

Supporting information

Visible-light-induced surfactant-promoted sulfonylation of alkenes and alkynes with sulfonyl chloride by the formation of EDA-complex with NaI in water at room temperature

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Table of Contents

1. General Information.....	2
2. General procedure for the synthesis of products	2
3. Table S1 Reaction in organic solvent free of catalyst. ^{a,b}	3
Table S2. Optimization of the reaction conditions in water. ^{a,b}	4
Table S3. Optimization of surfactants in water.	5
4. Gram scale synthesis.....	5
5. Proposed mechanism	7
6. UV-vis absorbance experiment.....	7
7. Stoichiometry of the EDA Complex in Solution (Job's plot).....	8
8. Stern-Volmer Quenching Studies with NaI.	9
9. NMR experiment.	9
10. Experimental for cyclic voltammetry.	12
11. Characterization Data of Products.	12
12. Single-crystal X-ray analysis of 8b.....	22
13. NMR Spectra	25

1. General Information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Both alkenes and sulfonyl chloride are purchased from Energy Chemical.

NMR spectra were obtained on a JNM-ECZ600R/S1 spectrometer. NMR data were obtained for ^1H at 600 MHz, and for ^{13}C at 150 MHz. The ^1H NMR (600 MHz) chemical shifts were measured relative to CDCl_3 or DMSO-d_6 or CD_3OD as the internal references (CDCl_3 : $\delta = 7.26$, DMSO-d_6 : $\delta = 2.50$, CD_3OD : $\delta = 3.31$). The ^{13}C NMR (150 MHz) chemical shifts were given using CDCl_3 or DMSO-d_6 or CD_3OD as the internal references (CDCl_3 : $\delta = 77.16$, DMSO-d_6 : $\delta = 39.52$, CD_3OD : $\delta = 49.00$). ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. TLC was performed on glass-backed silica plates. Column chromatography was performed on silicagel (300-400 mesh), eluting with petroleum ether and ethyl acetate.

2. General procedure for the synthesis of products

A 15 mL Schlenk tube equipped with a magnetic stirring bar was charged with alkenes (0.2 mmol), sulfonyl chlorides (0.2 mmol), NaI (0.2 mmol), HOAc (0.6 mmol), H_2O (4 mL) and CTAB (0.02 mmol). The mixture was then stirred at room temperature under nitrogen atmosphere and irradiated with a 3 W blue LEDs light bulb for 15 h. After completion of the reaction, the reaction mixture was extracted with ethyl acetate (3×4 mL). The combined organic phases were dried over anhydrous Na_2SO_4 , and then concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (PE: EA= 1:20) to afford the product.

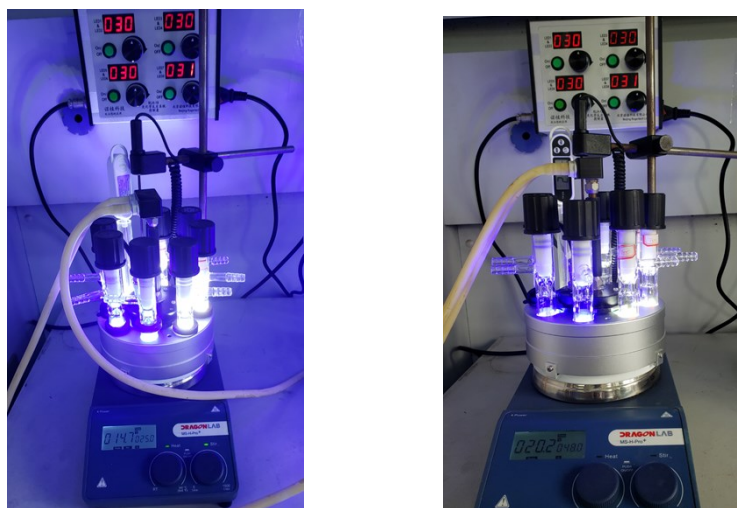
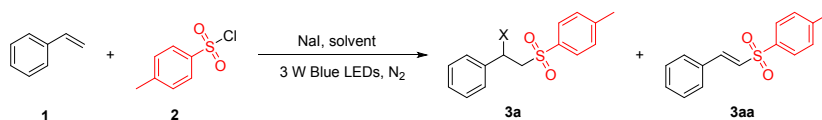


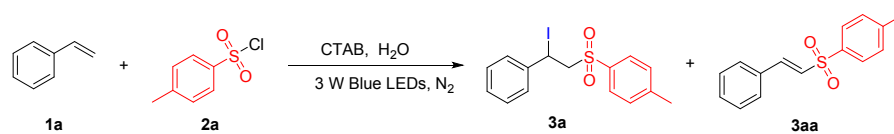
Figure S1. Synthesis of small batch equipment

3. Table S1 Reaction in organic solvent free of catalyst.^{a,b}



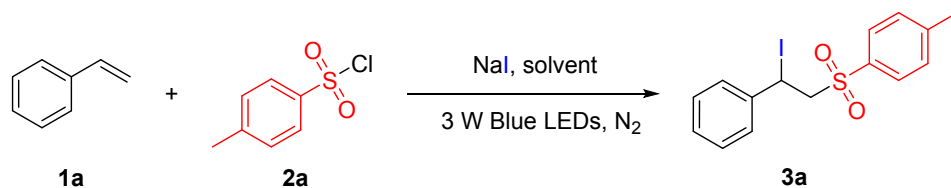
Entry	Solvent	Iodine source	Yield (%)		
			3a	3aa	Mixture 3a+3aa
1	CH ₃ CN	NaI	22	18	40
2	DMF	NaI	-	-	No reaction
3	DMSO	NaI	-	-	No reaction
4	MeOH	NaI	-	-	Trace
5	EtOH	NaI	-	-	Trace
6	THF	NaI	-	-	Trace
7	1,4-dioxane	NaI	-	-	No reaction
8	H ₂ O	NaI	-	-	Trace
9	CH ₃ CN	-	-	-	No reaction
10	CH ₃ CN	I ₂	-	-	No reaction
11	CH ₃ CN	KI	21	7	28
12	CH ₃ CN	CuI	16	10	26
13	CH ₃ CN	TBAI	40	35	75

^aReaction conditions: 0.2 mmol **1a**, 0.2 mmol **2a** (1 eq), iodine compound (2 eq), 4 mL Solvent, 15 h, rt, N₂, 3 W Blue LEDs; ^b¹H NMR yield.

Table S2. Optimization of the reaction conditions in water.^{a,b}

Entry	Iodine source (eq)	Acid/base	Yield(%)	
			3a	3aa
1	-	—	0	0
2	I ₂ (1 eq)	—	0	0
3	NaI (1 eq)	—	78	ND
4	KI (1 eq)	—	69	ND
5	NH ₄ I (1 eq)	—	45	ND
6	TBAI (1 eq)	—	65	ND
7	CuI (1 eq)	—	52	ND
8	NaF	—	0	0
9	NaCl	—	0	0
10	NaBr	—	0	0
11	NaI (0.2 eq)	—	15	ND
12	NaI (0.5 eq)	—	38	ND
13	NaI (2 eq)	—	65	ND
14	NaI (3 eq)	—	60	ND
15 ^c	NaI (1 eq)	—	0	ND
16 ^d	NaI (1 eq)	—	0	ND
17 ^e	NaI (1 eq)	—	0	15
18	NaI (1 eq)	HOAc (1eq)	80	ND
19	NaI (1 eq)	Na ₂ CO ₃ (1 eq)	47	9
20	NaI (1 eq)	NaOH (1 eq)	37	25
21	NaI (1 eq)	Et ₃ N (1 eq)	54	11
22	NaI (1 eq)	HCOOH (1 eq)	75	ND
23	NaI (1 eq)	HOAc (2 eq)	85	ND
24	NaI (1 eq)	HOAc (3 eq)	92	ND
25	NaI (1 eq)	HOAc (4 eq)	80	ND
26	NaI (1 eq)	HOAc (5 eq)	72	ND

^aReaction conditions: 0.2 mmol **1a**, 0.2 mmol **2a** (1 eq), 4 mL H₂O, 15 h, rt, N₂, CTAB (0.1eq), 3 W Blue LEDs; ^b¹H NMR yield; ^cair; ^d without light; ^e without CTAB; ND=Not detected.

Table S3. Optimization of surfactants in water.

Entry	Surfactant	Amount (eq)	Yield (%)
1	CTAB	0.04	45
2	CTAB	0.08	68
3	CTAB	0.10	78
4	CTAB	0.15	69
5	CTAB	0.2	45
6	CTAB	0.4	65
7	CTAB	0.8	58
8	CTAB	1.0	54
9	SDS	0.1	20
10	SDBS	0.1	26
11	Triton X-100	0.1	63
12	Brij L23	0.1	62
13	Tween 80	0.1	66
14	Cetylpyridine bromide	0.1	70
15	SDS	0.1	20

^a Reaction conditions: 0.2 mmol **1a**, 0.2 mmol **2a** (1 eq), 4 mL H₂O, 15 h, rt, N₂, surfactant, 3 W Blue LEDs; ^b ¹H NMR yield.

4. Gram scale synthesis

(1) General procedure for the gram scale synthesis

A 100 mL Schlenk tube equipped with a magnetic stirring bar was charged with alkenes (19.2 mmol), sulfonyl chlorides (19.2 mmol), NaI (19.2 mmol), HOAc (57.6 mmol), H₂O (80 mL) and CTAB (1.9 mmol). The mixture was then stirred at room temperature under nitrogen atmosphere and irradiated with a 3 W blue LEDs light. After completion of the reaction, the colored organic phase was separated with separatory funnel and the water phase extracted with ethyl acetate (30 mL). The combined organic phases were dried over anhydrous Na₂SO₄, and then concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel

column chromatography (PE: EA= 1:20) to afford the product.

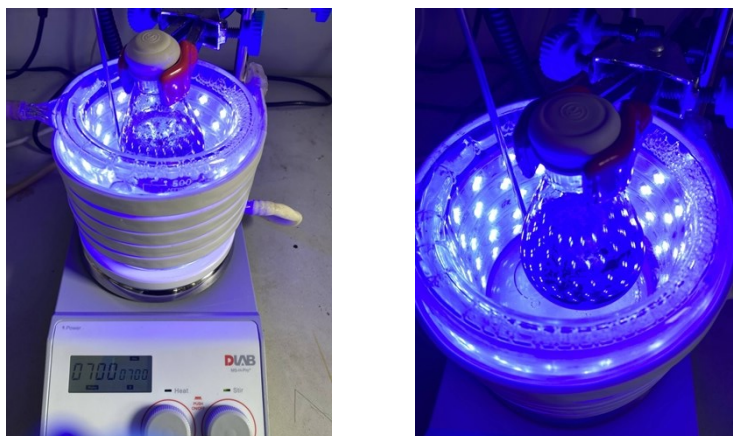
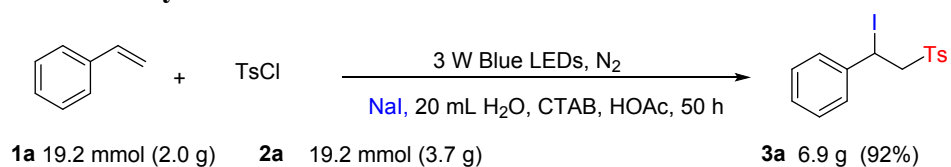


Figure S2 Gram scale synthesis of photochemical set up (cooled by water)

(2) Gram scale synthesis of **3a**



(a) Substrates

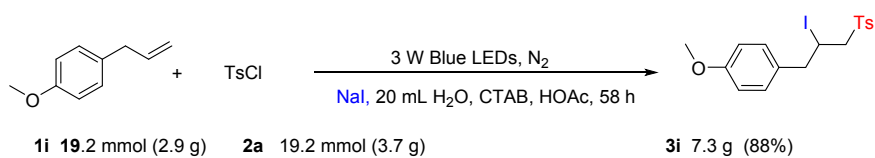
(b) Reaction for 5 min

(c) Reaction for 6 h

(d) Reaction for 50 h

Figure S3. Gram scale synthesis of **3a**

(3) Gram scale synthesis of **3i**



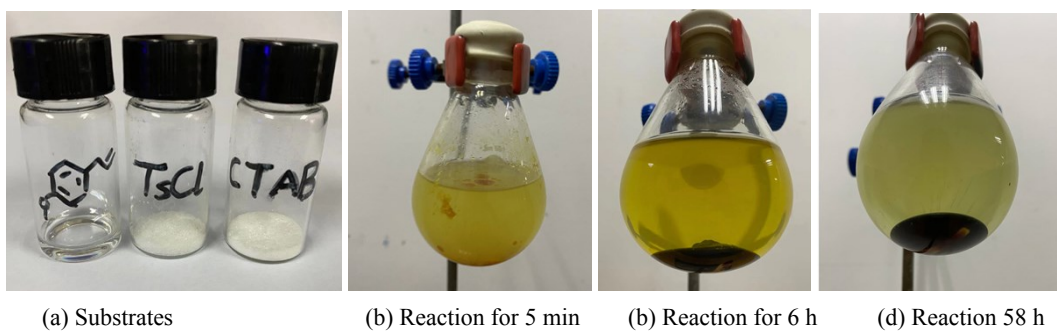


Figure S4. Gram scale synthesis of **3i**

5. Proposed mechanism

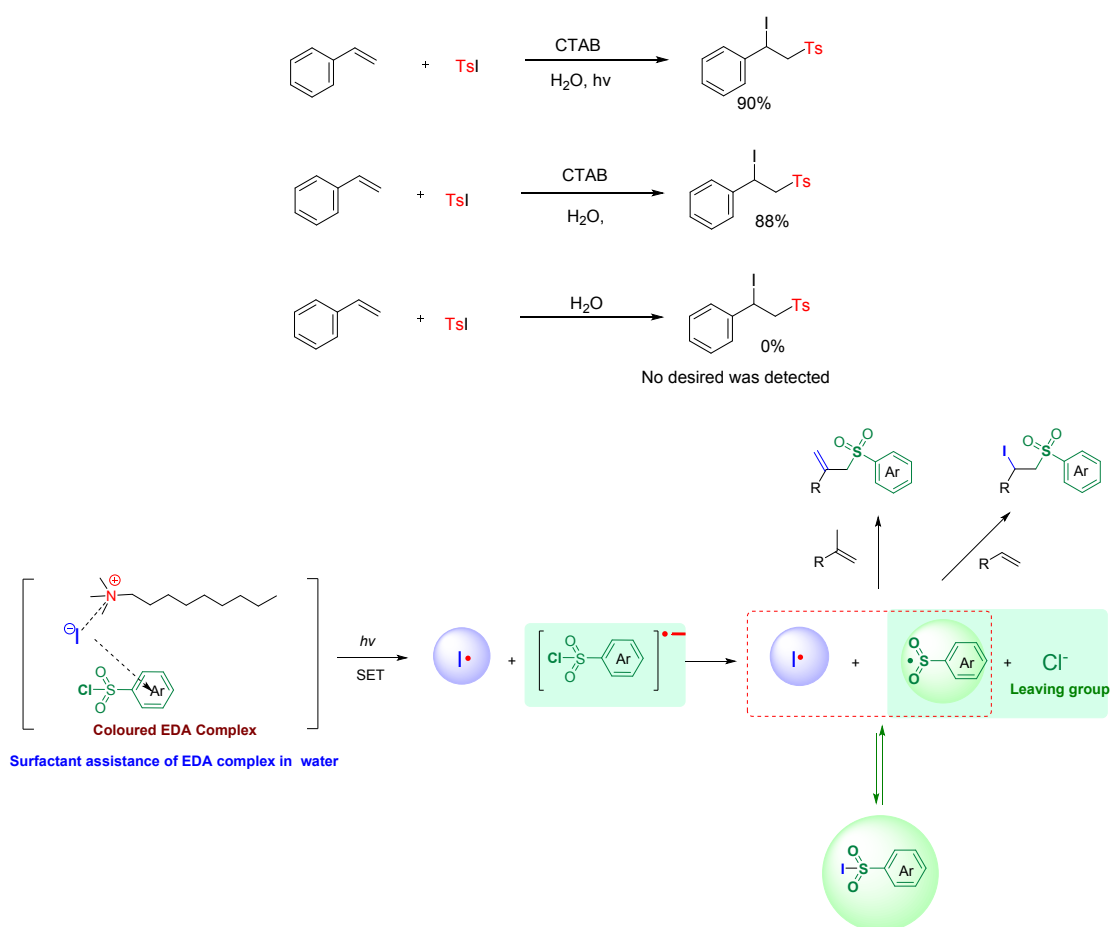


Figure S5. Proposed mechanism

6. UV-vis absorbance experiment.

All the UV-vis absorption spectra were recorded in 1 cm path quartz cuvettes using Agilent 8543 UV/Vis spectrophotometer.

A UV-vis absorbance experiment has been carried out for confirming the formation of EDA complex as illustrated in **Figure 1**. Condition: (a) Measured with water as a solvent. NaI (0.4

mmol), TsCl (0.4 mmol), styrene (0.4 mmol), CTAB (0.04 mmol), H₂O (4 mL). After weighing all the samples, ultrasound was carried out, and finally the supernatant was taken for testing. (b) Measured with acetonitrile as a solvent. NaI (0.4 mmol), TsCl (0.4 mmol), styrene (0.4 mmol), CH₃CN (4 mL).

UV/vis absorption spectrometry between TsI and [TsCl + NaI]

Measured with acetonitrile as a solvent. NaI (0.4 mmol), TsCl (0.4 mmol), TsI (0.4 mmol), styrene (0.4 mmol), CH₃CN (4 mL).

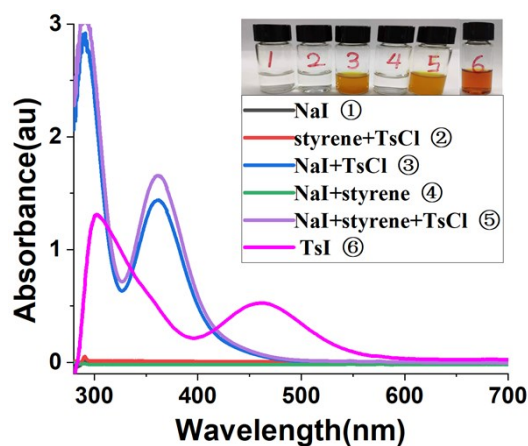


Figure S6 UV/vis absorption spectrometry between TsI and [TsCl + NaI]

7. Stoichiometry of the EDA Complex in Solution (Job's plot).

The Job's plot was constructed to evaluate the stoichiometry of the EDA complex between TsCl and TBAI. We measured the absorption of CH₃CN solutions at 420 nm with different donor/acceptor ratios with constant concentration (0.25 M) of the two components. All the absorption spectra were recorded in 1 cm path quartz cuvettes using Agilent 8543 UV/Vis spectrophotometer. The absorbance values were plotted against the molar fraction (%) of TBAI. The maximal absorbance at 50% molar fraction of TBAI indicated the 1:1 stoichiometry of the EDA complex in solution.

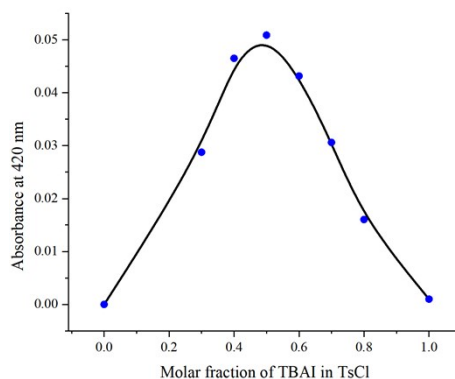


Figure S7. Job's plot of the EDA complex between TsCl and TBAI (in CH₃CN). [TsCl] + [TBAI] = 0.25 M.

8. Stern-Volmer Quenching Studies with NaI.

The samples were prepared mixing the TsCl with the required amount of NaI in a total volume of 1 mL of CH₃CN in a 10 × 10 mm light path quartz fluorescence cuvette. The excitation wavelength was fixed at 265 nm, the emission light was acquired from 320 nm to 600 nm.

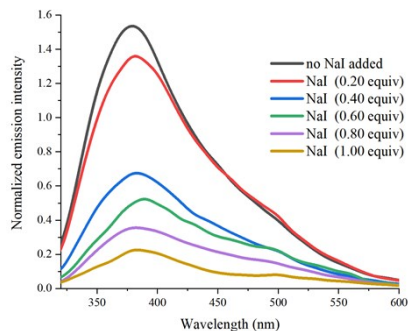


Figure S 8 Quenching of the TsCl emission in the presence of increasing amounts of NaI. The Stern-Volmer plot shows a linear correlation between the amounts of NaI and the ratio I_0/I .

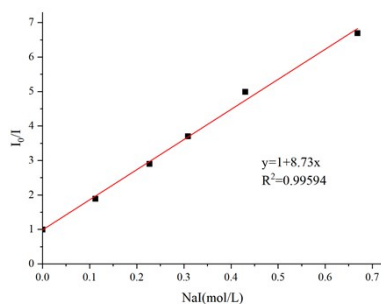
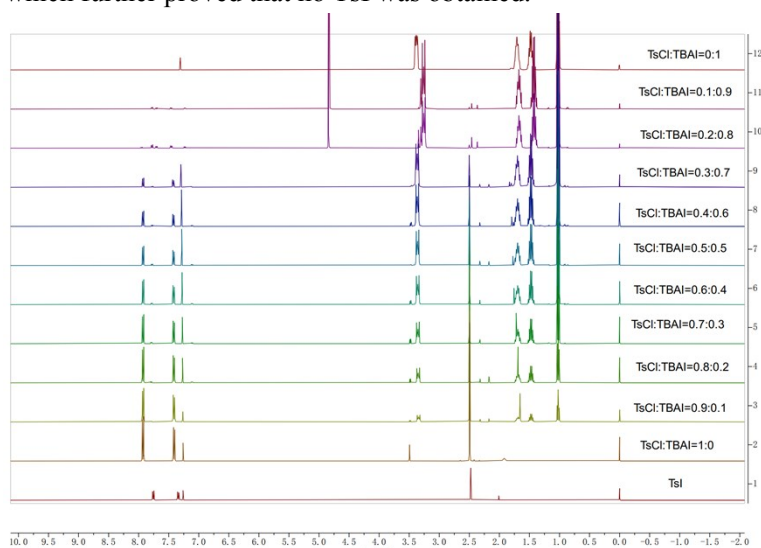


Figure S9. Stern-Volmer quenching plot.

9. NMR experiment.

Solutions containing equal molar concentrations of the TsCl (0.08 M in CDCl₃) and the TBAI (0.08 M in CDCl₃) were prepared and mixed to cover acceptor/donor ratio from 1:0, 0.9:0.1, 0.8:0.2 to 0:10. At the same time, we also added the nuclear magnetic resonance spectrum of TsI for comparison, which further proved that no TsI was obtained.



(a)

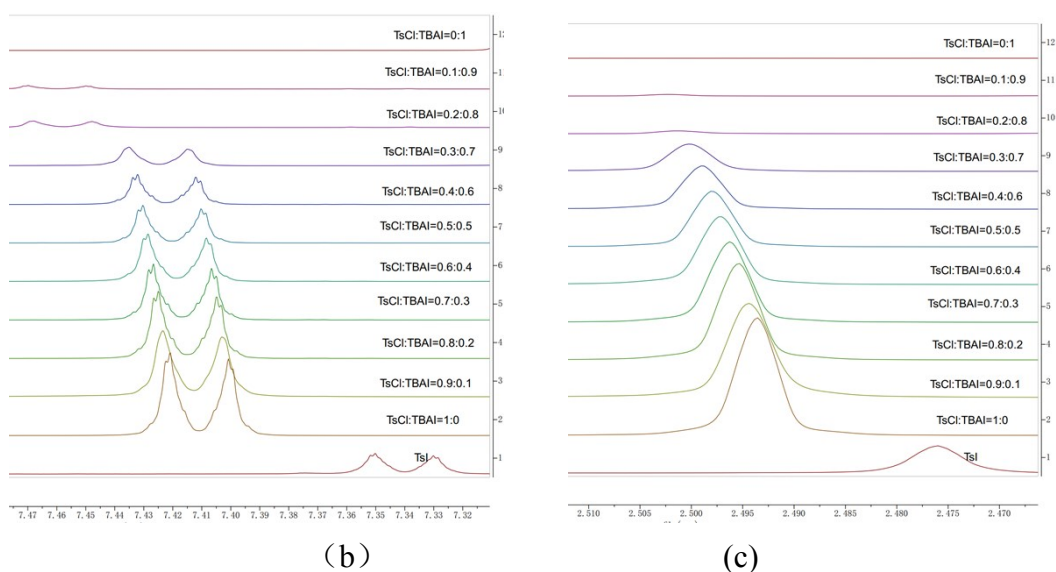
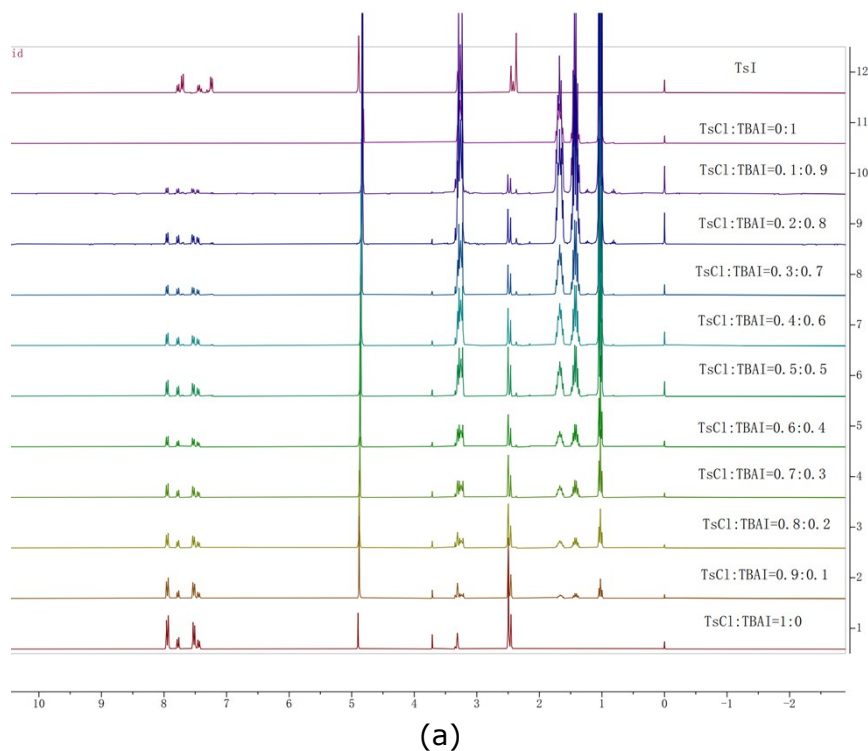
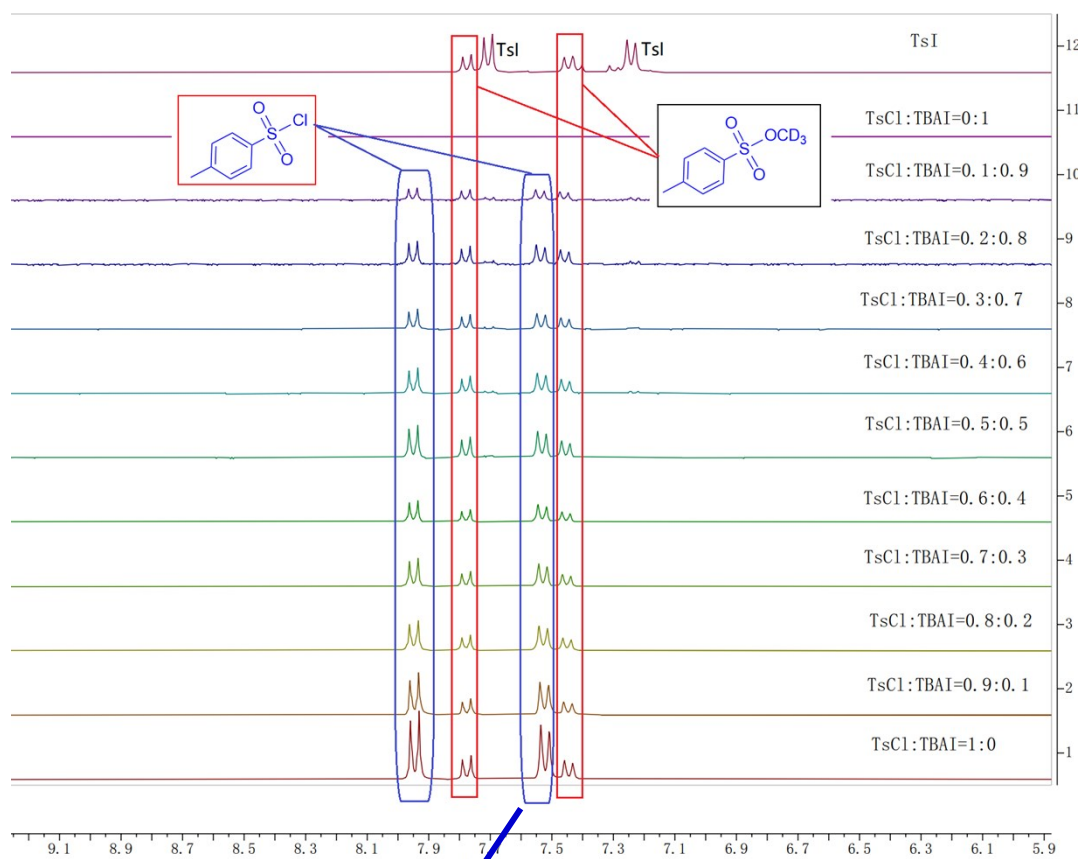


Figure S10. NMR study of mixture TsCl and I in $CDCl_3$

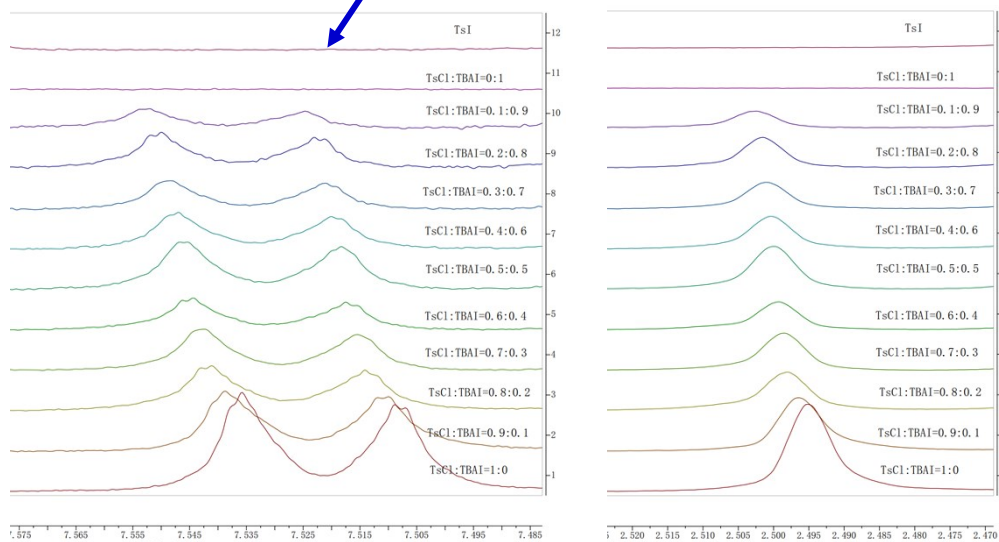
Solutions containing equal molar concentrations of the TsCl (0.08 M in CD_3OD) and the TBAI (0.08 M in CD_3OD) were prepared and mixed to cover acceptor/donor ratio from 1:0, 0.9:0.1, 0.8:0.2 to 0:10. At the same time, we also added the nuclear magnetic resonance spectrum of TsI for comparison, which further proved that no TsI was obtained.

Considering that TsCl and TsI can react quickly with CD_3OD , we mixed TsCl and TBAI in CD_3OD solvent and did NMR test immediately. Despite this, there were still many methyl sulfonate obtained from TsCl and CD_3OD , as shown in **Figure S11** (a,b). To our delight, as **Figure S11**(c,d) showed that there is an obvious chemical shift of unreacted TsCl.





(b)



(c)

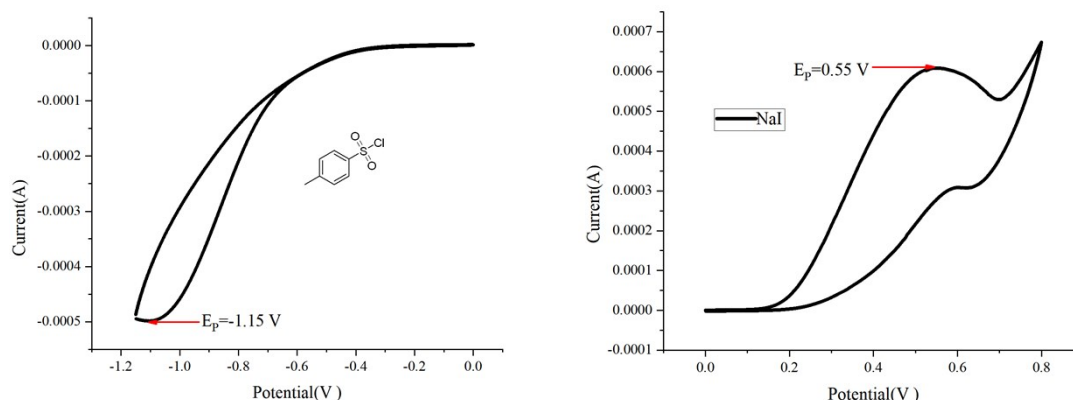
(d)

Figure S11. NMR study of mixture TsCl and I in CD₃OD

10. Experimental for cyclic voltammetry.

(a). Cyclic voltammetry was measured with CHI660E electrochemical workstation. Samples were prepared with 0.48 mmol of TsCl in 20 mL of 0.1 M tetra-*n*-butylammonium hexafluorophosphate in acetonitrile. At 0.1V/s scanning rate, the reduction potential was measured with glassy carbon working electrode, platinum wire counter electrode, and a KCl saturated Ag/AgCl reference electrode. A completely irreversible reduction wave was observed with $E_p = -1.15$ V.

(b). Cyclic voltammetry was measured with CHI660E electrochemical workstation. Samples were prepared with 0.96 mmol of NaI in 20 mL of 0.1 M tetra-*n*-butylammonium hexafluorophosphate in acetonitrile. At 0.1V/s scanning rate, the oxidation potential was measured with glassy carbon working electrode, platinum wire counter electrode, and a KCl saturated Ag/AgCl reference electrode. A completely irreversible oxidation wave was observed with $E_p = 0.55$ V.

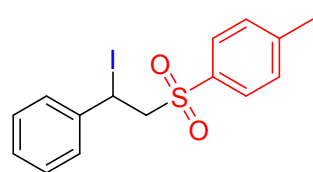


(a) The cyclic voltammogram of the TsCl.

(b) The cyclic voltammogram of the NaI.

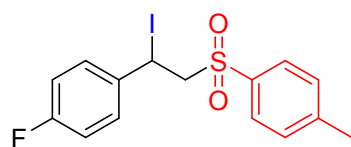
Figure S12. Electrochemical Measurements

11. Characterization Data of Products.



1-((2-iodo-2-phenylethyl)sulfonyl)-4-methylbenzene (3a)

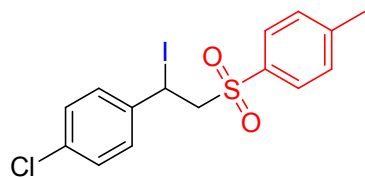
.White solid (90% yield) ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 8.3$ Hz, 2H), 7.22 (dd, $J = 7.8, 1.6$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 5H), 5.55 (dd, $J = 11.2, 4.3$ Hz, 1H), 4.28 (dd, $J = 14.6, 11.2$ Hz, 1H), 4.03 (d, $J = 4.3$ Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 144.80, 140.71, 136.21, 129.81, 128.86, 128.60, 128.14, 127.28, 66.06, 21.71, 18.27 ppm. ESI HRMS: calcd. for $\text{C}_{15}\text{H}_{15}\text{IO}_2\text{S}$ [$\text{M}+\text{Na}$] 408.9730, found 408.9726.



1-fluoro-4-(1-iodo-2-tosylethyl)benzene (3b)

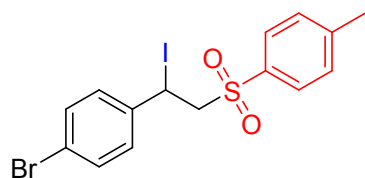
.White solid (76% yield) ^1H NMR (600 MHz, CDCl_3) δ 7.42 (d, $J = 10.0$ Hz, 2H), 7.20 (dd, $J = 8.7, 5.2$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 6.83 – 6.76 (m, 2H), 5.54 (dd, $J = 11.6,$

4.0 Hz, 1H), 4.25 (dd, $J = 14.9, 11.6$ Hz, 1H), 4.04 (dd, $J = 14.5, 4.1$ Hz, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 163.21, 161.56, 145.03, 136.56, 136.16, 129.84, 129.15, 129.09, 128.07, 115.87, 115.73, 66.20, 21.69, 17.16 ppm. ESI HRMS: calcd. for $\text{C}_{15}\text{H}_{14}\text{FIO}_2\text{S}$ [$\text{M}+\text{Na}$] 426.9635, found 426.9631.



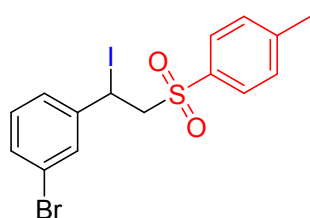
1-chloro-4-(1-iodo-2-tosylethyl)benzene (3c). White solid (72% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 8.2$ Hz, 3H), 7.14 (dd, $J = 8.2, 5.7$ Hz, 4H), 7.06 (d, $J = 8.6$ Hz, 2H), 5.50 (dd, $J = 11.7, 4.0$ Hz, 1H), 4.25 (dd, $J = 14.6, 11.7$ Hz, 1H), 4.02 (dd, $J = 14.6, 4.0$

Hz, 1H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 145.13, 139.10, 136.09, 134.43, 129.86, 128.96, 128.60, 128.07, 65.99, 21.72, 16.85 ppm. ESI HRMS: calcd. for $\text{C}_{15}\text{H}_{14}\text{ClIO}_2\text{S}$ [$\text{M}+\text{Na}$] 442.9340, found 442.9340.



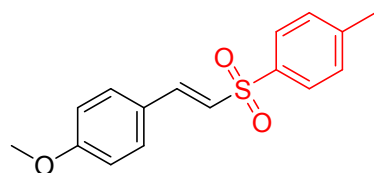
1-bromo-4-(1-iodo-2-tosylethyl)benzene (3d). White solid (58% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 6.7$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.5$ Hz, 2H), 5.48 (dd, $J = 11.7, 4.0$ Hz, 1H), 4.24 (dd, $J = 14.6, 11.8$ Hz, 1H),

4.02 (dd, $J = 14.6, 4.0$ Hz, 1H), 2.41 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 16.89, 21.69, 65.77, 76.94, 77.15, 77.36, 122.48, 127.97, 128.81, 129.80, 131.82, 135.96, 139.49, 145.06$ ppm. ESI HRMS: calcd. for $\text{C}_{15}\text{H}_{14}\text{BrIO}_2\text{S}$ [$\text{M}+\text{Na}$] 486.8835, found 486.8831.



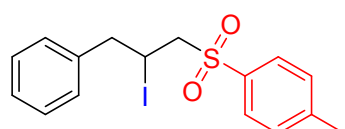
1-bromo-3-(1-iodo-2-tosylethyl)benzene (3e). White solid (70% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.39 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.2$ Hz, 1H), 7.19 – 7.16 (m, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 7.00 (t, $J = 8.0$ Hz, 1H), 5.46 (dd, $J = 11.7, 3.9$ Hz, 1H), 4.25 (dd, $J = 14.7, 11.7$ Hz, 1H), 4.03 (dd, $J = 14.7, 4.0$ Hz, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (150

MHz, CDCl_3) δ 145.14, 142.52, 135.84, 131.59, 130.30, 130.20, 129.86, 127.96, 126.10, 122.71, 65.61, 21.77, 16.29 ppm. ESI HRMS: calcd. for $\text{C}_{15}\text{H}_{14}\text{BrIO}_2\text{S}$ [$\text{M}+\text{Na}$] 486.8835, found 486.8830.



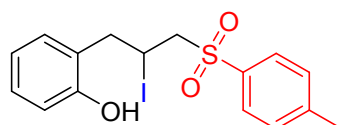
(E)-1-methoxy-4-(2-tosylvinyl)benzene (3f). White solid (66% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.3$ Hz, 2H), 7.60 (d, $J = 15.4$ Hz, 1H), 7.42 (d, $J = 8.8$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 6.69 (d, $J = 15.4$ Hz, 1H), 3.83 (s, 3H),

2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 162.13, 144.27, 141.89, 138.35, 130.45, 130.04, 127.72, 125.24, 124.98, 114.64, 55.58, 21.72 ppm. ESI HRMS: calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{S}$ [$\text{M}+\text{Na}$] 311.0712, found 311.0714.

