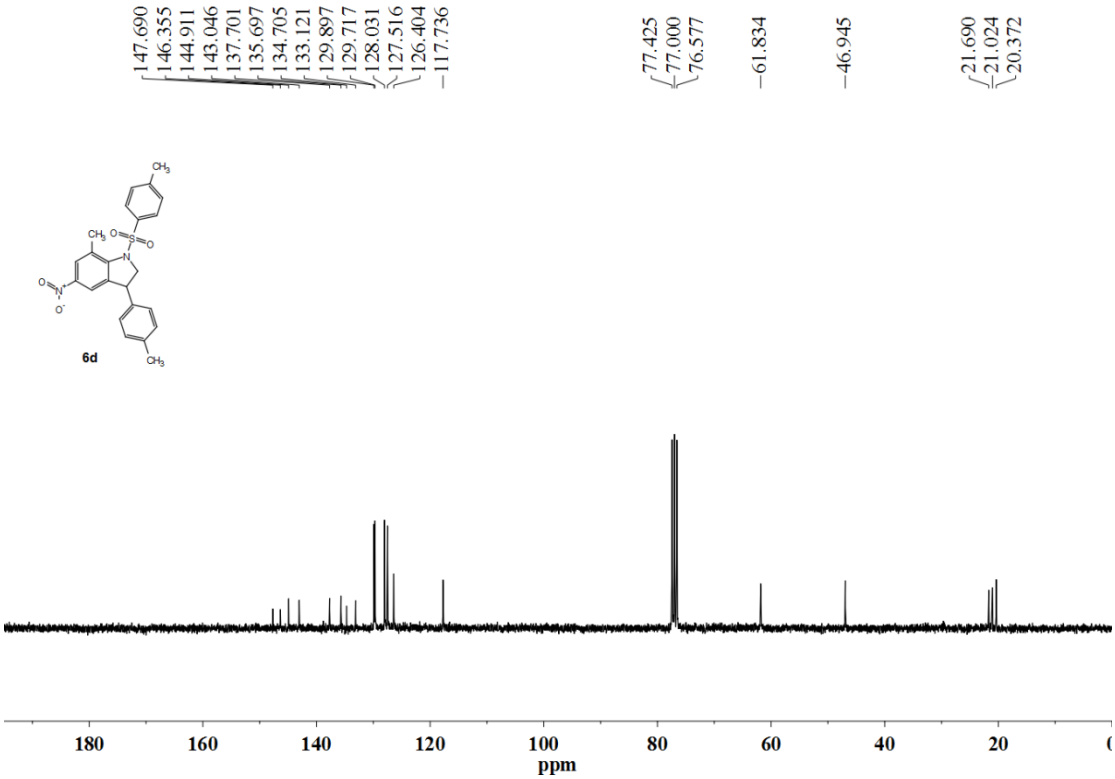
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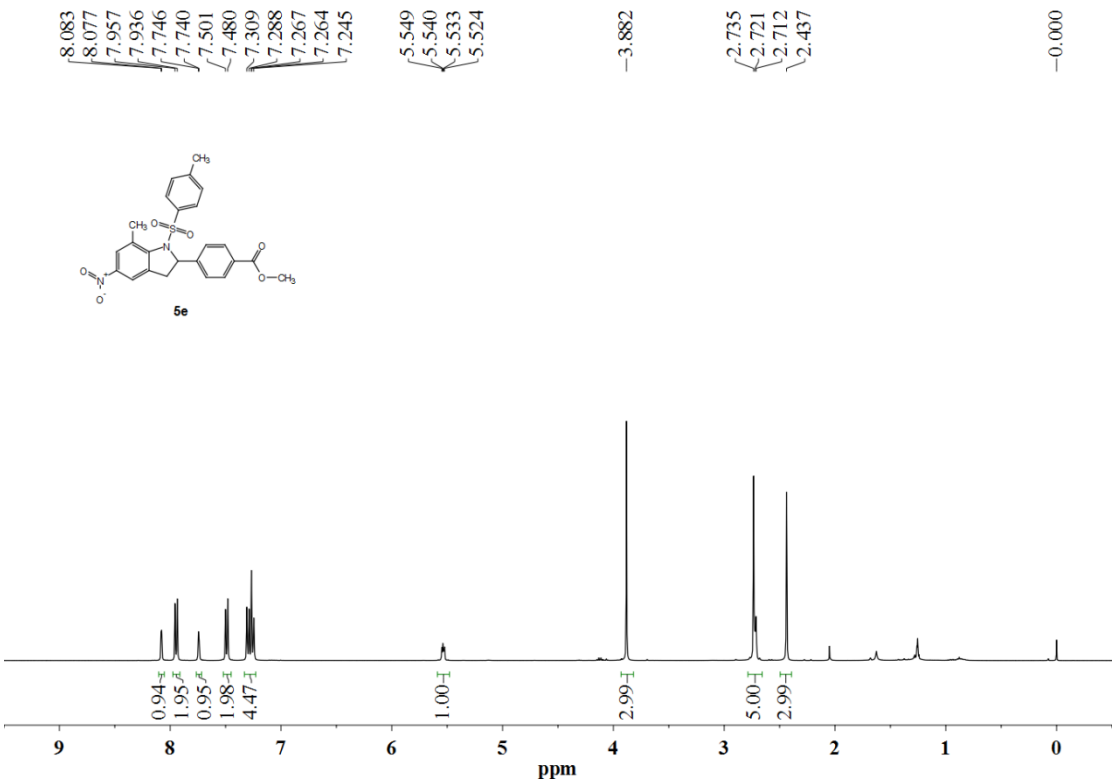
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7.245
5.549
5.540
5.533
5.524
3.882
2.735
2.721
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2.437
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6
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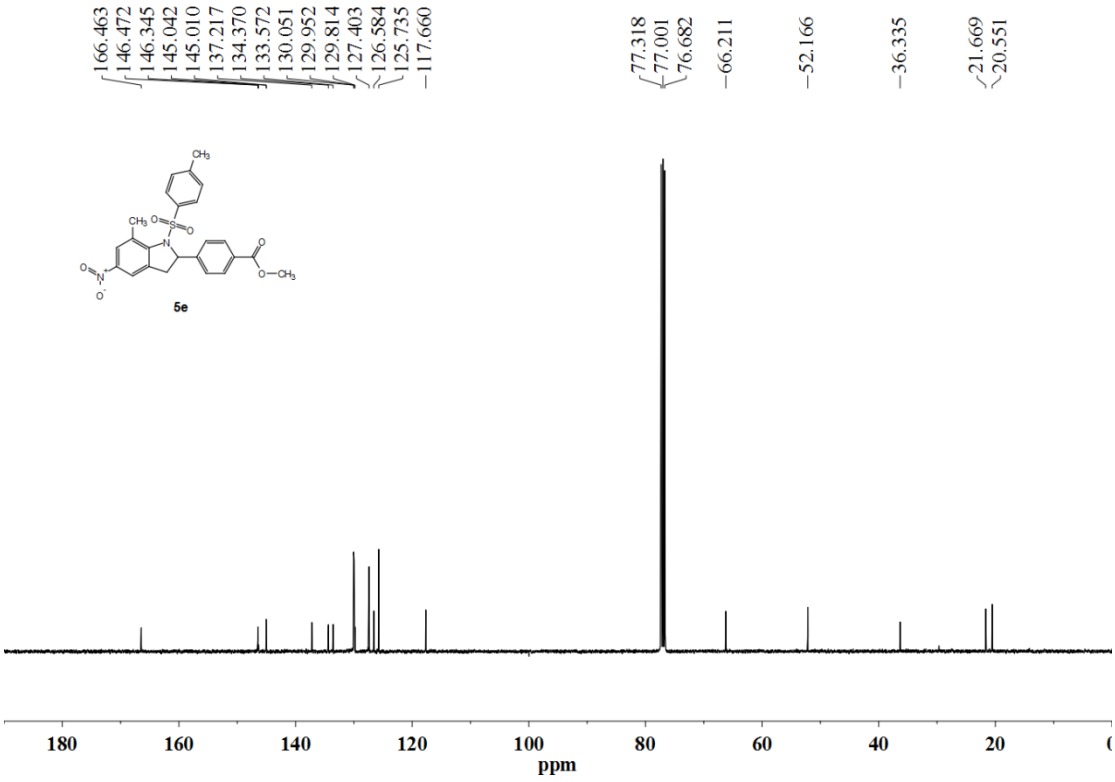
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117.660
77.318
77.001
76.682
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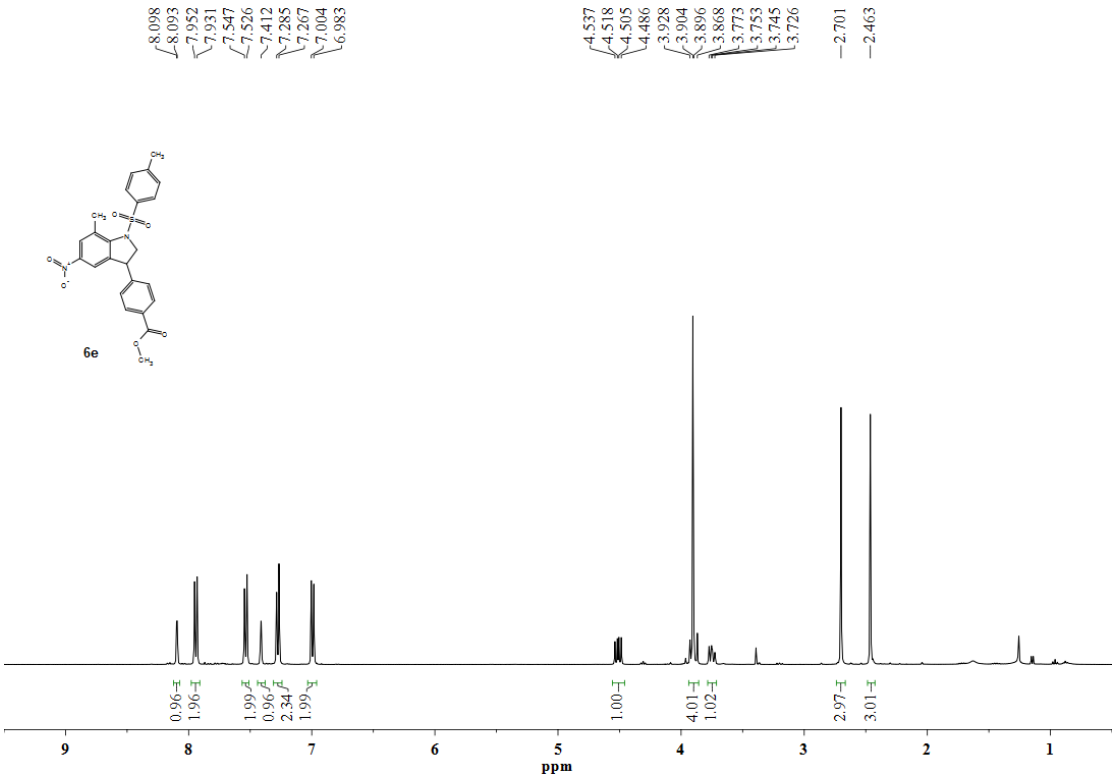
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6e
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1.96
1.99
0.96
2.34
1.99
1.00
4.01
1.02
2.97
3.01
9
8
7
6
5
4
3
2
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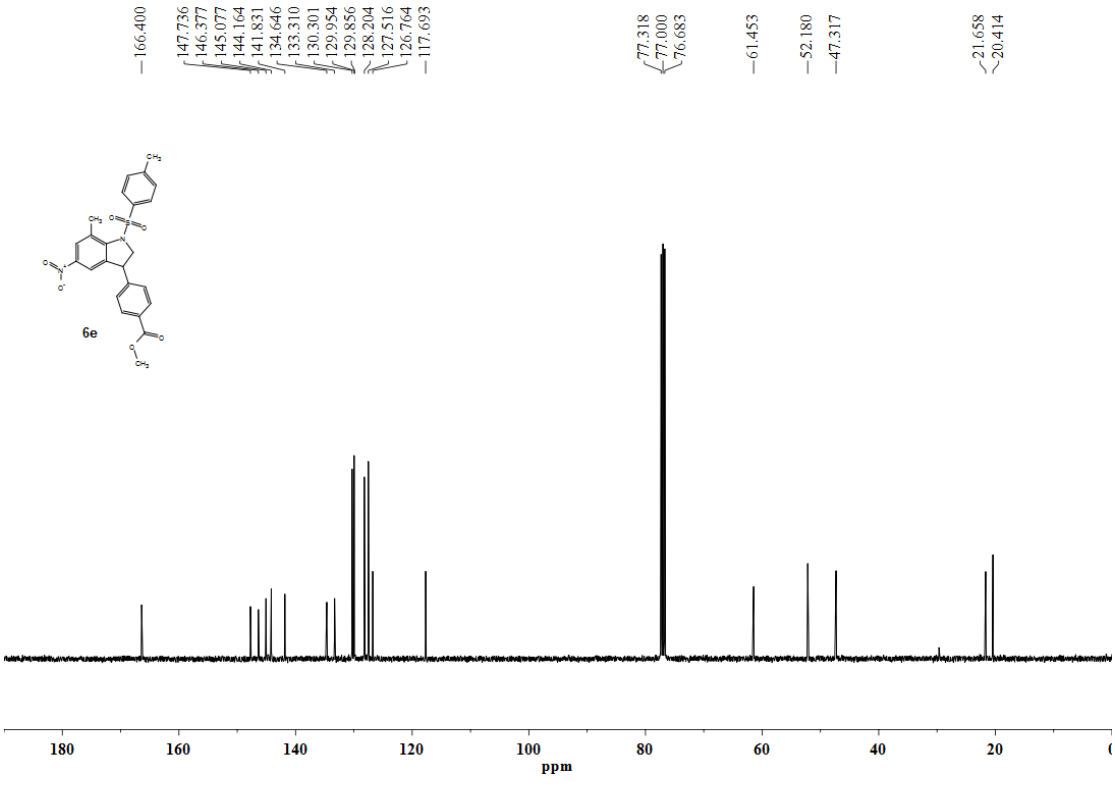
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126.764
117.693
