Supporting Information

Visible-light Induced Oxidant-free Oxidative Cross-Coupling for Constructing Allylic Sulfones from Olefins and Sulfinic Acids

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General Considerations

All manipulations were carried out by using standard Schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200−300 mesh silica gel in petroleum ether (bp. 60−90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the ethyl acetate. $Co(dmgH)_2pyCl$[1], sulfinic acids[2] an α-methylstyrene derivatives[3] were all prepared following literature procedures. All new compounds were characterized by ^1H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^1H NMR and ^{13}C NMR. The ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to DMSO-d_6 (2.5 ppm for ^1H), DMSO-d_6 (39.6 ppm for ^{13}C). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion + Hydrogen (M+H). Hydrogen gas content was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, argon as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector). EPR spectra were recorded on a Bruker X-band A200 spectrometer.

Experimental Procedures

2. General Procedure for allyl sulfones:

A solution of sulfinic acids **1** (0.2 mmol), α-methylstyrene derivatives **2** (0.6 mmol), pyridine (0.4 mmol), TBA_2-eosin Y (0.01 mmol, 5 mol %) and $Co^{III}(dmgH)_2PyCl$ (0.02 mmol, 10 mol %) in degased $CHCl_3$ (6 mL) was stirred under an argon atmosphere and irradiation of 3W green LEDs for 5 h. After completion of the reaction, H_2 was detected by GC-TCD, and then the reaction was treated with 1M HCl. The aqueous solution was extracted with ethyl acetate (3 × 5 mL) and the combined extracts were dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure by an aspirator, then the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 10:1) to afford **3**.

Mechanistic Studies

1. UV-visible absorption spectra of the reaction.

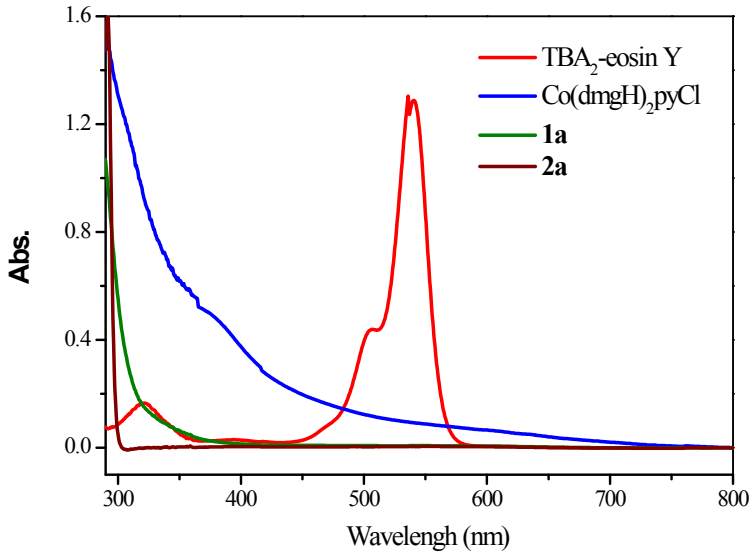


Figure S1. UV-visible absorption spectra of TBA_2-eosin Y (red), $Co(dmgH)_2pyCl$ (blue), **1a** (green) and **2a** (brown).