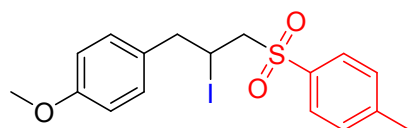


1-((2-iodo-3-phenylpropyl)sulfonyl)-4-methylbenzene

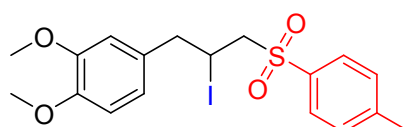
(3g) .White solid (90% yield) .¹H NMR (600 MHz, CDCl₃) δ 7.84 – 7.78 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.31 (dt, *J* = 13.3, 6.8 Hz, 3H), 7.21 (d, *J* = 6.9 Hz, 2H), 4.55 (tt, *J* = 9.1, 4.7 Hz, 1H), 3.83 – 3.73 (m, 2H), 3.55 (dd, *J* = 14.7, 4.5 Hz, 1H), 3.14 (dd, *J* = 14.7, 9.2 Hz, 1H), 2.47 (s, 3H) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 145.48, 138.46, 136.39, 130.33, 129.30, 128.64, 128.19, 127.36, 65.09, 45.60, 21.84, 21.74 ppm. ESI HRMS: calcd. for C₁₆H₁₇IO₂S [M+Na] 422.9886, found 422.9882.



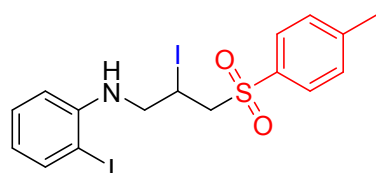
2-(2-iodo-3-tosylpropyl)phenol (3h) .White solid (86% yield) .¹H NMR (400 MHz, DMSO-*d*₆) δ 9.59 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.78 – 6.65 (m, 2H), 4.53 (dq, *J* = 12.2, 6.3 Hz, 1H), 4.03 (dd, *J* = 15.2, 6.3 Hz, 1H), 3.93 (dd, *J* = 15.2, 6.7 Hz, 1H), 3.29 (d, *J* = 5.7 Hz, 1H), 3.03 – 2.92 (m, 1H), 2.40 (s, 3H) ppm; ¹³C NMR (100 MHz, DMSO) δ 155.74, 145.24, 136.44, 131.39, 130.42, 128.66, 128.39, 125.80, 119.25, 115.47, 64.03, 41.56, 40.45, 40.24, 40.03, 39.83, 39.62, 39.41, 39.20, 21.61, 21.28 ppm. ESI HRMS: calcd. for C₁₆H₁₇IO₃S [M+Na] 438.9835, found 438.9831.



1-((2-iodo-3-(4-methoxyphenyl)propyl)sulfonyl)-4-methylbenzene (3j) .White solid (88% yield) .¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.51 (tt, *J* = 8.8, 5.0 Hz, 1H), 3.83 – 3.73 (m, 5H), 3.44 (dd, *J* = 14.8, 4.6 Hz, 1H), 3.10 (dd, *J* = 14.8, 8.9 Hz, 1H), 2.46 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 158.84, 145.45, 136.36, 130.45, 130.39, 130.30, 128.18, 113.95, 64.84, 55.35, 44.70, 22.63, 21.83 ppm. ESI HRMS: calcd. for C₁₇H₁₉IO₃S [M+Na] 452.9992, found 452.9990.

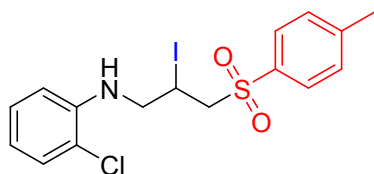


4-(2-iodo-3-tosylpropyl)-1,2-dimethoxybenzene (3j) .White solid (92% yield) .¹H NMR (600 MHz, CDCl₃) δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 2H), 6.88 – 6.59 (m, 3H), 4.52 (s, 1H), 3.87 (s, 6H), 3.71 (s, 2H), 3.41 (s, 1H), 3.10 (s, 1H), 2.45 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 148.92, 148.29, 145.35, 136.44, 130.80, 130.27, 128.19, 121.63, 112.52, 111.17, 64.75, 55.96, 45.20, 22.02, 21.80 ppm. ESI HRMS: calcd. for C₁₈H₂₁IO₄S [M+Na] 483.0097, found 483.0088.

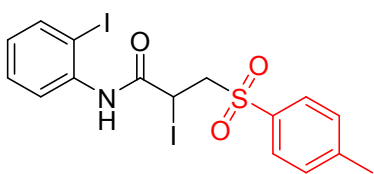


2-iodo-N-(2-iodo-3-tosylpropyl)aniline (3k) .White solid (85% yield) .¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.67 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.65 (d, *J* = 9.3 Hz, 1H), 6.50 (t, *J* = 6.9 Hz, 1H), 4.74 – 4.53 (m, 2H), 3.94 – 3.72 (m, 3H), 3.59 (dt, *J* = 14.5, 6.8 Hz, 1H), 2.43 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 145.82, 145.59, 139.41, 135.99, 130.35, 129.68, 128.05, 119.92, 111.43, 86.21, 63.08, 51.03, 21.83, 20.21 ppm. ESI HRMS: calcd. for

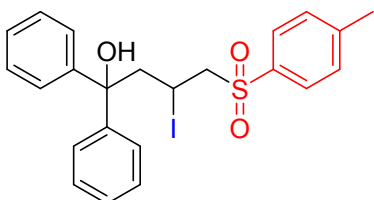
C₁₆H₁₇I₂NO₂S [M+Na] 563.8962, found 563.8958.



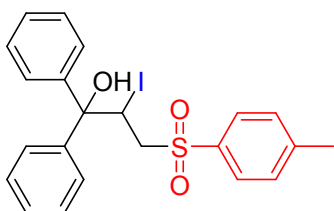
2-chloro-N-(2-iodo-3-tosylpropyl)aniline (3l). White solid (82% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.20 – 7.10 (m, 1H), 6.76 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.68 (td, *J* = 7.6, 1.4 Hz, 1H), 4.81 (t, *J* = 6.7 Hz, 1H), 4.71 – 4.60 (m, 1H), 3.91 – 3.72 (m, 3H), 3.67 – 3.54 (m, 1H), 2.43 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 145.60, 142.61, 136.06, 131.63, 130.52, 130.35, 129.54, 128.07, 119.94, 118.52, 111.97, 63.19, 50.66, 21.82, 20.43 ppm. ESI HRMS: calcd. for C₁₆H₁₅ClINO₃S [M+Na] 471.9611, found 471.9598.



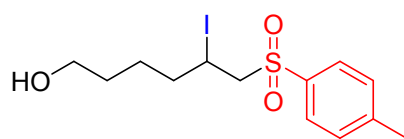
2-iodo-N-(2-iodophenyl)-3-tosylpropanamide (3m). White solid (70% yield). ¹H NMR (600 MHz) δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 11.6 Hz, 3H), 7.57 (s, 1H), 7.27 (d, *J* = 8.2 Hz, 3H), 6.87 (t, *J* = 7.5 Hz, 1H), 4.91 (dd, *J* = 10.8, 2.8 Hz, 1H), 4.43 (dd, *J* = 14.2, 10.7 Hz, 1H), 3.66 (dd, *J* = 14.3, 2.7 Hz, 1H), 2.34 (s, 3H) ppm; ¹³C NMR (150 MHz) δ 166.27, 145.66, 139.05, 137.18, 135.52, 130.20, 129.26, 128.49, 126.85, 122.49, 90.37, 61.78, 21.76, 9.89 ppm. ESI HRMS: calcd. for C₁₆H₁₅I₂NO₃S [M+Na] 577.8754, found 577.8748.



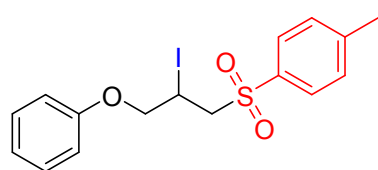
3-iodo-1,1-diphenyl-4-tosylbutan-1-ol (3n). White solid (72% yield). ¹H NMR (400 MHz) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.28 (m, 12H), 4.24 (p, *J* = 6.1 Hz, 1H), 3.97 (dd, *J* = 15.0, 7.2 Hz, 1H), 3.76 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.43 (dd, *J* = 15.3, 6.5 Hz, 1H), 3.16 (dd, *J* = 15.3, 5.9 Hz, 1H), 2.93 (s, 1H), 2.45 (s, 3H) ppm; ¹³C NMR (100 MHz) δ 146.31, 145.27, 144.87, 136.00, 130.15, 128.59, 128.56, 128.32, 127.55, 127.42, 126.11, 126.03, 79.03, 66.12, 51.47, 21.84, 11.68 ppm. ESI HRMS: calcd. for C₂₃H₂₃IO₃S [M+Na] 529.0305, found 529.0300.



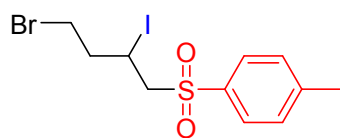
2-iodo-1,1-diphenyl-3-tosylpropan-1-ol (3o). White solid (68% yield). ¹H NMR (400 MHz) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.45 (t, *J* = 8.3 Hz, 4H), 7.32 (dt, *J* = 7.9, 3.6 Hz, 4H), 7.26 – 7.15 (m, 4H), 5.40 (d, *J* = 9.5 Hz, 1H), 3.79 (dd, *J* = 16.1, 9.6 Hz, 1H), 3.59 (d, *J* = 16.1 Hz, 1H), 2.85 (s, 1H), 2.45 (s, 3H) ppm; ¹³C NMR (100 MHz) δ 146.60, 145.18, 139.23, 136.43, 130.08, 129.04, 128.67, 128.46, 127.71, 127.68, 125.54, 125.03, 80.87, 62.00, 33.88, 21.84 ppm. ESI HRMS: calcd. for C₂₂H₂₁IO₃S [M+Na] 515.0148, found 515.0144.



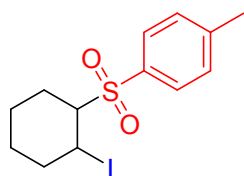
5-iodo-6-tosylhexan-1-ol (3p). White solid (85% yield). ^1H NMR (400 MHz) δ 7.78 (dd, $J = 8.3, 1.9$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 4.57 – 4.37 (m, 1H), 3.83 – 3.65 (m, 2H), 3.58 (s, 1H), 3.37 (dt, $J = 9.4, 4.7$ Hz, 1H), 3.28 – 3.19 (m, 1H), 2.46 (s, 3H), 2.39 – 1.49 (m, 6H) ppm; ^{13}C NMR (100 MHz) δ 145.55, 136.25, 130.34, 128.14, 70.48, 69.82, 65.63, 36.21, 36.08, 35.55, 35.17, 21.85, 21.43, 21.07, 15.91, 15.71 ppm. ESI HRMS: calcd. for $\text{C}_{13}\text{H}_{19}\text{IO}_3\text{S}$ $[\text{M}+\text{Na}]$ 404.9992, found 404.9990.



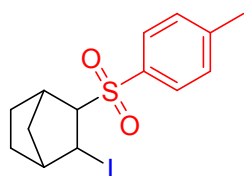
1-((2-iodo-3-phenoxypropyl)sulfonyl)-4-methylbenzene (3q). White solid (90% yield). ^1H NMR (400 MHz) δ 7.78 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.6$ Hz, 1H), 7.25 (s, 1H), 6.98 (t, $J = 7.4$ Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 2H), 4.66 (dq, $J = 9.9, 5.0$ Hz, 1H), 4.27 (t, $J = 5.0$ Hz, 2H), 4.04 (dd, $J = 14.7, 8.9$ Hz, 1H), 3.71 (dd, $J = 14.7, 5.1$ Hz, 1H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 157.73, 145.50, 136.10, 130.26, 129.66, 128.14, 121.82, 115.02, 71.41, 61.98, 21.82, 14.96. ESI HRMS: calcd. for $\text{C}_{16}\text{H}_{17}\text{IO}_3\text{S}$ $[\text{M}+\text{Na}]$ 438.9835, found 438.9830.



1-((4-bromo-2-iodobutyl)sulfonyl)-4-methylbenzene (3r). White solid (70% yield). ^1H NMR (600 MHz) δ 7.80 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 4.50 (t, $J = 10.8$ Hz, 1H), 3.85 (dd, $J = 14.4, 3.5$ Hz, 1H), 3.75 (dd, $J = 14.4, 10.5$ Hz, 1H), 3.61 (ddd, $J = 9.9, 6.0, 3.7$ Hz, 1H), 3.43 (td, $J = 10.1, 5.4$ Hz, 1H), 2.68 – 2.60 (m, 1H), 2.47 (s, 3H), 2.29 (ddd, $J = 15.7, 11.0, 5.2$ Hz, 1H) ppm; ^{13}C NMR (150 MHz) δ 145.69, 135.77, 130.39, 128.35, 65.70, 41.06, 33.19, 21.87, 19.71 ppm. ESI HRMS: calcd. for $\text{C}_{11}\text{H}_{14}\text{BrIO}_2\text{S}$ $[\text{M}+\text{Na}]$ 438.8835, found 438.8830.

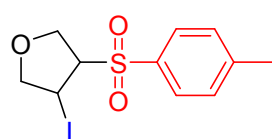


1-((2-iodocyclohexyl)sulfonyl)-4-methylbenzene (3s). White solid (65% yield). ^1H NMR (400 MHz) δ 7.75 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 7.9$ Hz, 2H), 5.09 (s, 1H), 3.33 (s, 1H), 2.45 (s, 3H), 2.21 (tdd, $J = 19.6, 9.7, 4.6$ Hz, 2H), 1.96 (ddt, $J = 21.9, 13.4, 4.0$ Hz, 3H), 1.67 (dddd, $J = 18.0, 13.8, 10.0, 3.7$ Hz, 2H), 1.52 (dp, $J = 12.7, 4.2, 3.6$ Hz, 1H) ppm; ^{13}C NMR (100 MHz) δ 145.17, 135.15, 130.14, 128.63, 67.62, 33.61, 25.54, 22.58, 21.82, 21.80, 21.10 ppm. ESI HRMS: calcd. for $\text{C}_{13}\text{H}_{17}\text{IO}_2\text{S}$ $[\text{M}+\text{Na}]$ 386.9986, found 386.9881.

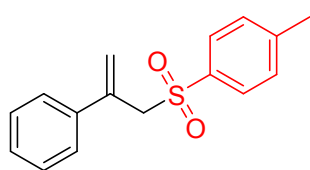


2-iodo-3-tosylbicyclo[2.2.1]heptane (3t). White solid (68% yield). ^1H NMR (600 MHz) δ 7.77 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 4.37 (s, 1H), 3.03 (d, $J = 5.7$ Hz, 1H), 2.77 (s, 1H), 2.50 (s, 1H), 2.47 (s, 3H), 2.06 (d, $J = 10.7$ Hz, 1H), 1.79 (t, $J = 9.9$ Hz, 1H), 1.65 (d, $J = 9.5$ Hz, 2H), 1.32 (d, $J = 11.8$ Hz, 1H), 1.26 (t, $J = 8.8$ Hz, 1H) ppm; ^{13}C NMR (150 MHz) δ 145.20, 135.62, 130.21, 128.92,

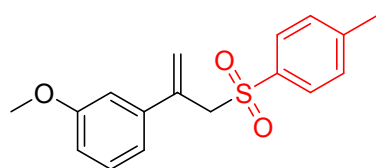
76.88, 45.46, 38.64, 34.80, 29.41, 27.66, 26.71, 21.88 ppm. ESI HRMS: calcd. for $C_{14}H_{17}IO_2S$ [M+Na] 398.9886, found 398.9882.



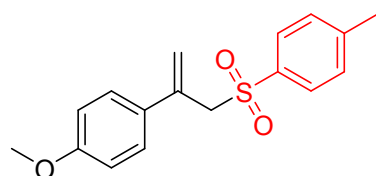
3-iodo-4-tosyltetrahydrofuran (3u). White solid (70% yield). 1H NMR (400 MHz) δ 7.80 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 4.51 – 4.43 (m, 1H), 4.36 (dd, J = 10.5, 4.3 Hz, 1H), 4.26 (dd, J = 10.1, 6.0 Hz, 1H), 4.17 (dd, J = 10.5, 8.1 Hz, 1H), 4.02 – 3.89 (m, 2H), 2.48 (s, 3H) ppm; ^{13}C NMR (100 MHz) δ 145.90, 134.94, 130.48, 128.79, 78.81, 74.14, 66.98, 21.90, 13.71 ppm. ESI HRMS: calcd. for $C_{11}H_{13}IO_3S$ [M+Na] 374.9522, found 374.9517.



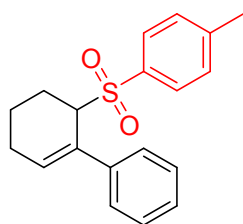
1-methyl-4-((2-phenylallyl)sulfonyl)benzene (5a). White solid (76% yield). 1H NMR (600 MHz) δ 7.65 (s, 2H), 7.25 – 7.00 (m, 7H), 5.59 (s, 1H), 5.21 (s, 1H), 4.25 (s, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (150 MHz) δ 144.52, 139.02, 136.67, 135.64, 129.64, 128.83, 128.50, 128.07, 126.38, 121.86, 62.32, 21.75 ppm. ESI HRMS: calcd. for $C_{16}H_{16}O_2S$ [M+Na] 295.0763, found 295.0758.



1-methoxy-3-(3-tosylprop-1-en-2-yl)benzene (5b). White solid (78% yield). 1H NMR (600 MHz,) δ 7.66 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.15 (t, J = 7.9 Hz, 1H), 6.85 (d, J = 7.4 Hz, 1H), 6.77 (dd, J = 9.3, 6.8 Hz, 2H), 5.58 (s, 1H), 5.22 (s, 1H), 4.23 (s, 2H), 3.77 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (151 MHz,) δ 159.60, 144.73, 140.54, 136.65, 135.56, 129.61, 129.48, 128.81, 122.05, 118.88, 113.45, 112.26, 62.38, 55.32, 21.70 ppm. ESI HRMS: calcd. for $C_{17}H_{18}O_3S$ [M+Na] 325.0869, found 325.0866.

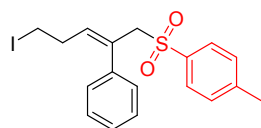


1-methoxy-4-(3-tosylprop-1-en-2-yl)benzene (5c). White solid (82% yield). 1H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.9 Hz, 4H), 6.77 (d, J = 8.9 Hz, 2H), 5.49 (s, 1H), 5.06 (s, 1H), 4.22 (s, 2H), 3.79 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (151 MHz,) δ 143.080, 131.13, 124.23, 123.87, 119.08, 118.43, 117.54, 117.47, 111.47, 106.47, 65.43, 59.72, 32.76 ppm. ESI HRMS: calcd. for $C_{17}H_{18}O_3S$ [M+Na] 325.0869, found 325.0866.

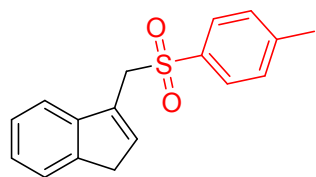


2-tosyl-2,3,4,5-tetrahydro-1,1'-biphenyl (5d). White solid (66% yield). 1H NMR (400 MHz) δ 7.41 – 7.36 (m, 2H), 7.09 – 6.95 (m, 7H), 6.23 (t, J = 3.9 Hz, 1H), 4.36 (s, 1H), 2.80 (d, J = 16.7 Hz, 1H), 2.30 (s, 5H), 2.13 (ddq, J = 13.6, 7.0, 3.5 Hz, 1H), 1.94 – 1.83 (m, 1H), 1.78 – 1.69 (m, 1H) ppm; ^{13}C NMR (100 MHz) δ 143.81, 141.13, 137.00, 135.34, 131.18, 129.23, 128.72, 128.16,

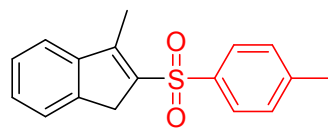
126.67, 126.45, 62.88, 25.64, 23.56, 21.59, 17.52 ppm. ESI HRMS: calcd. for $C_{19}H_{20}O_2S$ [M+Na] 335.1076, found 335.1074.



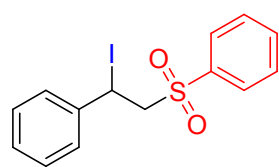
(E)-1-((4-iodo-2-phenylbut-2-en-1-yl)sulfonyl)-4-methylbenzene (5e). White solid (83% yield). 1H NMR (600 MHz) δ 7.61 (d, J = 8.2 Hz, 2H), 7.21 – 7.17 (m, 7H), 5.93 (t, J = 7.3 Hz, 1H), 4.33 (s, 2H), 3.15 (t, J = 6.9 Hz, 2H), 2.72 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (150 MHz) δ 144.81, 140.62, 136.29, 135.95, 130.24, 129.71, 128.51, 128.43, 127.53, 126.60, 58.14, 33.14, 21.69, 4.38 ppm. ESI HRMS: calcd. for $C_{18}H_{19}IO_2S$ [M+Na] 449.0043, found 449.0039.



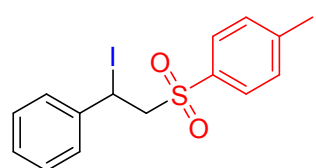
3-(tosylmethyl)-1H-indene (5f). White solid (42% yield). 1H NMR (600 MHz,) δ 7.65 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 7.2 Hz, 1H), 7.25 – 7.17 (m, 5H), 6.36 (s, 1H), 4.35 (s, 2H), 3.35 (s, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR (151 MHz,) δ 144.83, 143.50, 143.26, 137.41, 135.58, 132.11, 129.65, 128.74, 126.35, 125.28, 123.88, 119.66, 55.97, 38.51, 21.73 ppm. ESI HRMS: calcd. for $C_{17}H_{16}O_2S$ [M+Na] 307.0763, found 307.0759.



3-methyl-2-tosyl-1H-indene (5ff). White solid (45% yield). 1H NMR (600 MHz,) δ 7.85 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 6.9 Hz, 1H), 7.43 (d, J = 6.9 Hz, 1H), 7.40 – 7.28 (m, 4H), 3.68 (s, 2H), 2.58 (s, 3H), 2.41 (s, 3H) ppm; ^{13}C NMR (151 MHz,) δ 149.95, 144.12, 142.75, 139.32, 137.43, 130.00, 128.46, 127.36, 127.21, 124.17, 121.69, 39.27, 21.71, 11.69 ppm. ESI HRMS: calcd. for $C_{17}H_{16}O_2S$ [M+Na] 307.0763, found 307.0758.

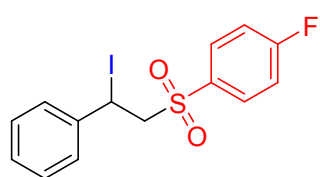


(1-iodo-2-(phenylsulfonyl)ethyl)benzene (6a). White solid (87% yield). 1H NMR (600 MHz) δ 7.54 (d, J = 8.5 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.35 – 7.29 (m, 2H), 7.21 (d, J = 8.3 Hz, 2H), 7.15 – 7.05 (m, 3H), 5.57 (dd, J = 11.3, 4.2 Hz, 1H), 4.32 (dd, J = 14.7, 11.3 Hz, 1H), 4.08 (dd, J = 14.7, 4.2 Hz, 1H) ppm; ^{13}C NMR (150 MHz) δ 140.49, 139.24, 133.69, 129.16, 128.87, 128.77, 128.05, 127.26, 66.00, 18.10 ppm. ESI HRMS: calcd. for $C_{14}H_{13}IO_2S$ [M+Na] 394.9573, found 394.9568.



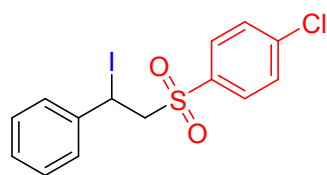
1-((2-iodo-2-phenylethyl)sulfonyl)-4-methylbenzene (6b). White solid (90% yield). 1H NMR (400 MHz) δ 7.43 (d, J = 8.3 Hz, 2H), 7.22 (dd, J = 7.8, 1.6 Hz, 2H), 7.12 (d, J = 8.4 Hz, 5H), 5.55 (dd, J = 11.2, 4.3 Hz, 1H), 4.28 (dd, J = 14.6, 11.2 Hz, 1H), 4.03 (d, J = 4.3 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz) δ 144.80, 140.71, 136.21, 129.81, 128.86, 128.60, 128.14, 127.28, 66.06, 21.71, 18.27 ppm. ESI HRMS: calcd. for $C_{15}H_{15}IO_2S$ [M+Na]

408.9730, found 408.9726.



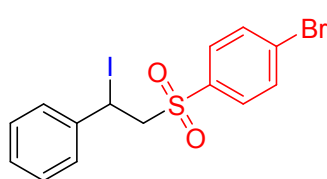
1-fluoro-4-((2-iodo-2-phenylethyl)sulfonyl)benzene (6c)

.White solid (83% yield) .¹H NMR (400 MHz) δ 7.55 – 7.46 (m, 2H), 7.23 – 7.07 (m, 5H), 6.96 (t, *J* = 8.6 Hz, 2H), 5.56 (dd, *J* = 11.4, 4.2 Hz, 1H), 4.31 (dd, *J* = 14.7, 11.4 Hz, 1H), 4.09 (dd, *J* = 14.7, 4.2 Hz, 1H) ppm; ¹³C NMR (100 MHz) δ 140.33, 131.03, 130.93, 128.95, 128.85, 127.29, 116.52, 116.30, 66.14, 17.84 ppm. ESI HRMS: calcd. for C₁₄H₁₂FIO₂S [M+Na] 412.9479, found 412.9479.



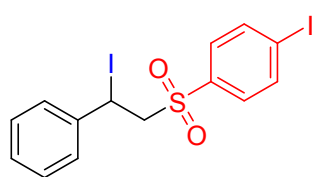
1-chloro-4-((2-iodo-2-phenylethyl)sulfonyl)benzene (6d)

.White solid (85% yield) .¹H NMR (400 MHz) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.21 – 7.14 (m, 3H), 7.14 – 7.07 (m, 2H), 5.55 (dd, *J* = 11.5, 4.2 Hz, 1H), 4.31 (dd, *J* = 14.8, 11.5 Hz, 1H), 4.08 (dd, *J* = 14.8, 4.2 Hz, 1H) ppm; ¹³C NMR (100 MHz) δ 140.50, 140.25, 137.61, 129.53, 129.39, 128.97, 128.82, 127.30, 66.10, 17.71 ppm. ESI HRMS: calcd. for C₁₄H₁₂ClIO₂S [M+Na] 428.9183, found 428.9179.



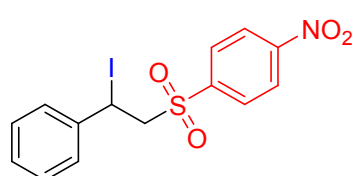
1-bromo-4-((2-iodo-2-phenylethyl)sulfonyl)benzene (6e)

.White solid (58% yield) .¹H NMR (400 MHz) δ 7.42 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.17 (t, *J* = 6.0 Hz, 3H), 7.14 – 7.07 (m, 2H), 5.54 (dd, *J* = 11.5, 4.2 Hz, 1H), 4.31 (dd, *J* = 14.7, 11.5 Hz, 1H), 4.07 (dd, *J* = 14.8, 4.2 Hz, 1H) ppm; ¹³C NMR (100 MHz) δ 140.22, 138.12, 132.79, 132.38, 129.57, 129.36, 129.11, 128.97, 128.79, 127.29, 66.07, 17.68 ppm. ESI HRMS: calcd. for C₁₄H₁₂BrIO₂S [M+Na] 472.8678, found 472.8674.



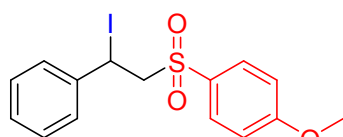
1-iodo-4-((2-iodo-2-phenylethyl)sulfonyl)benzene (6f)

.White solid (80% yield) .¹H NMR (400 MHz) δ 7.63 (d, *J* = 8.6 Hz, 2H), 7.22 – 7.14 (m, 5H), 7.13 – 7.06 (m, 2H), 5.54 (dd, *J* = 11.5, 4.1 Hz, 1H), 4.31 (dd, *J* = 14.7, 11.5 Hz, 1H), 4.07 (dd, *J* = 14.7, 4.1 Hz, 1H) ppm; ¹³C NMR (100 MHz) δ 140.19, 138.73, 138.36, 129.34, 128.99, 128.75, 127.28, 101.81, 66.02, 17.70 ppm. ESI HRMS: calcd. for C₁₄H₁₂I₂O₂S [M+Na] 520.8540, found 520.8537.

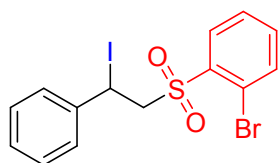


1-((2-iodo-2-phenylethyl)sulfonyl)-4-nitrobenzene (6g)

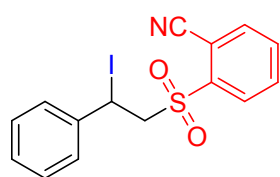
.White solid (82% yield) .¹H NMR (400 MHz) δ 8.08 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 8.9 Hz, 2H), 7.22 – 6.98 (m, 5H), 5.56 (dd, *J* = 11.6, 4.1 Hz, 1H), 4.38 (dd, *J* = 14.9, 11.6 Hz, 1H), 4.14 (dd, *J* = 14.9, 4.1 Hz, 1H) ppm; ¹³C NMR (150 MHz) δ 144.77, 139.69, 136.55, 131.95, 129.38, 129.05, 127.40, 116.74, 113.73, 66.06, 17.04 ppm. ESI HRMS: calcd. for C₁₄H₁₂INO₄S [M+Na] 439.9424, found 439.9420.



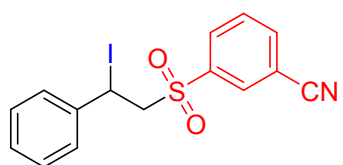
1-((2-iodo-2-phenylethyl)sulfonyl)-4-methoxybenzene (6h). White solid (85% yield). ^1H NMR (600 MHz) δ 7.45 (d, $J = 8.9$ Hz, 2H), 7.23 – 7.18 (m, 2H), 7.13 (d, $J = 7.1$ Hz, 3H), 6.76 (d, $J = 8.9$ Hz, 2H), 5.54 (dd, $J = 11.2$, 4.2 Hz, 1H), 4.26 (dd, $J = 14.7$, 11.3 Hz, 1H), 4.05 (dd, $J = 14.6$, 4.2 Hz, 1H), 3.81 (s, 3H) ppm; ^{13}C NMR (150 MHz) δ 163.75, 140.70, 130.59, 130.31, 128.89, 128.67, 127.26, 114.38, 66.11, 55.81, 18.47 ppm. ESI HRMS: calcd. for $\text{C}_{15}\text{H}_{15}\text{IO}_3\text{S}$ [$\text{M}+\text{Na}$] 424.9679, found 424.9675.



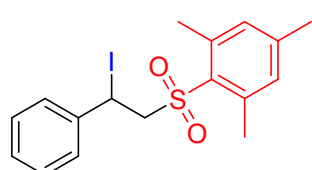
1-bromo-2-((2-iodo-2-phenylethyl)sulfonyl)benzene (6i). White solid (78% yield). ^1H NMR (600 MHz) δ 7.57 (d, $J = 8.0$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.24 (d, $J = 7.8$ Hz, 1H), 7.21 (dd, $J = 6.5$, 2.8 Hz, 2H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.04 – 6.98 (m, 3H), 5.55 (dd, $J = 11.4$, 4.2 Hz, 1H), 4.90 (dd, $J = 14.9$, 11.4 Hz, 1H), 4.19 (dd, $J = 14.9$, 4.2 Hz, 1H) ppm; ^{13}C NMR (150 MHz) δ 139.95, 138.32, 135.03, 134.55, 132.10, 128.81, 128.71, 127.86, 127.15, 120.70, 63.05, 18.11 ppm. ESI HRMS: calcd. for $\text{C}_{14}\text{H}_{12}\text{BrIO}_2\text{S}$ [$\text{M}+\text{Na}$] 472.8678, found 472.8673.



2-((2-iodo-2-phenylethyl)sulfonyl)benzonitrile (6j). White solid (42% yield). ^1H NMR (600 MHz) δ 7.69 (d, $J = 7.6$ Hz, 1H), 7.57 (d, $J = 8.1$ Hz, 1H), 7.56 – 7.51 (m, 1H), 7.44 (d, $J = 7.2$ Hz, 1H), 7.33 (d, $J = 4.2$ Hz, 1H), 7.23 – 7.19 (m, 2H), 7.02 (d, $J = 1.7$ Hz, 2H), 5.56 (dd, $J = 11.4$, 4.2 Hz, 1H), 4.74 (dd, $J = 15.2$, 11.6 Hz, 1H), 4.25 (dd, $J = 15.2$, 4.2 Hz, 1H) ppm; ^{13}C NMR (150 MHz) δ 141.60, 139.94, 134.99, 133.45, 132.98, 130.57, 128.92, 127.32, 125.81, 124.41, 115.63, 111.15, 64.66, 16.77 ppm. ESI HRMS: calcd. for $\text{C}_{15}\text{H}_{12}\text{NO}_2\text{S}$ [$\text{M}+\text{Na}$] 419.9526, found 419.9522.

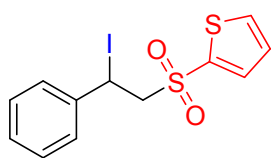


3-((2-iodo-2-phenylethyl)sulfonyl)benzonitrile (6k). White solid (85% yield). ^1H NMR (600 MHz) δ 7.77 (s, 1H), 7.69 (d, $J = 8.8$ Hz, 1H), 7.53 (s, 1H), 7.46 (d, $J = 7.9$ Hz, 1H), 7.19 – 7.16 (m, 3H), 7.12 – 7.07 (m, 2H), 5.56 (dd, $J = 11.8$, 4.0 Hz, 1H), 4.35 (dd, $J = 15.1$, 11.8 Hz, 1H), 4.13 (dd, $J = 15.1$, 4.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz) δ 144.77, 141.02, 139.69, 136.55, 131.95, 131.76, 130.03, 129.38, 129.05, 127.40, 116.74, 113.73, 66.06, 17.04 ppm. ESI HRMS: calcd. for $\text{C}_{15}\text{H}_{12}\text{INO}_2\text{S}$ [$\text{M}+\text{Na}$] 419.9526, found 419.9521.



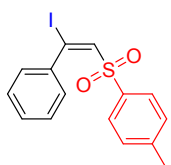
2-((2-iodo-2-phenylethyl)sulfonyl)-1,3,5-trimethylbenzene (6l). White solid (92% yield). ^1H NMR (600 MHz) δ 7.25 – 7.22 (m, 2H), 7.17 – 7.08 (m, 3H), 6.79 (s, 2H), 5.64 (dd, $J = 10.8$, 4.4 Hz, 1H), 4.37 (dd, $J = 14.5$,

10.9 Hz, 1H), 4.03 (dd, $J = 14.6, 4.3$ Hz, 1H), 2.49 (s, 6H), 2.23 (s, 3H) ppm; ^{13}C NMR (150 MHz) δ 143.68, 140.93, 139.86, 133.12, 132.37, 128.76, 128.54, 126.86, 65.63, 22.72, 21.05, 18.52 ppm. ESI HRMS: calcd. for $\text{C}_{17}\text{H}_{19}\text{IO}_2\text{S}$ [$\text{M}+\text{Na}$] 437.0043, found 437.0039.



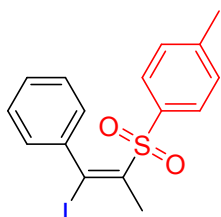
2-((2-iodo-2-phenylethyl)sulfonyl)thiophene (6m) .White solid (90% yield) . ^1H NMR (600 MHz) δ 7.60 – 7.55 (m, 1H), 7.29 (dd, $J = 6.7, 2.8$ Hz, 2H), 7.24 – 7.22 (m, 1H), 7.20 – 7.15 (m, 3H), 6.92 – 6.87 (m, 1H), 5.60 (dd, $J = 11.1, 4.2$ Hz, 1H), 4.41 (dd, $J = 14.9, 11.1$ Hz, 1H), 4.17 (dd, $J = 15.0, 4.2$ Hz, 1H)

ppm; ^{13}C NMR (150 MHz) δ 140.65, 140.12, 134.93, 134.65, 128.98, 128.84, 127.96, 127.23, 67.20, 17.94 ppm. ESI HRMS: calcd. for $\text{C}_{12}\text{H}_{11}\text{IO}_2\text{S}_2$ [$\text{M}+\text{Na}$] 400.9137, found 400.9133.



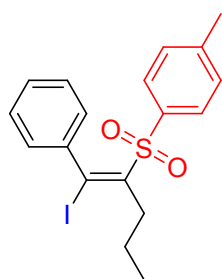
(E)-1-((2-iodo-2-phenylvinyl)sulfonyl)-4-methylbenzene (8a)

.White solid (73% yield) . ^1H NMR (600 MHz) δ 7.46 (d, $J = 8.2$ Hz, 2H), 7.36 (s, 1H), 7.29 (dt, $J = 14.5, 6.9$ Hz, 3H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (150 MHz) δ 144.70, 141.40, 139.81, 137.47, 129.92, 129.80, 128.05, 128.02, 127.84, 114.29, 21.77 ppm. ESI HRMS: calcd. for $\text{C}_{15}\text{H}_{13}\text{IO}_2\text{S}$ [$\text{M}+\text{Na}$] 406.9573, found 406.9568.



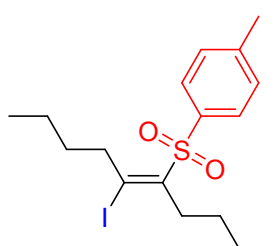
(E)-1-((1-iodo-1-phenylprop-1-en-2-yl)sulfonyl)-4-

methylbenzene (8b) .White solid (93% yield) . ^1H NMR (600 MHz) δ 7.39 (d, $J = 8.1$ Hz, 2H), 7.25 – 7.21 (m, 3H), 7.16 (d, $J = 8.1$ Hz, 2H), 7.11 (dd, $J = 6.8, 2.9$ Hz, 2H), 2.51 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (150 MHz) δ 144.29, 144.05, 143.11, 137.38, 129.63, 128.76, 127.90, 127.79, 127.69, 115.89, 27.20, 21.75 ppm. ESI HRMS: calcd. for $\text{C}_{16}\text{H}_{15}\text{IO}_2\text{S}$ [$\text{M}+\text{Na}$] 420.9730, found 420.9732.



(E)-1-((1-iodo-1-phenylpent-1-en-2-yl)sulfonyl)-4-

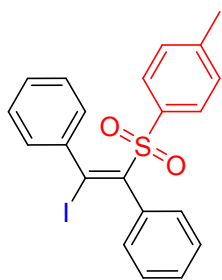
methylbenzene (8c) .White solid (89% yield) . ^1H NMR (400 MHz) δ 7.23 (d, $J = 8.3$ Hz, 2H), 7.19 – 7.10 (m, 3H), 7.06 (d, $J = 8.1$ Hz, 2H), 6.99 (dd, $J = 8.0, 1.5$ Hz, 2H), 2.96 – 2.80 (m, 2H), 2.35 (s, 3H), 1.81 (dq, $J = 15.0, 7.4$ Hz, 2H), 1.09 (t, $J = 7.3$ Hz, 3H) ppm; ^{13}C NMR (100 MHz) δ 149.11, 143.82, 142.90, 137.92, 129.35, 128.58, 127.94, 127.69, 127.65, 115.40, 41.72, 22.03, 21.68, 14.21 ppm. ESI HRMS: calcd. for $\text{C}_{18}\text{H}_{19}\text{IO}_2\text{S}$ [$\text{M}+\text{Na}$] 449.0043, found 449.0040.



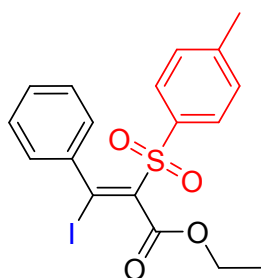
(E)-1-((6-iododec-5-en-5-yl)sulfonyl)-4-methylbenzene (8d)

.White solid (88% yield) . ^1H NMR (400 MHz) δ 7.74 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 3.18 – 3.07 (m, 2H), 2.64 – 2.53 (m, 2H), 2.44 (s, 3H), 1.57 – 1.47 (m, 2H), 1.41 (q, $J = 8.1, 7.5$ Hz, 2H), 1.37 – 1.24 (m, 4H), 0.89 (q, $J = 7.1$ Hz, 6H) ppm ; ^{13}C NMR (100 MHz) δ 144.65, 144.50, 138.78,

129.97, 127.86, 127.46, 43.56, 40.42, 32.59, 30.40, 22.80, 22.01, 21.75, 14.05, 13.79 ppm. ESI HRMS: calcd. for C₁₇H₂₅IO₂S [M+Na] 443.0512, found 443.0508.