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77.000
76.683
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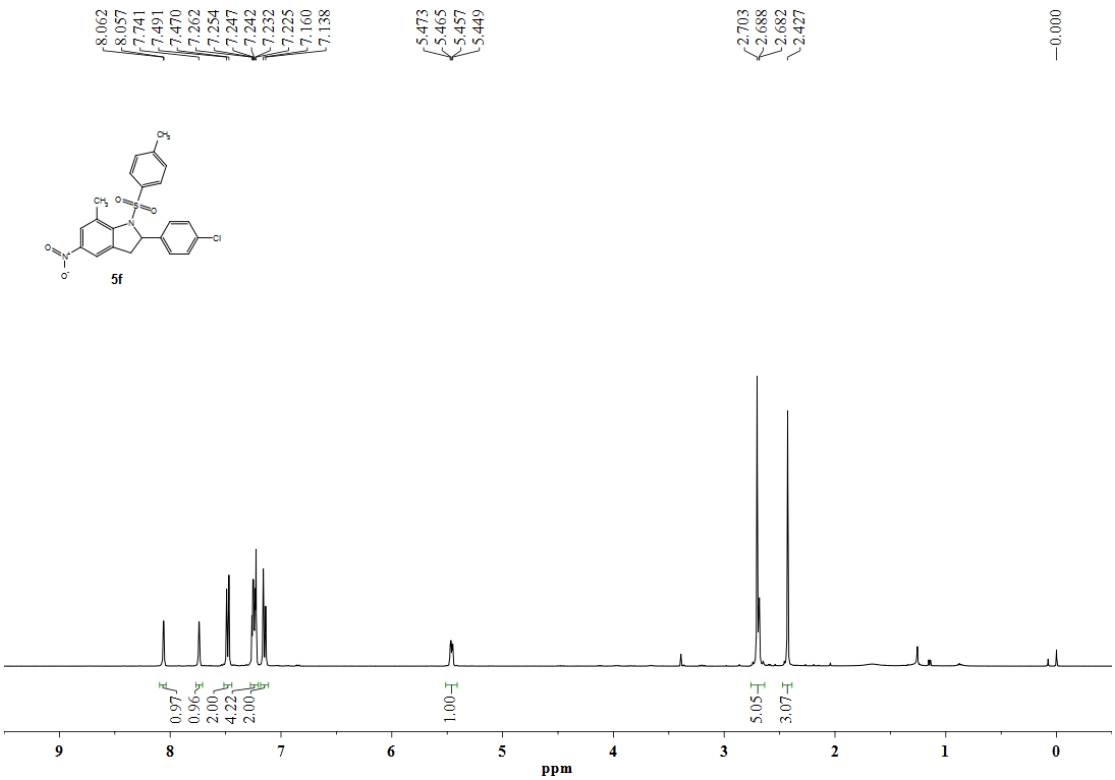
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5.457
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2.688
2.682
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0.96
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6
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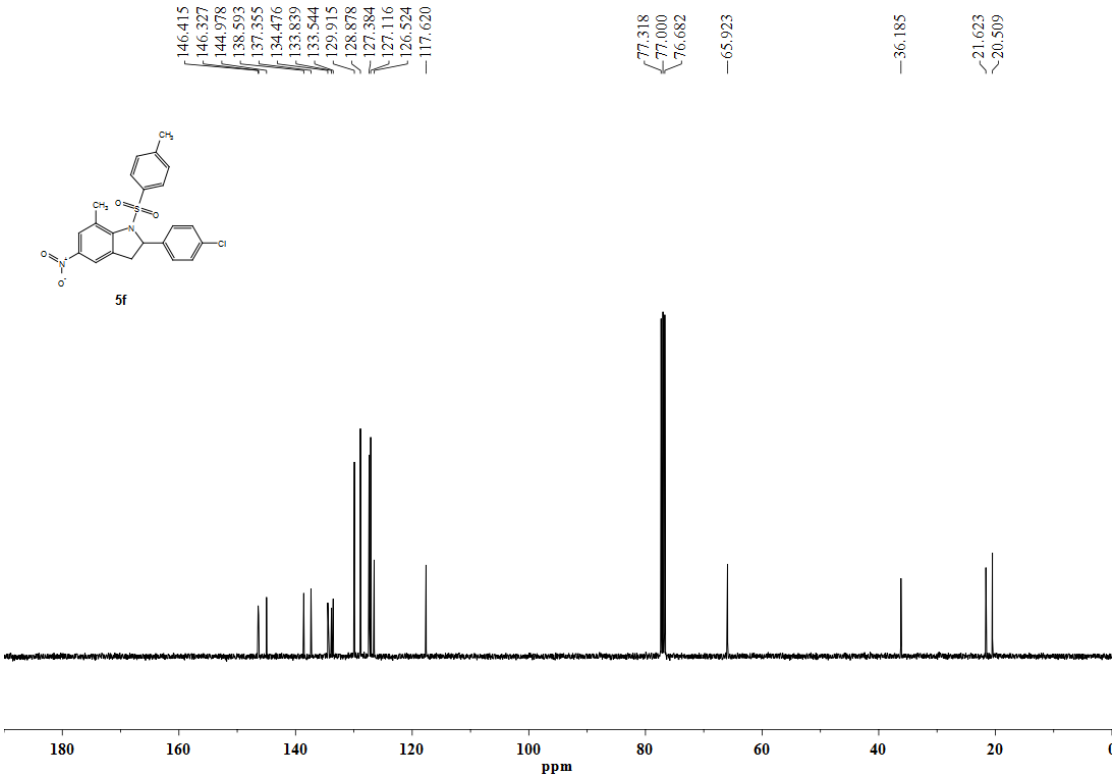
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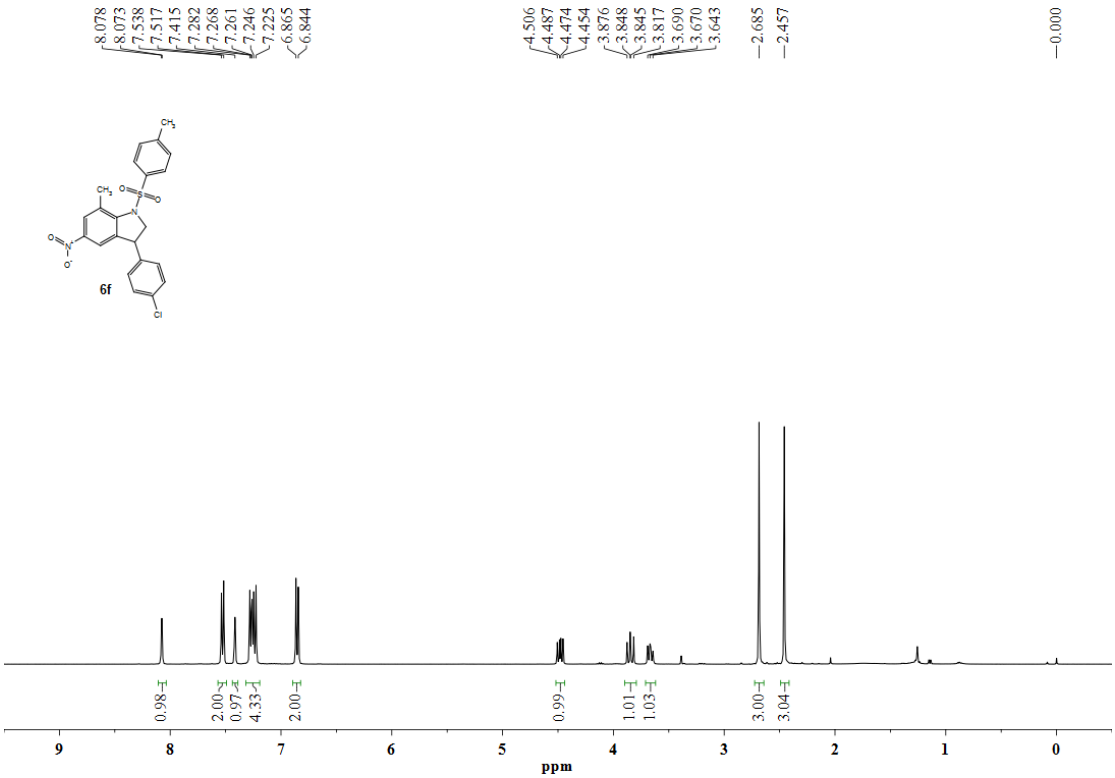
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3.845
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3.690
3.670
3.643
2.685
2.457
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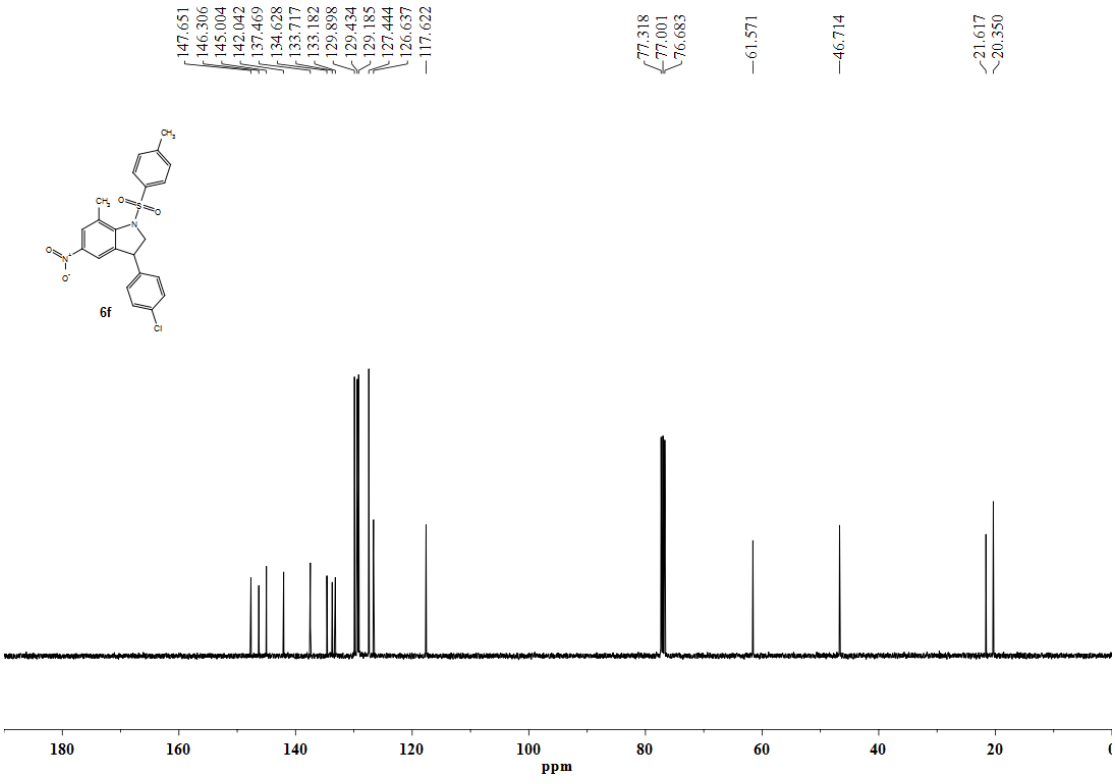
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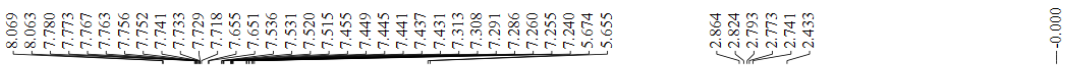
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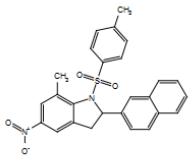