2. The acid–base neutralizing reaction between sulfinic acid and pyridine

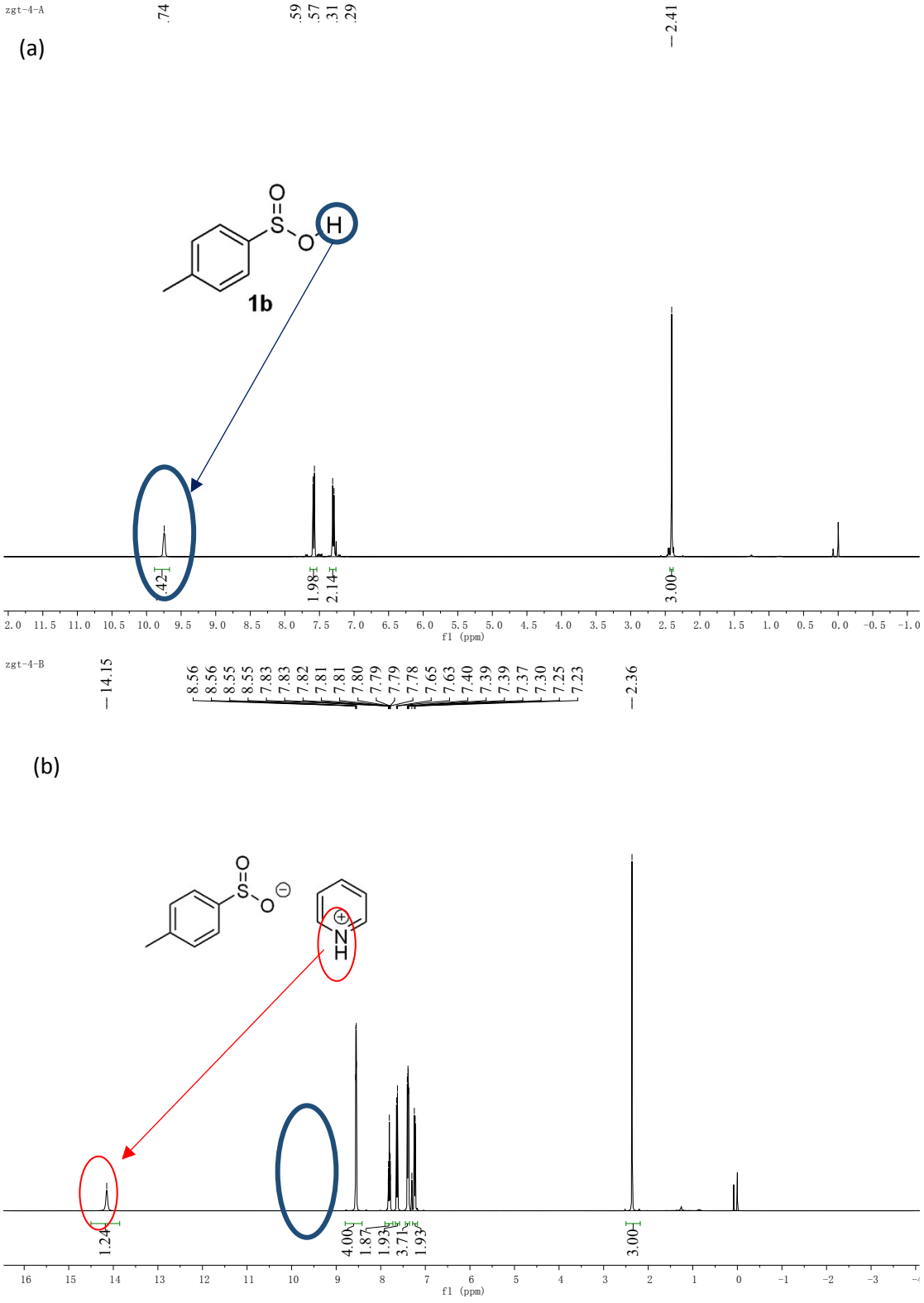
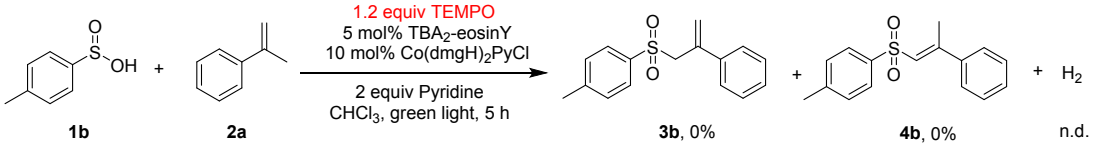


Figure S2. The difference between the ^{1}H NMR of the (a) sulfinic acid **1b** and (b) sulfinc acid **1b** was neutralized by 2 equiv. pyridine.

3. Radical trapping experiments:



Procedure: A solution of 4-methylbenzenesulfinic acid **1b** (0.2 mmol), α-methylstyrene **2a** (0.6 mmol), pyridine (0.4 mmol), TBA_2-eosin Y (0.01 mmol, 5 mol %), TEMPO (0.24 mmol) and $Co^{III}(dmgH)_2PyCl$ (0.02 mmol, 10 mol %) in degased $CHCl_3$ (6 mL) was stirred under an argon atmosphere and irradiation of 3W green LEDs for 5 h. After completion of the reaction, H_2 was detected by GC-TCD, and then the reaction was analysis by TLC and ^1H NMR. No desired product and H_2 were observed.

4. ESR experiments:

A solution of 4-methylbenzenesulfinic acid **1b** (0.2 mmol), α-methylstyrene **2a** (0.6 mmol), pyridine (0.4 mmol), TBA_2-eosin Y (0.01 mmol, 5 mol %) and $Co^{III}(dmgH)_2PyCl$ (0.02 mmol, 10 mol %) in degased $CHCl_3$ (6 mL) was stirred under an argon atmosphere and irradiation of 3W green LEDs. After 30 mins, DMPO (10 μL) was added, then the solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.417 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3352 G; time constant: 163.84 ms; scan time: 61.44 s modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×10^5; microwave power: 19.54 mW.