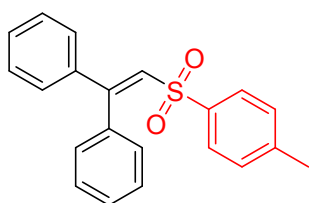


(E)-(1-iodo-2-tosylethene-1,2-diyl)dibenzene (8e). White solid (90% yield). ¹H NMR (600 MHz) δ 7.39 – 7.29 (m, 8H), 7.25 (s, 5H), 7.19 – 7.14 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H) ppm; ¹³C NMR (150 MHz) δ 149.19, 144.40, 142.64, 139.50, 136.88, 130.42, 129.34, 129.14, 128.68, 128.47, 128.00, 127.50, 118.21, 21.77 ppm. ESI HRMS: calcd. for C₂₁H₁₇IO₂S [M+Na] 482.9886, found 482.9884.



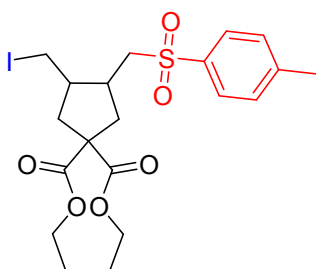
ethyl (E)-3-iodo-3-phenyl-2-tosylacrylate (8f). White solid (95% yield). ¹H NMR (600 MHz) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.27-7.29 (m, 1H), 7.24-7.22 (m, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.0 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (150 MHz) δ 163.79, 146.64, 144.99, 139.75, 137.28, 131.57, 130.51, 129.71, 129.45, 128.40, 127.93, 127.45, 114.17, 63.34, 21.76, 14.02 ppm. ESI HRMS: calcd. for C₁₈H₁₇IO₄S [M+Na] 478.9790, found

478.9984.



(2-tosylethene-1,1-diyl)dibenzene (9a). White solid (78% yield). ¹H NMR (400 MHz) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 4H), 7.20 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H) ppm; ESI HRMS: calcd. for C₂₁H₁₈O₂S [M+Na] 357.0920, found 357.0916.

Diethyl 3-(iodomethyl)-4-(tosylmethyl)cyclopentane-1,1-dicarboxylate (10a)



White solid (62% yield). White solid (90% yield). ¹H NMR (300 MHz) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 4.23 – 4.14 (m, 4H), 3.12 – 3.02 (m, 4H), 2.61 – 2.40 (m, 8H), 2.22-2.17 (m, 1H), 1.26-1.21 (t, *J* = 6.9 Hz, 6H) ppm; ¹³C NMR (75 MHz) δ 172.37, 171.95, 145.11, 136.44, 130.19, 128.24, 62.11, 61.95, 58.51, 55.48, 45.16, 39.71, 37.69, 37.25, 21.81, 14.16, 14.13, 5.28 ppm. ESI HRMS:

calcd. for C₂₀H₂₇IO₆S [M+Na] 522.0573, found 522.0570.

12. Single-crystal X-ray analysis of 8b.

Suitable single crystals for ligand **8b** were obtained by slow volatilization of the chloroform solution of ligand for two weeks. Crystallographic data for **8b** were collected on a Bruker D8 VENTURE single-crystal diffractometer equipped with Mo K α radiation (λ = 0.71073 Å) at 150 K. Data reduction was performed with the CrysAlisPro package [1], and an analytical absorption correction was performed. The

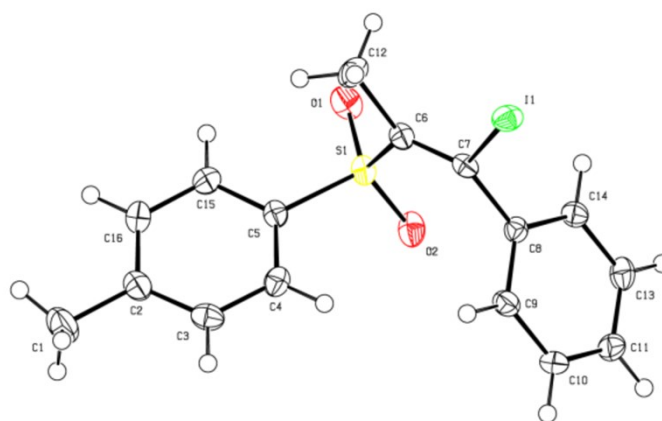
structure was solved by direct method and refined by full-matrix least-squares on F₂ using SHELXTL^[2].

Crystal data and details of data collection and refinement of **8b** are summarized in **Table S4**. CCDC 2069855 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[1] Agilent Technologies, *CrysAlisPro* v. 1.171.36.28, **2013**.

[2] Heldrick, G. M., *Acta Crystallogr. Sect. A*, **2008**, *64*, 112.

Table S4 Crystallographic data and structure of **8b**.



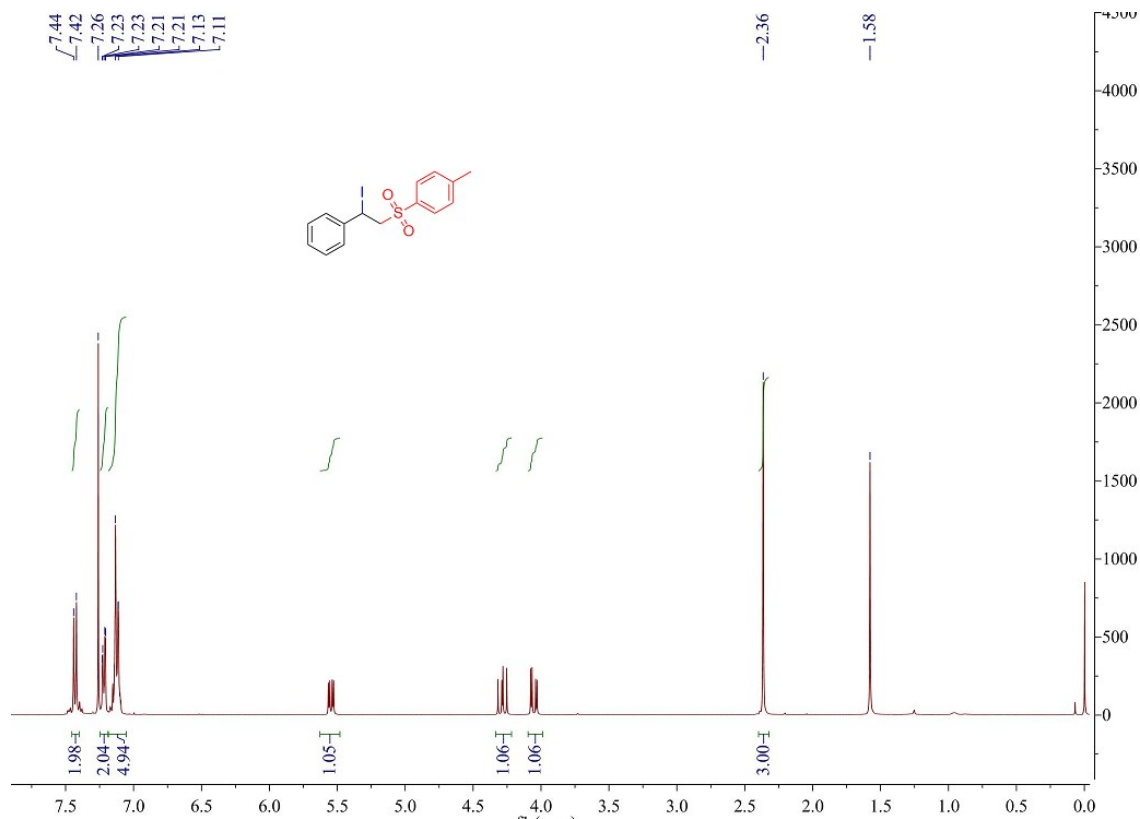
8b CCDC 2069855

8b	
Formula	C ₁₆ H ₁₅ IO ₂ S
Molecular weight / gmol⁻¹	398.24
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
a/Å	5.4771(2)
b/Å	9.0324(4)
c/Å	31.6646(14)
α/°	90
β/°	90
γ/°	90
Cell volume/Å³	1566.49(11)

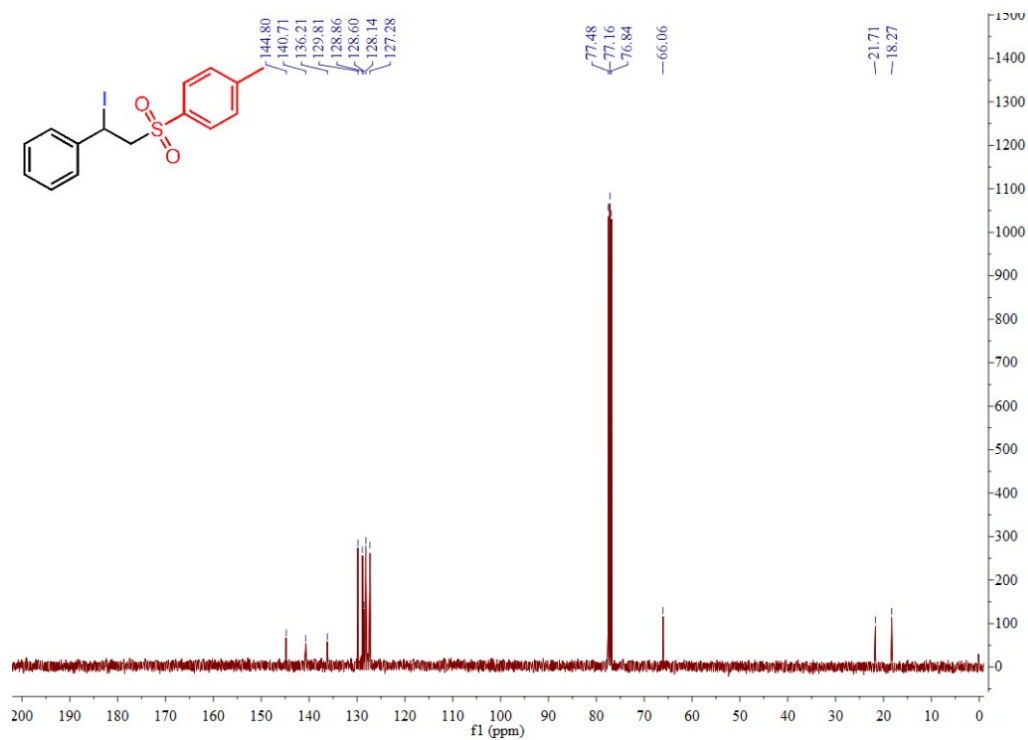
Z	4
Absorption coefficient / mm⁻¹	2.176
Reflections collected	8920
Independent reflections, R(int)	2771, 0.0239
Restraints / parameters	0 / 183
Final R indices[I>2sigma(I)]:R1,wR2	0.0149, 0.0346
CCDC number	2069855

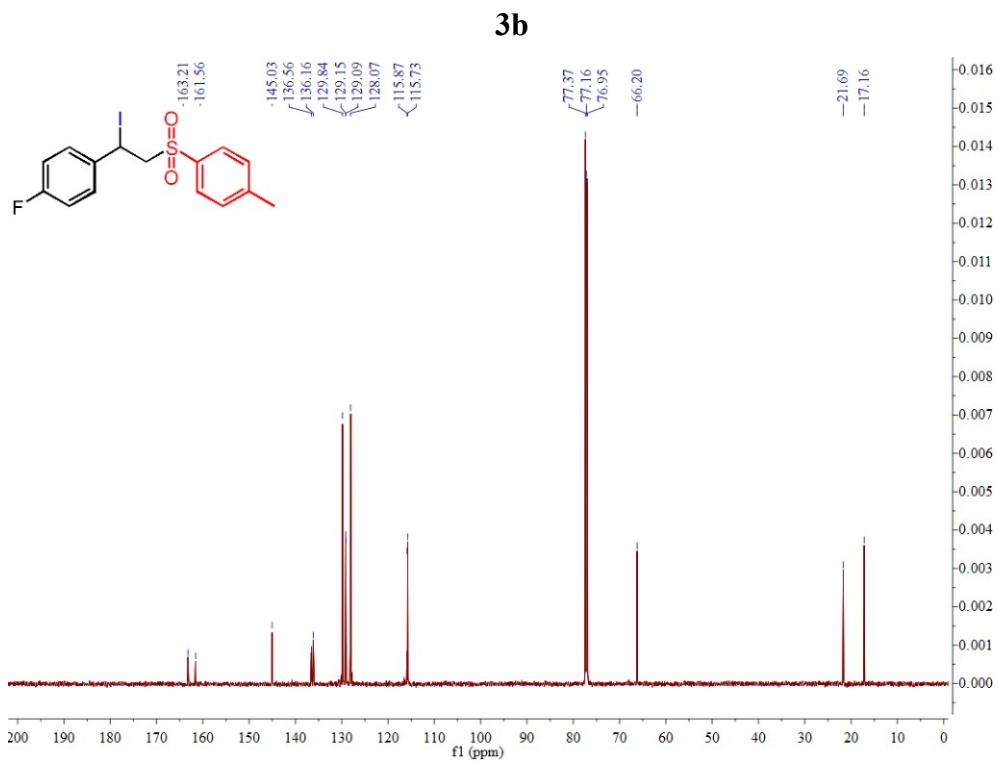
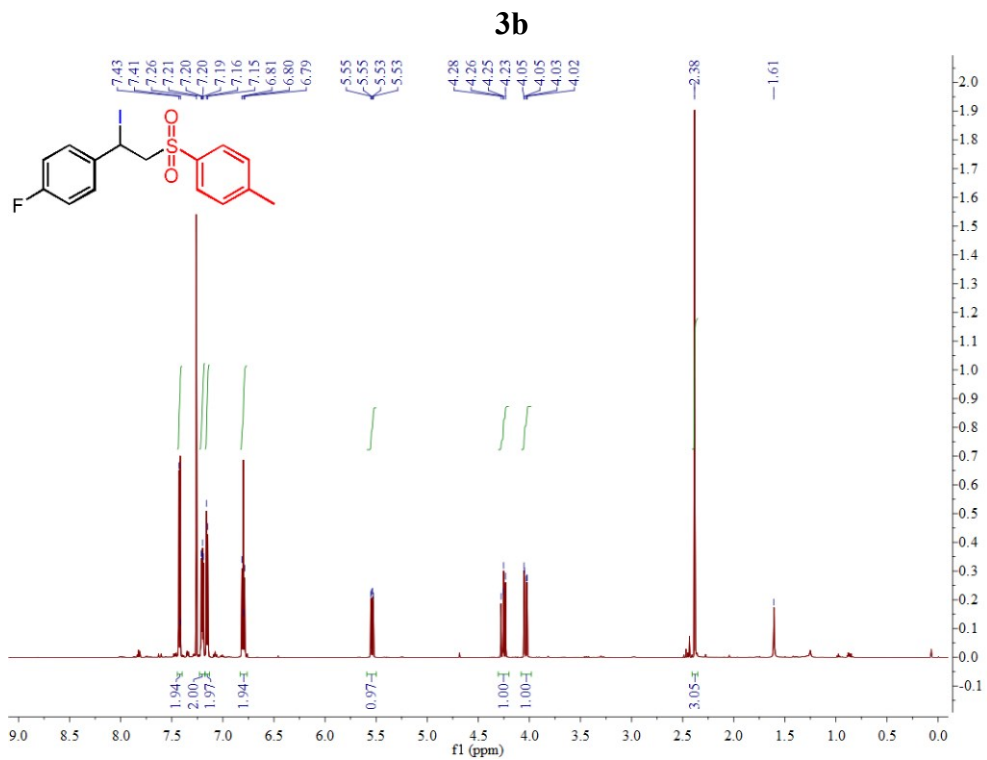
13. NMR Spectra

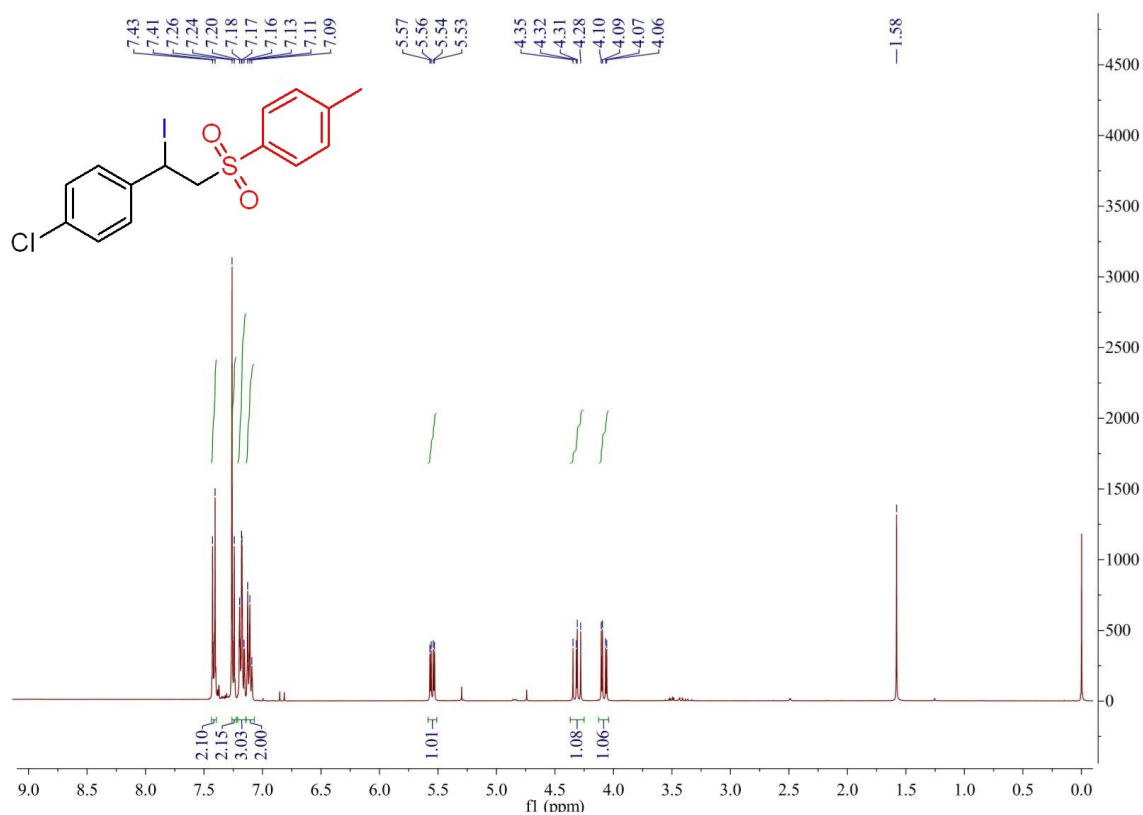
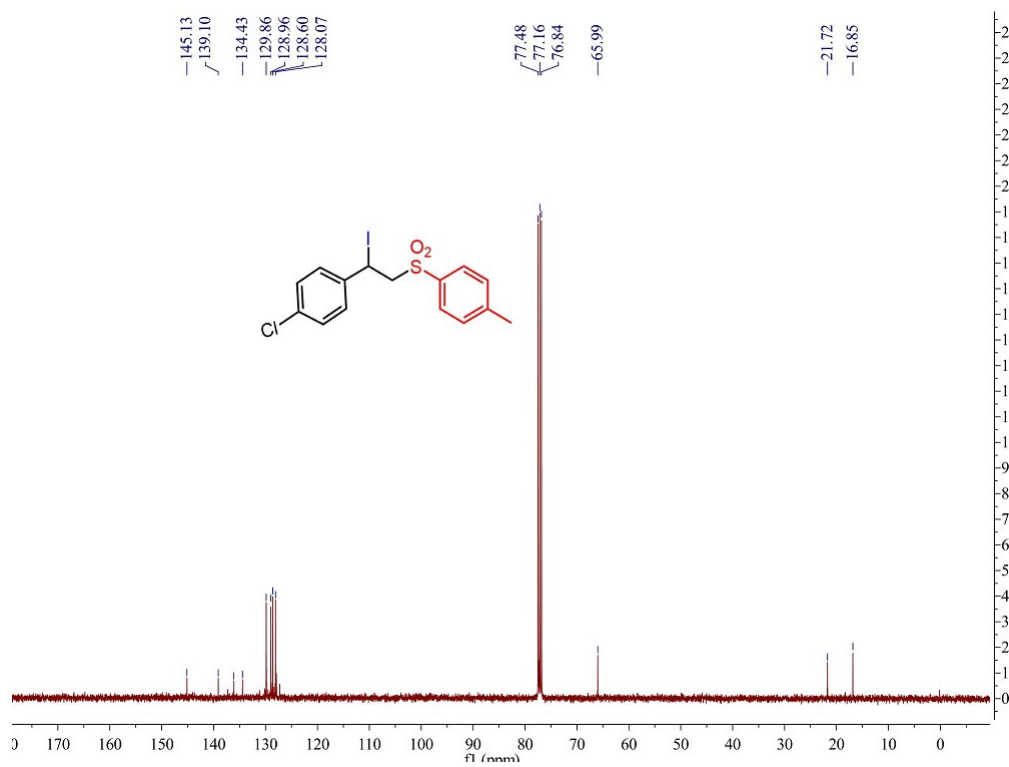
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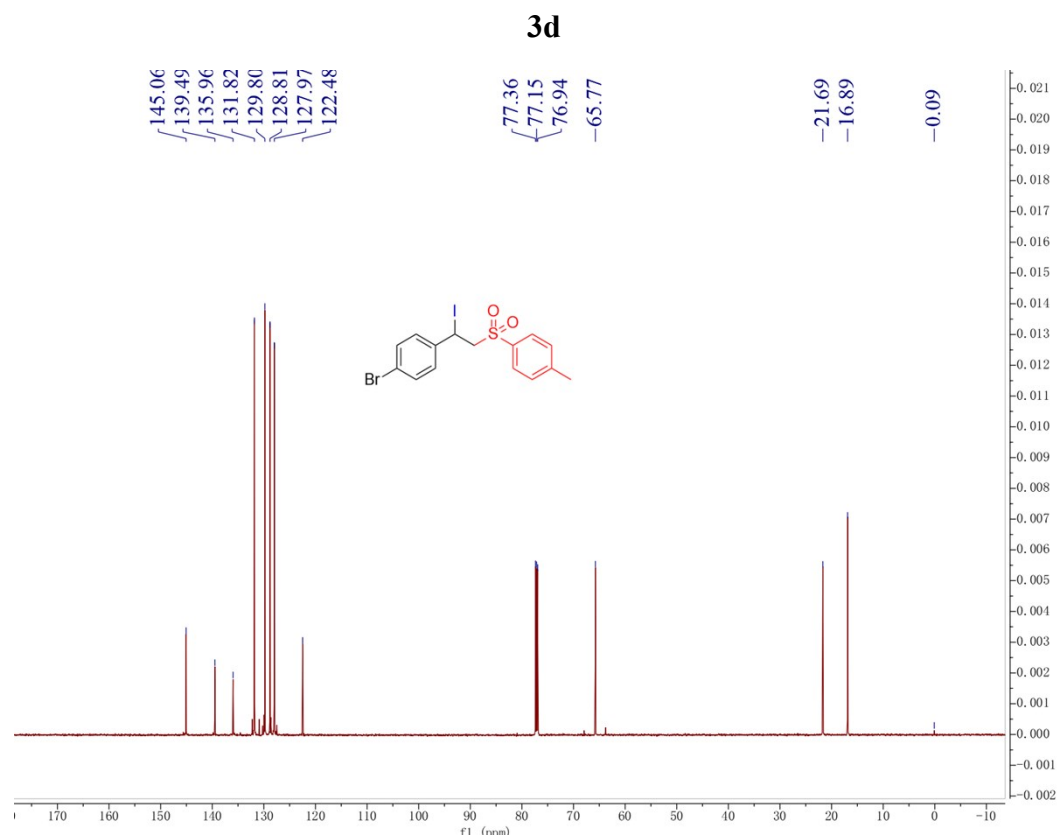
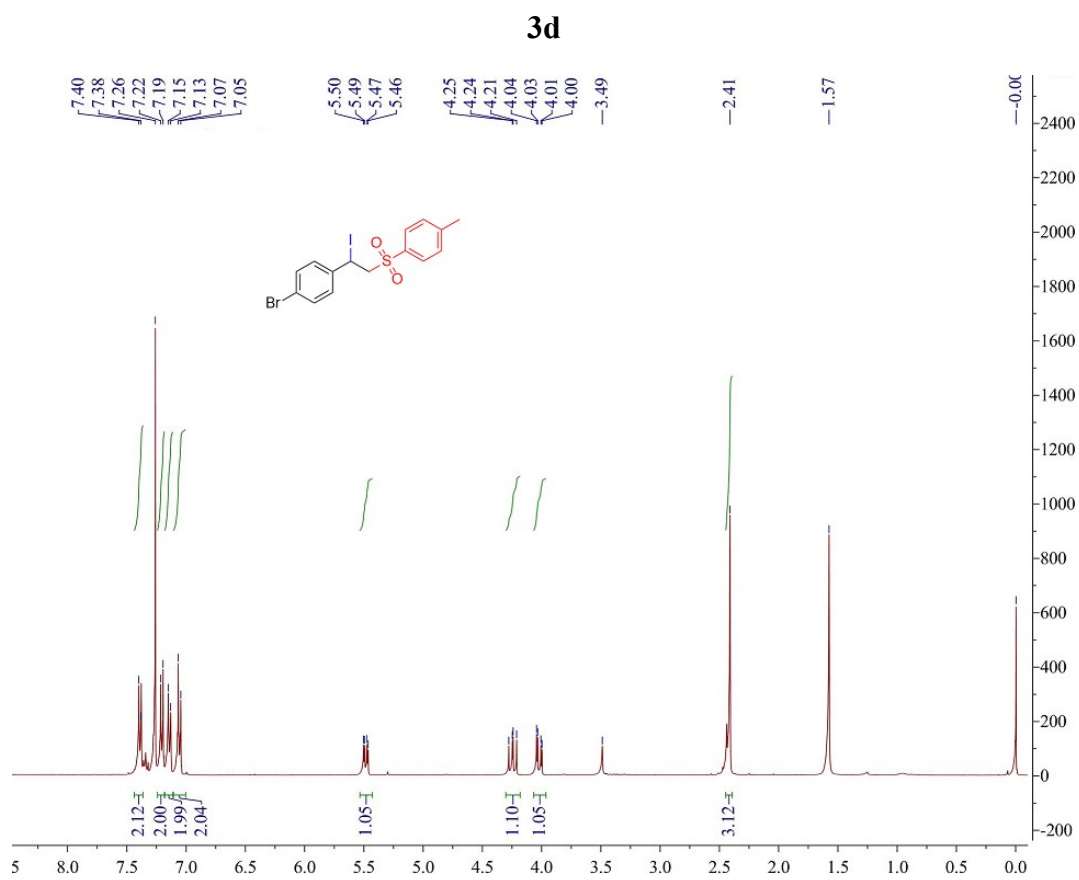


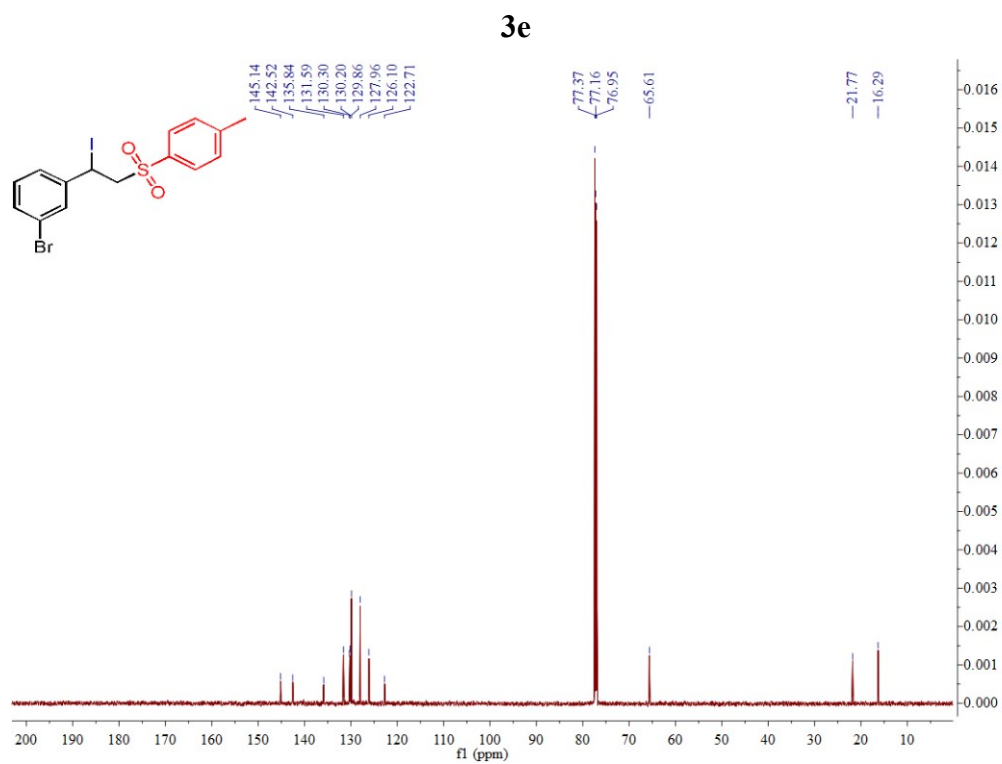
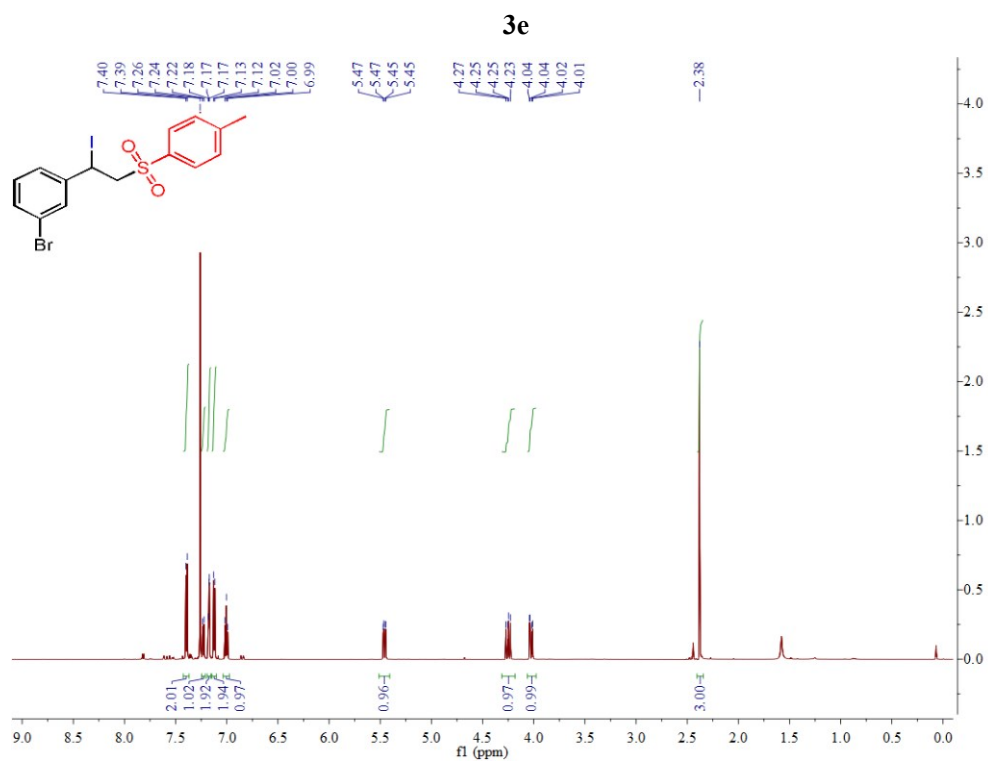
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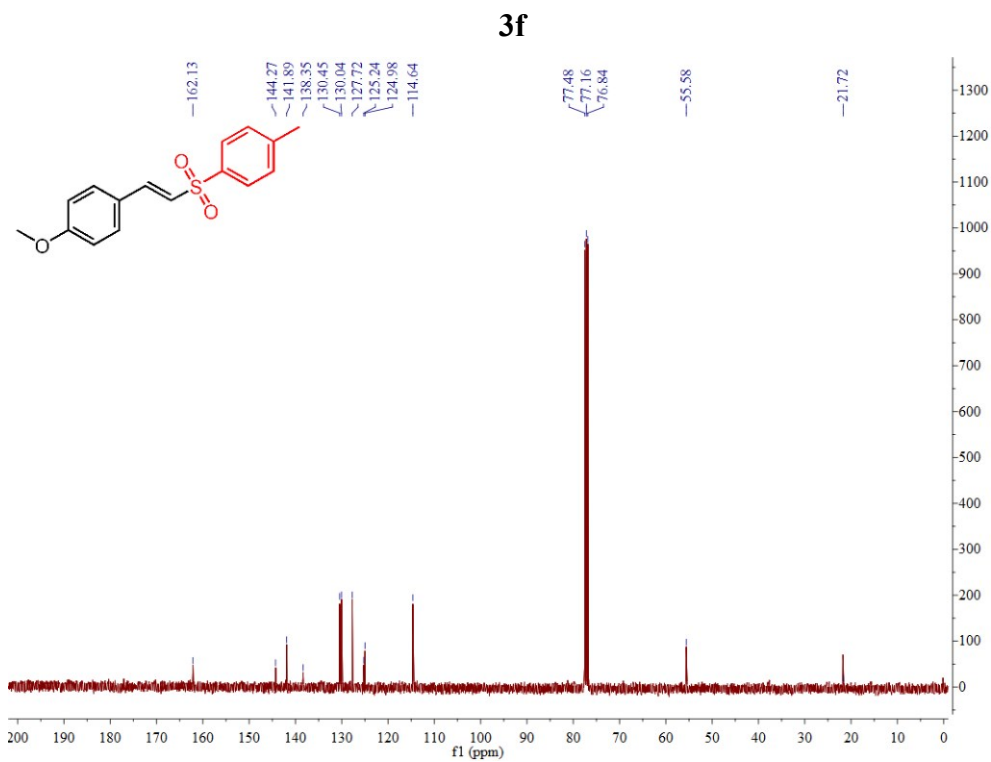
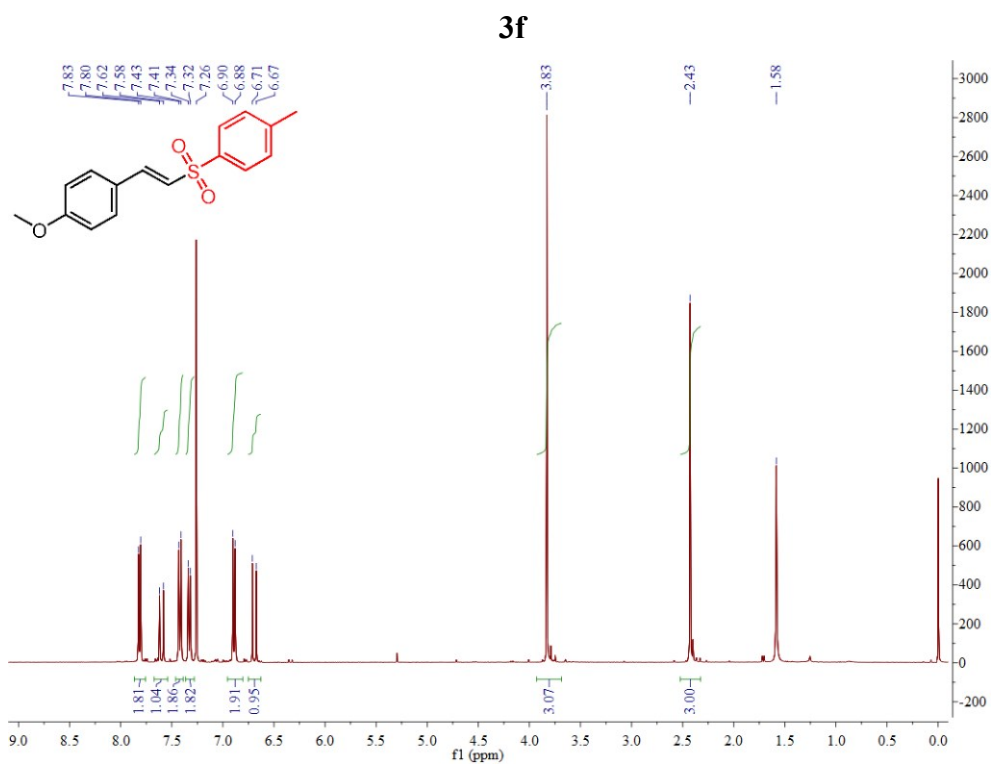


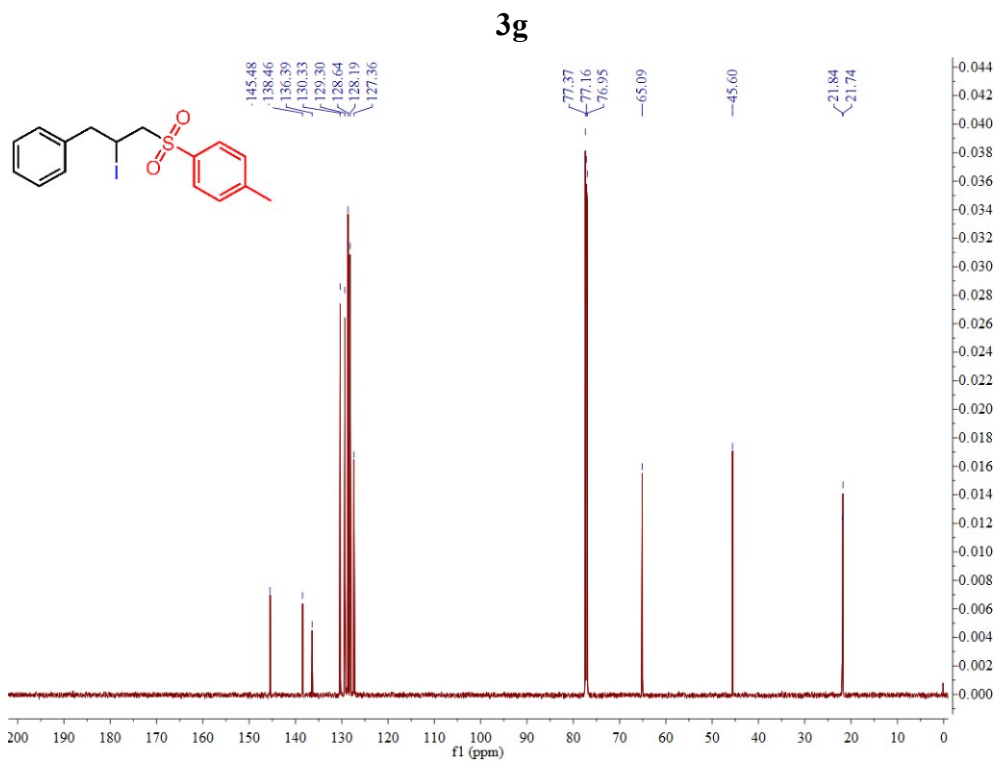
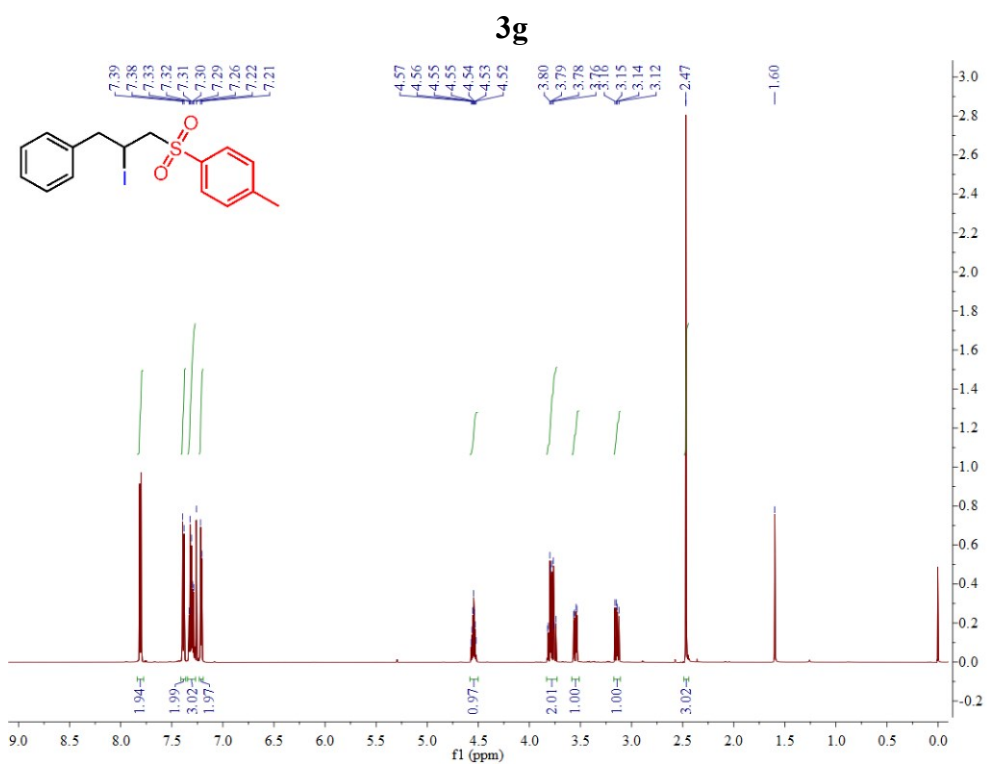