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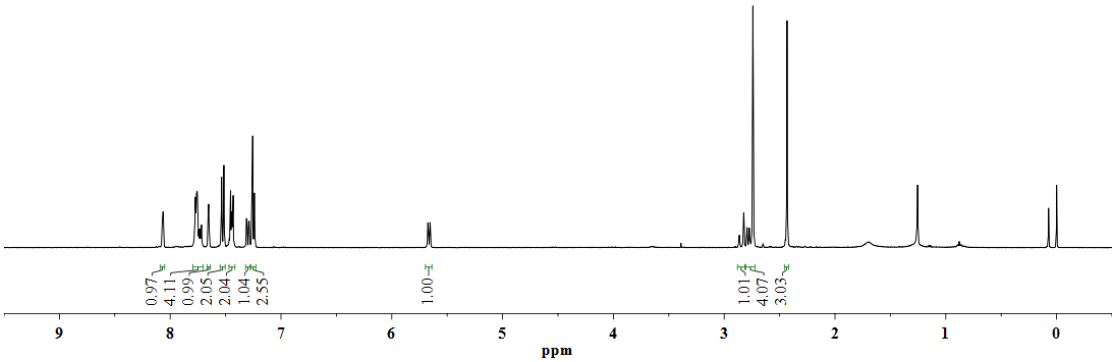
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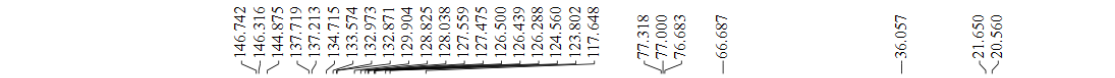
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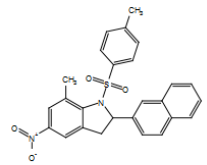
20.560