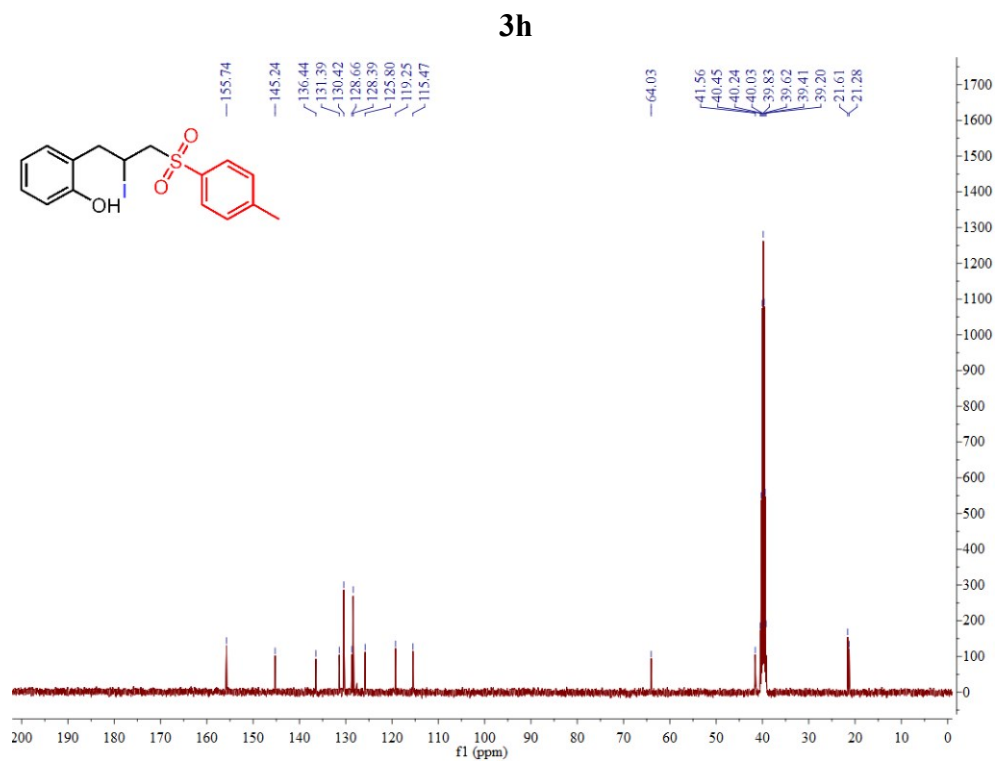
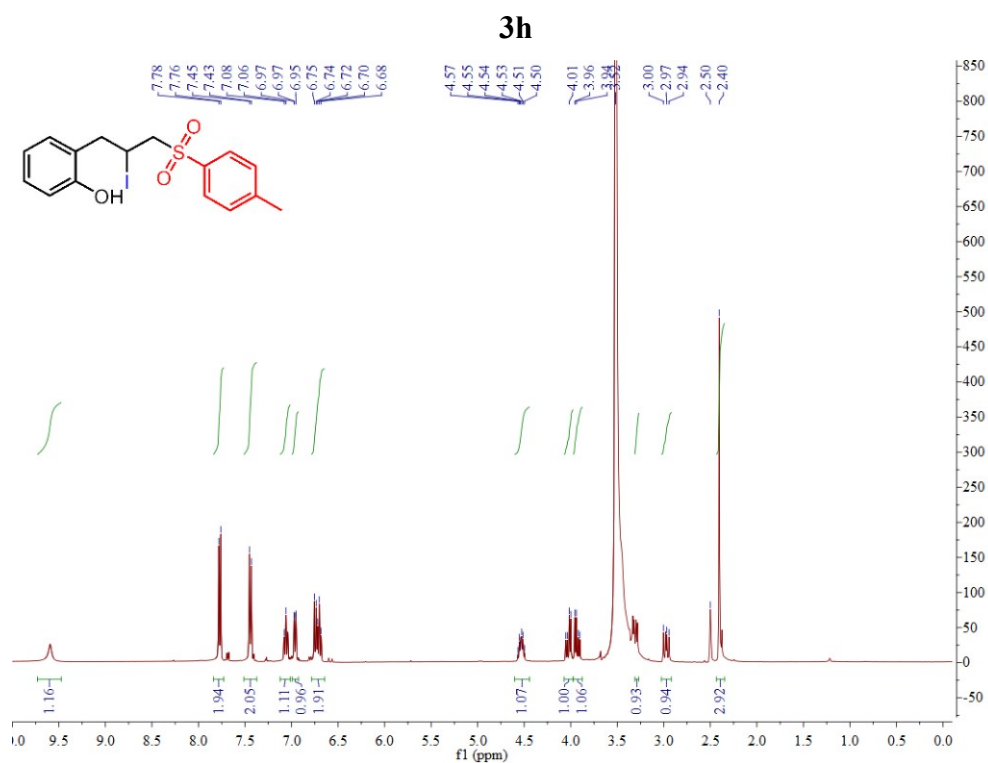
3c**3c**

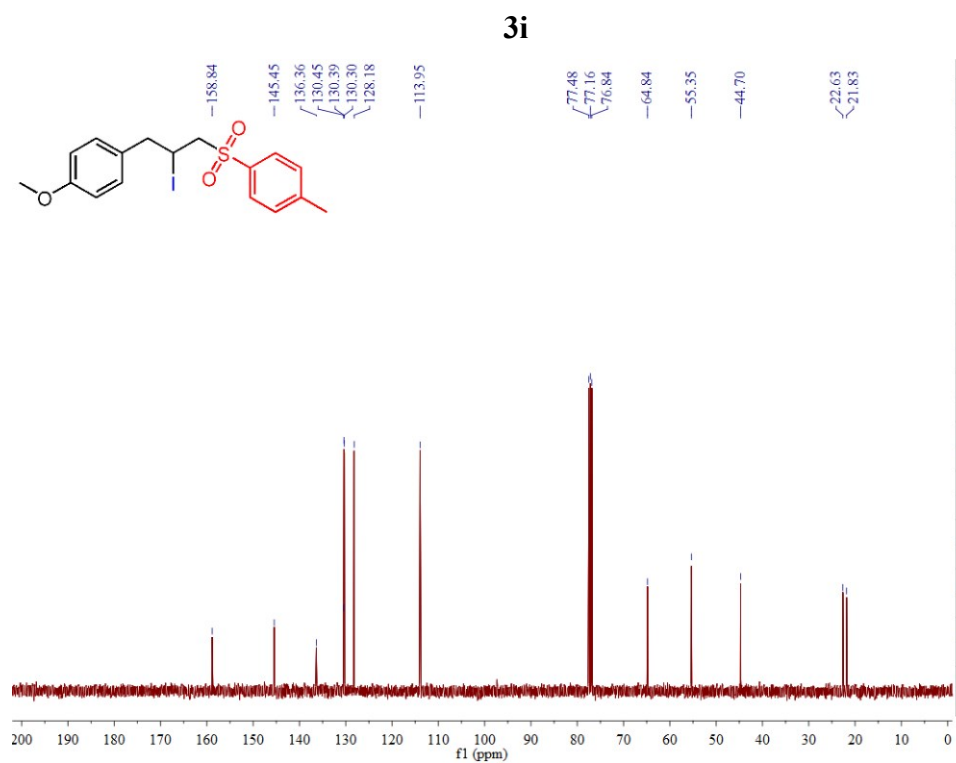
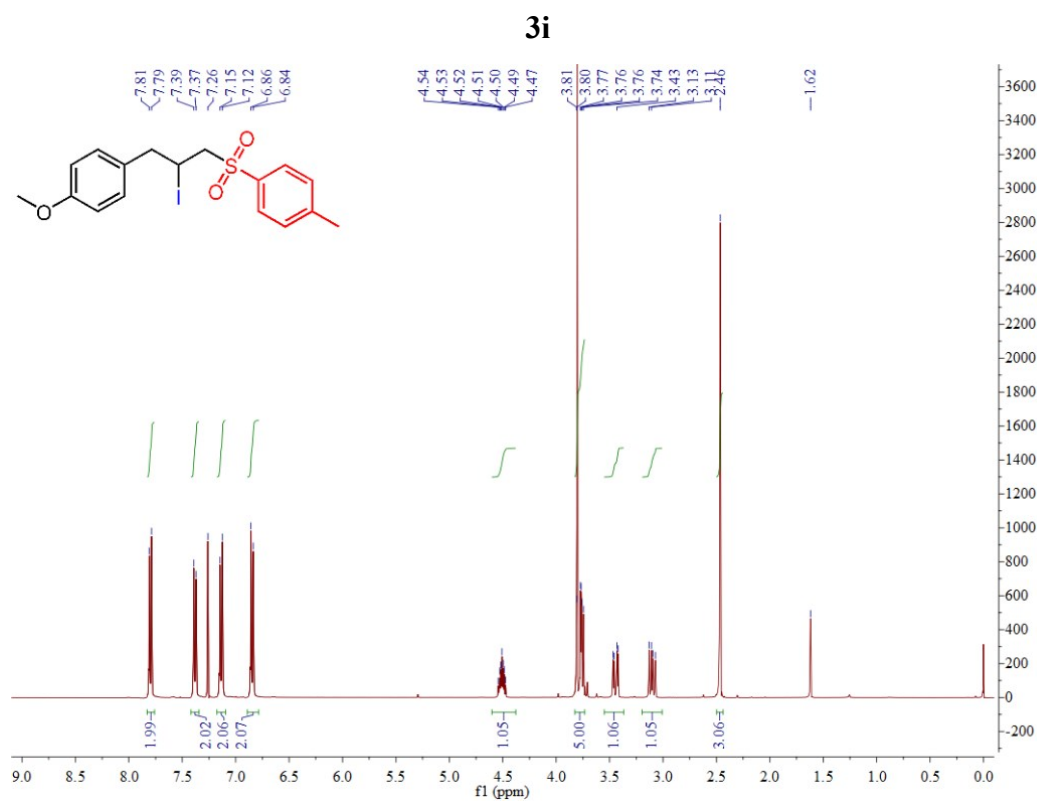


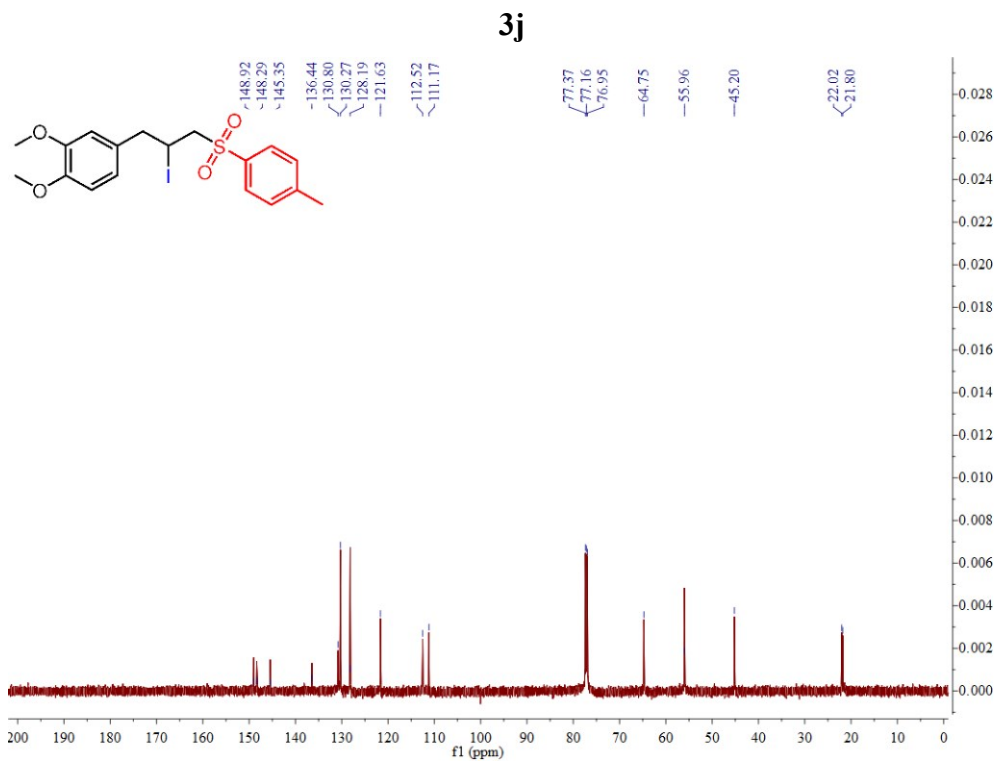
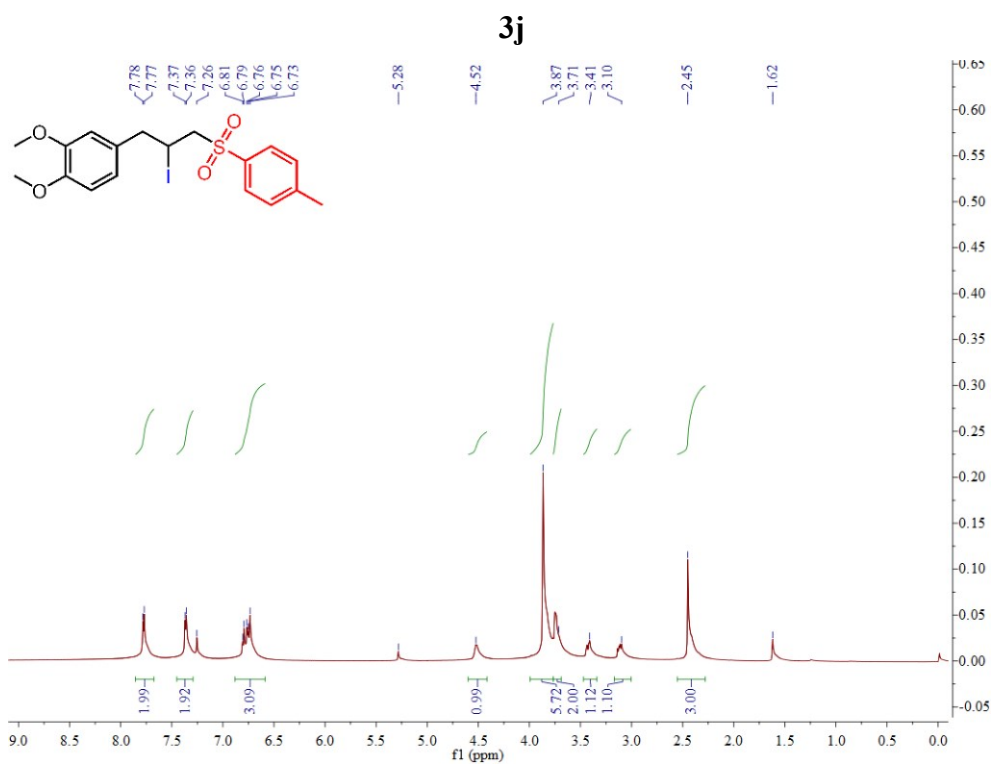




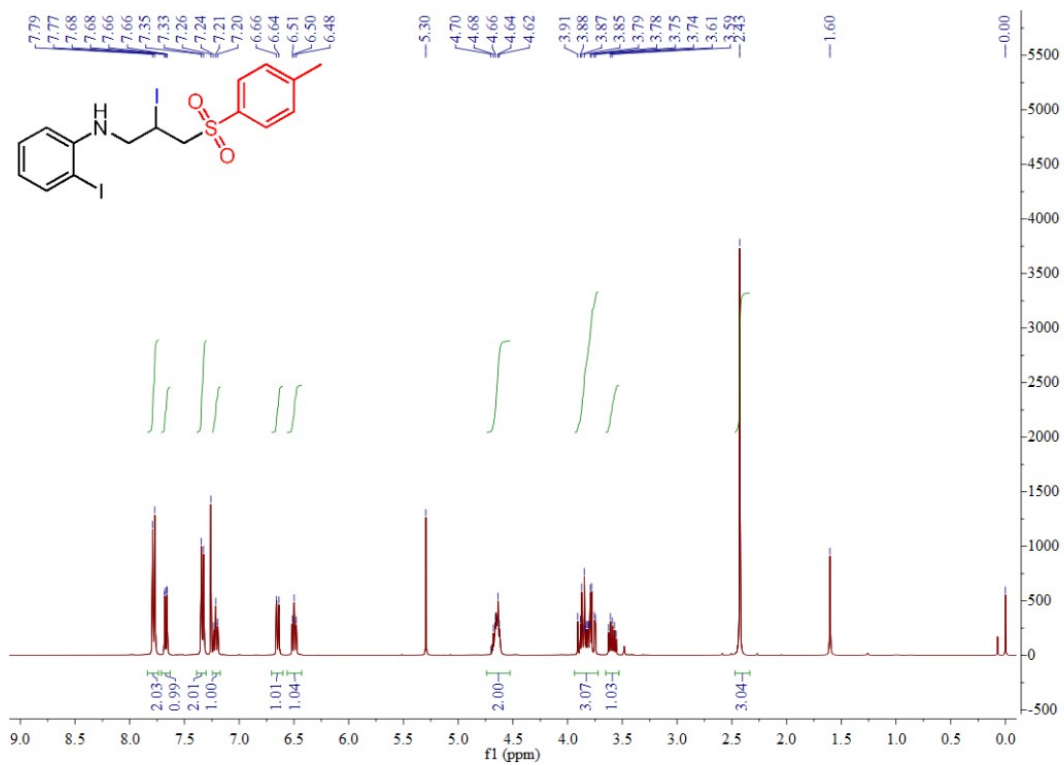




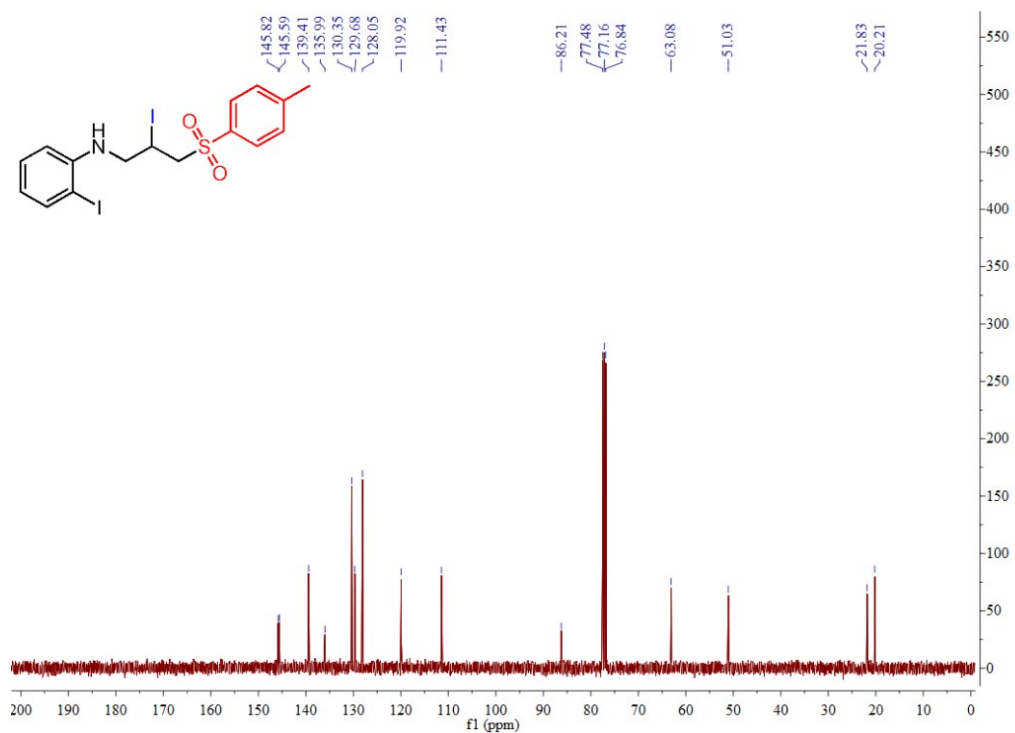




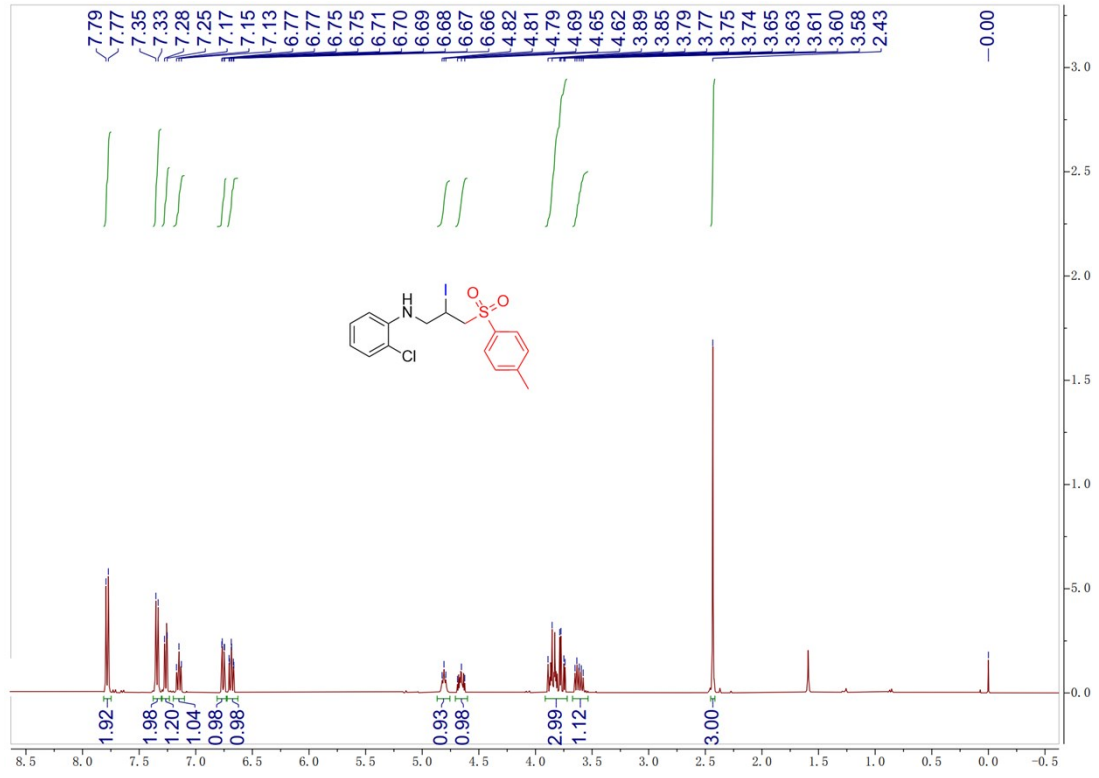
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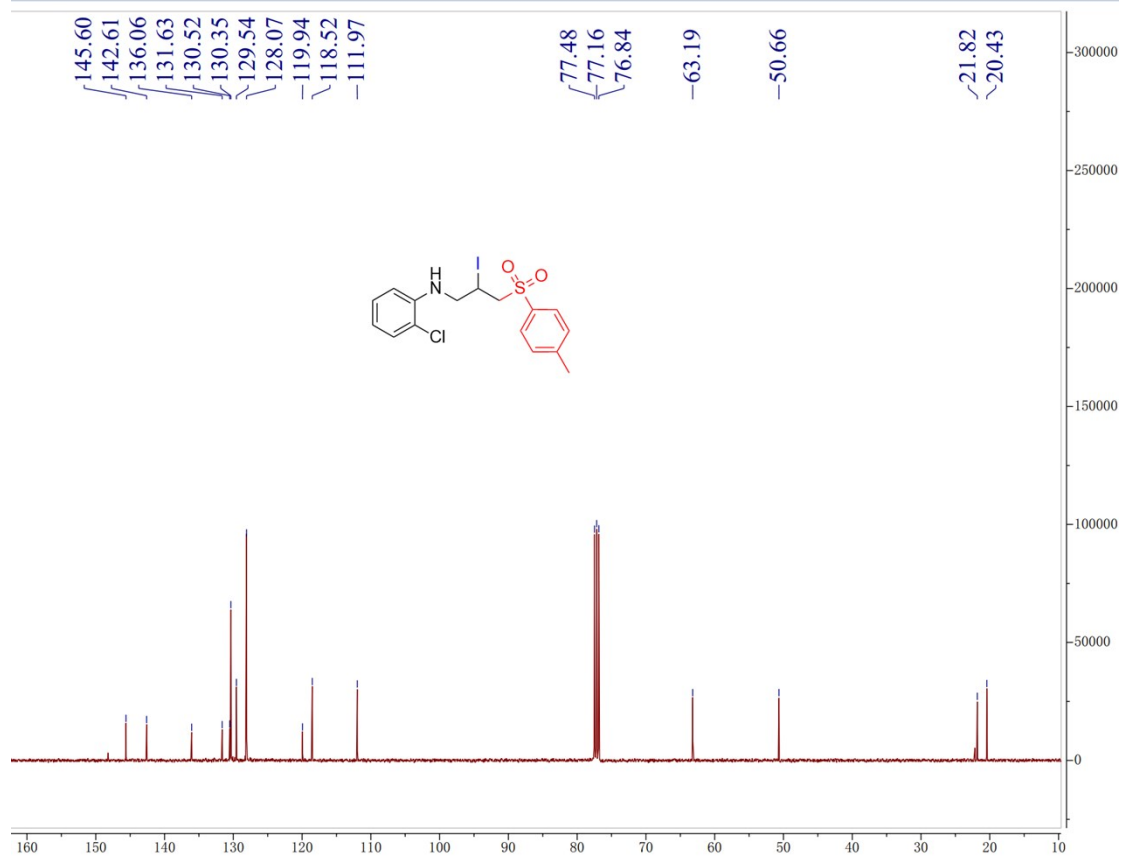
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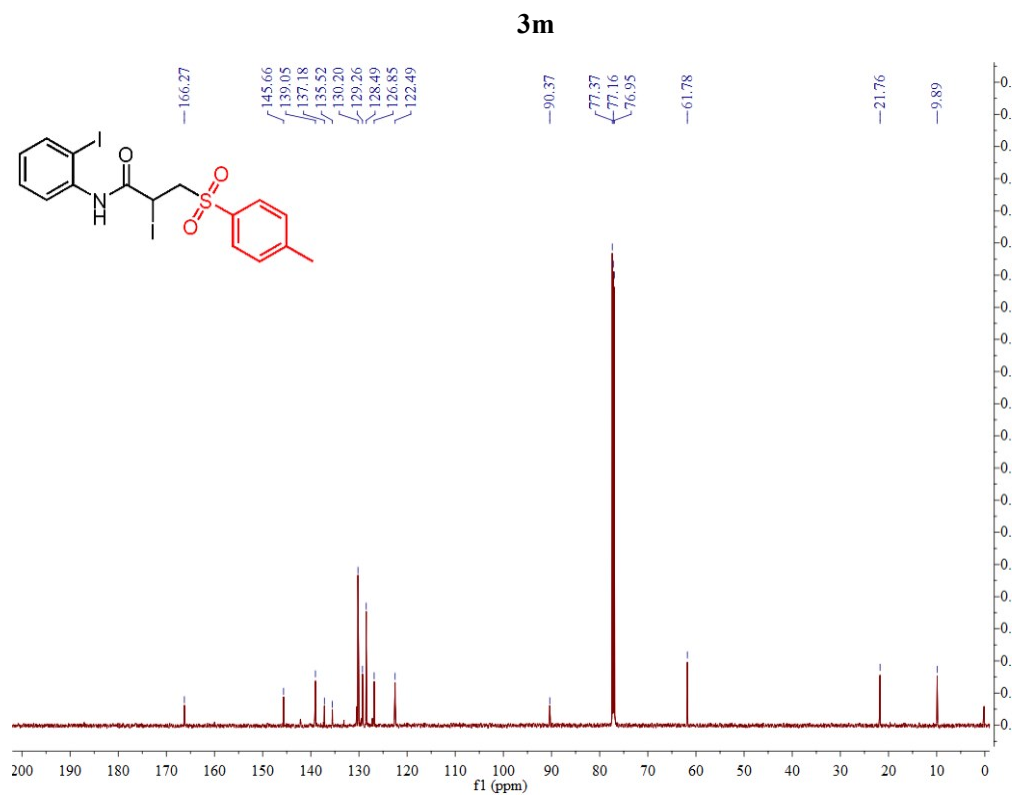
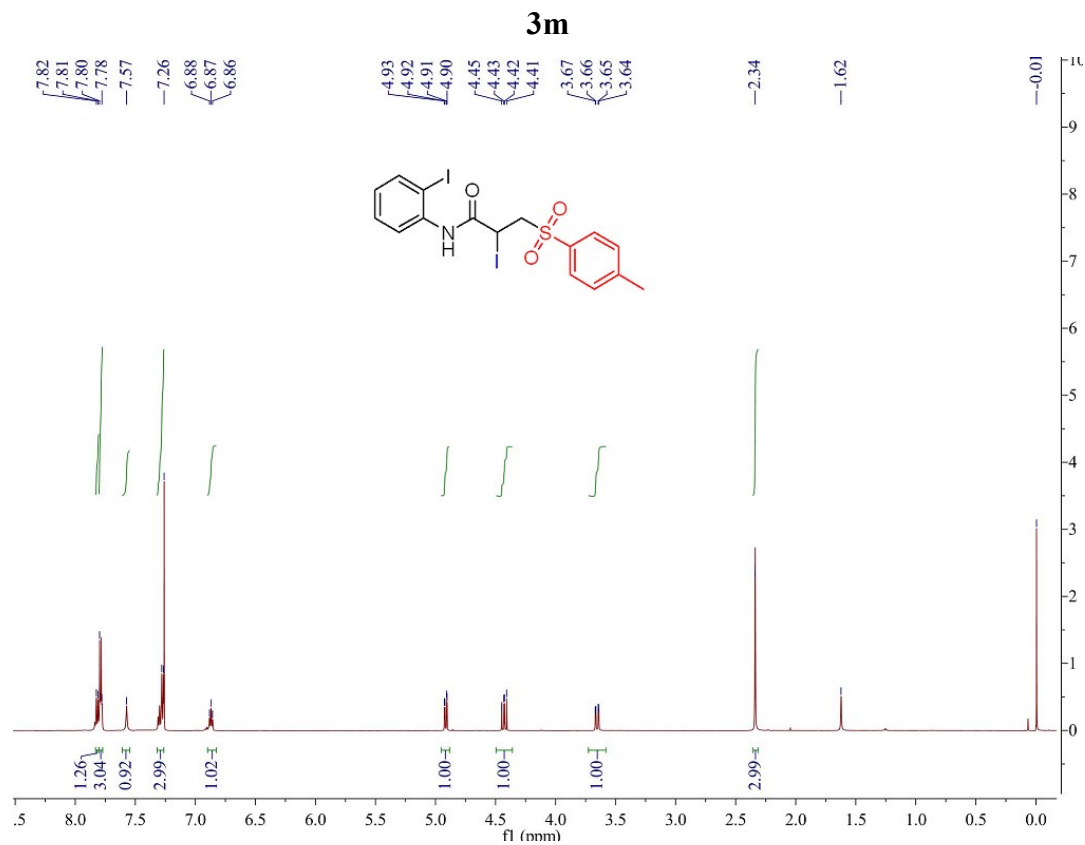


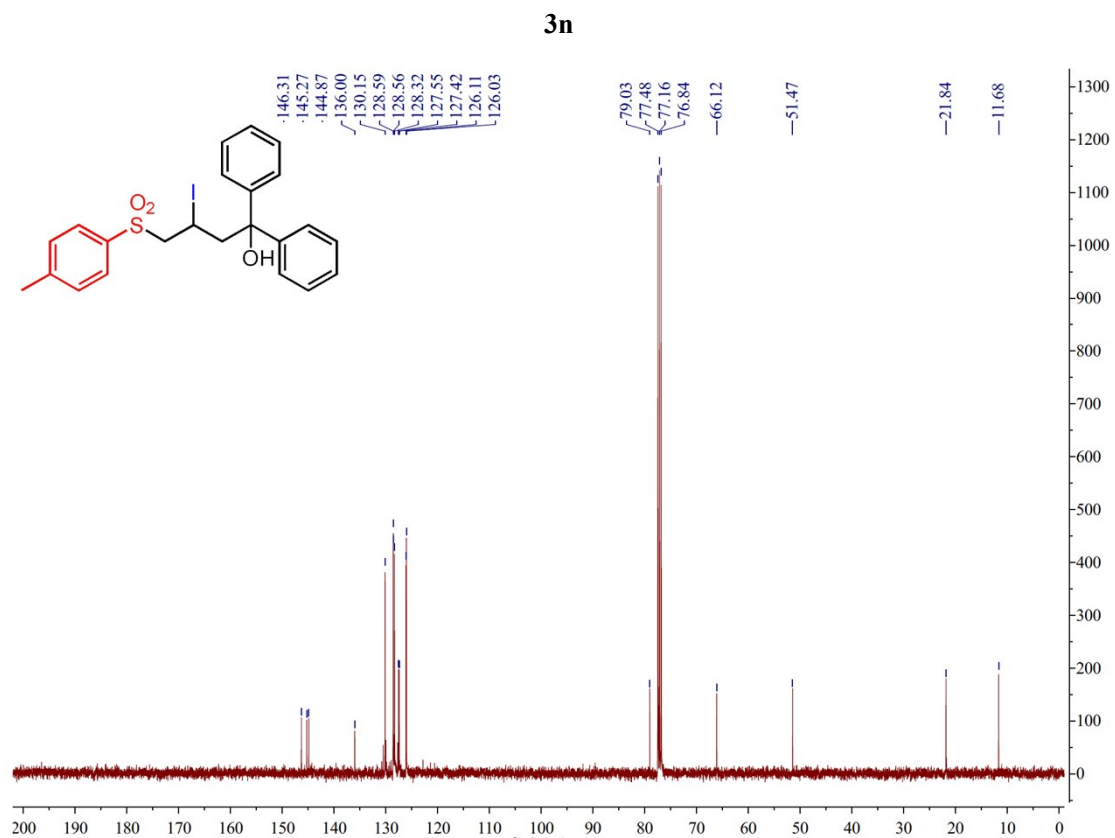
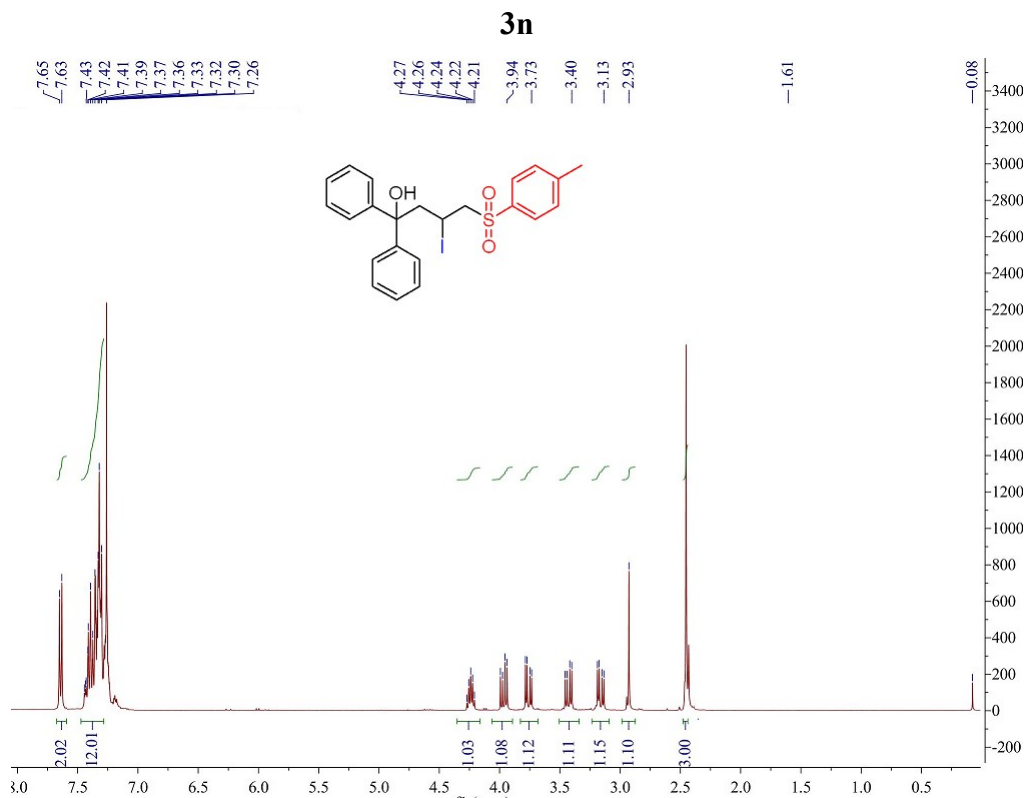
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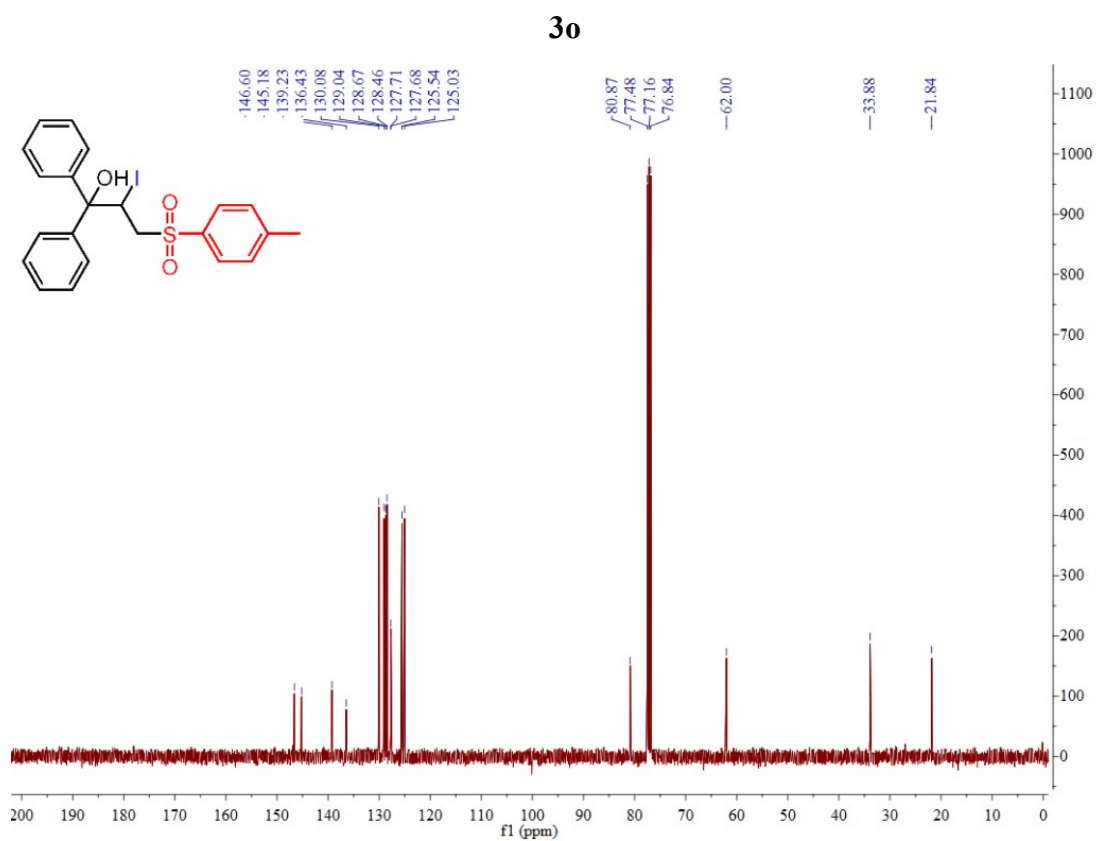
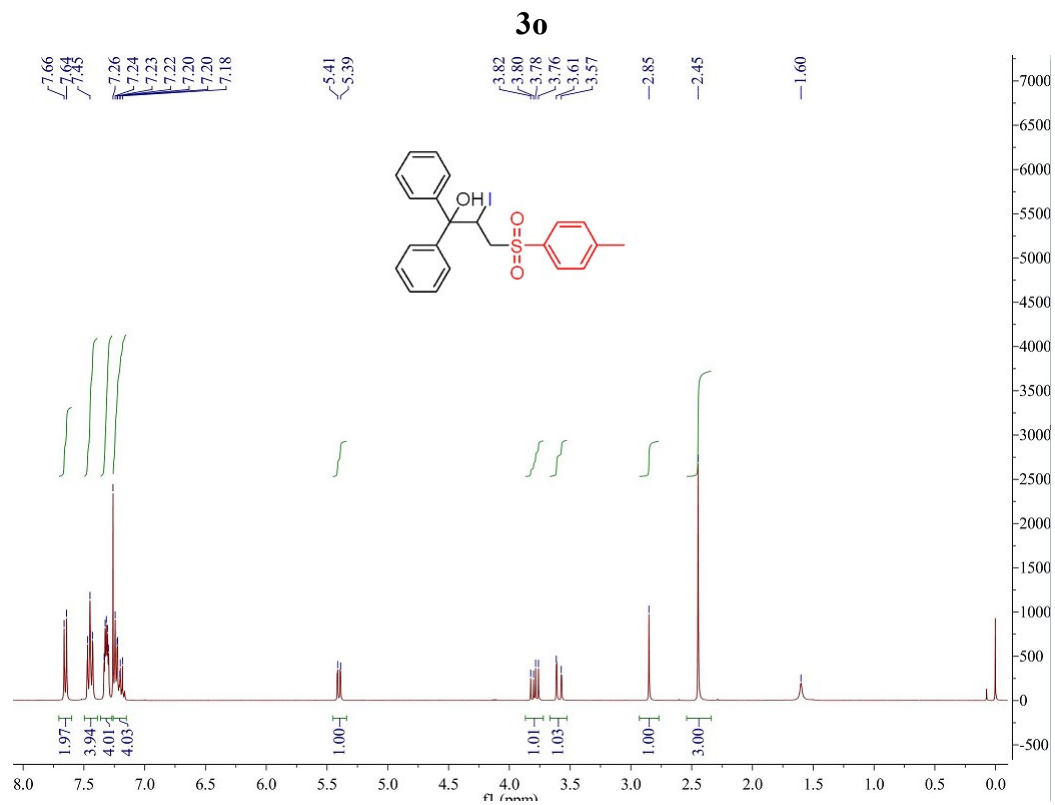


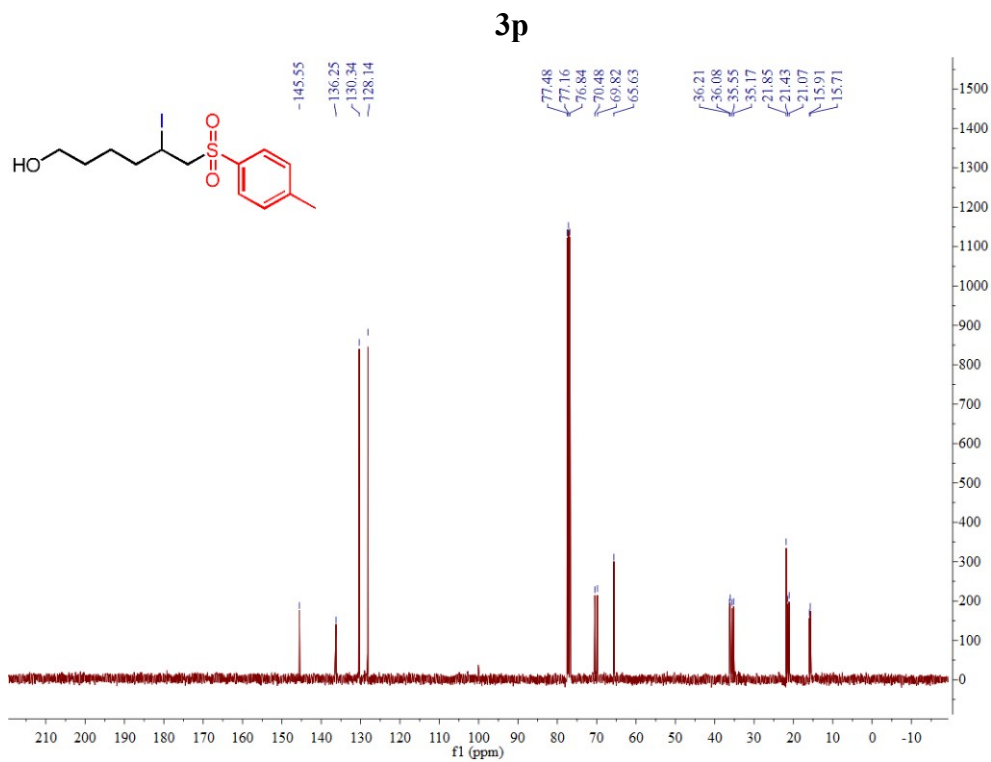
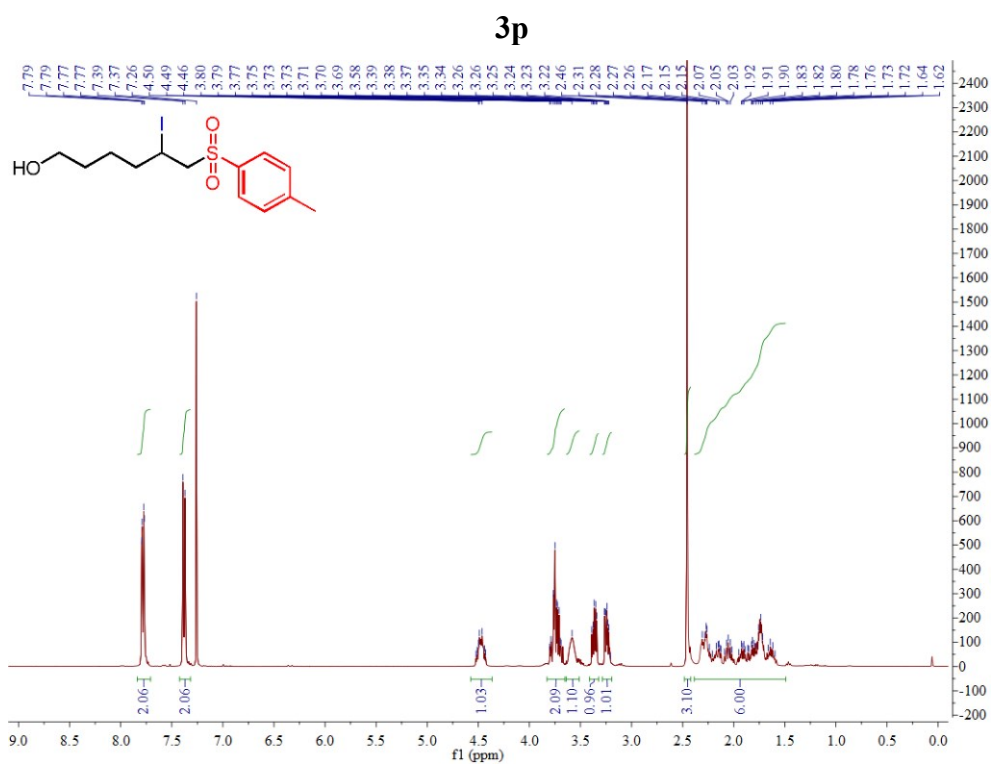
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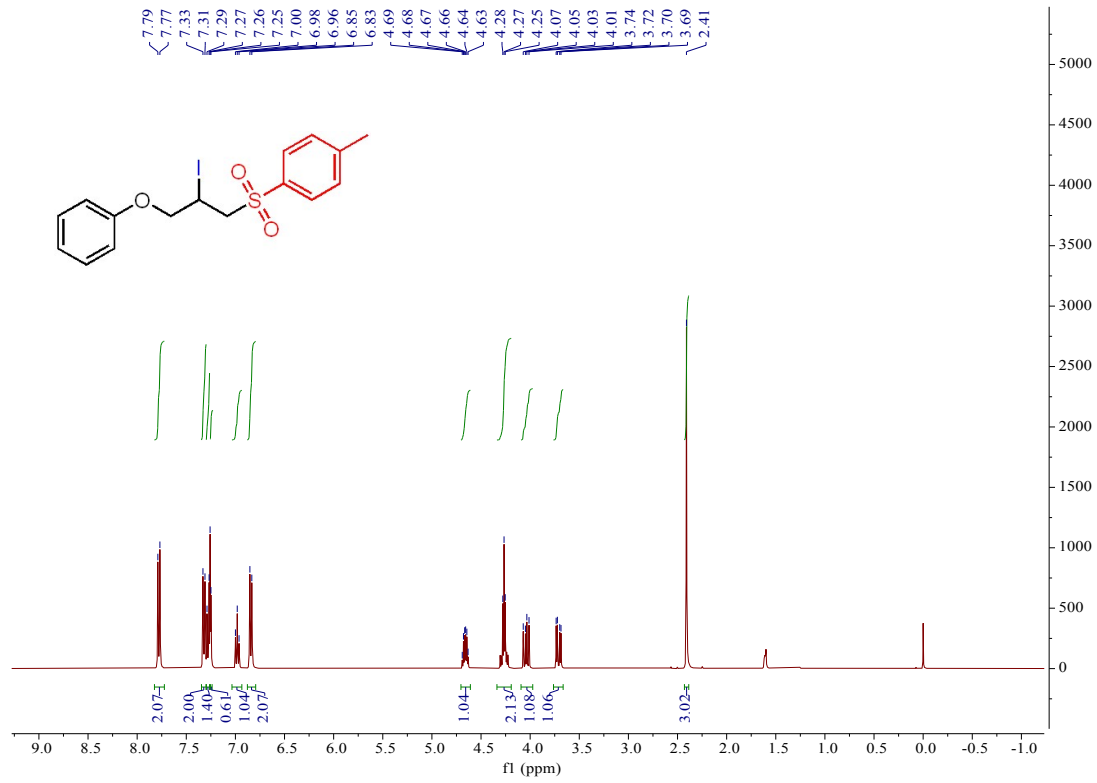




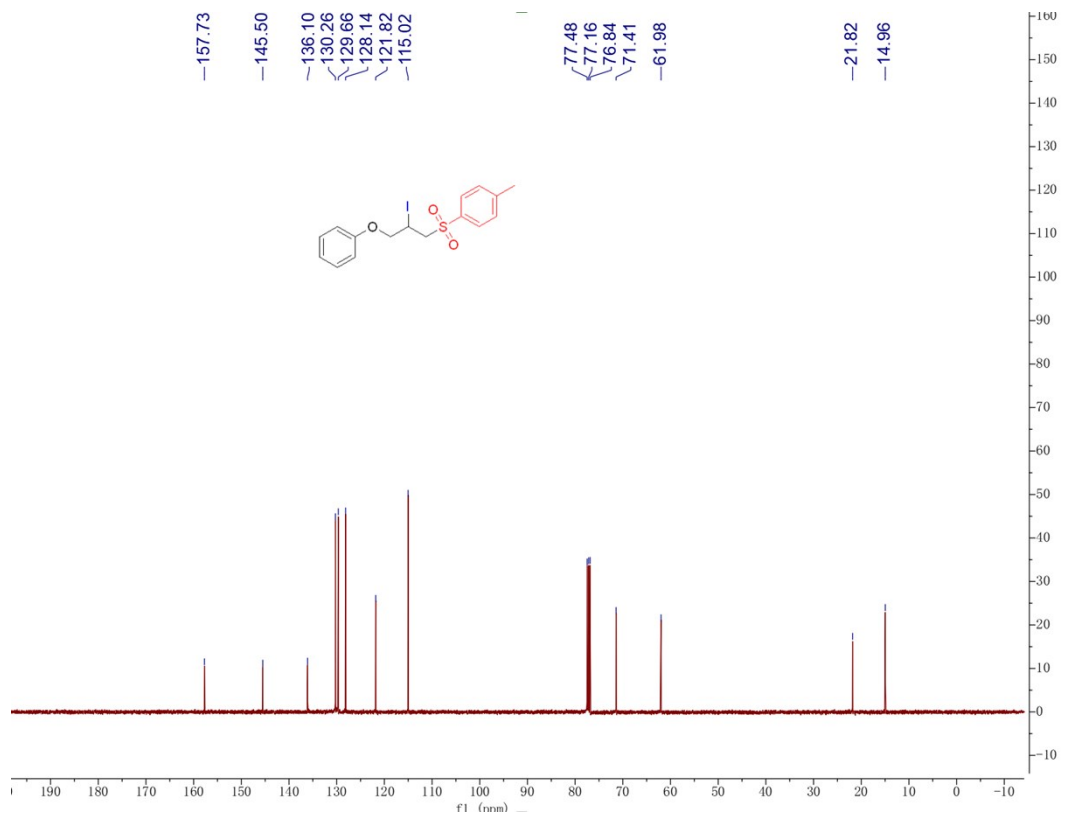


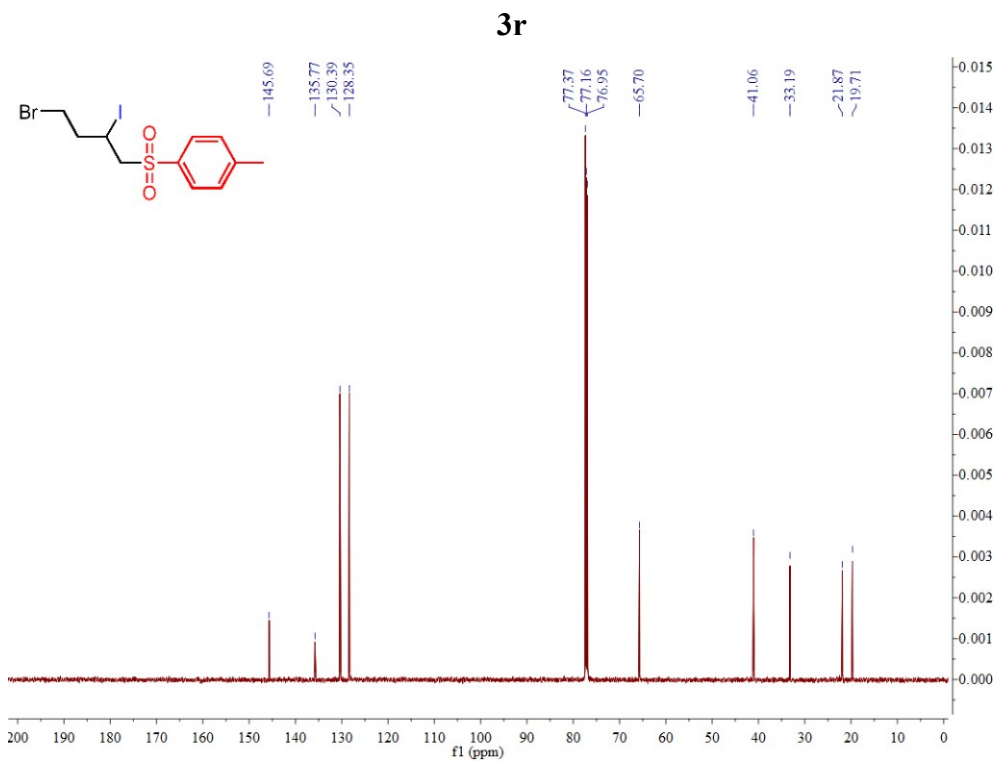
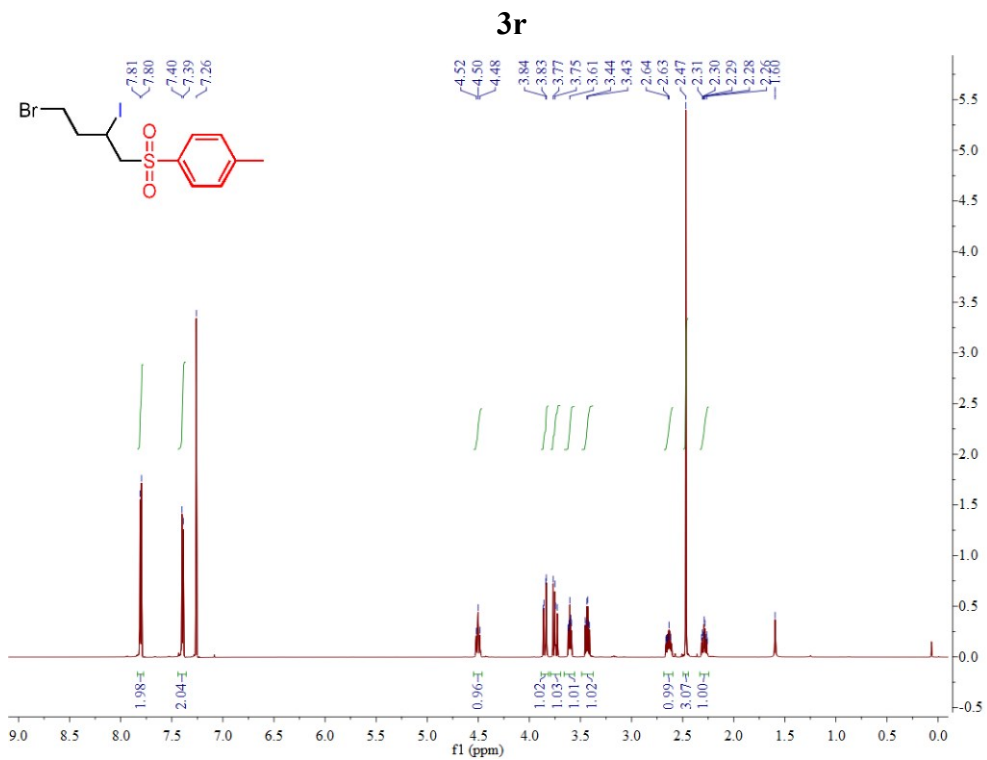


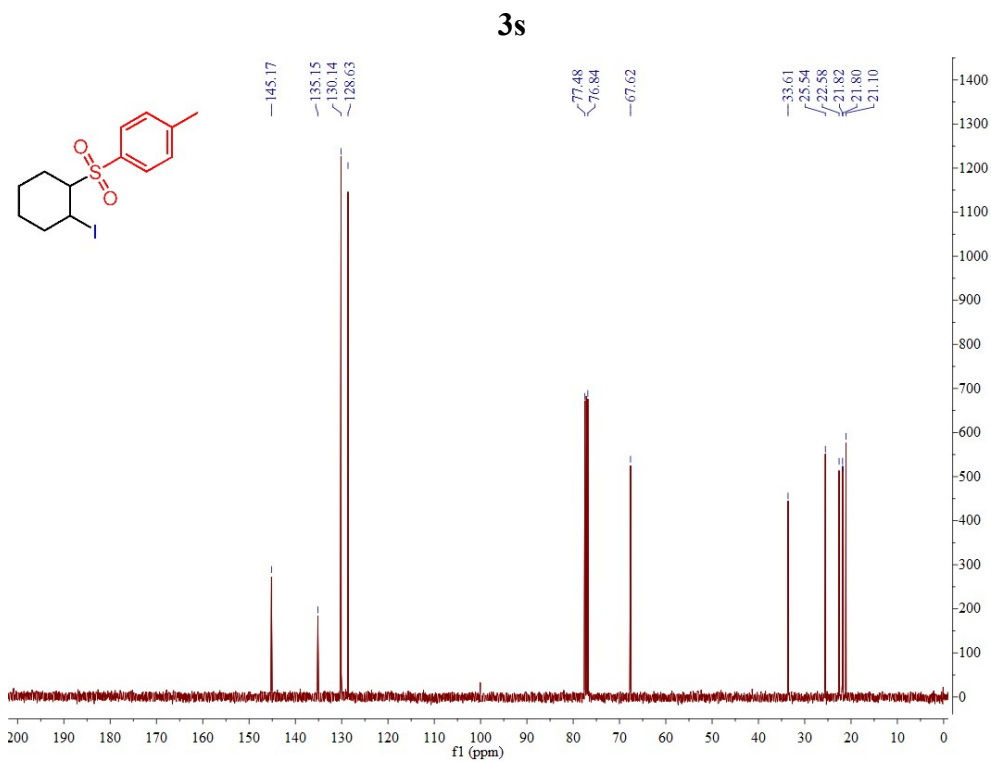
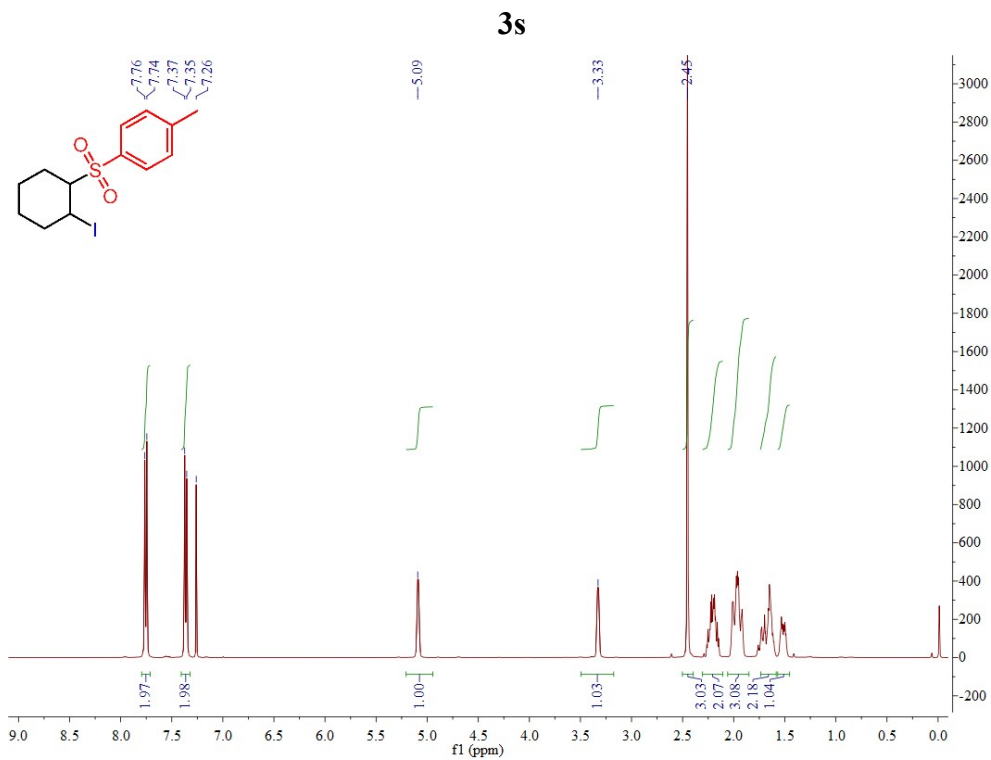
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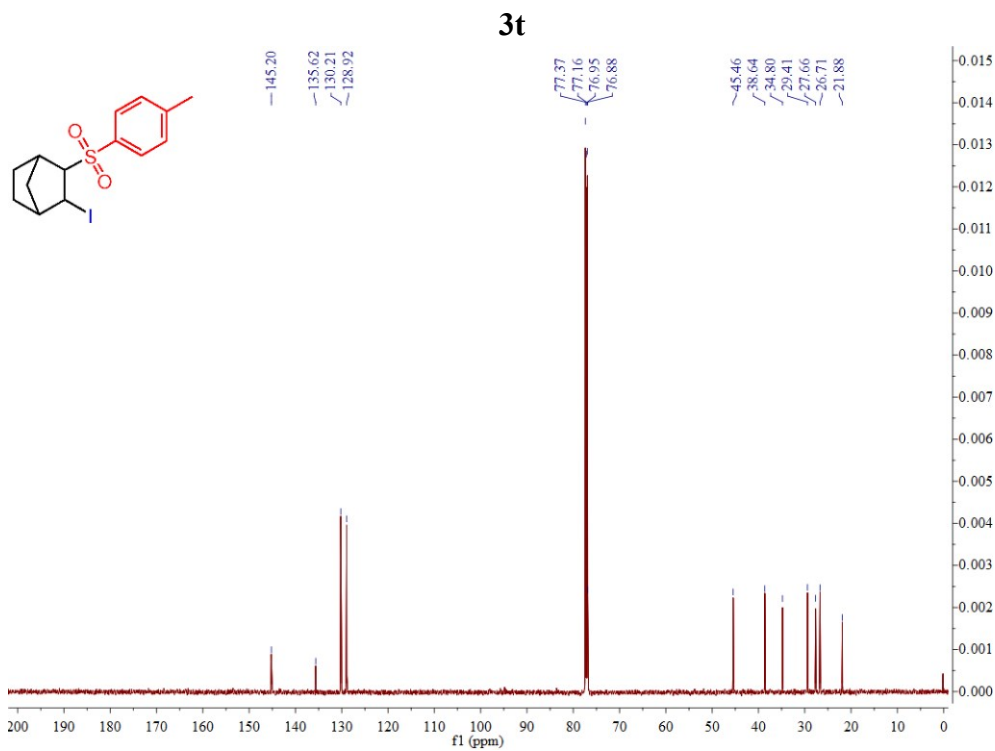
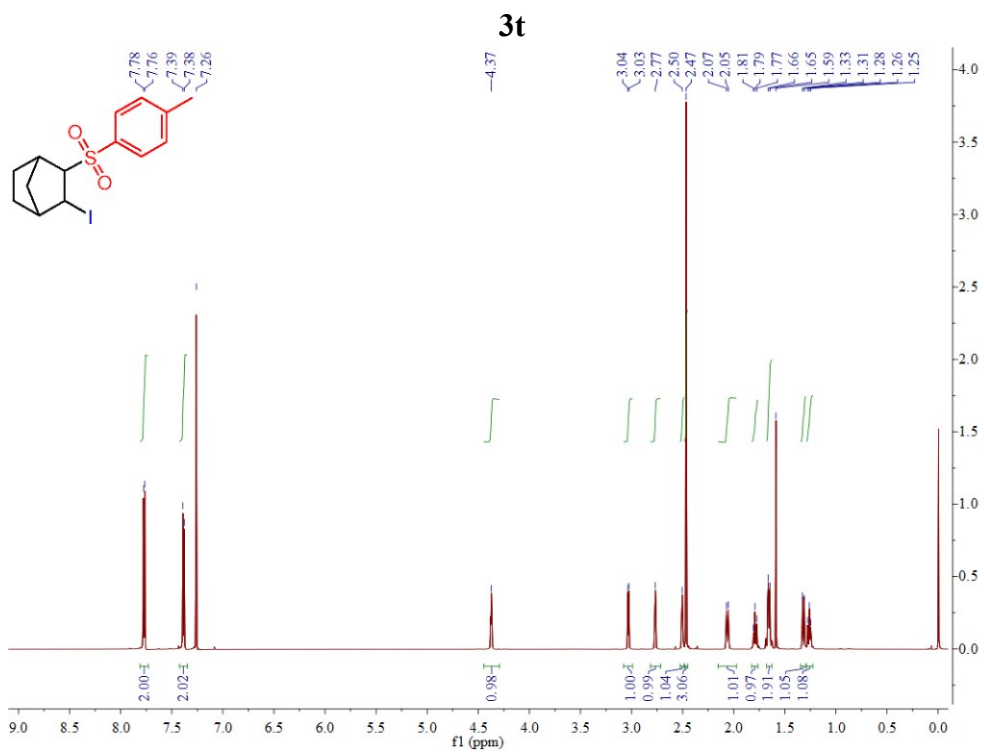


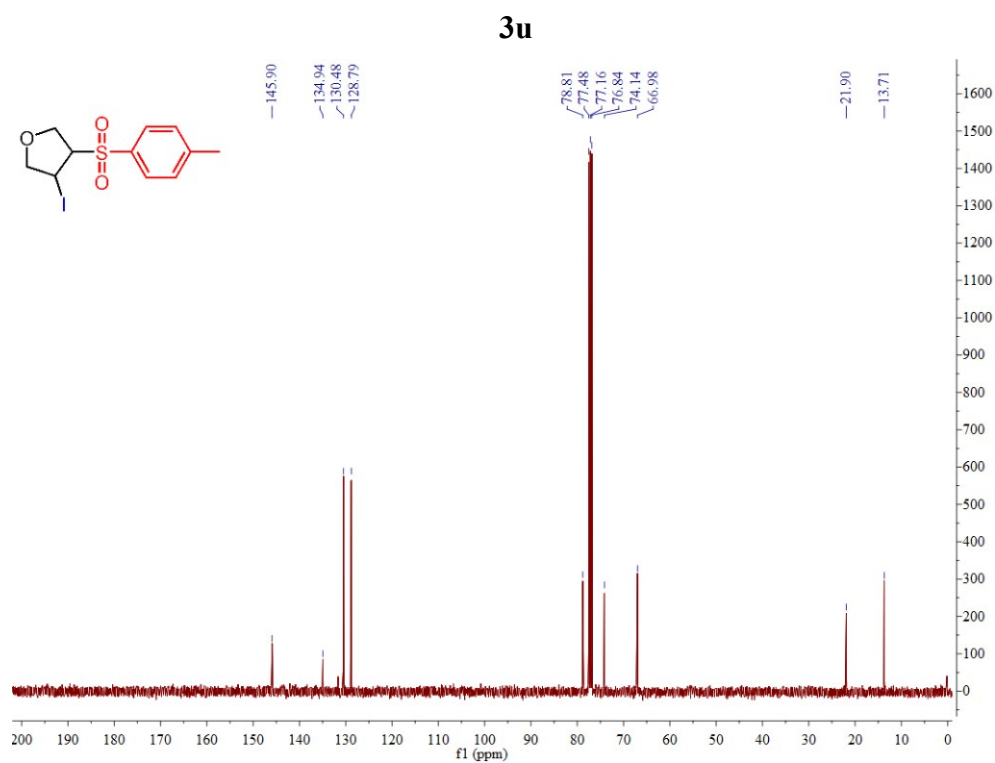
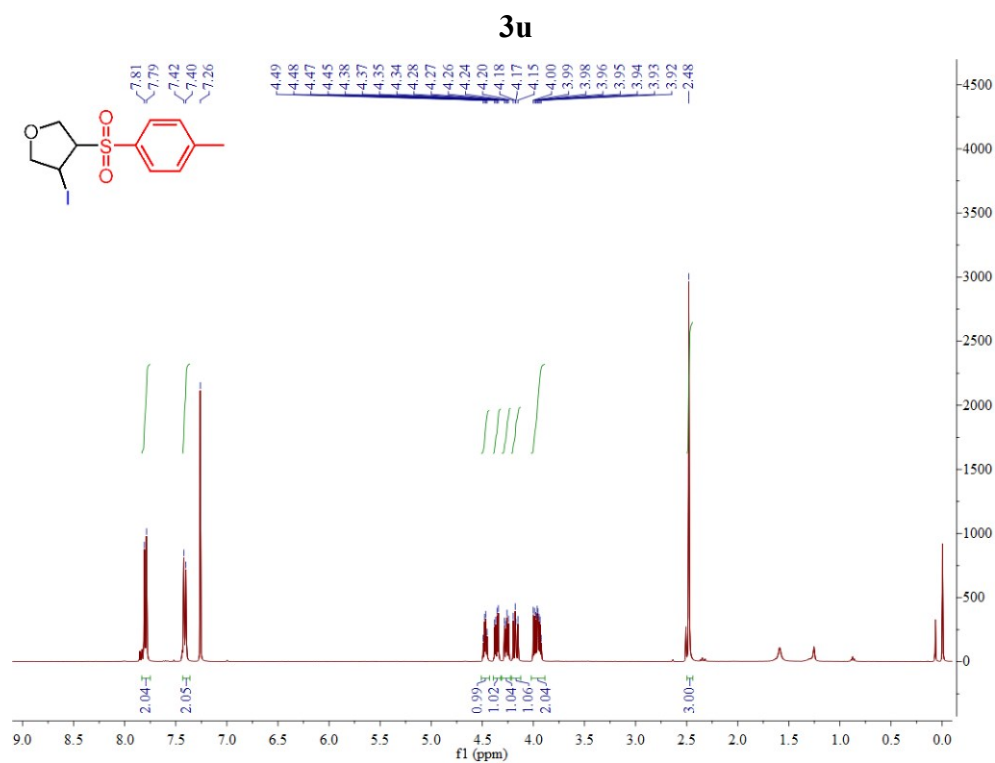
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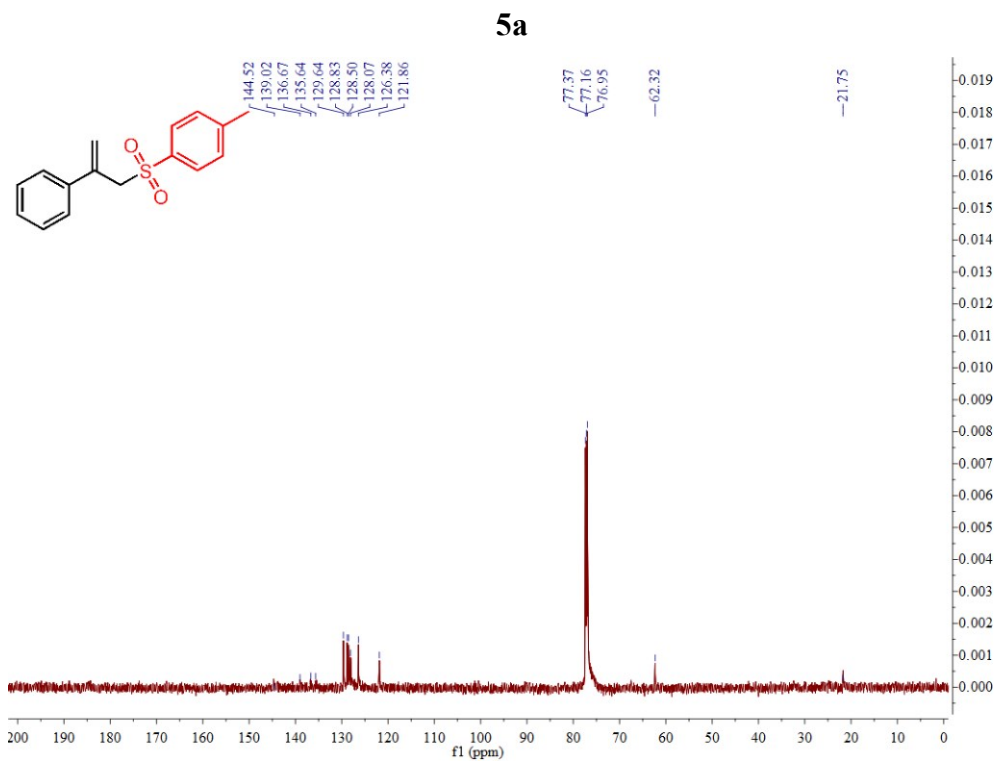
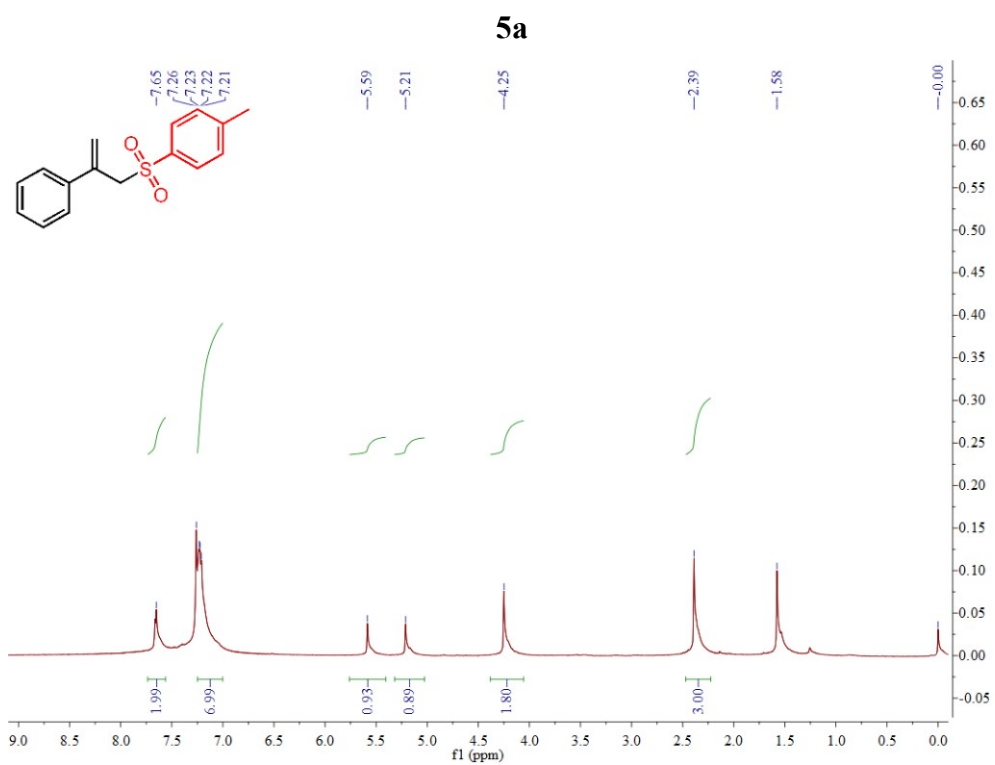


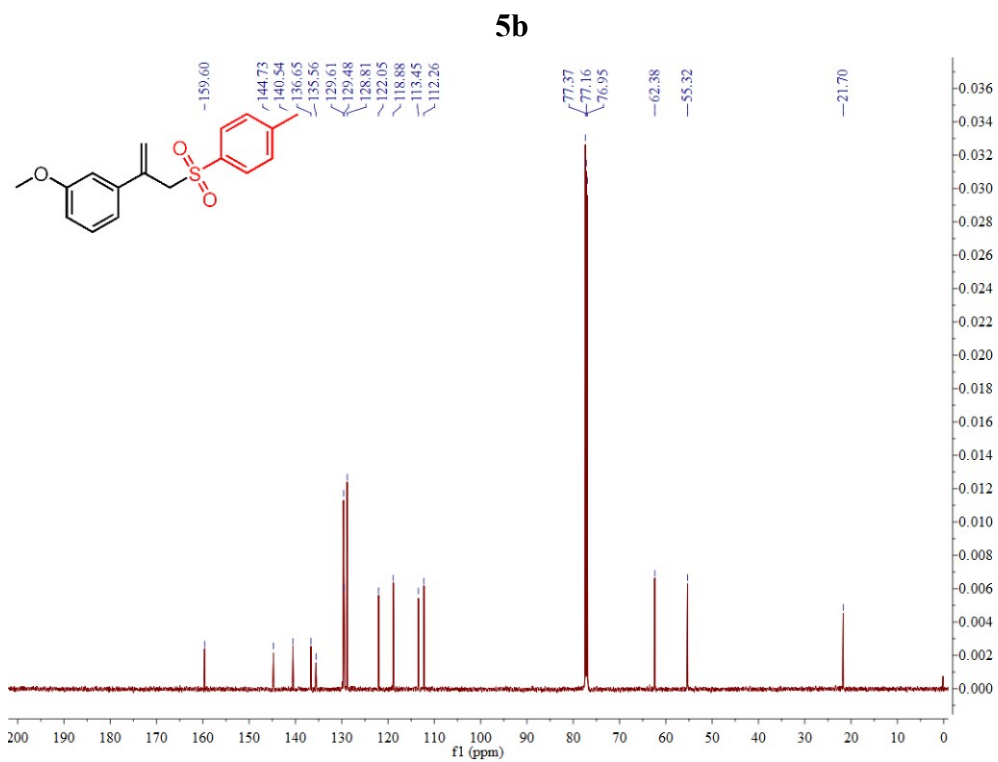
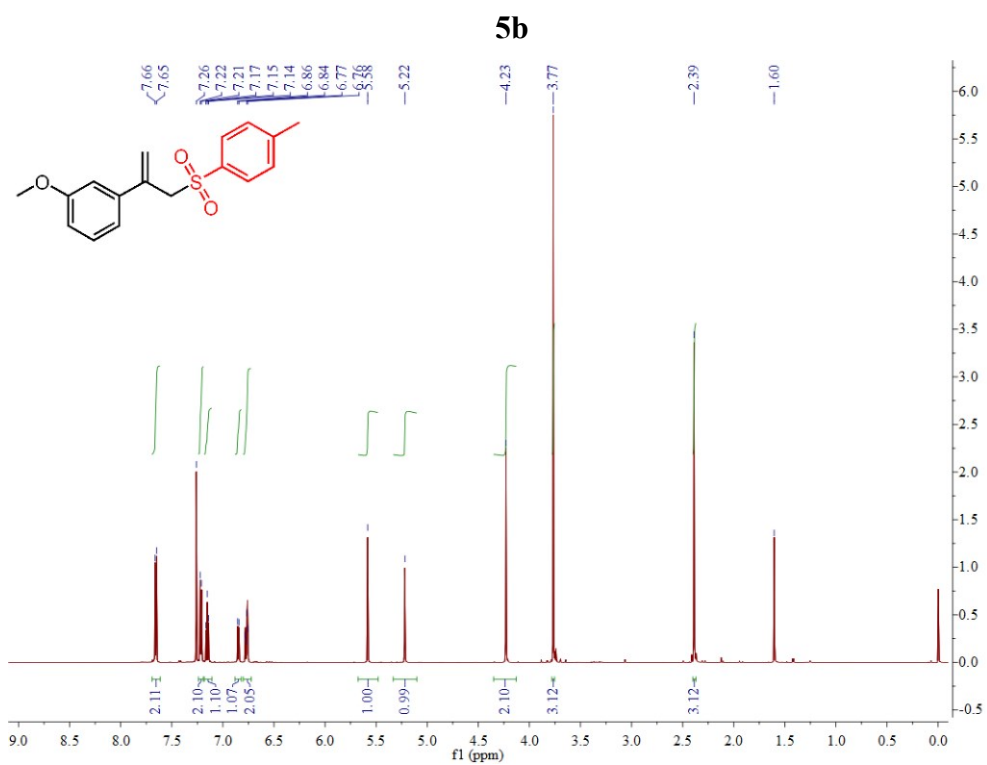