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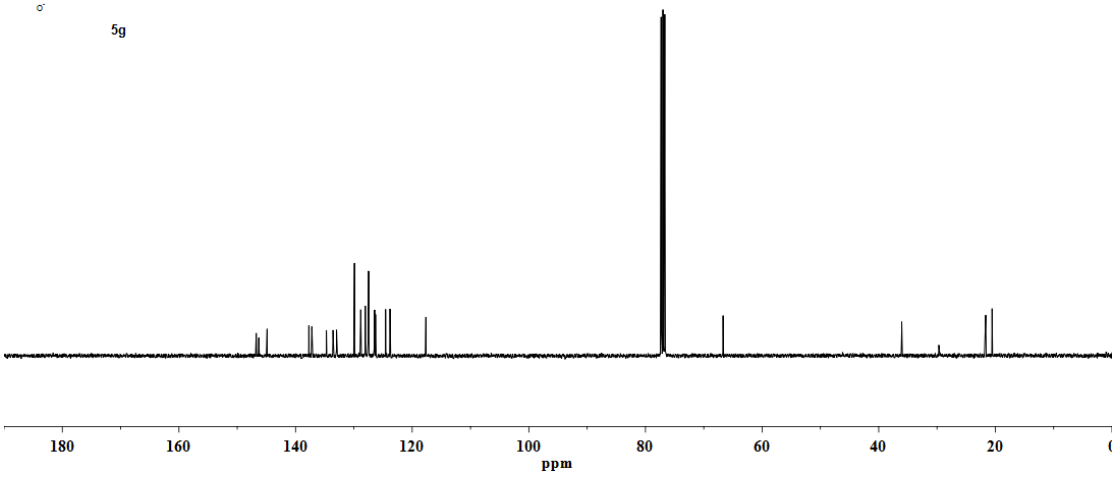
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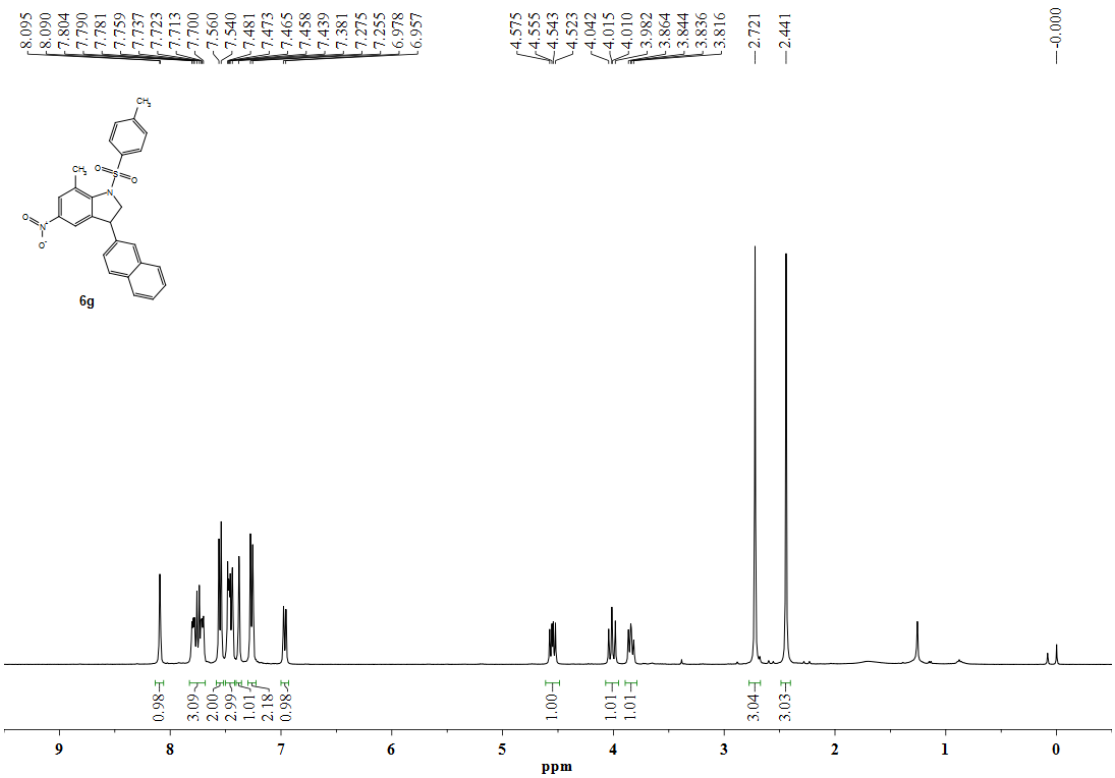
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7.458
7.439
7.381
7.275
7.255
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6.957
4.575
4.555
4.543
4.523
4.042
4.015
4.010
3.982
3.864
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3.836
3.816
2.721
2.441
0.000
6g
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3.09
2.00
2.99
1.01
2.18
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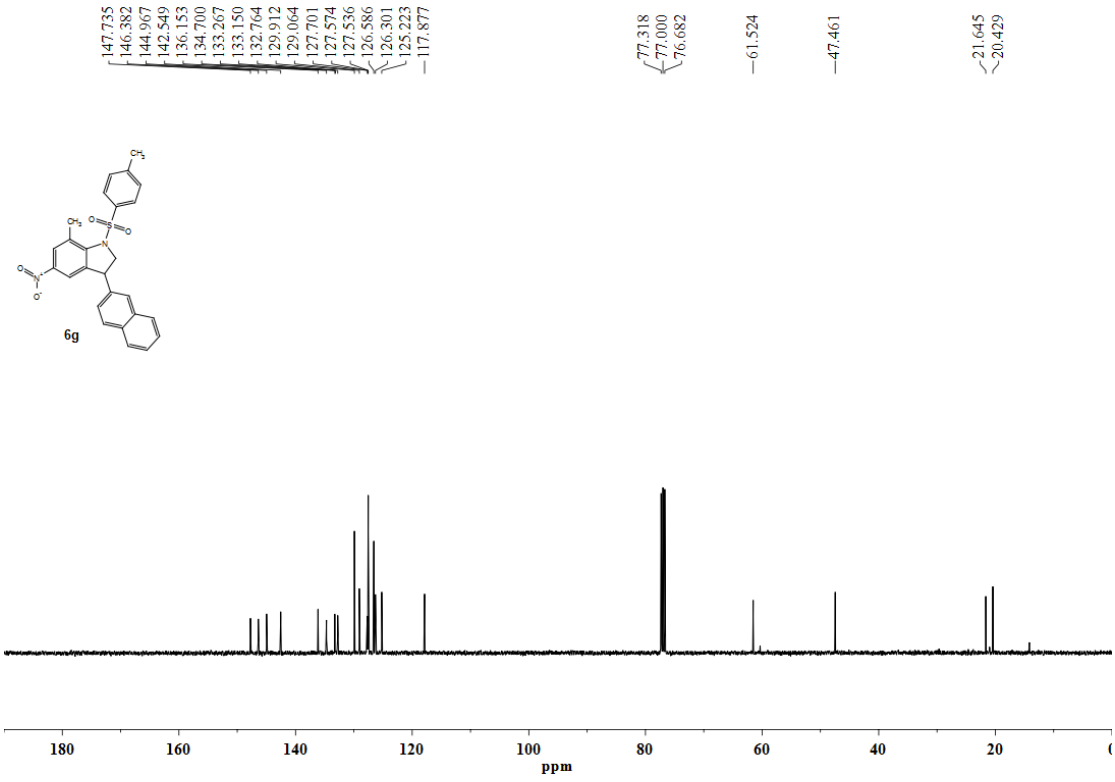
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6g
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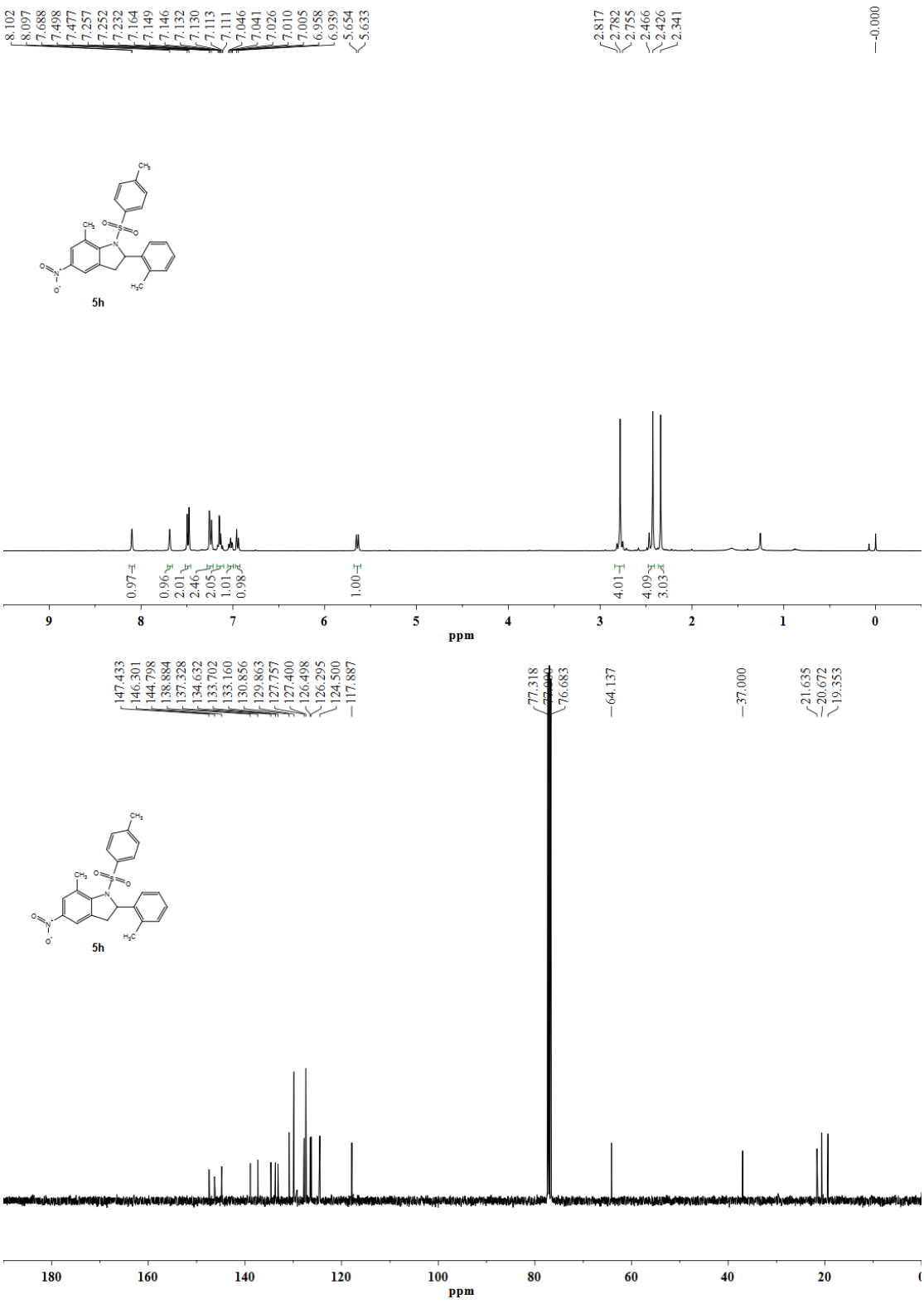
20
ppm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7.041
7.026
7.010
7.005
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2.05
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0.98
1.00
4.01
4.09
3.03
ppm
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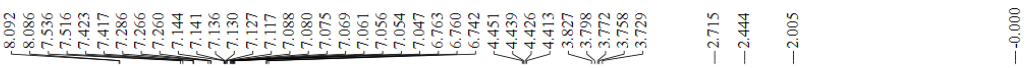
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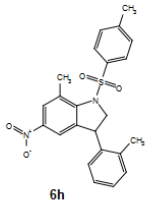
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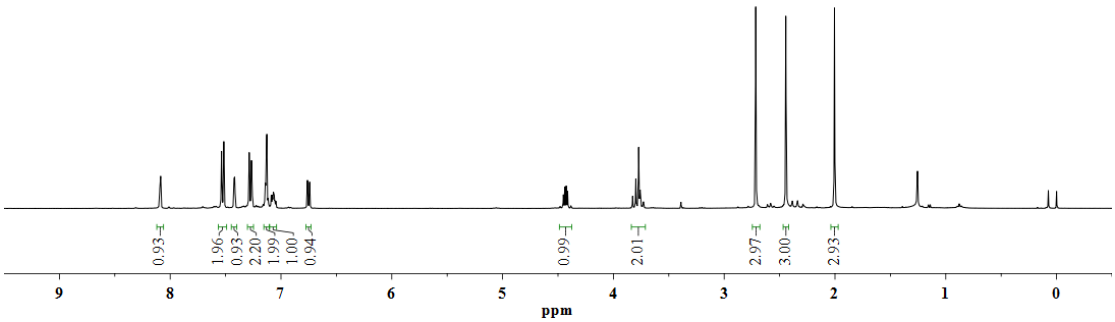
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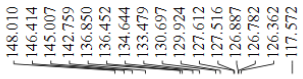
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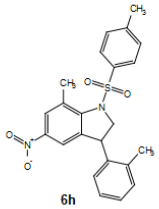
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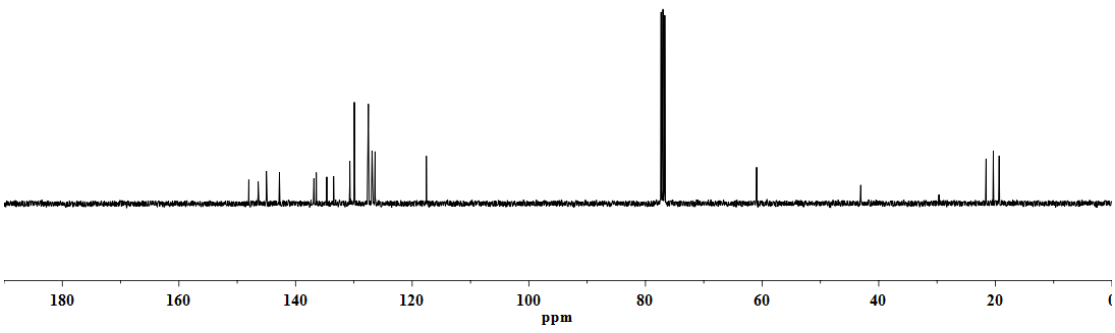
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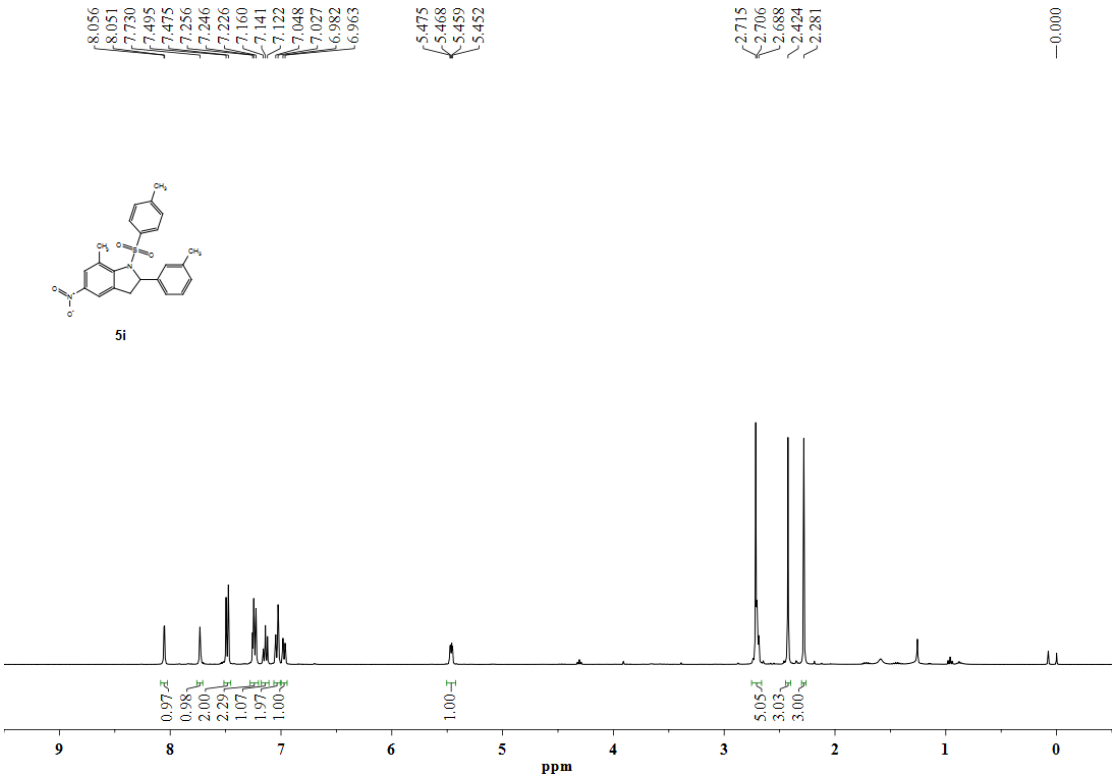
ppm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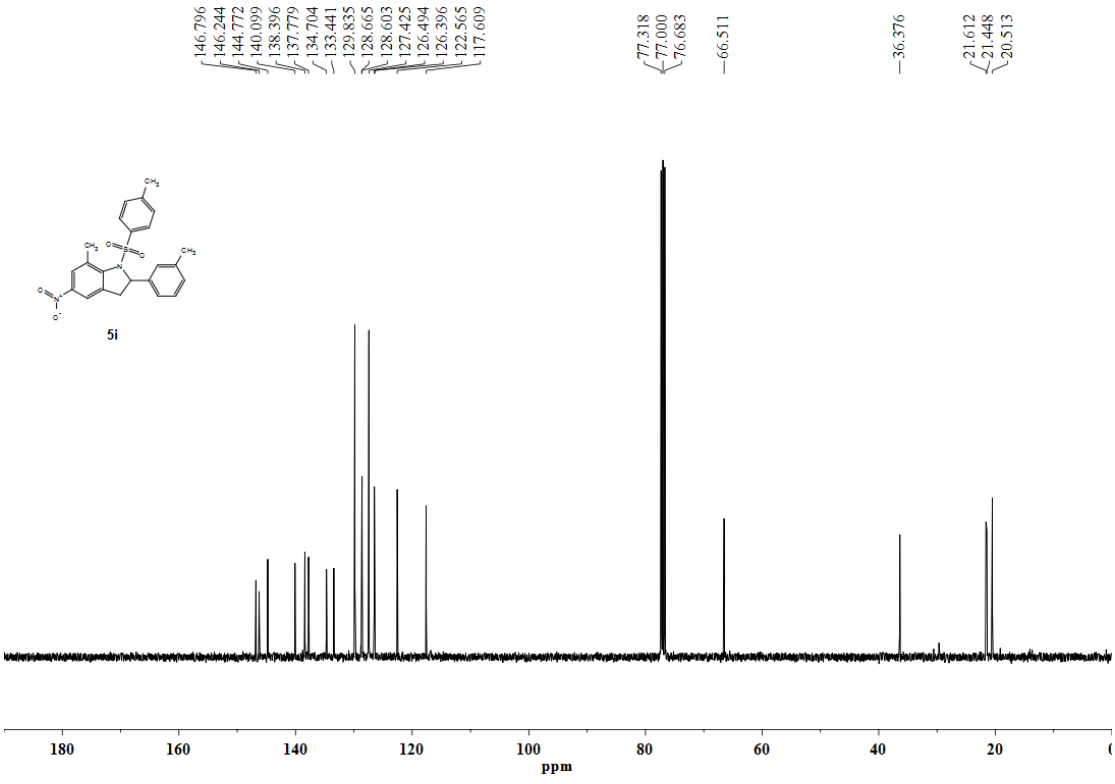
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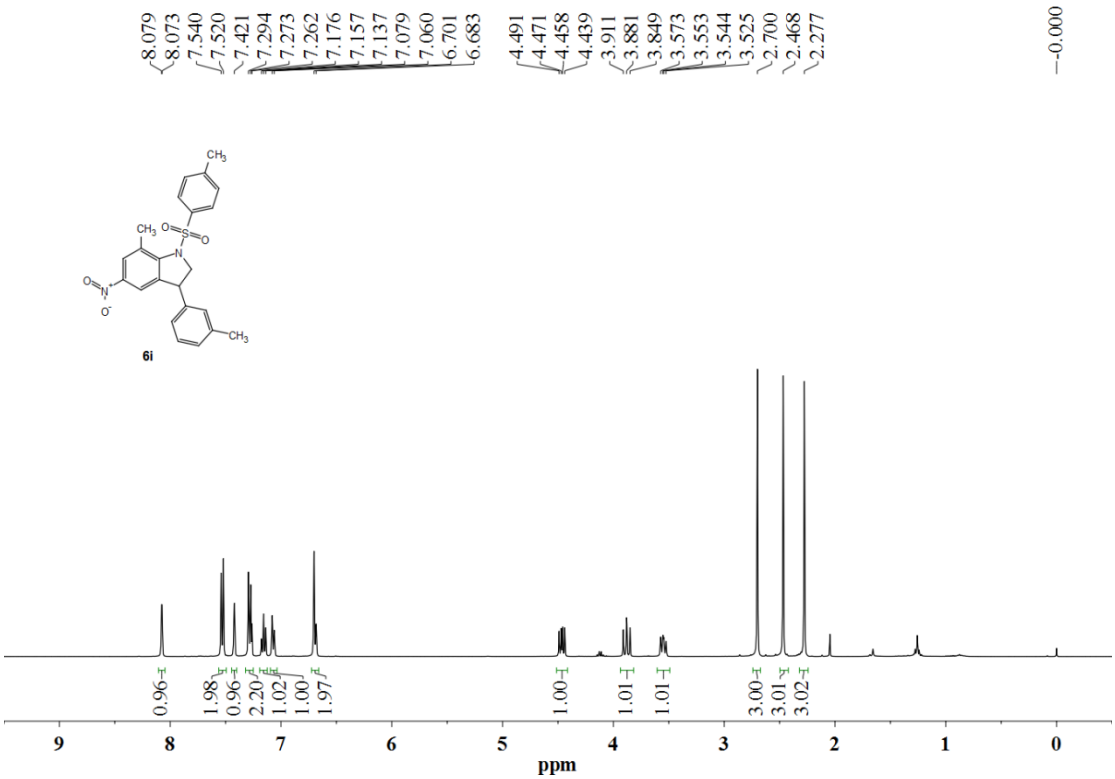
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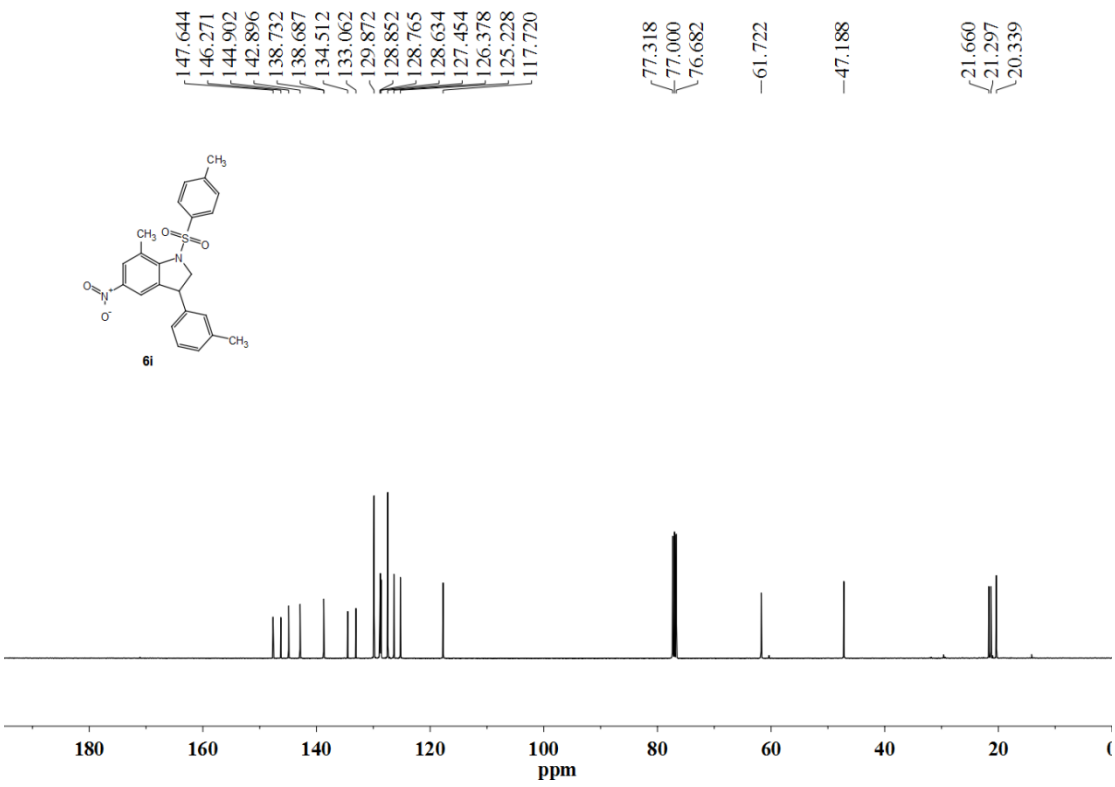
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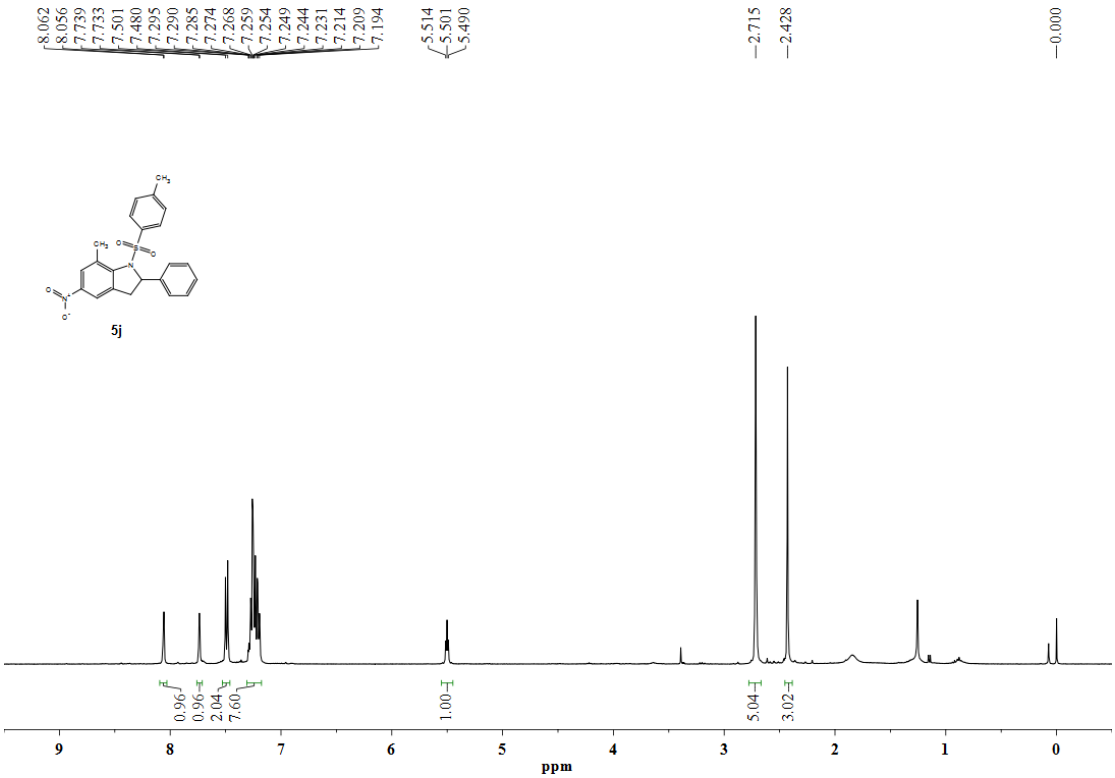
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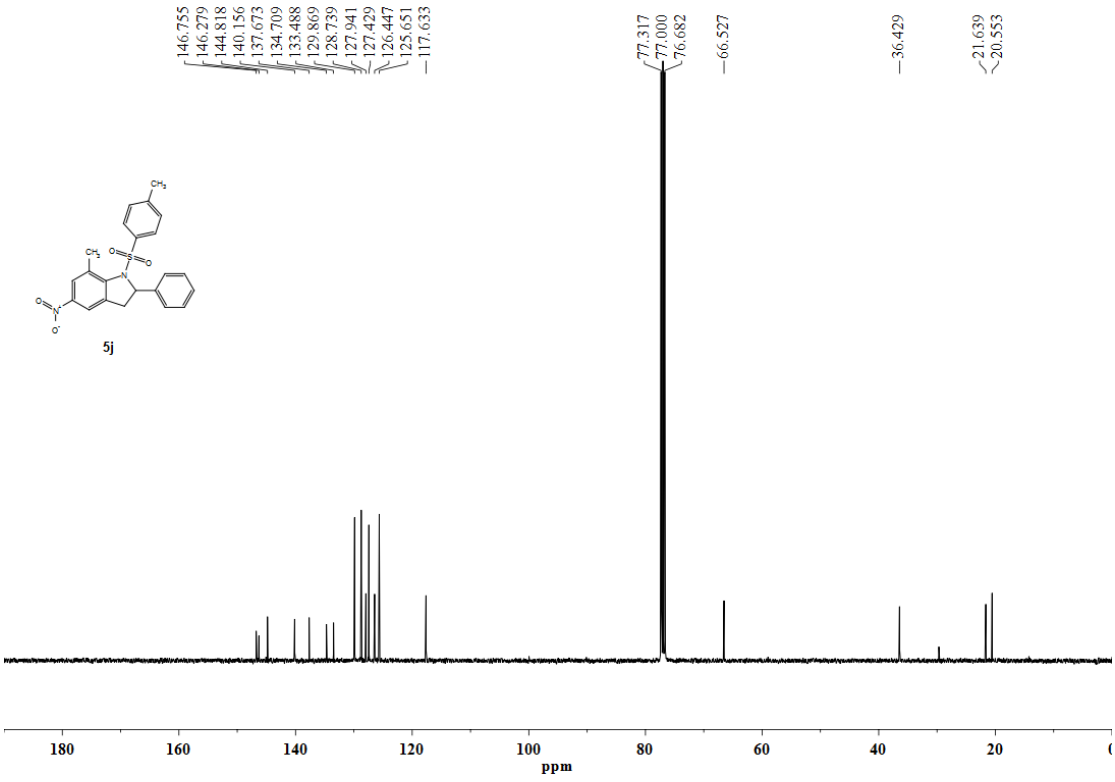
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77.317
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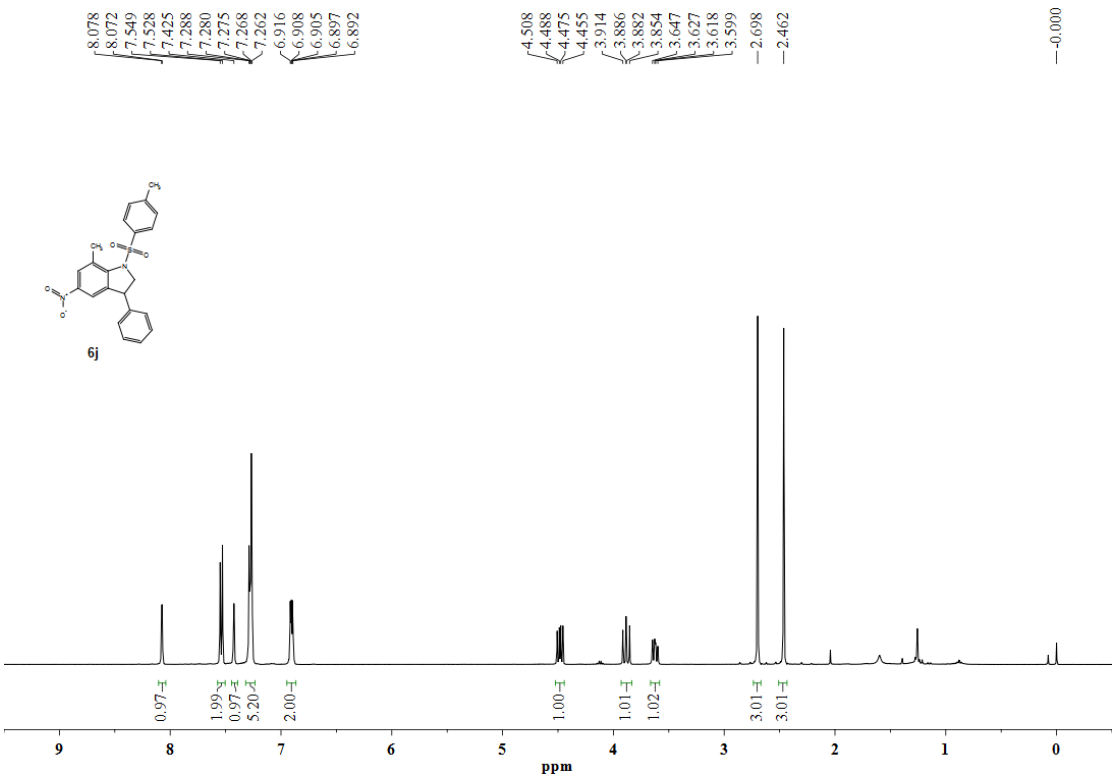