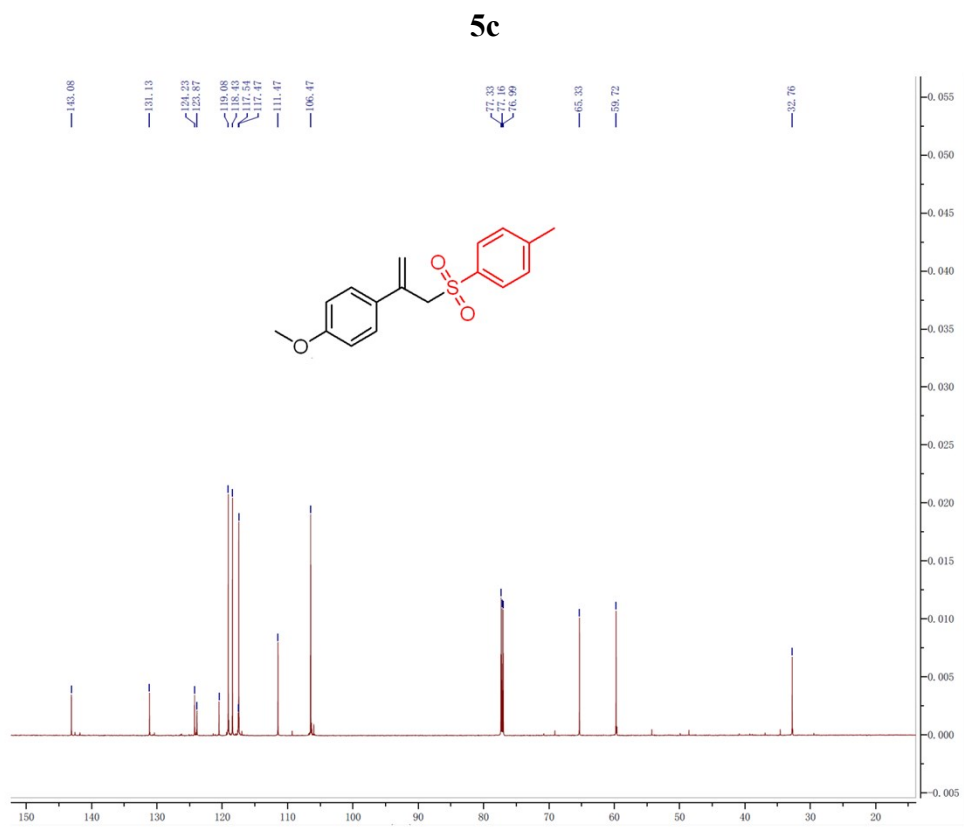
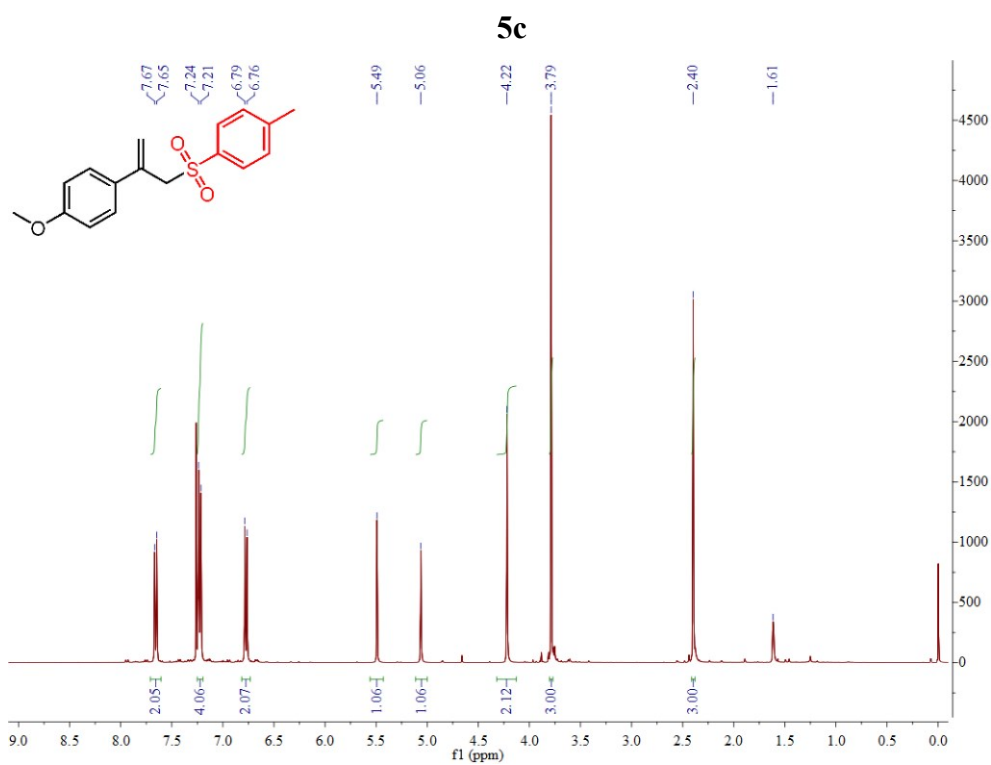


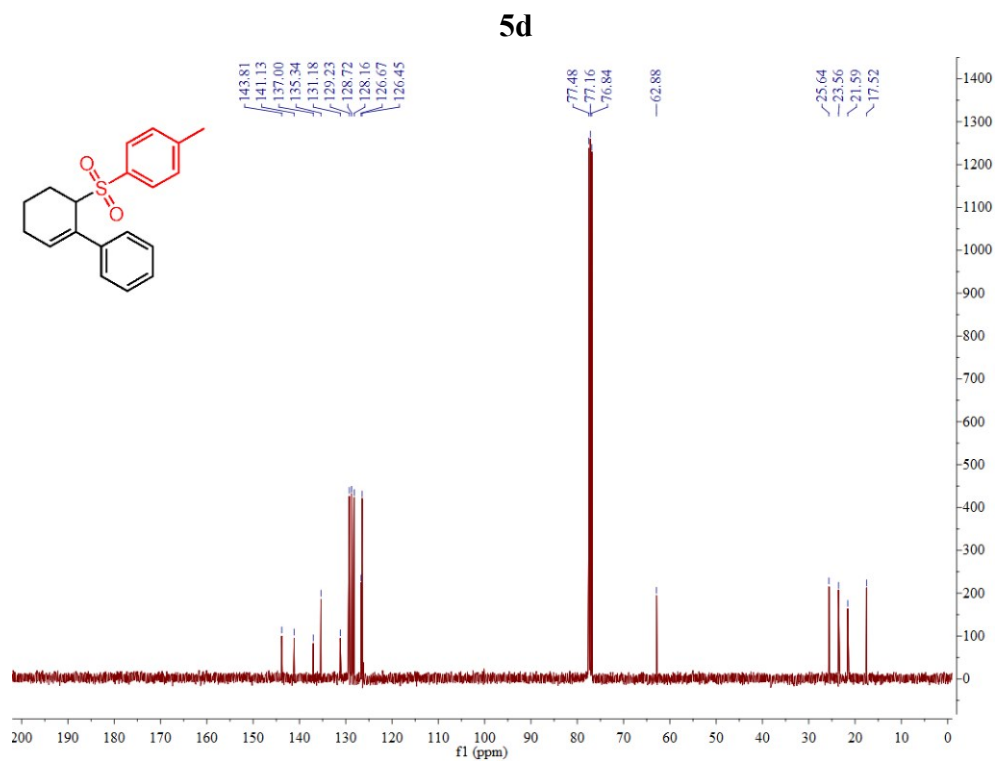
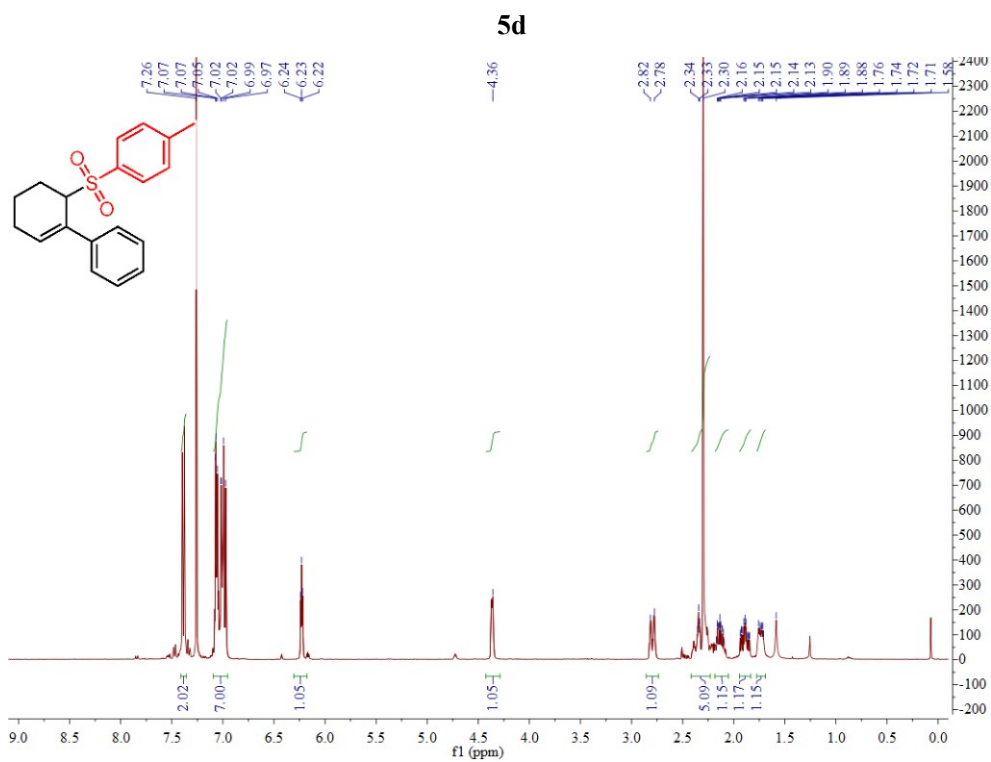


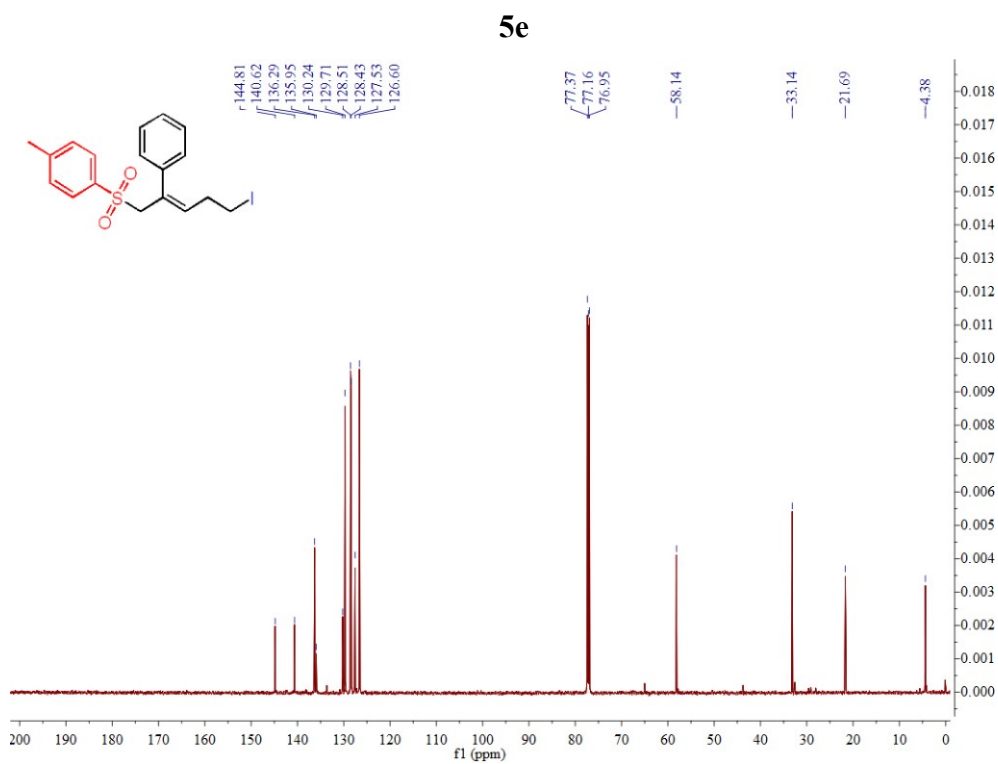
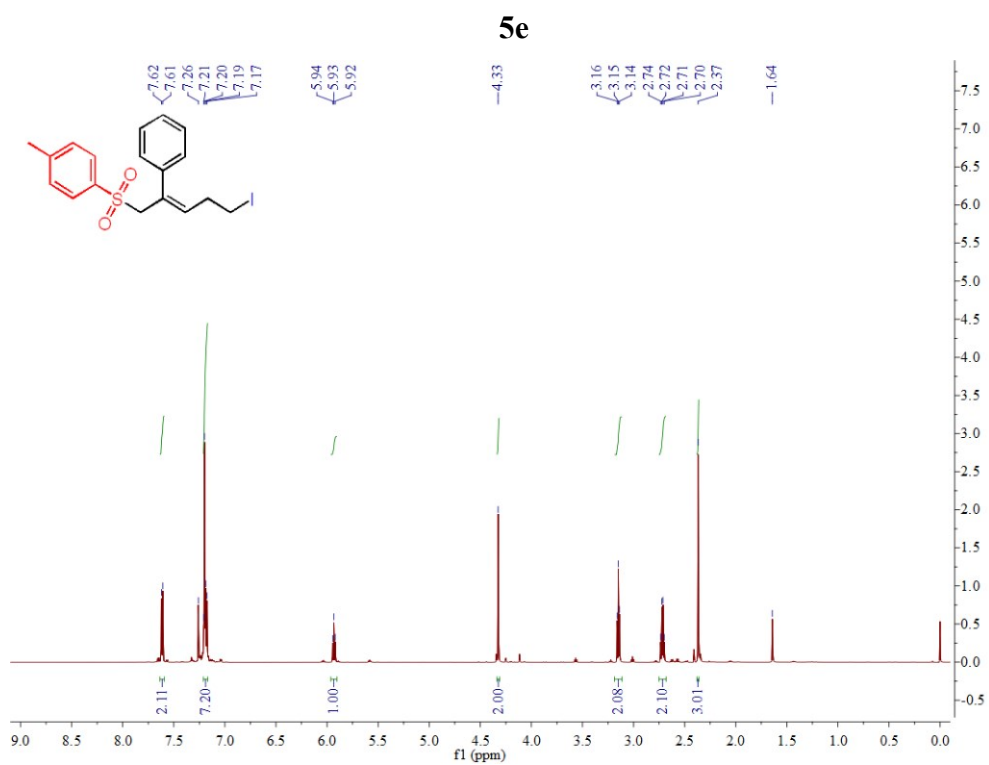


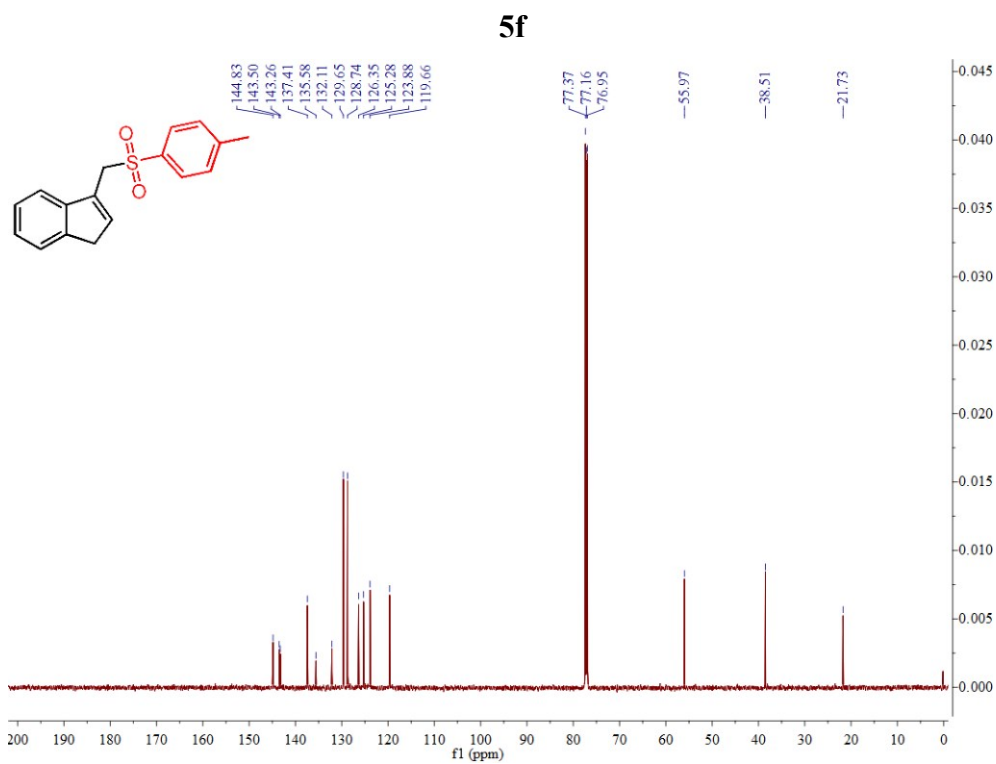
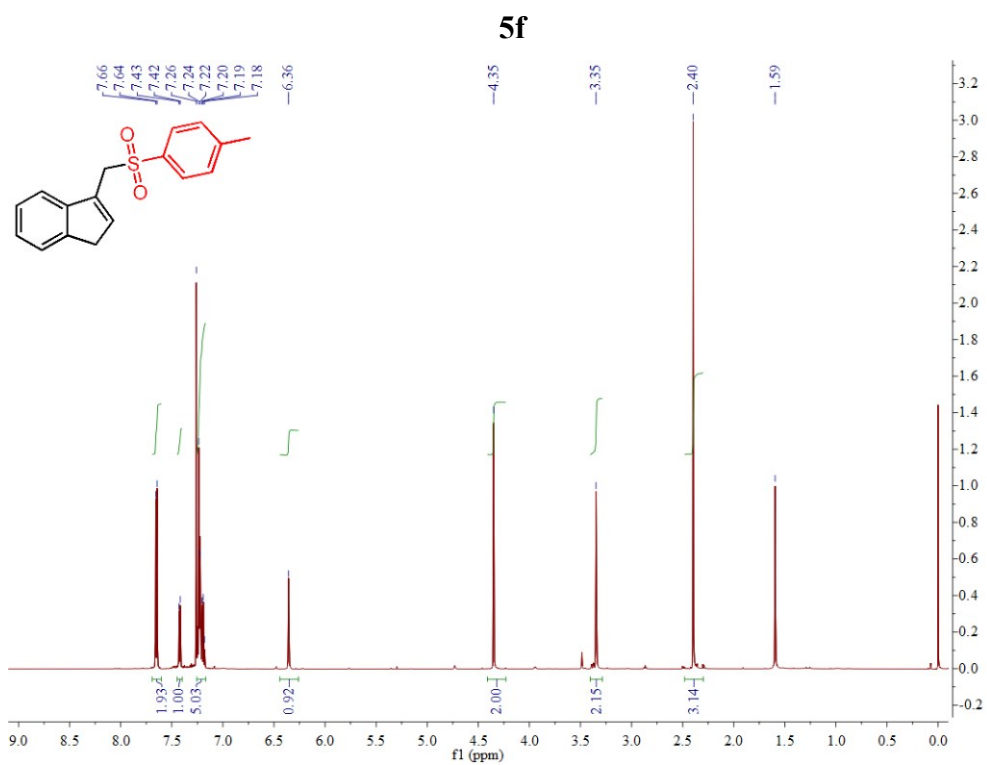




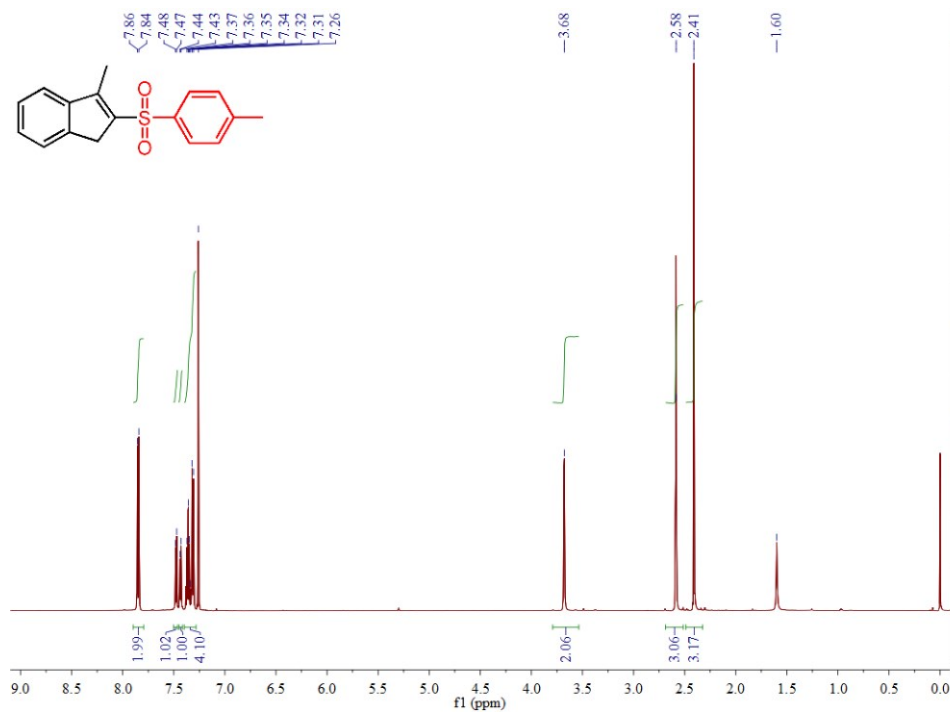




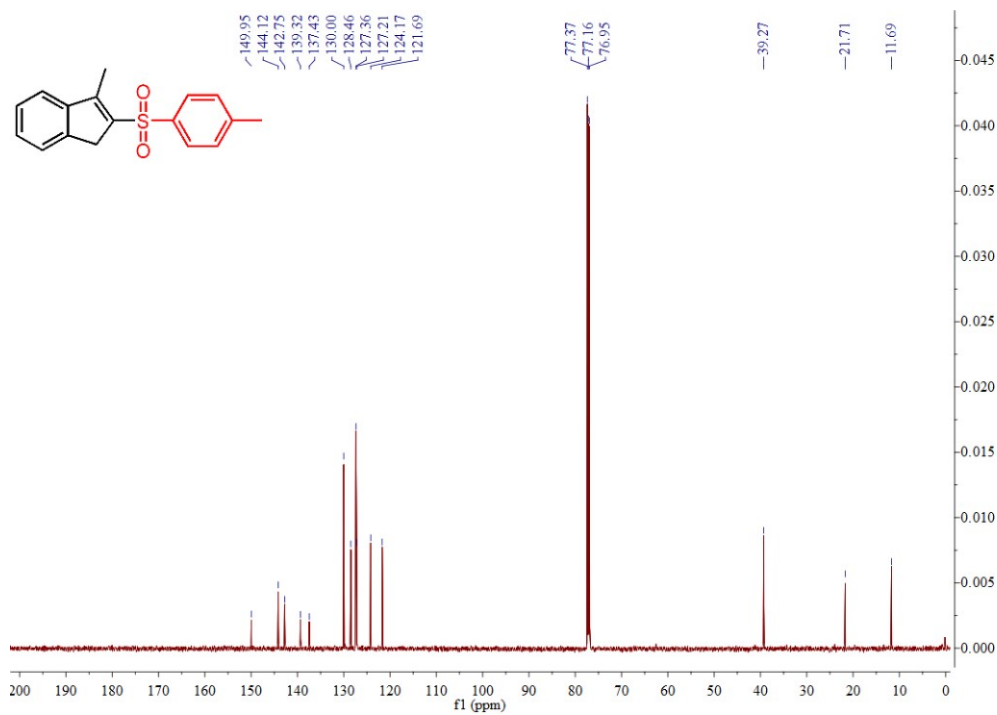




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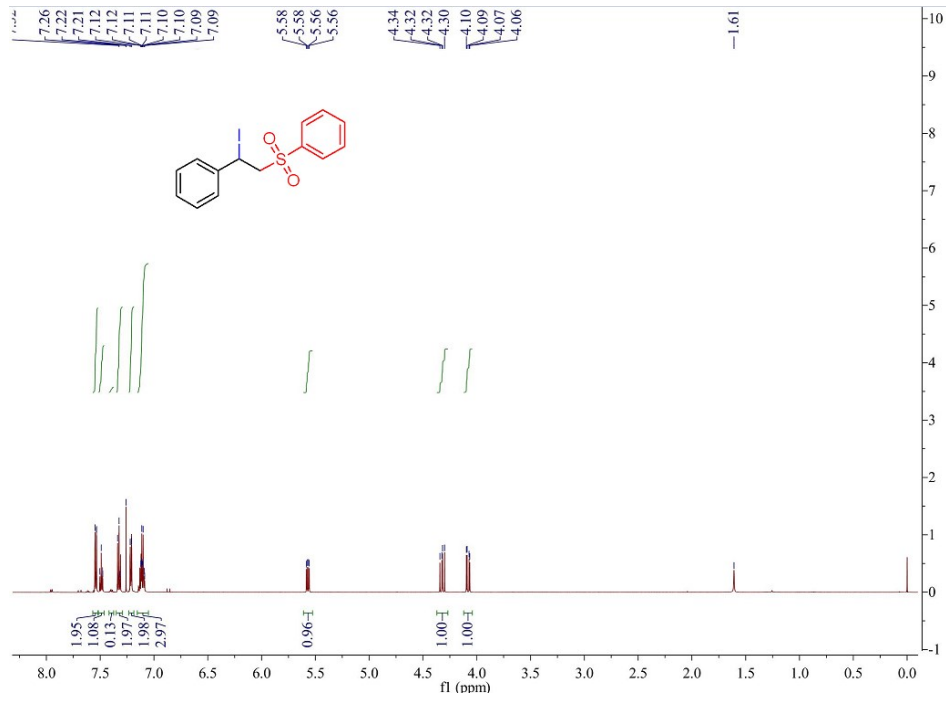


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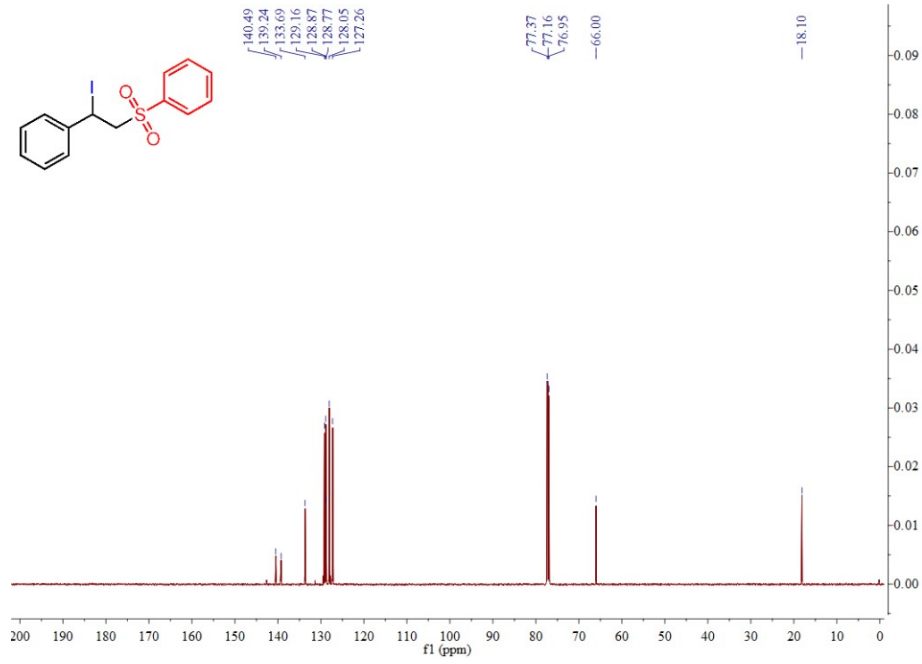


S52

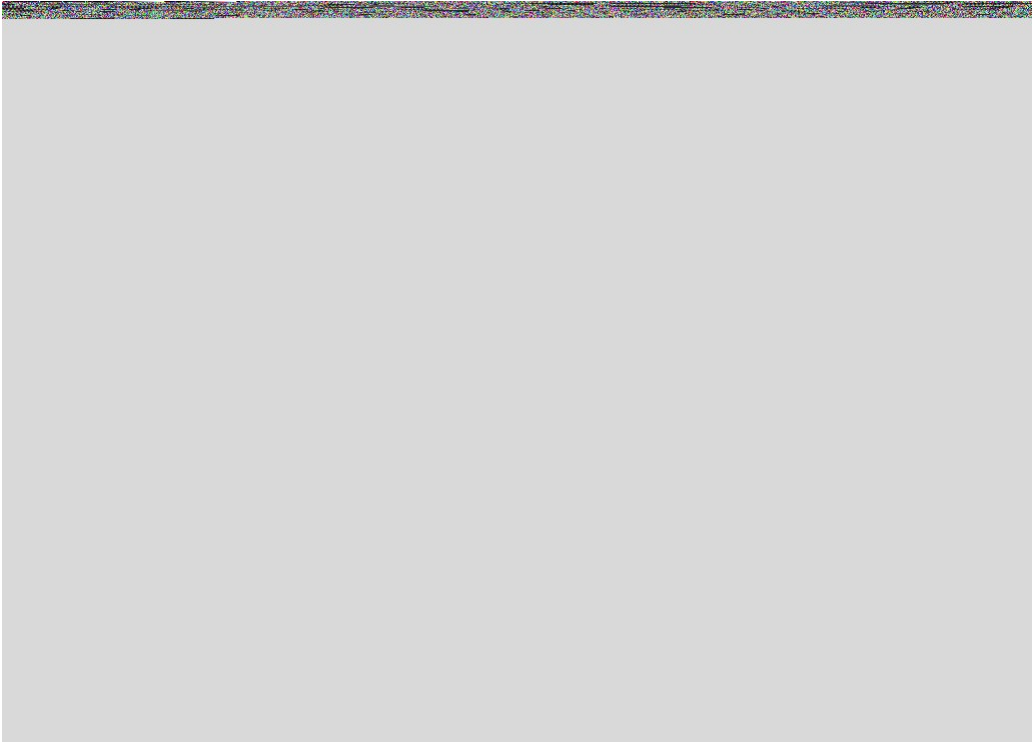
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6a



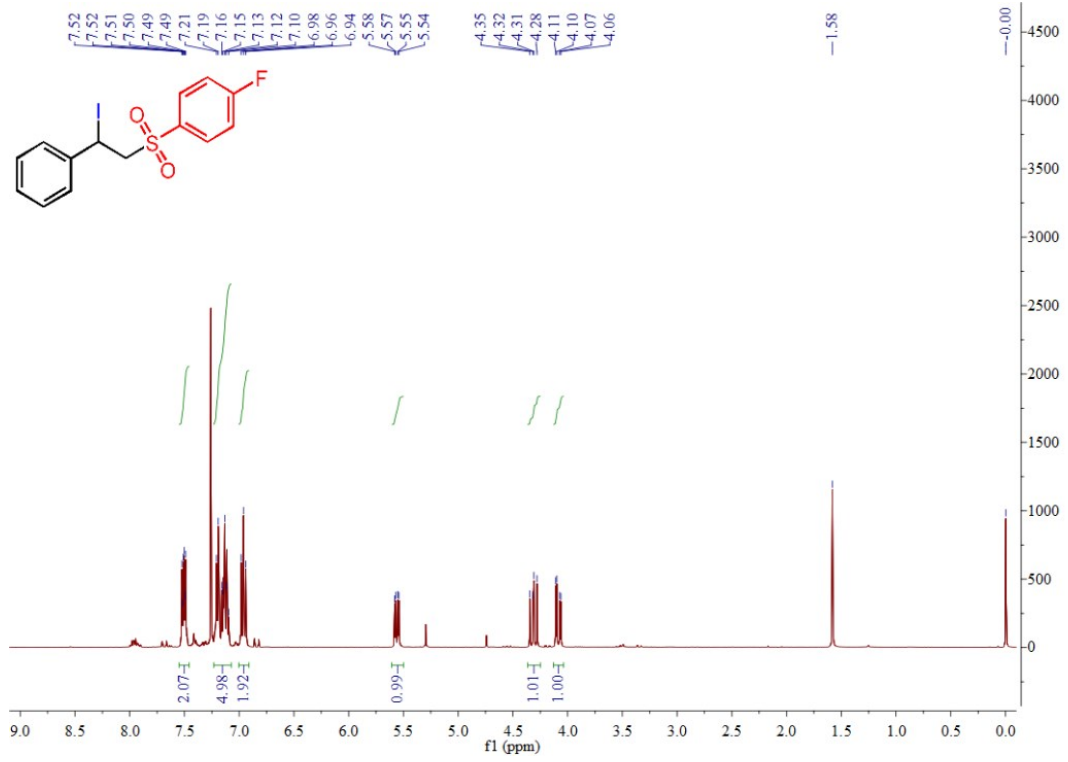
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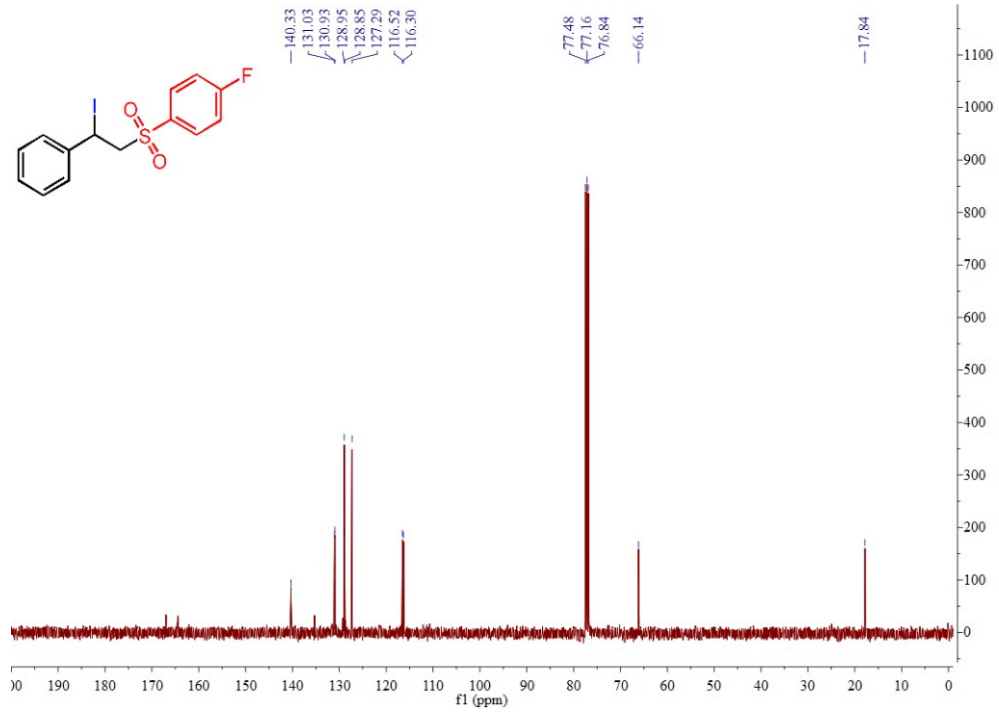
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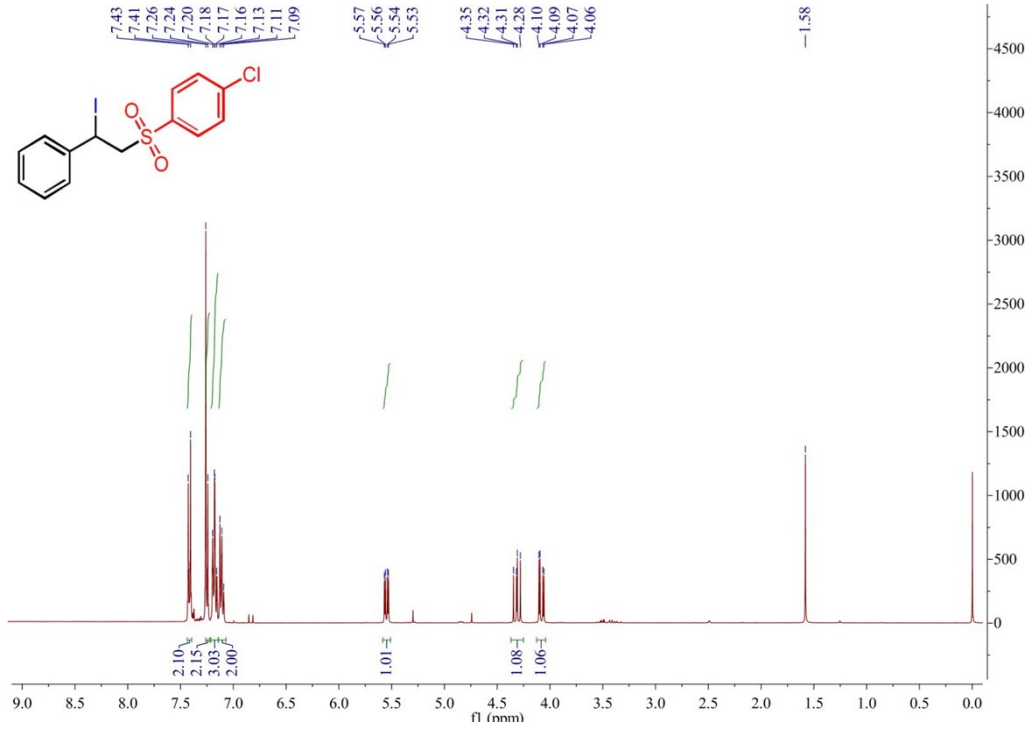
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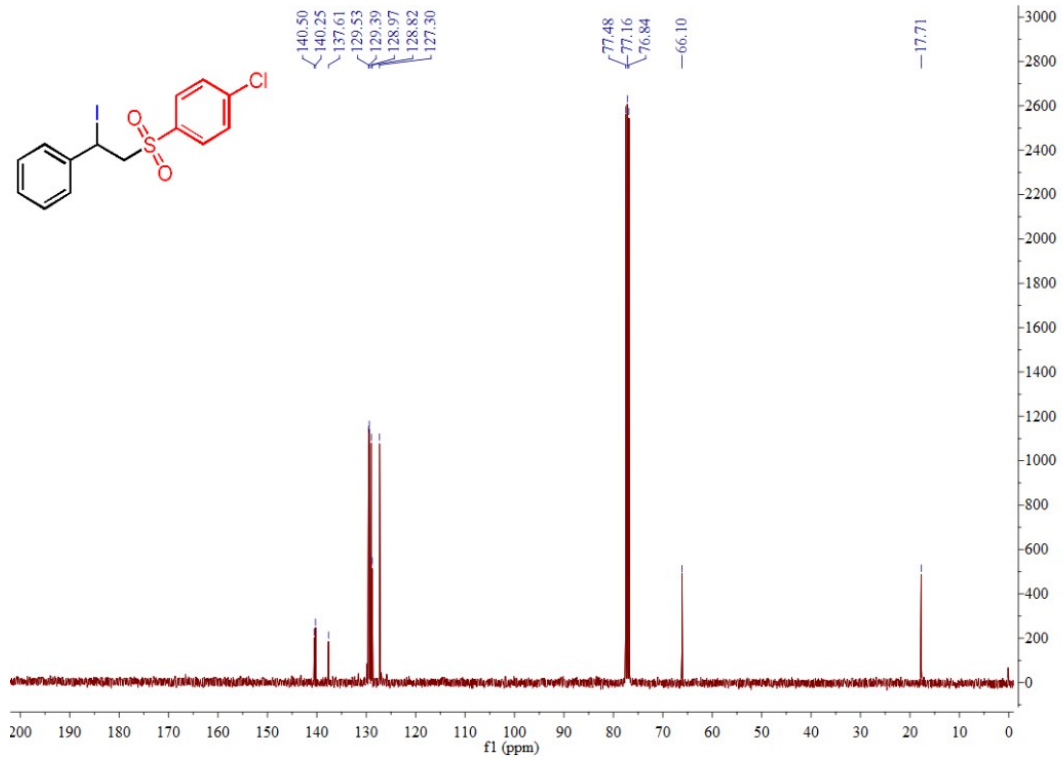
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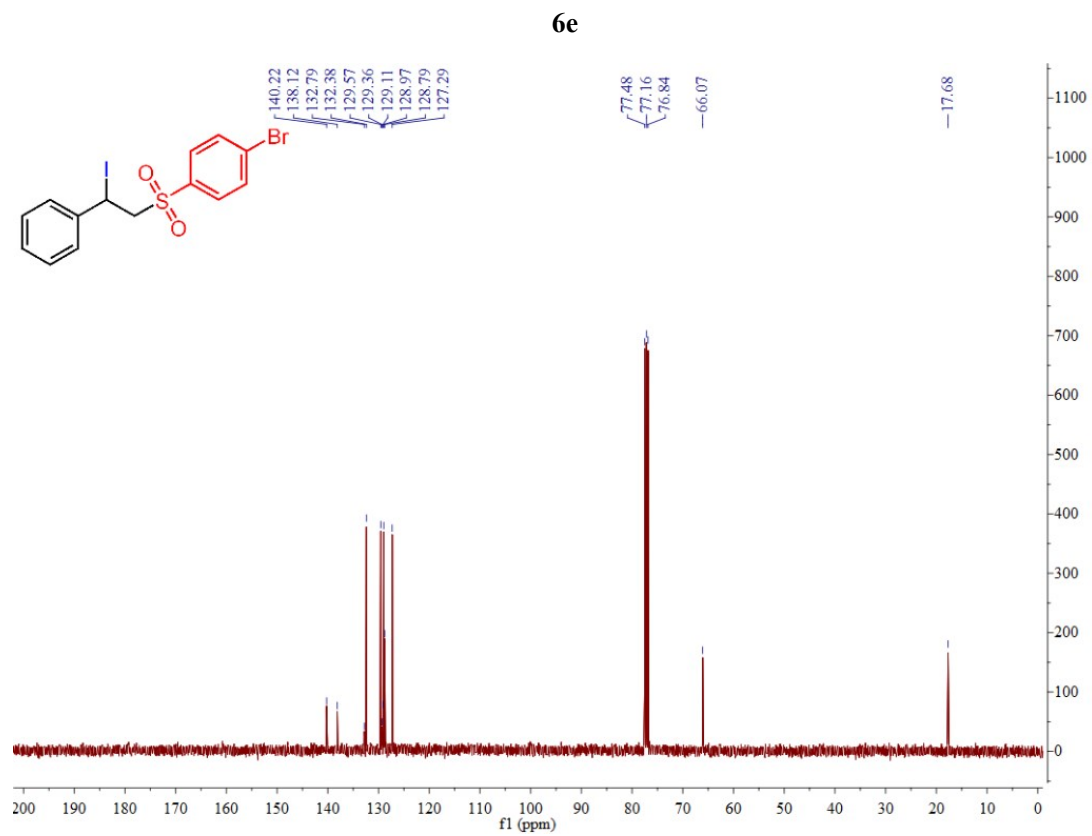
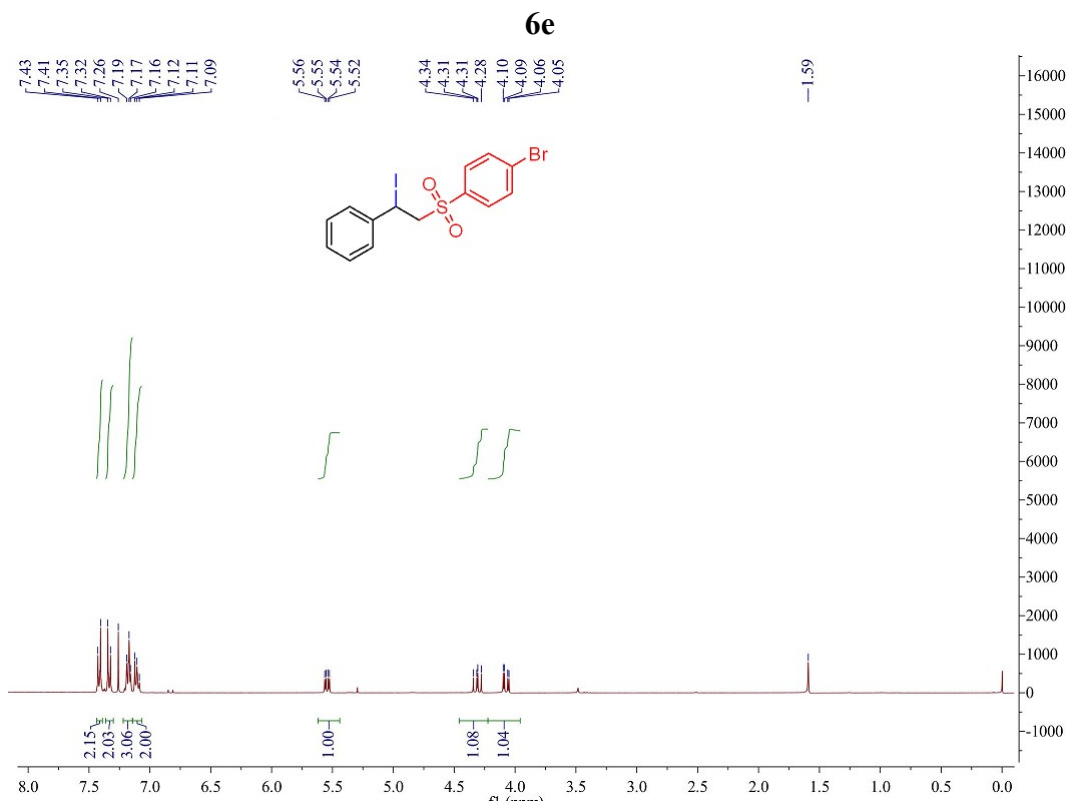