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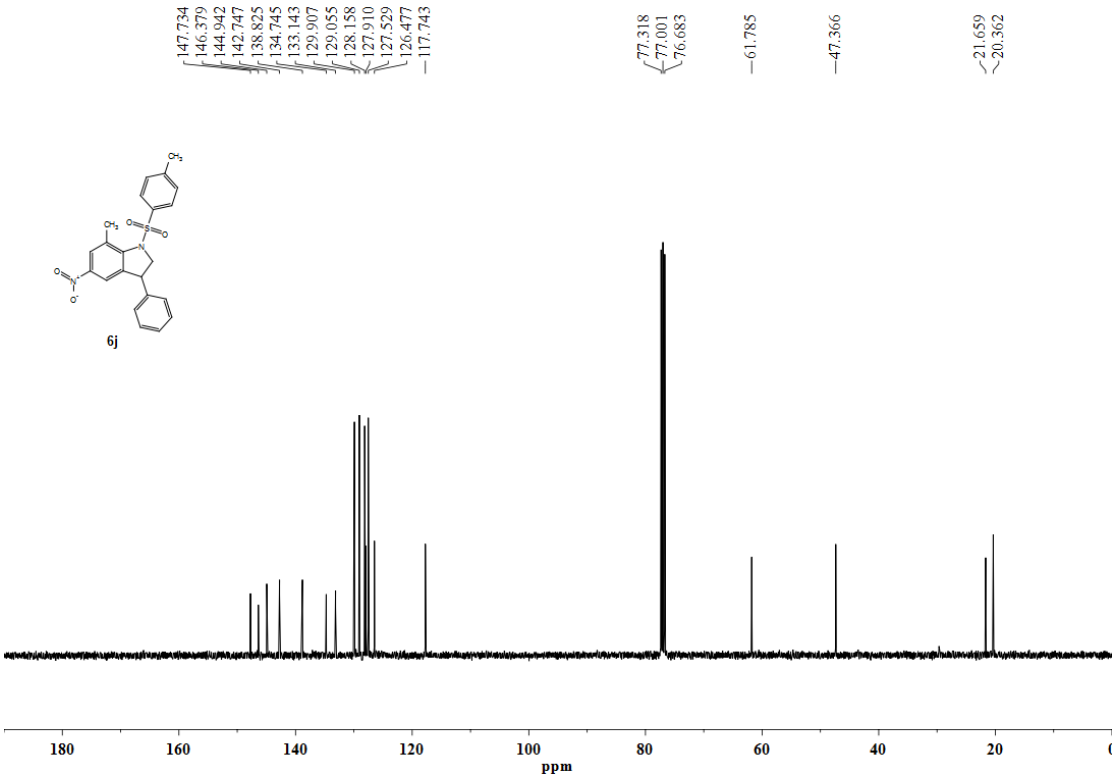
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77.318
77.001
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21.659
20.362
6j
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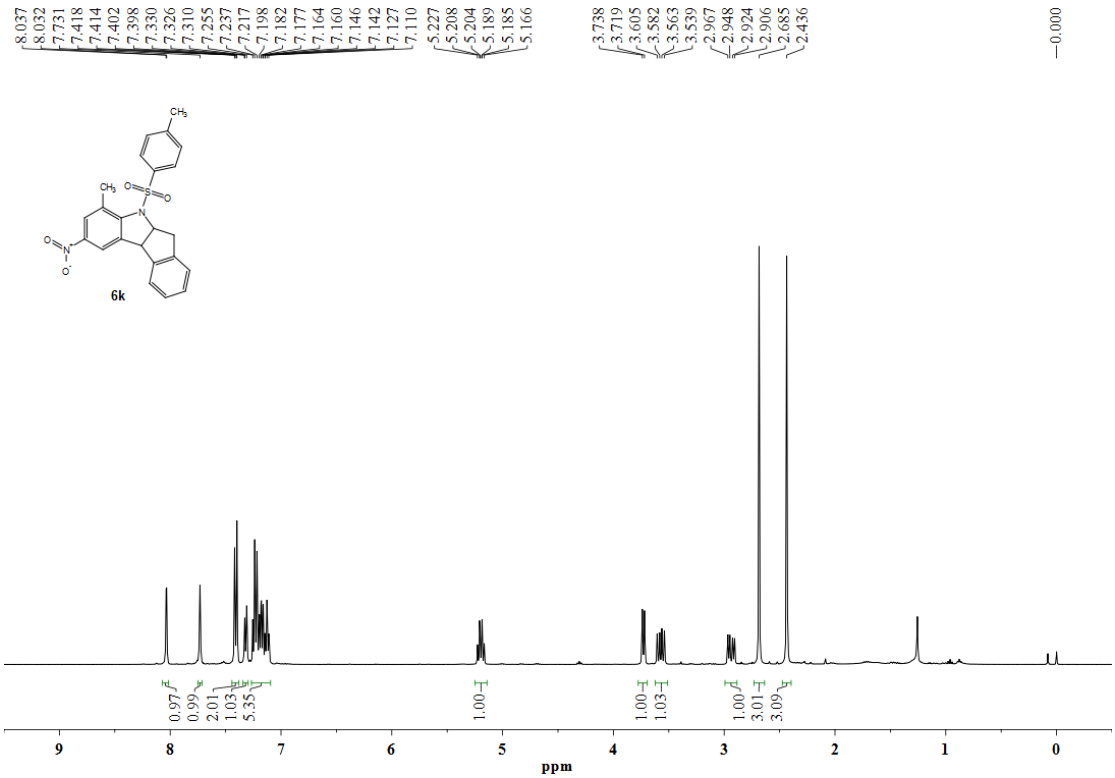
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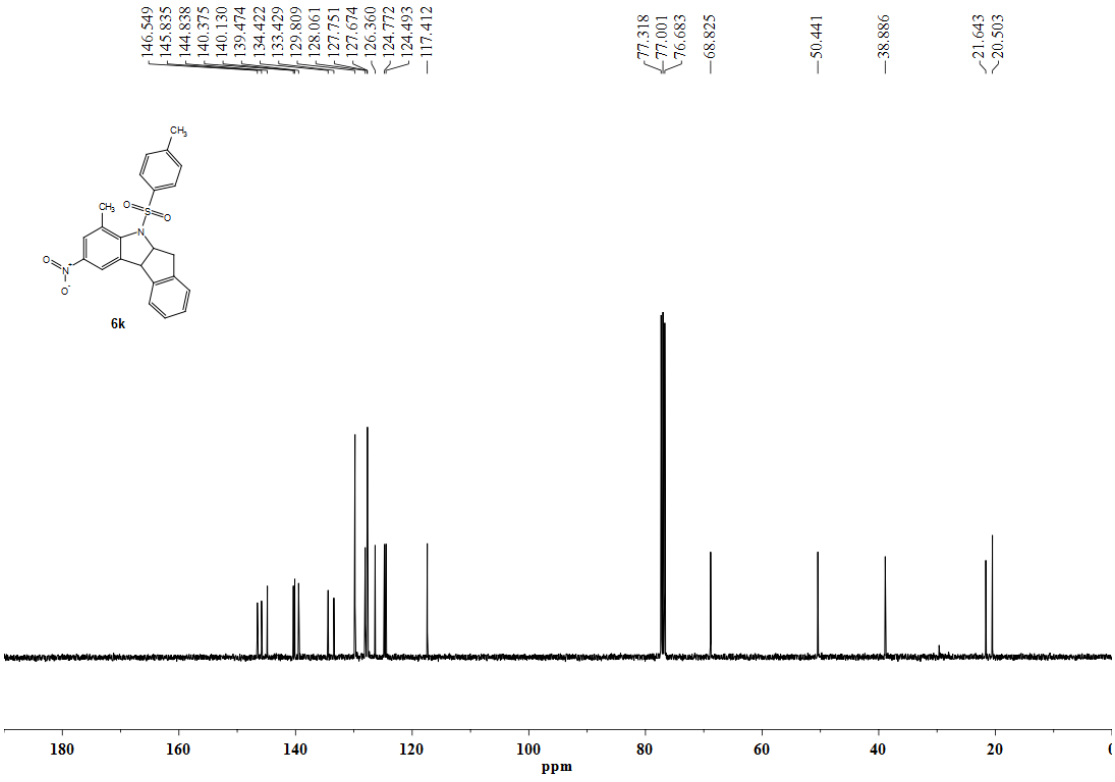
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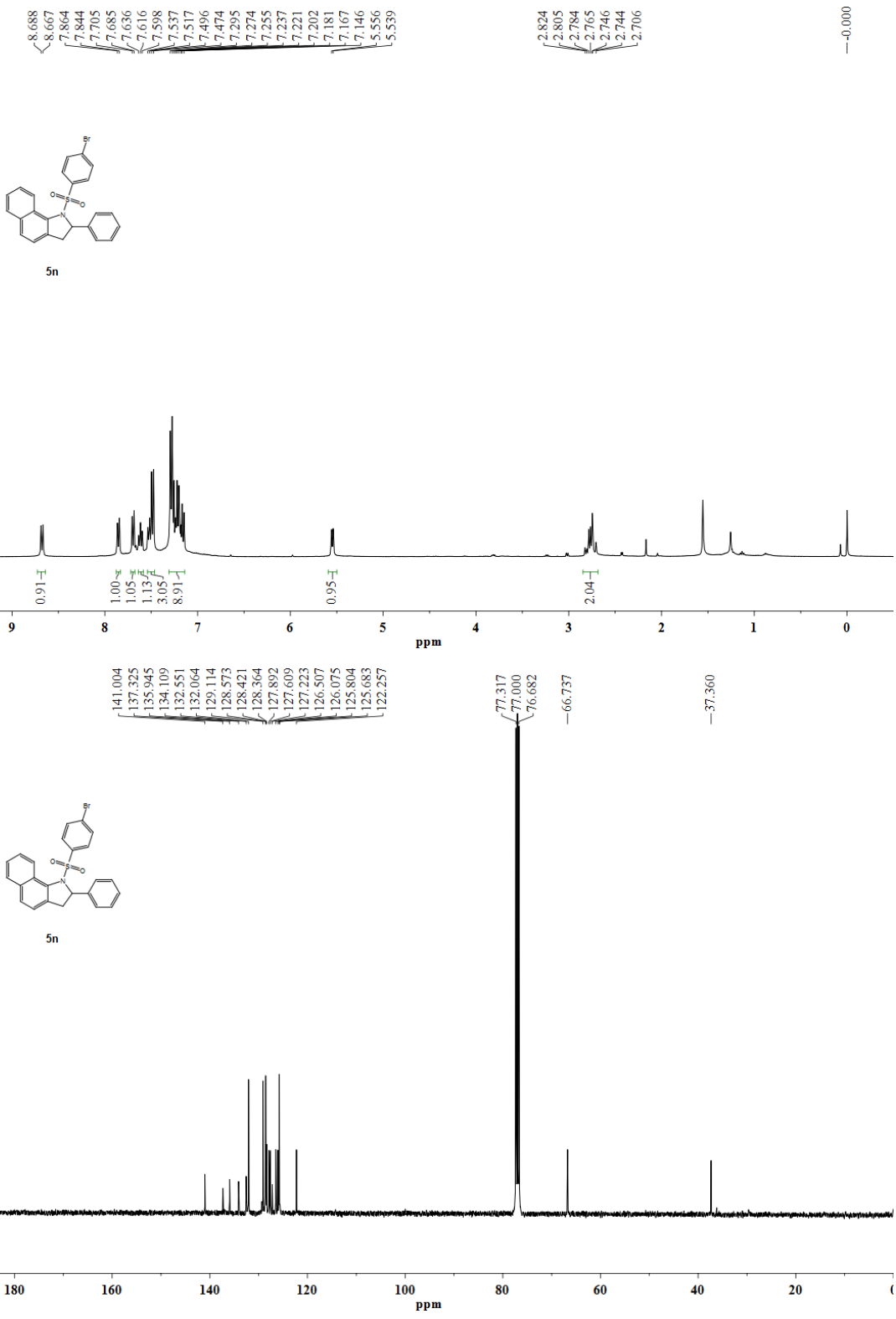
77.001
76.683
68.825
50.441
38.886
21.643
20.503
6k
ppm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8.667
7.864
7.844
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7.685
7.636
7.616
7.598
7.537
7.517
7.496
7.474
7.295
7.274
7.255
7.237
7.221
7.202
7.181
7.167
7.146
5.556
5.539
2.824
2.805
2.784
2.765
2.746
2.744
2.706
0.000
5n
0.91
1.00
1.05
1.13
3.05
8.91
0.95
2.04
ppm
141.004
137.325
135.945
134.109
132.551
132.064
129.114
128.573
128.421
128.364
127.892
127.609
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125.804
125.683
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77.000
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37.360
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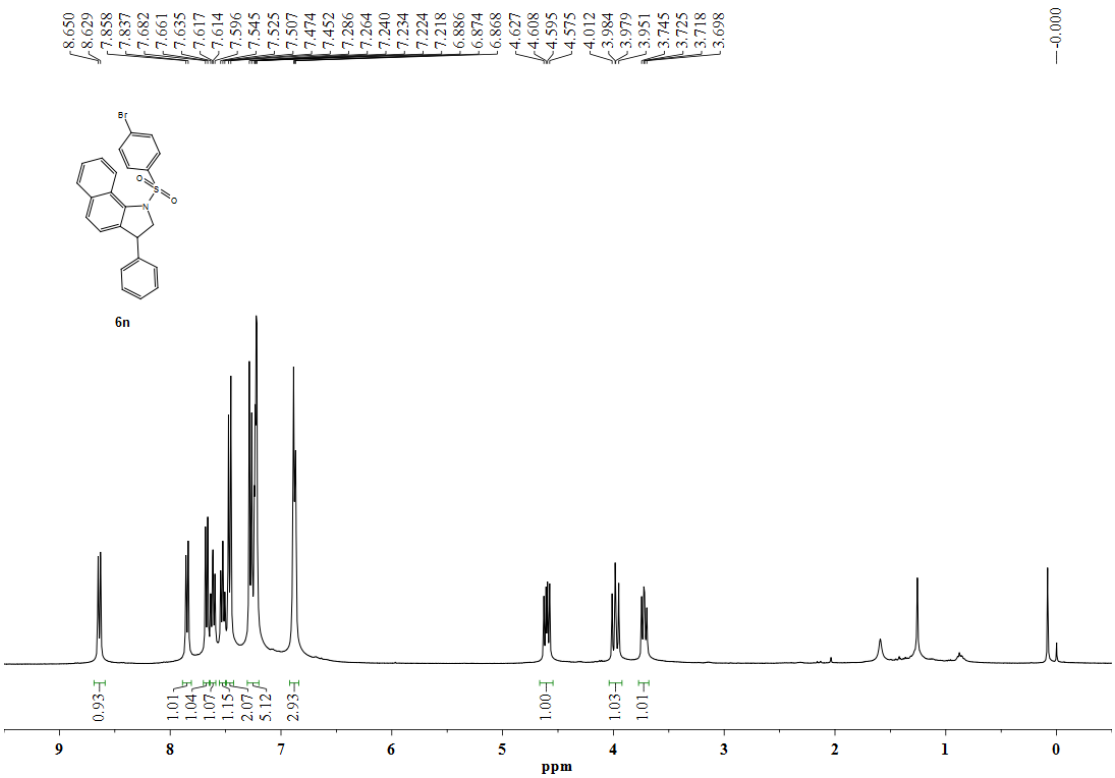
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8.629
7.858
7.837
7.682
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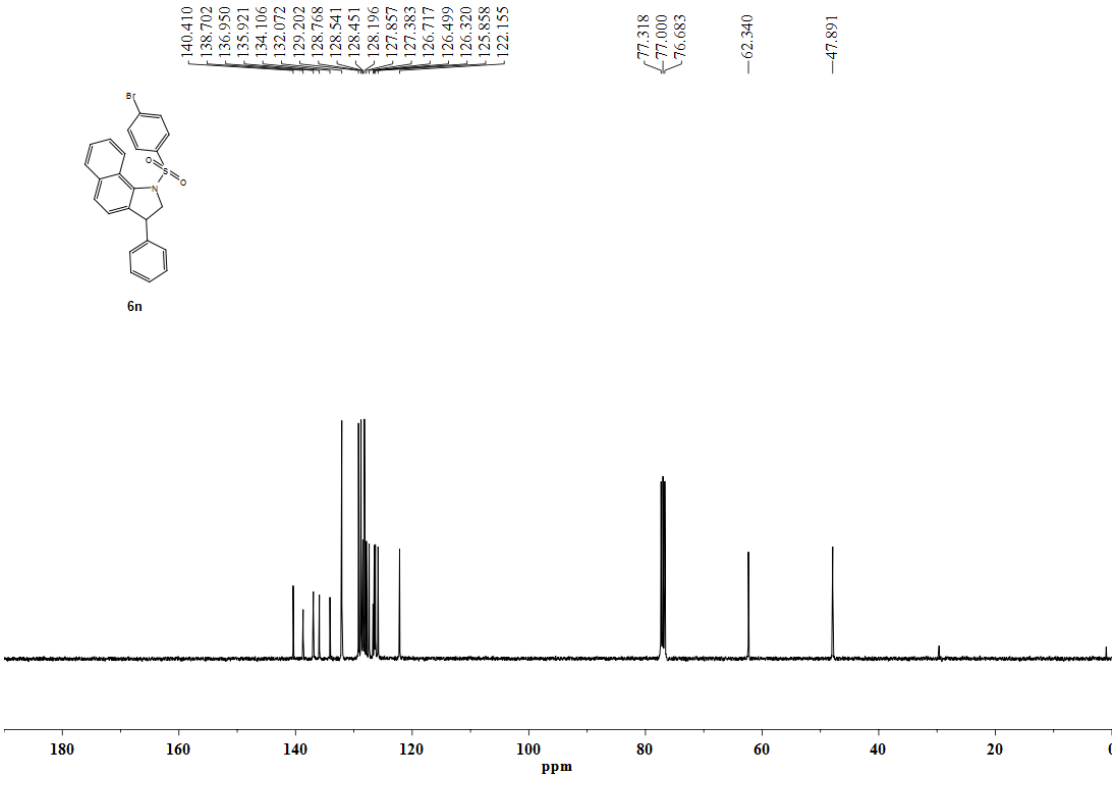
7.635
7.617
7.614
7.596
7.545
7.525
7.507
7.474
7.452
7.286
7.264
7.240
7.234
7.224
7.218
6.886
6.874
6.868
4.627
4.608
4.595
4.575
4.012
3.984
3.979
3.951
3.745
3.725
3.718
3.698
0.000
Br
O
S
O
N
6n
0.93
1.01
1.04
1.07
1.15
2.07
5.12
2.93
1.00
1.03
1.01
9
8
7
6
5
4
3
2
1
0
ppm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134.106
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129.202
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128.196
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126.717
126.499
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125.858
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77.000
76.683
62.340
47.891
Br
O
S
O
N
6n
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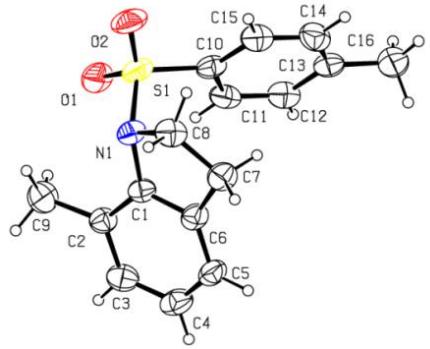
160
140
120
100
80
60
40
20
ppm