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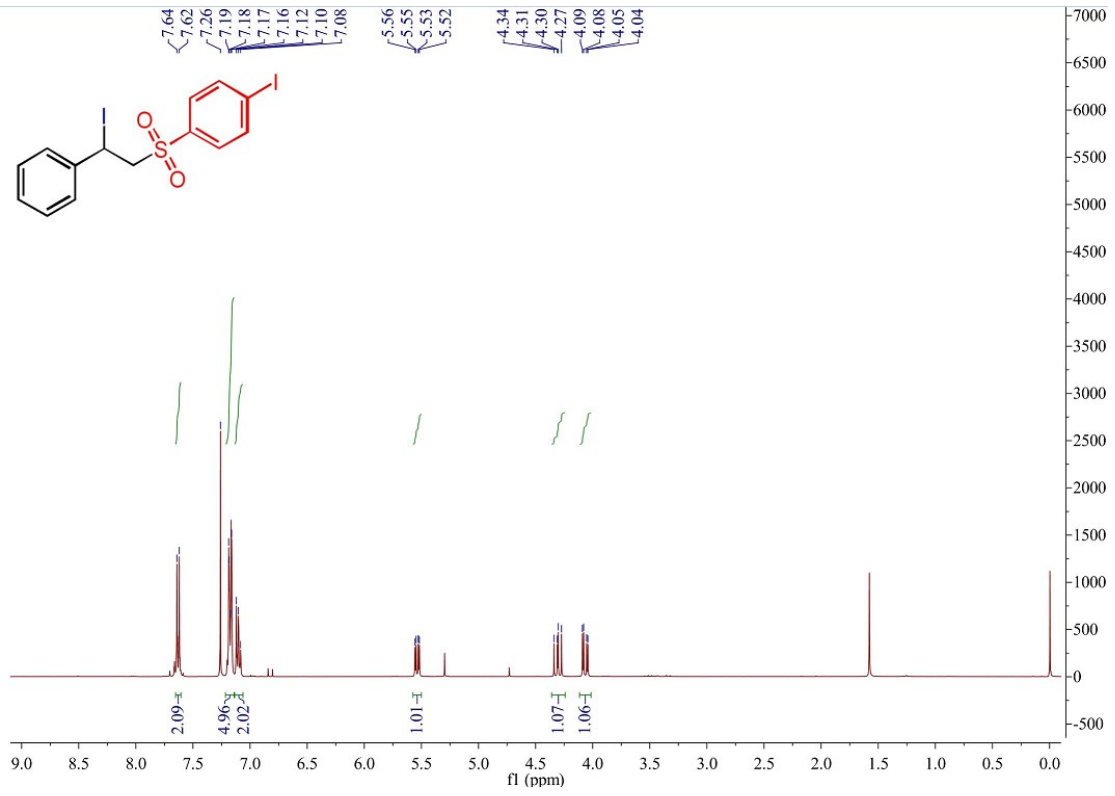


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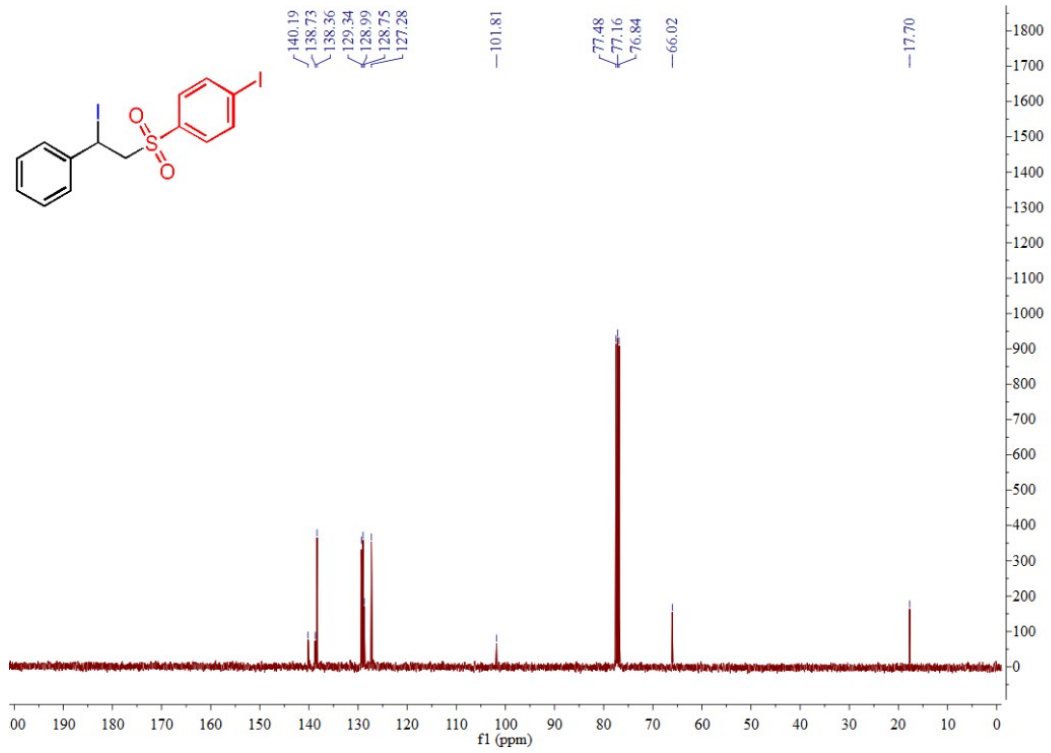


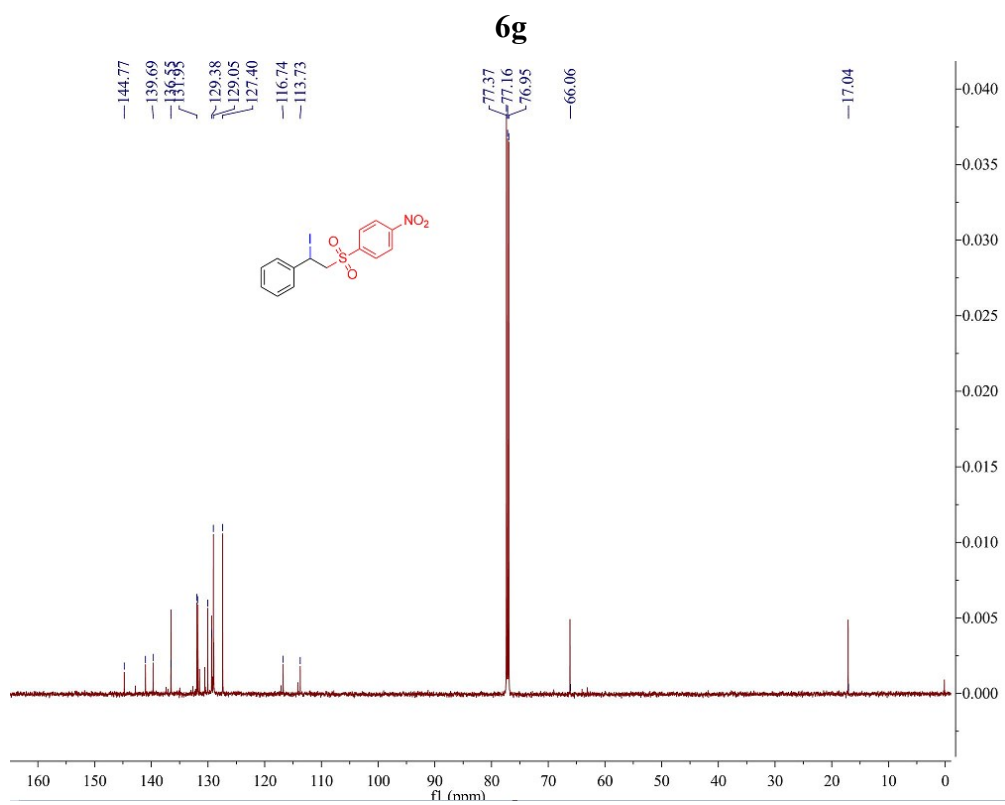
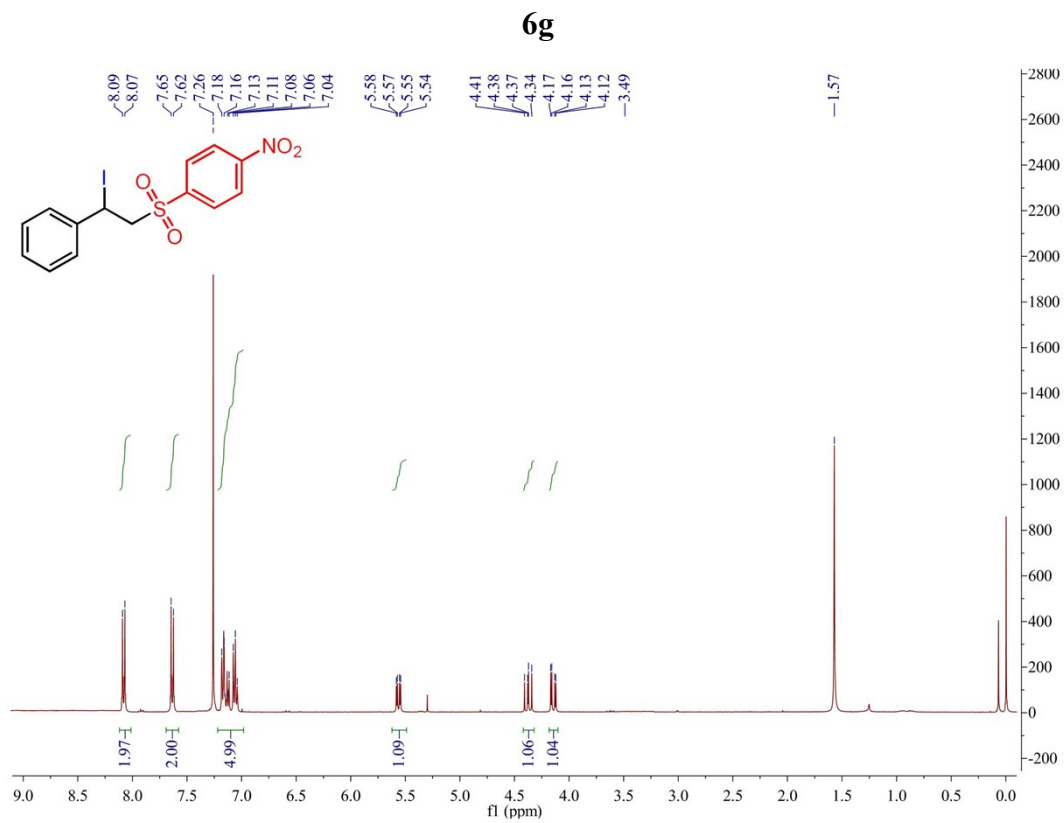


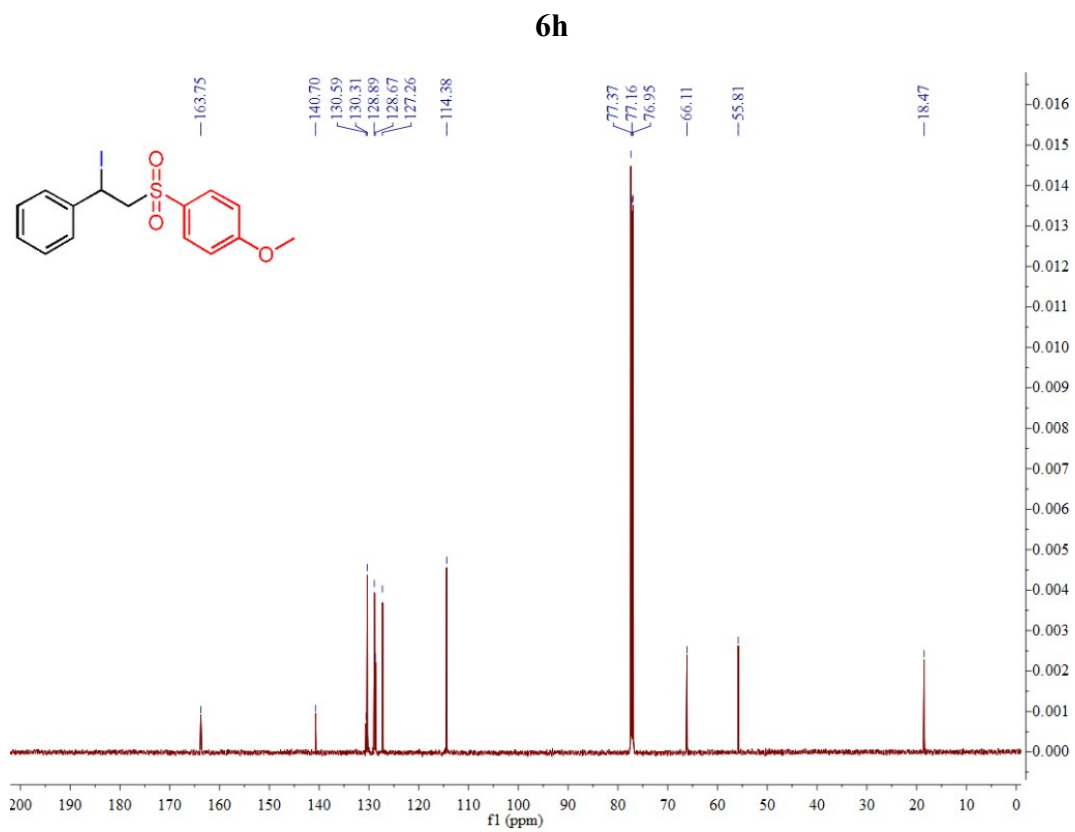
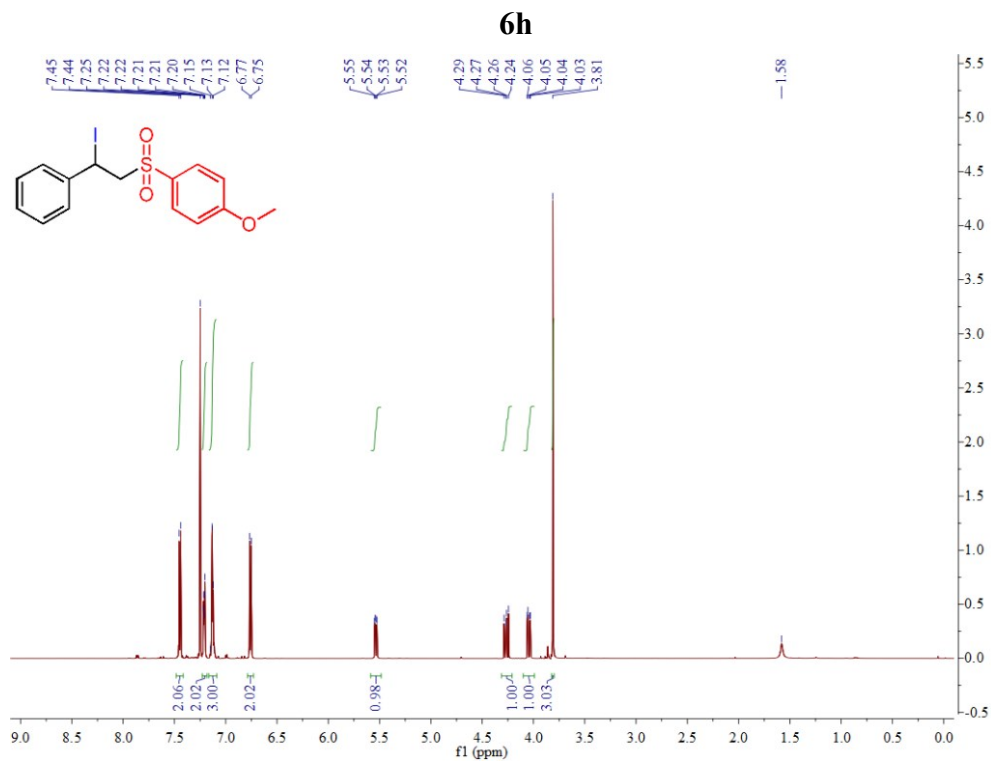
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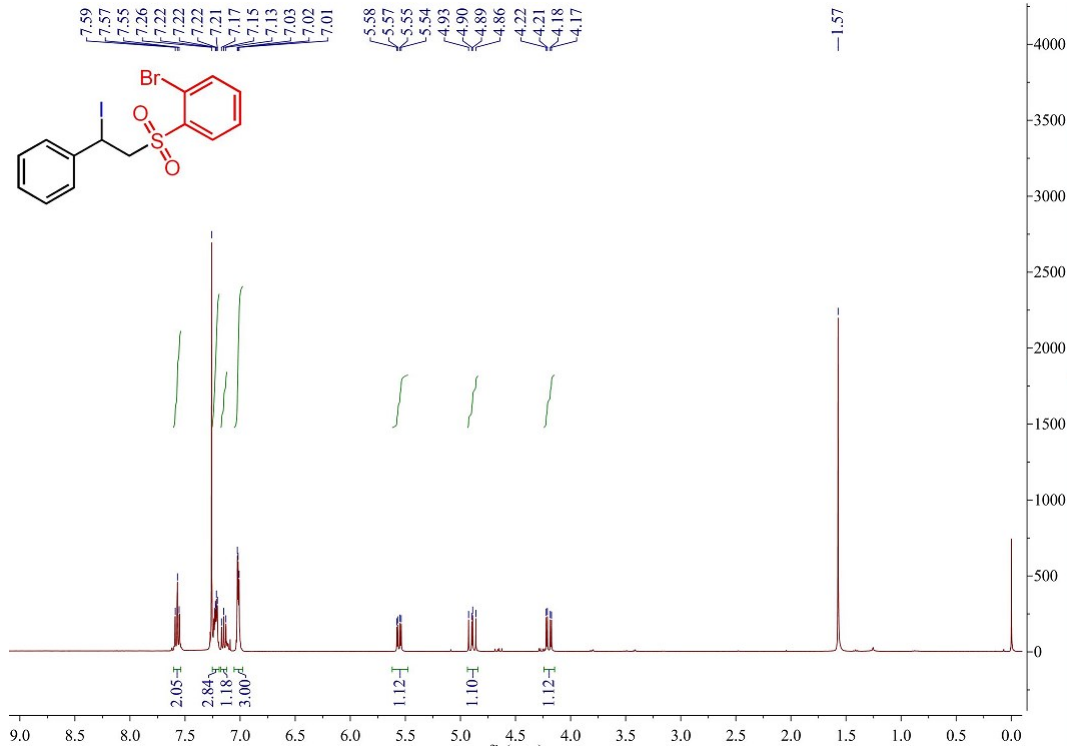
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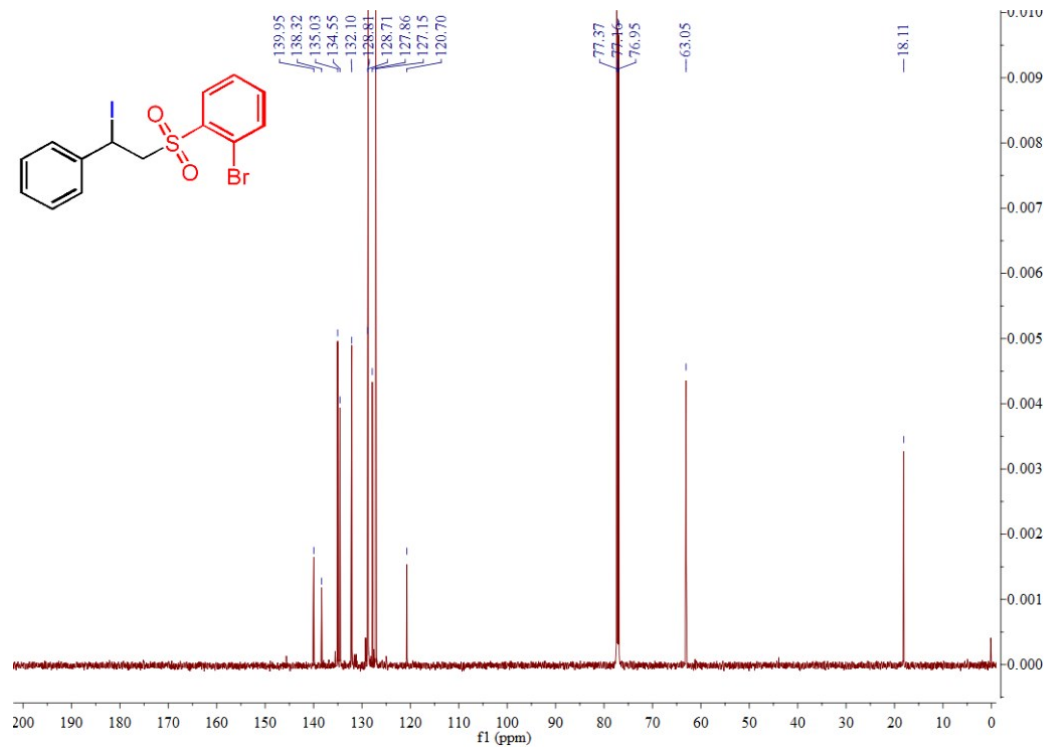


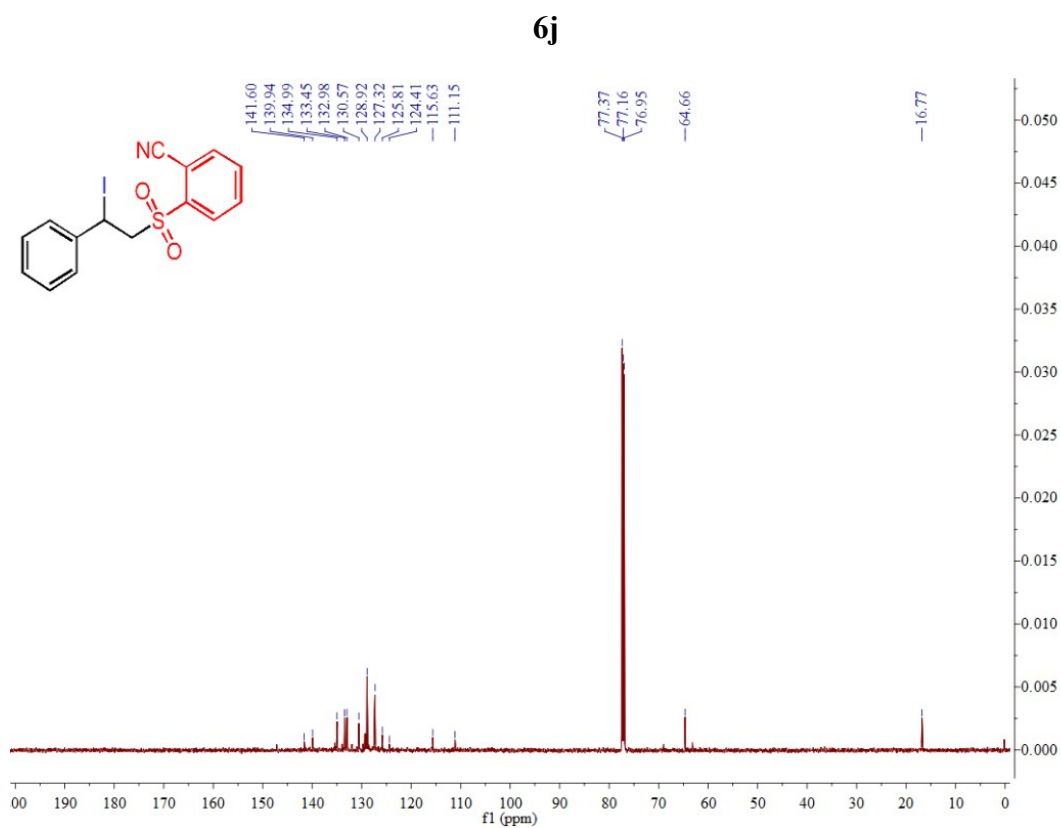
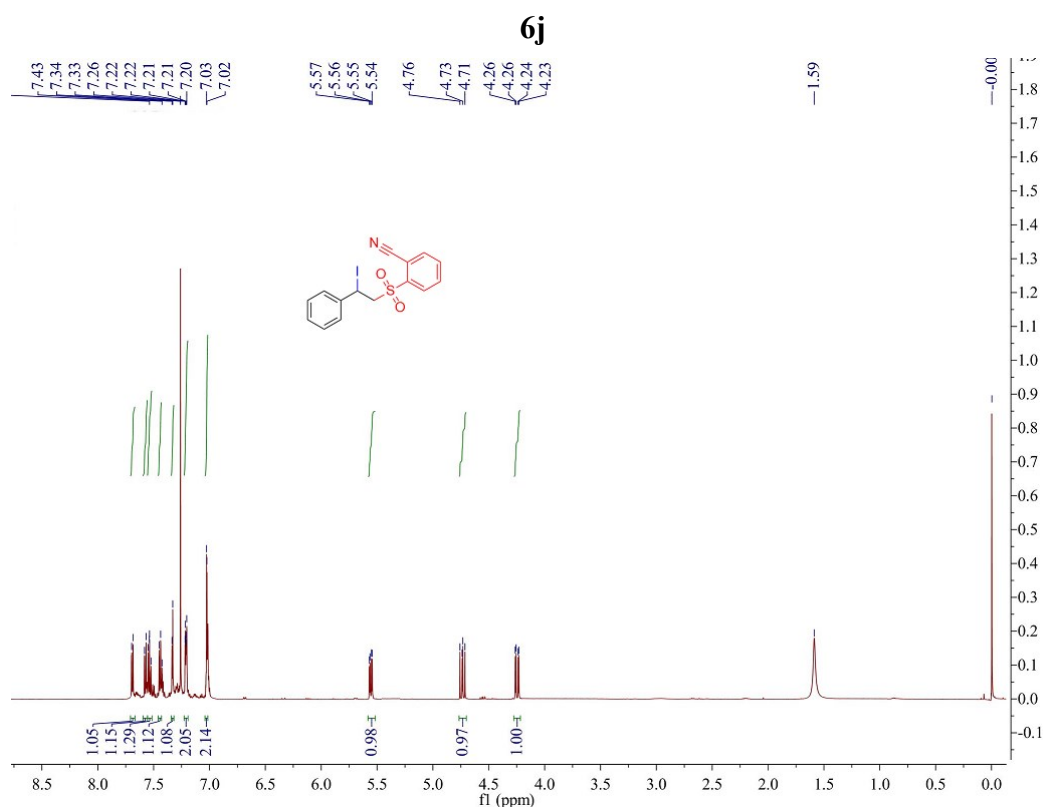


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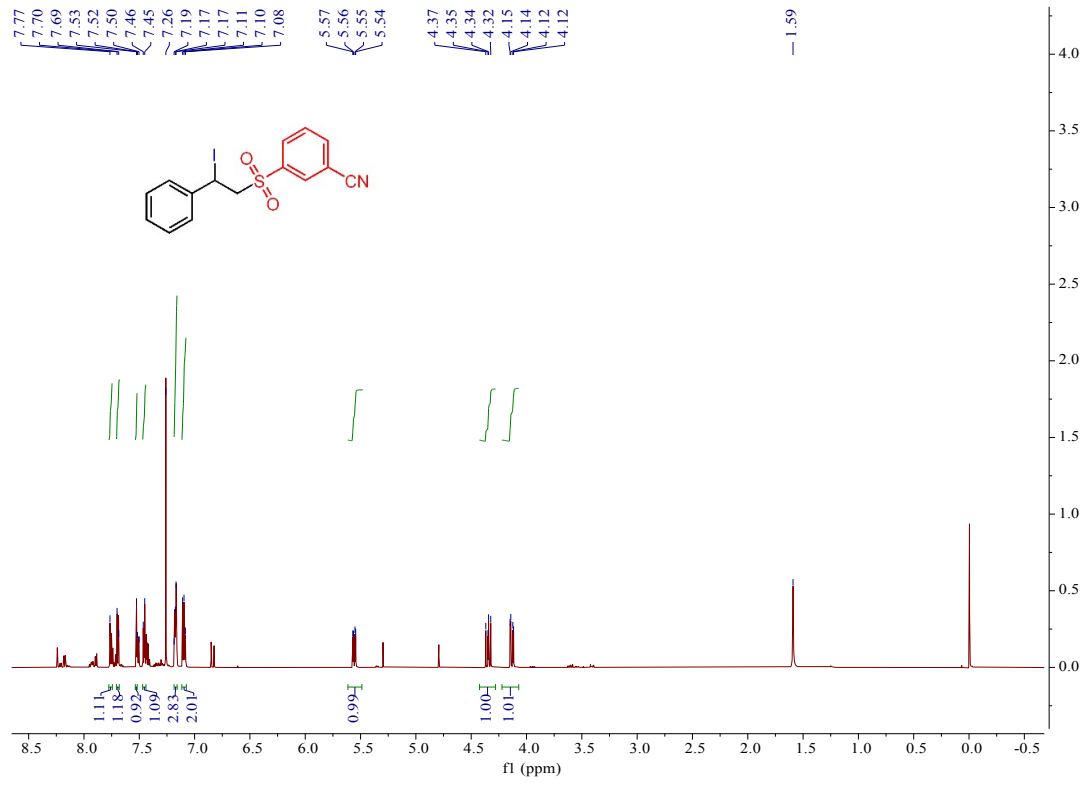


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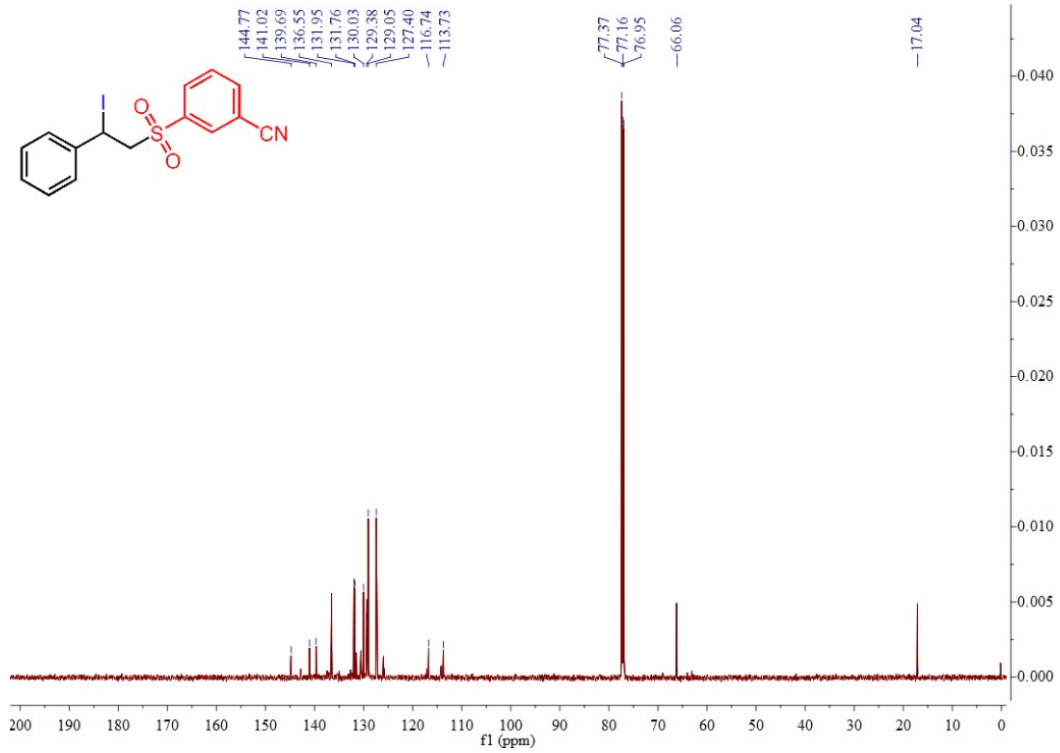




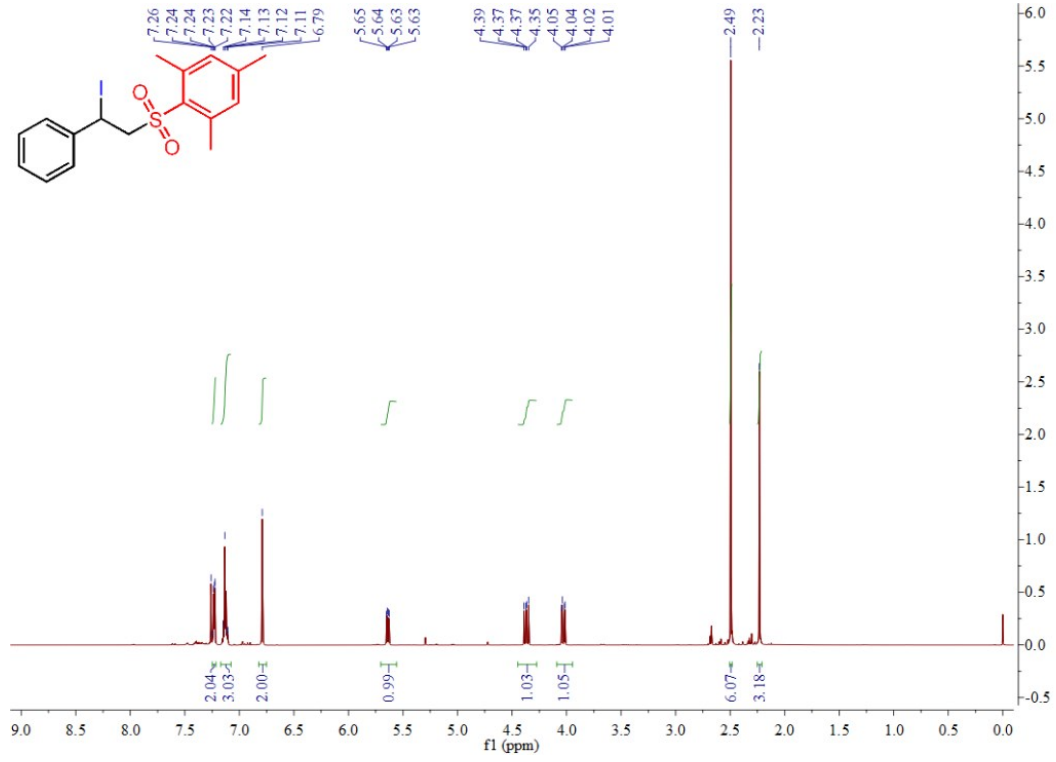
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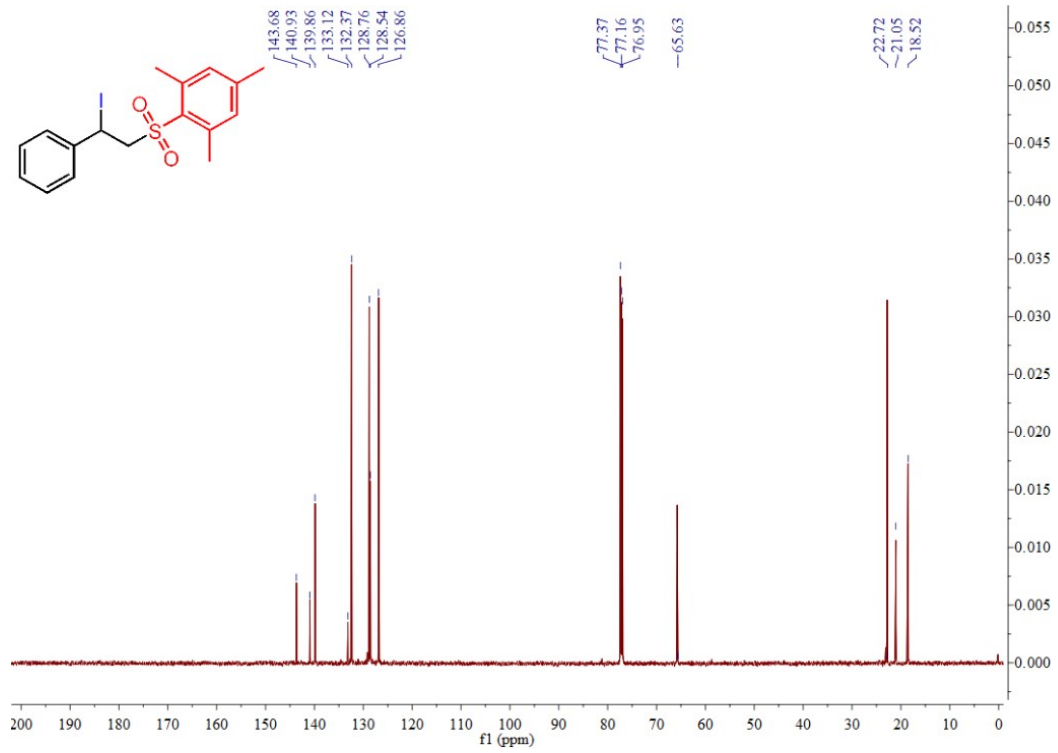
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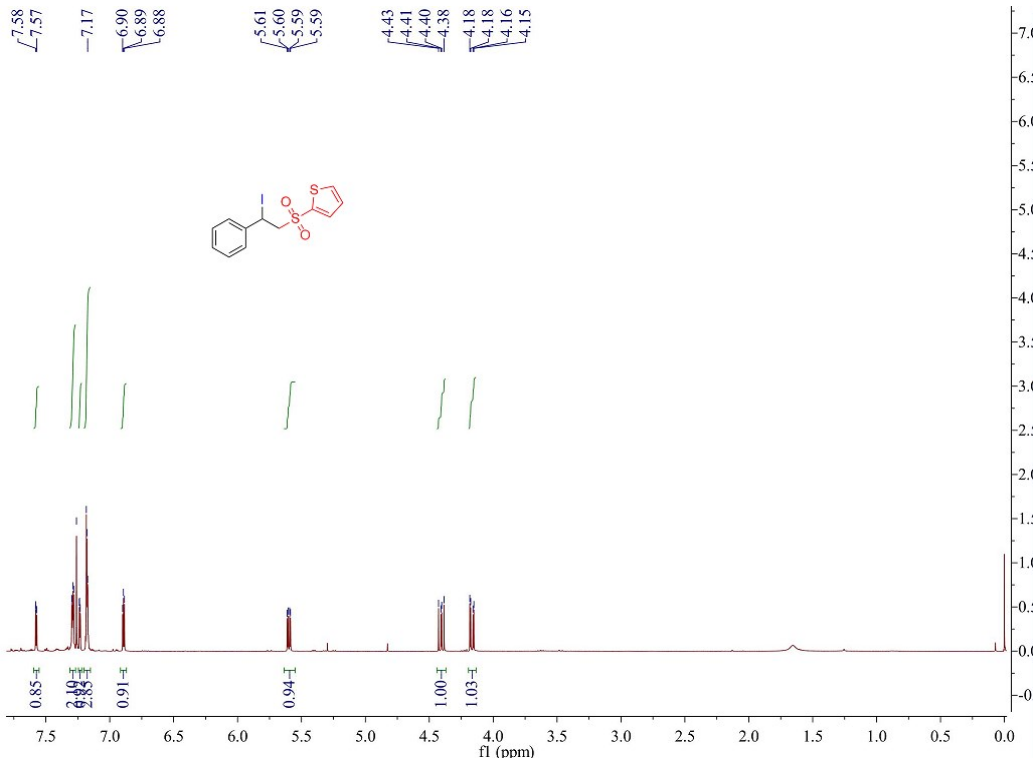
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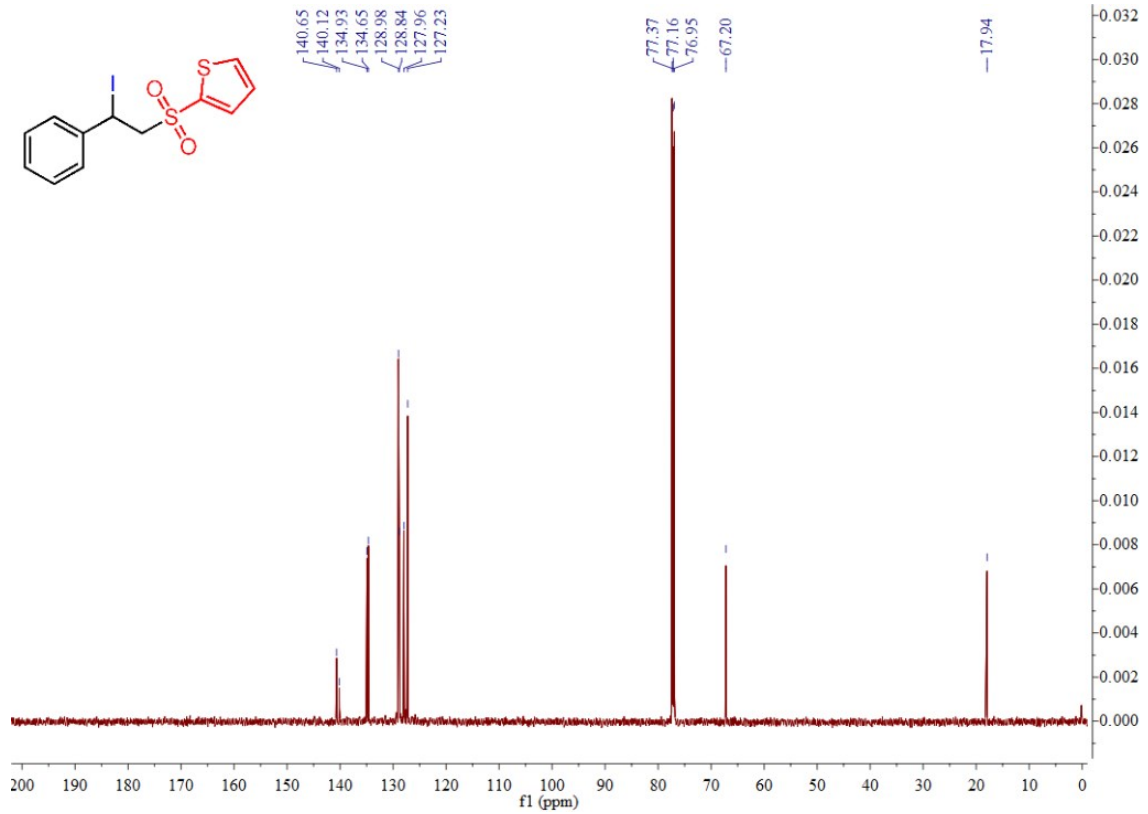
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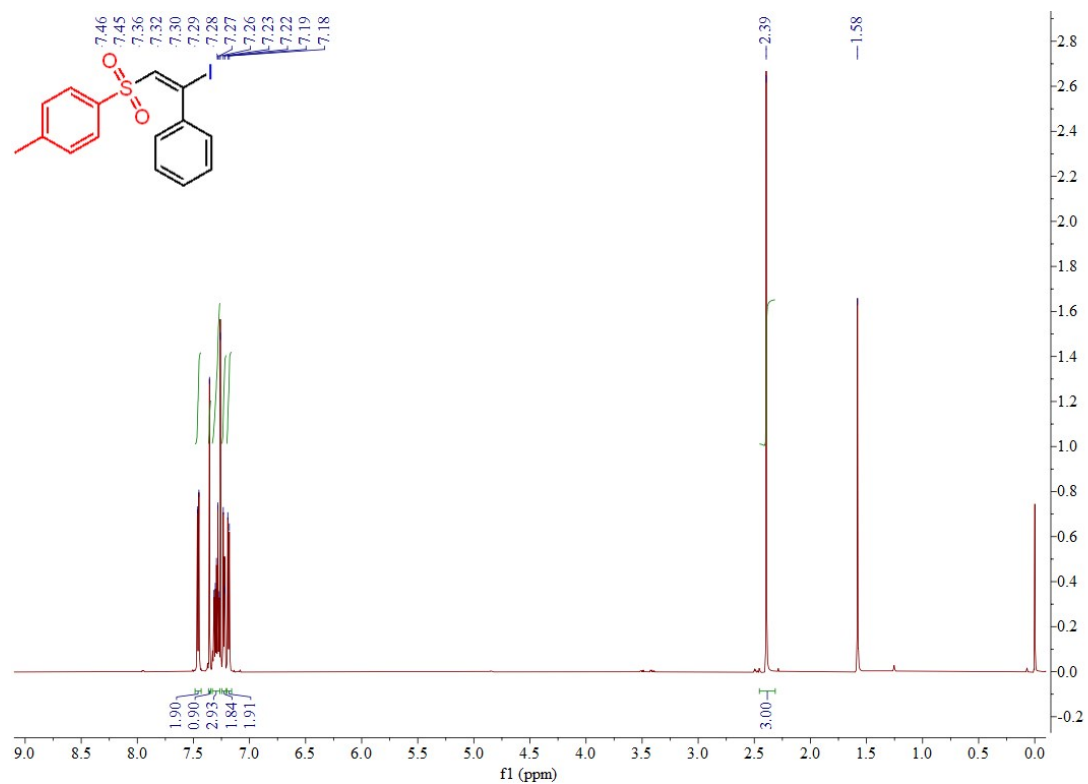
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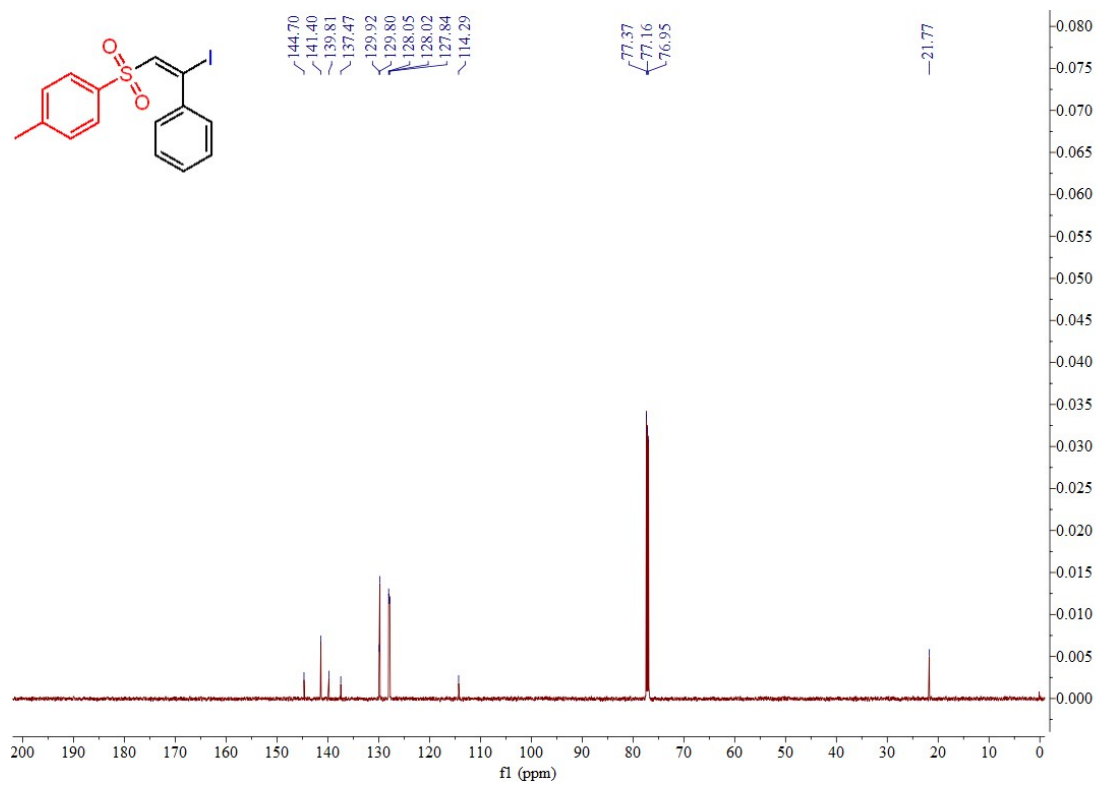
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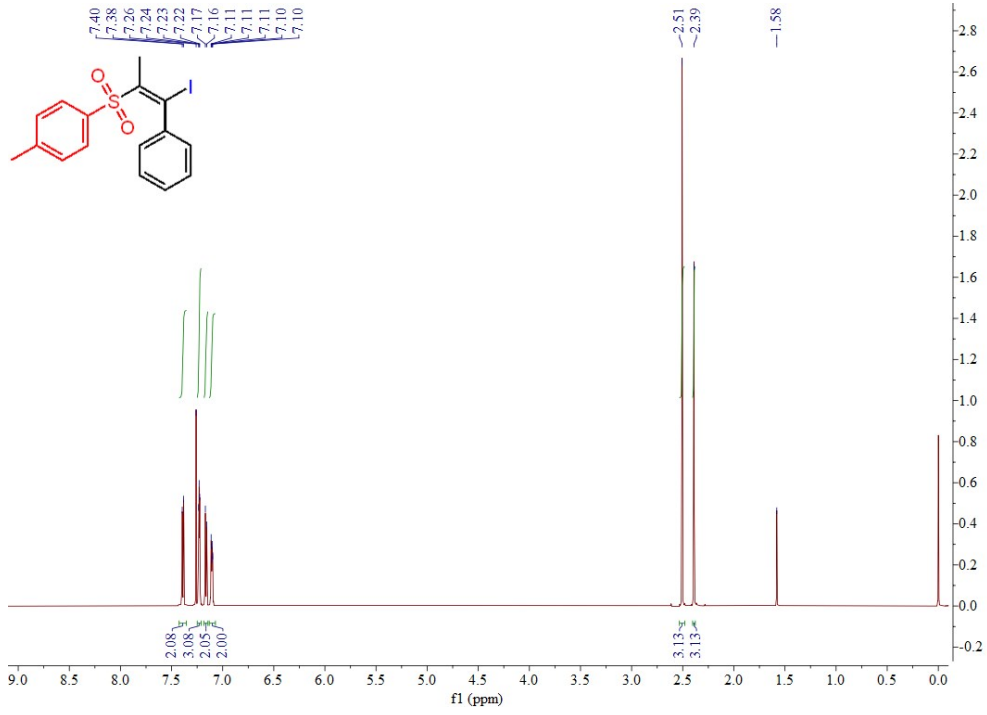
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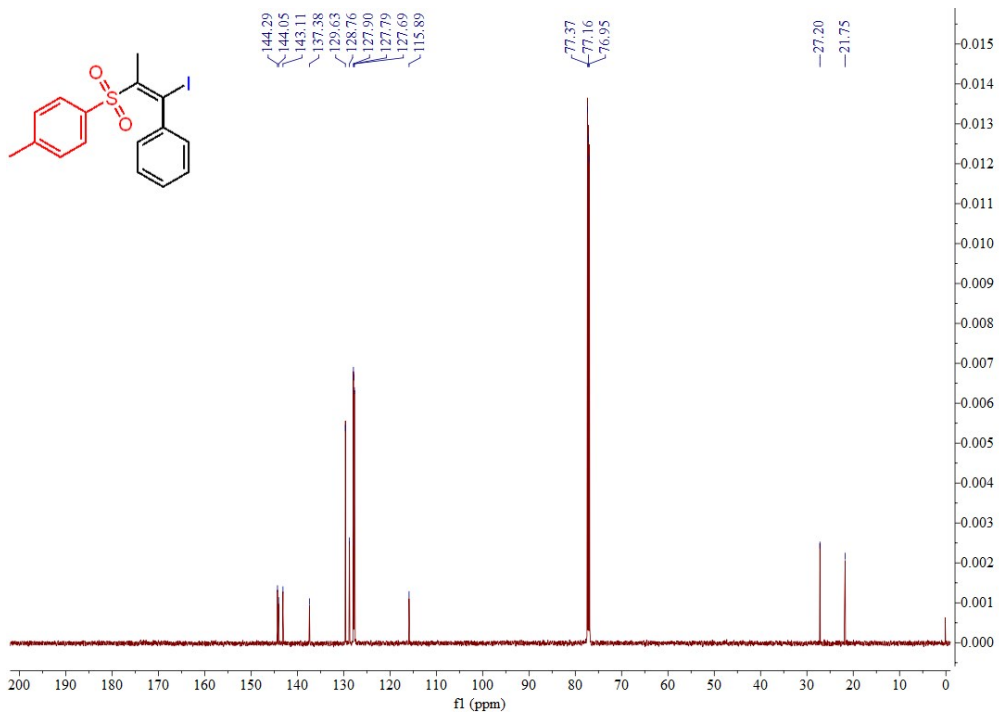
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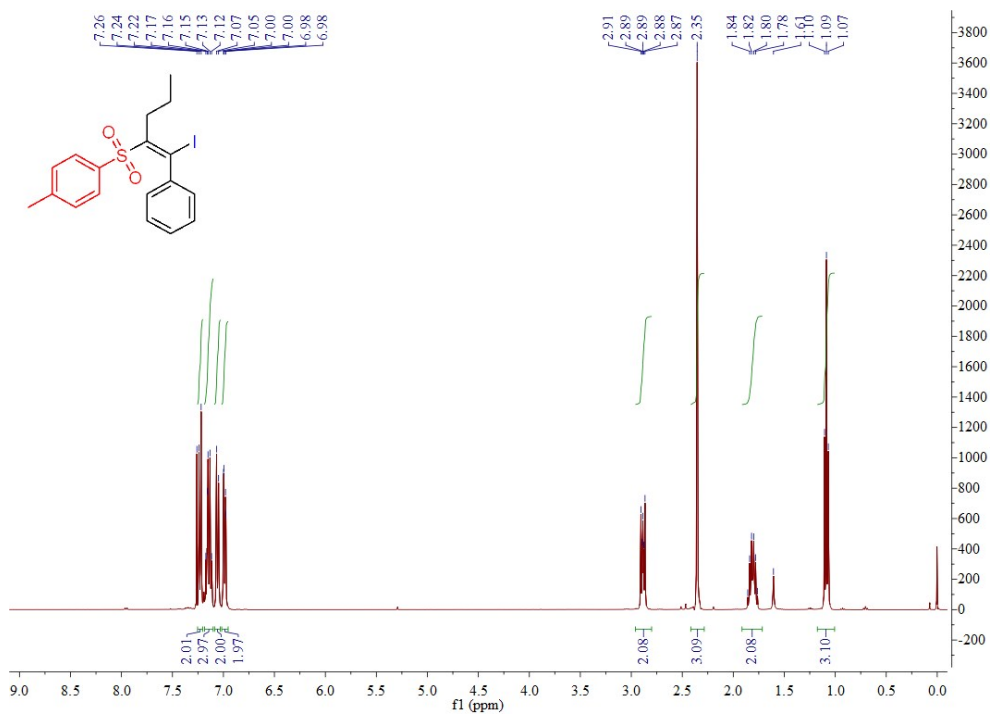
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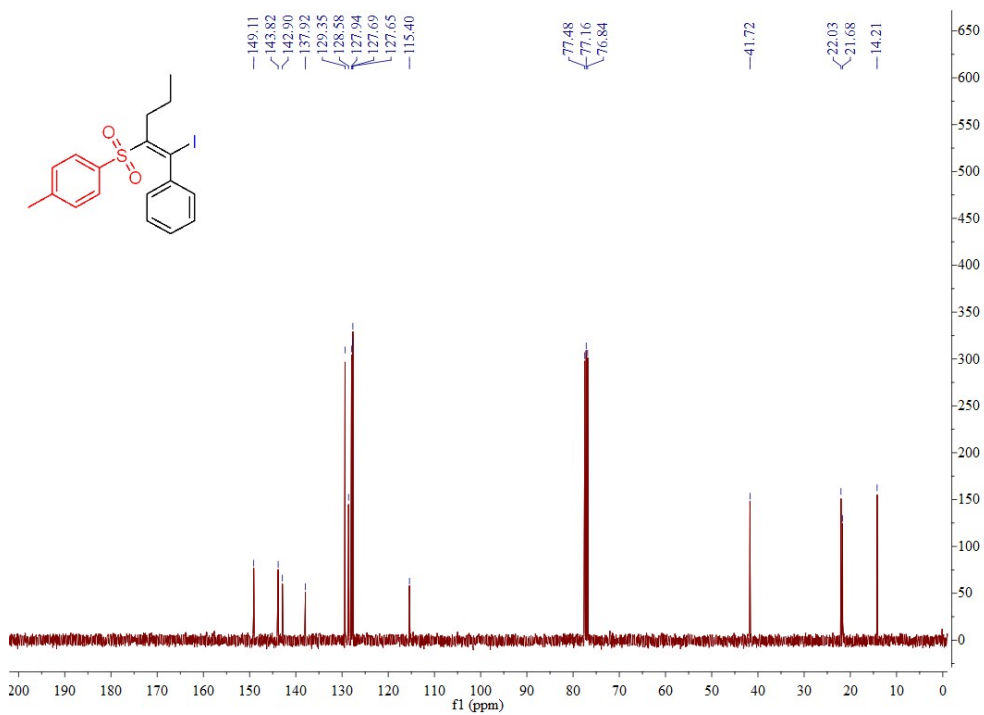
8b



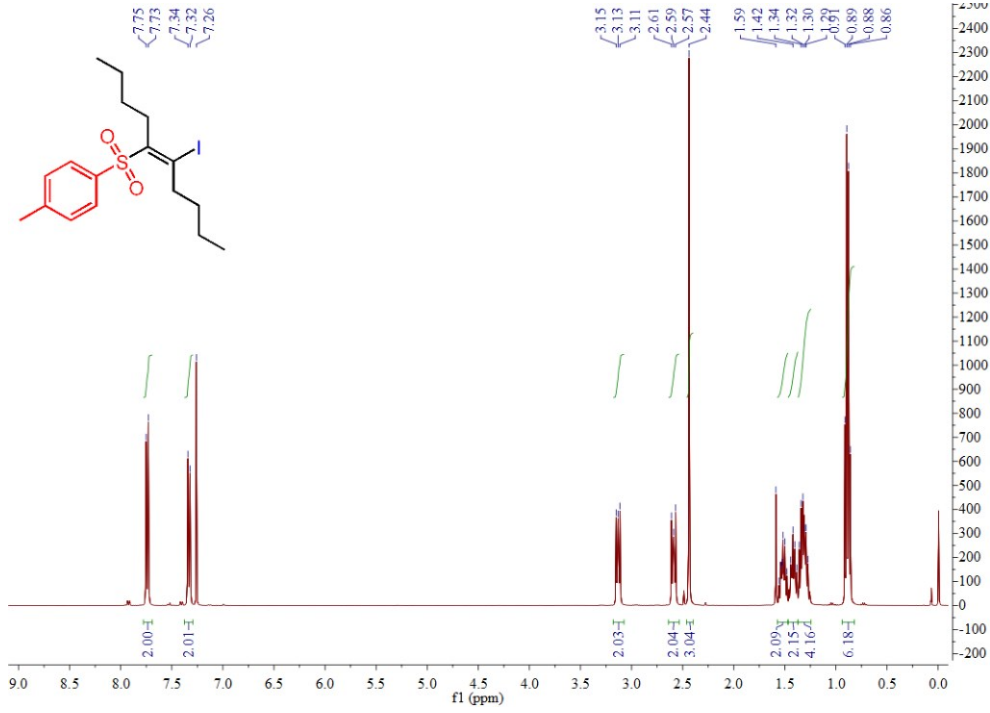
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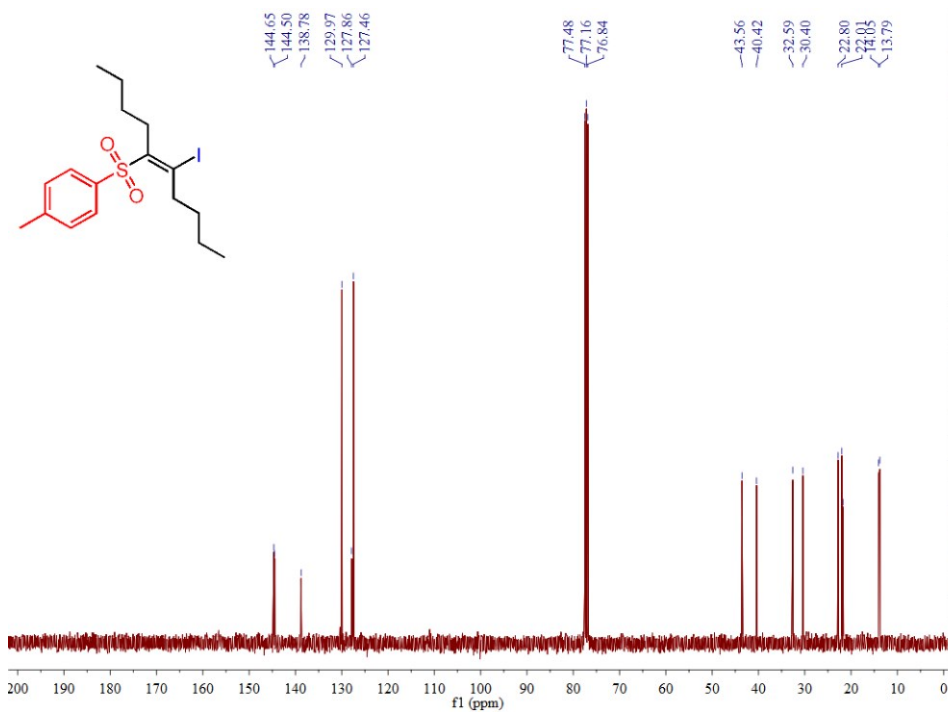
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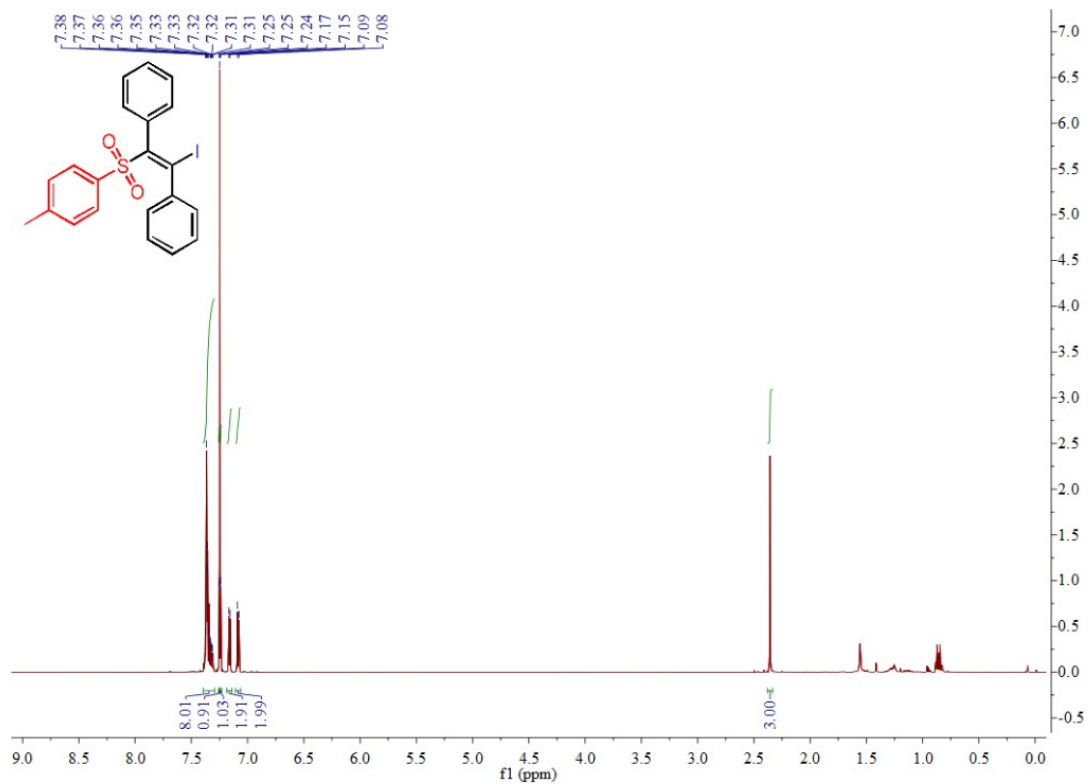
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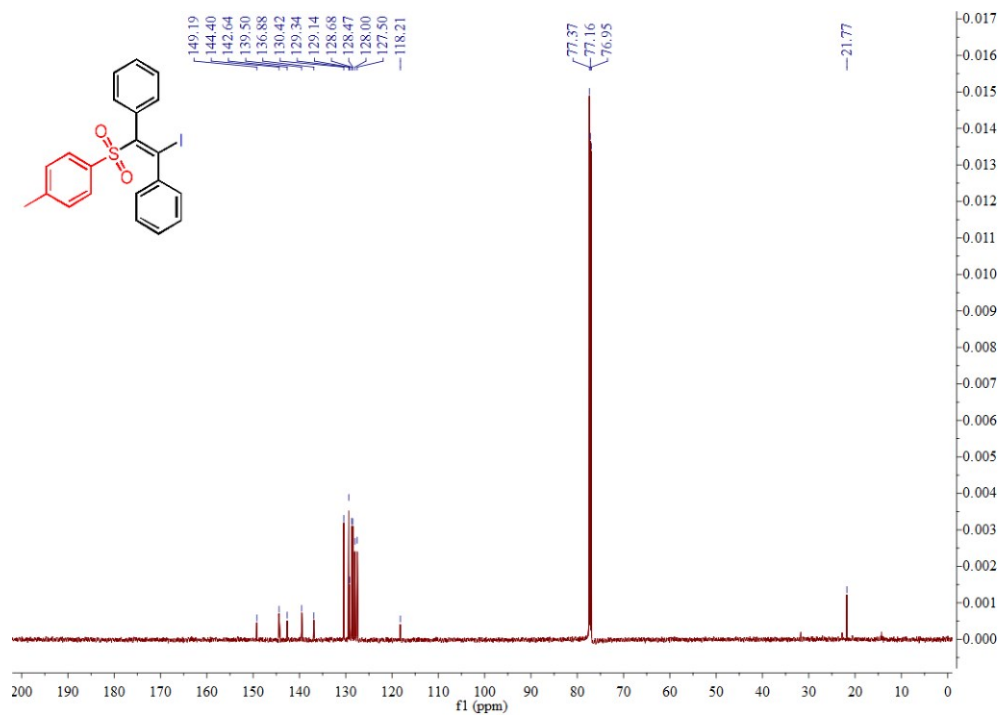
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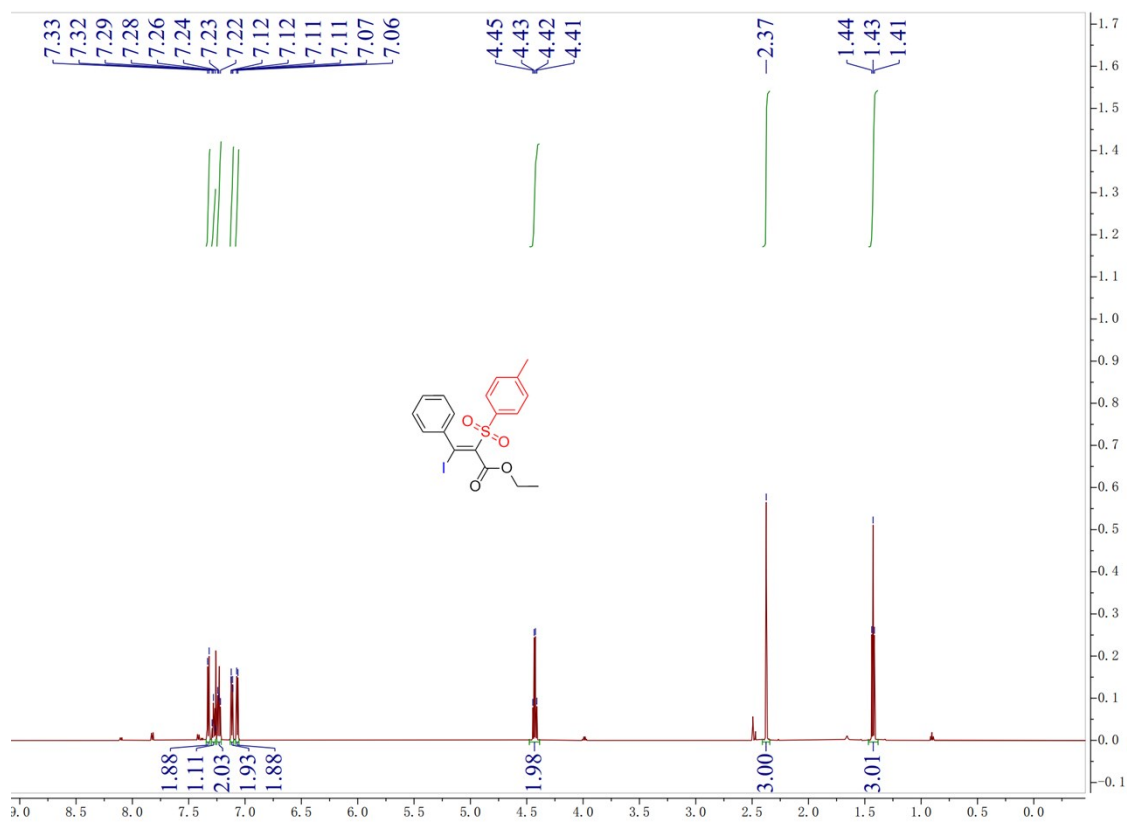
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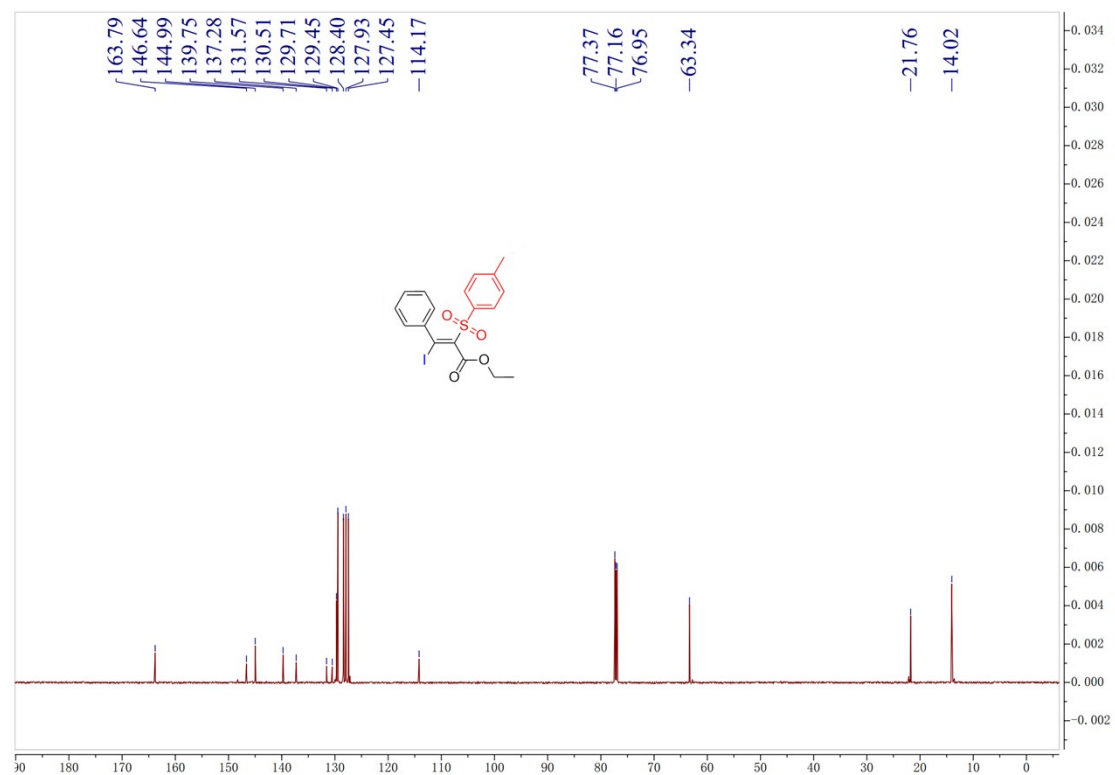
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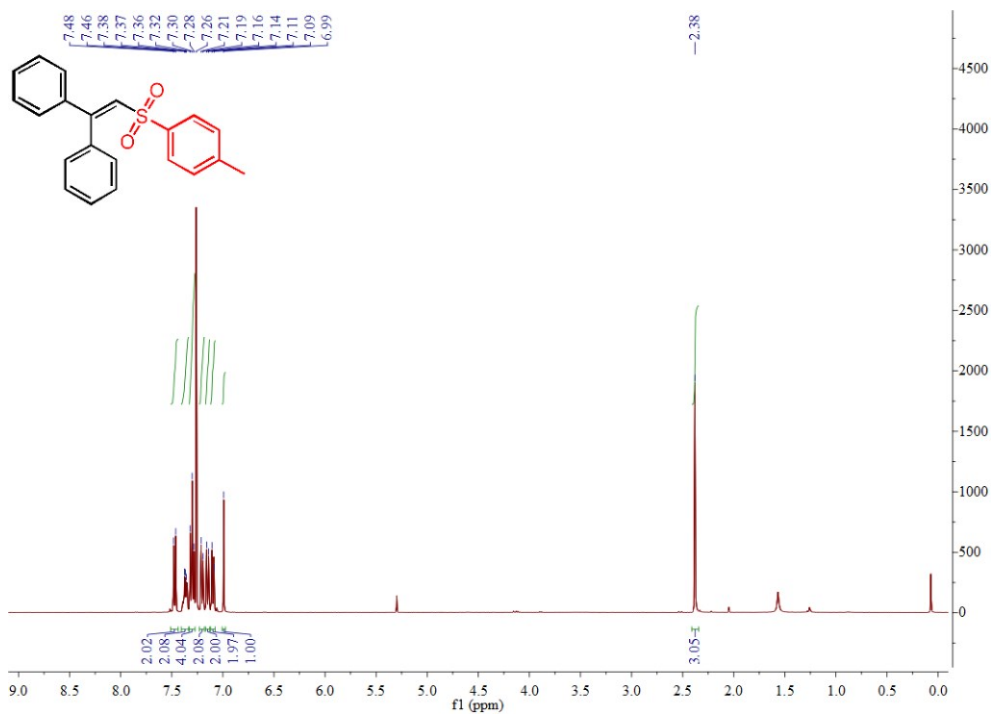
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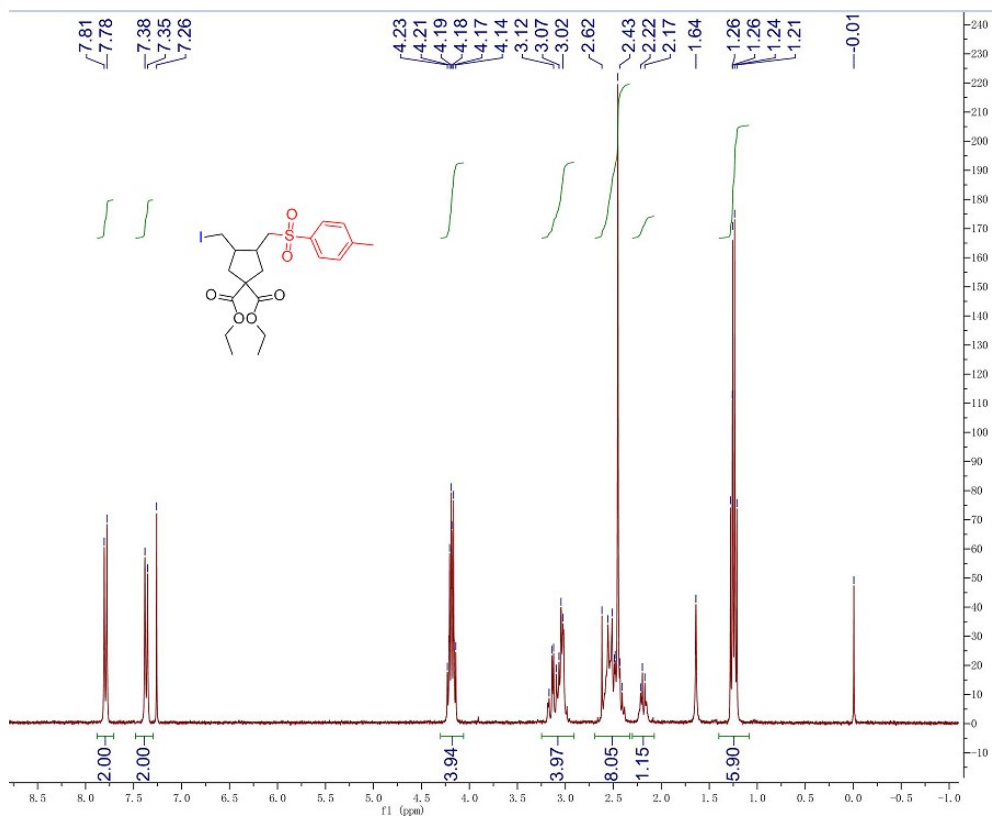
8f



9a



10a



10a