7 X-ray Crystallographic Information

7.1 X-ray crystallographic data of 3a

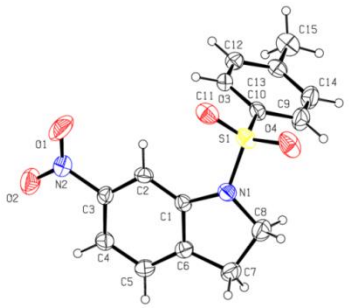


CCDC 1815728

Table 1 Crystal data and structure refinement for huahl_0328_2.

Identification code	huahl_0328_2
Empirical formula	$C_{16}H_{17}NO_2S$
Formula weight	287.37
Temperature/K	290.83(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.2125(8)
b/Å	15.041(2)
c/Å	12.8713(8)
α/°	90.00
β/°	90.483(5)
γ/°	90.00
Volume/Å^3	2945.1(5)
Z	8
ρ_{calc}g/cm^3	1.296
μ/mm^{-1}	0.220
F(000)	1216.0
Crystal size/mm^3	0.21 × 0.17 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.76 to 52.04
Index ranges	-17 ≤ h ≤ 18, -8 ≤ k ≤ 18, -15 ≤ l ≤ 15
Reflections collected	11725
Independent reflections	5798 [R_{int} = 0.0637, R_{sigma} = 0.1338]
Data/restraints/parameters	5798/0/365
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0677, wR_2 = 0.1158
Final R indexes [all data]	R_1 = 0.1895, wR_2 = 0.1784
Largest diff. peak/hole / e Å^{-3}	0.29/-0.29

7.2 X-ray crystallographic data of 3s

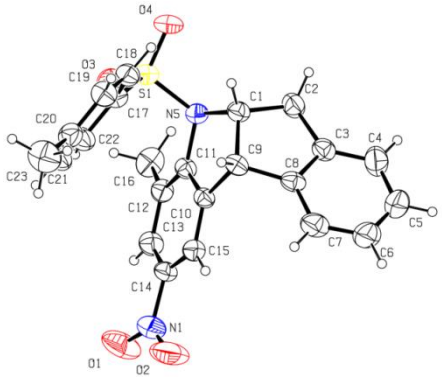


CCDC 1815733

Table 1 Crystal data and structure refinement for liuce_1114_2.

Identification code	liuce_1114_2
Empirical formula	$C_{15}H_{14}N_2O_4S$
Formula weight	318.34
Temperature/K	291.37(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.7131(9)
b/Å	7.8152(8)
c/Å	21.654(2)
α/°	90.00
β/°	92.171(9)
γ/°	90.00
Volume/Å^3	1473.5(3)
Z	4
ρ_{calc}g/cm^3	1.435
μ/mm^{-1}	0.240
F(000)	664.0
Crystal size/mm^3	0.25 × 0.24 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7 to 52.02
Index ranges	$-10 \le h \le 10$, $-9 \le k \le 9$, $-26 \le l \le 14$
Reflections collected	5031
Independent reflections	2900 [R_{int} = 0.0332, R_{sigma} = 0.0635]
Data/restraints/parameters	2900/0/200
Goodness-of-fit on F^2	1.107
Final R indexes [I>=2σ (I)]	R_1 = 0.0566, wR_2 = 0.1092
Final R indexes [all data]	R_1 = 0.0986, wR_2 = 0.1406
Largest diff. peak/hole / e Å^{-3}	0.21/-0.33

7.3 X-ray crystallographic data of 6k

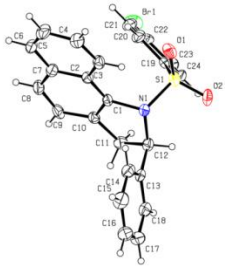


CCDC 1815734

Table 1 Crystal data and structure refinement for liuc_0831-sr.

Identification code	liuc_0831-sr
Empirical formula	$C_{23}H_{20}N_2O_4S$
Formula weight	420.47
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.0329(9)
b/Å	24.1681(14)
c/Å	8.5244(5)
α/°	90
β/°	103.965(7)
γ/°	90
Volume/Å^3	2405.7(3)
Z	4
ρ_{calc}g/cm^3	1.161
μ/mm^{-1}	0.163
F(000)	880.0
Crystal size/mm^3	0.25 × 0.22 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.744 to 52.038
Index ranges	$-14 \le h \le 14$, $0 \le k \le 29$, $0 \le l \le 10$
Reflections collected	4738
Independent reflections	4738 [R_{int} = 0.0000, R_{sigma} = 0.0969]
Data/restraints/parameters	4738/0/273
Goodness-of-fit on F^2	0.902
Final R indexes [I>=2σ (I)]	R_1 = 0.0621, wR_2 = 0.1335
Final R indexes [all data]	R_1 = 0.1344, wR_2 = 0.1645
Largest diff. peak/hole / e Å^{-3}	0.19/-0.26

7.4 X-ray crystallographic data of *(R)*-5n

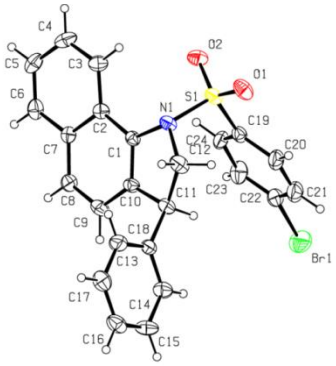


CCDC 1815739

Table 1 Crystal data and structure refinement for liuc_547_2.

Identification code	liuc_547_2
Empirical formula	$C_{24}H_{18}BrNO_2S$
Formula weight	464.36
Temperature/K	289.50(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.2737(10)
b/Å	8.0033(8)
c/Å	11.9357(10)
α/°	90.00
β/°	108.605(9)
γ/°	90.00
Volume/Å^3	1020.64(16)
Z	2
ρ_{calc}g/cm^3	1.511
μ/mm^{-1}	2.137
F(000)	472.0
Crystal size/mm^3	0.21 × 0.15 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.68 to 52.04
Index ranges	$-13 \le h \le 12$, $-4 \le k \le 9$, $-14 \le l \le 9$
Reflections collected	3728
Independent reflections	2564 [R_{int} = 0.0330, R_{sigma} = 0.0678]
Data/restraints/parameters	2564/1/262
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0494, wR_2 = 0.0838
Final R indexes [all data]	R_1 = 0.0763, wR_2 = 0.0963
Largest diff. peak/hole / e Å^{-3}	0.29/-0.35
Flack parameter	-0.009(13)

7.5 X-ray crystallographic data of *(S)*-6n

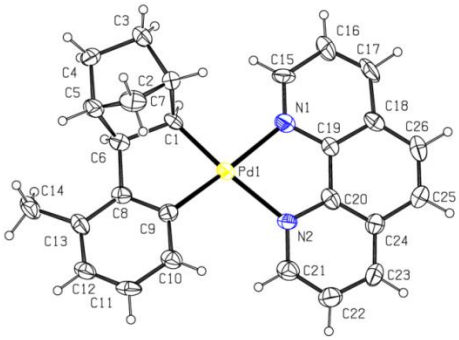


CCDC 1815740

Table 1 Crystal data and structure refinement for liuc_0516.

Identification code	liuc_0516
Empirical formula	$C_{24}H_{18}BrNO_2S$
Formula weight	464.36
Temperature/K	292.4(5)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.0085(4)
b/Å	10.9667(7)
c/Å	26.5254(15)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2038.7(2)
Z	4
ρ_{calc}g/cm^3	1.513
μ/mm^{-1}	2.139
F(000)	944.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.58 to 52.04
Index ranges	-8 ≤ h ≤ 8, -13 ≤ k ≤ 6, -18 ≤ l ≤ 32
Reflections collected	7932
Independent reflections	4020 [R_{int} = 0.0517, R_{sigma} = 0.0891]
Data/restraints/parameters	4020/0/262
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.0843
Final R indexes [all data]	R_1 = 0.1005, wR_2 = 0.1007
Largest diff. peak/hole / e Å^{-3}	0.28/-0.53
Flack parameter	-0.013(11)

7.6 X-ray crystallographic data of B

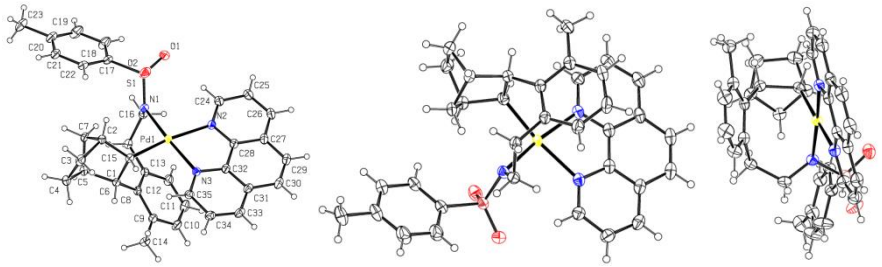


CCDC 1815736

Table 1 Crystal data and structure refinement for Xray_0104.

Identification code	Xray_0104
Empirical formula	$C_{26}H_{24}N_2Pd$
Formula weight	470.87
Temperature/K	294.8(3)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	18.5168(5)
b/Å	22.2325(12)
c/Å	9.8110(4)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	4038.9(3)
Z	8
ρ_{calc}g/cm^3	1.549
μ/mm^{-1}	0.934
F(000)	1920.0
Crystal size/mm^3	0.06 × 0.04 × 0.03
Radiation	Mo Kα (λ = 0.7107)
2Θ range for data collection/°	6.86 to 52.04
Index ranges	-20 ≤ h ≤ 22, -27 ≤ k ≤ 19, -6 ≤ l ≤ 12
Reflections collected	10207
Independent reflections	5431 [R_{int} = 0.0655, R_{sigma} = 0.1008]
Data/restraints/parameters	5431/1/525
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0529, wR_2 = 0.0734
Final R indexes [all data]	R_1 = 0.0901, wR_2 = 0.0943
Largest diff. peak/hole / e Å^{-3}	0.90/-0.53
Flack parameter	-0.02(4)

7.7 X-ray crystallographic data of E

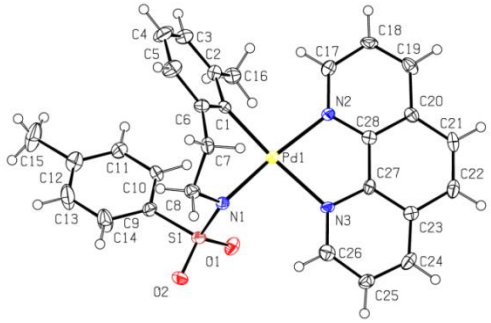


CCDC 1822354

Table 1 Crystal data and structure refinement for liuc_3.

Identification code	liuc_3
Empirical formula	$C_{38}H_{42}N_4O_3PdS$
Formula weight	741.26
Temperature/K	173
Crystal system	triclinic
Space group	P-1
a/Å	10.2072(5)
b/Å	13.9301(10)
c/Å	15.1016(13)
α/°	66.531(8)
β/°	75.760(6)
γ/°	88.492(5)
Volume/Å^3	1902.9(3)
Z	2
ρ_{calc}g/cm^3	1.2936
μ/mm^{-1}	4.753
F(000)	771.0
Crystal size/mm^3	0.21 × 0.15 × 0.14
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.68 to 133.2
Index ranges	-12 ≤ h ≤ 11, -16 ≤ k ≤ 16, -17 ≤ l ≤ 18
Reflections collected	12232
Independent reflections	6479 [R_{int} = 0.0237, R_{sigma} = 0.0315]
Data/restraints/parameters	6479/0/428
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0323, wR_2 = 0.0873
Final R indexes [all data]	R_1 = 0.0338, wR_2 = 0.0890
Largest diff. peak/hole / e Å^{-3}	1.41/-0.62

7.8 X-ray crystallographic data of F



CCDC 1815737

Table 1 Crystal data and structure refinement for liuc_0308_2.

Identification code	liuc_0308_2
Empirical formula	$C_{28}H_{25}N_3O_2PdS$
Formula weight	573.97
Temperature/K	291.17(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.1719(16)
b/Å	9.5500(11)
c/Å	15.502(3)
α/°	87.411(13)
β/°	88.915(16)
γ/°	80.386(13)
Volume/Å^3	1191.5(4)
Z	2
ρ_{calc}g/cm^3	1.600
μ/mm^{-1}	0.899
F(000)	584.0
Crystal size/mm^3	0.17 × 0.15 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/ °	6.672 to 52.036
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -13 ≤ l ≤ 19
Reflections collected	7926
Independent reflections	4671 [R_{int} = 0.0591, R_{sigma} = 0.1214]
Data/restraints/parameters	4671/0/318
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0590, wR_2 = 0.0909
Final R indexes [all data]	R_1 = 0.0929, wR_2 = 0.1088
Largest diff. peak/hole / e Å^{-3}	1.04/-0.67