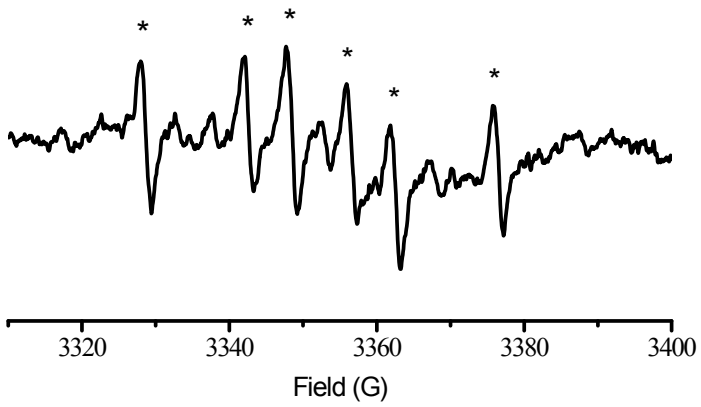


Figure S3. EPR measurements of a solution in $CHCl_3$ of eosin Y, $Co(dmgH)_2pyCl$, pyridine, **1b** and **2a** in the presence of DMPO under the irradiation of green LEDs for 30 min.

No EPR signal was observed in the absence of either of photo-sensitizer, cobalt catalyst, pyridine or light.

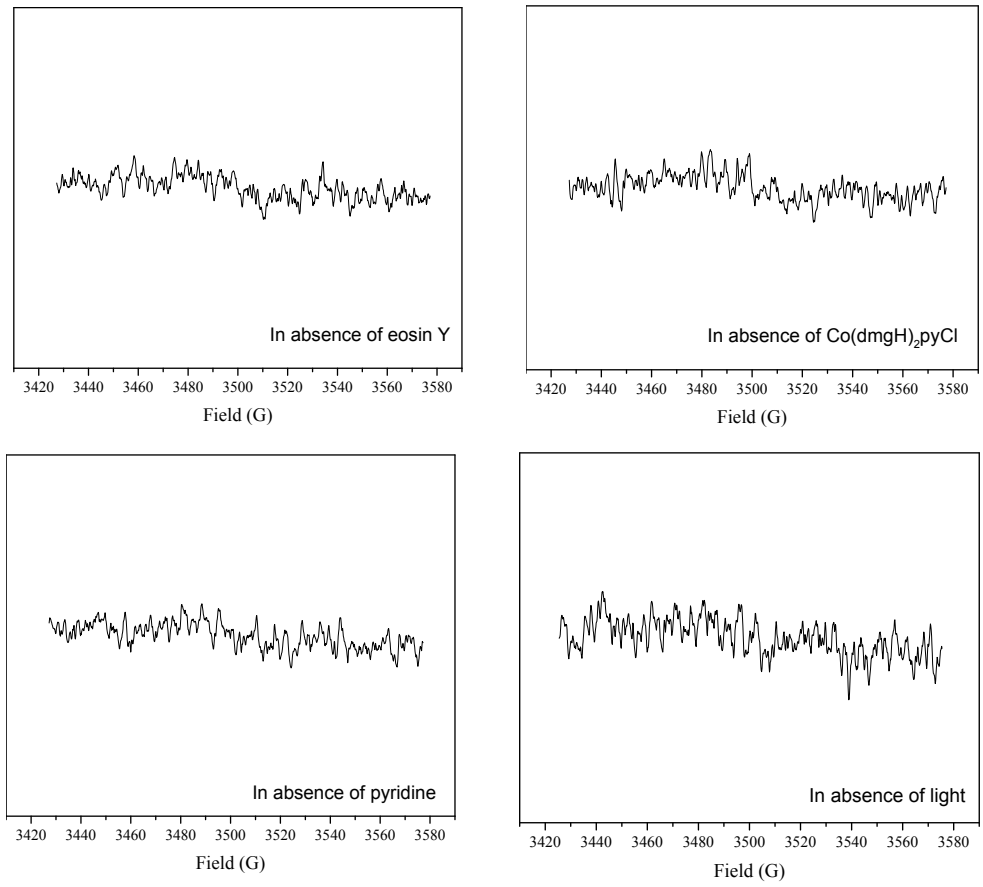


Figure S4. Control experiments of EPR experiment.

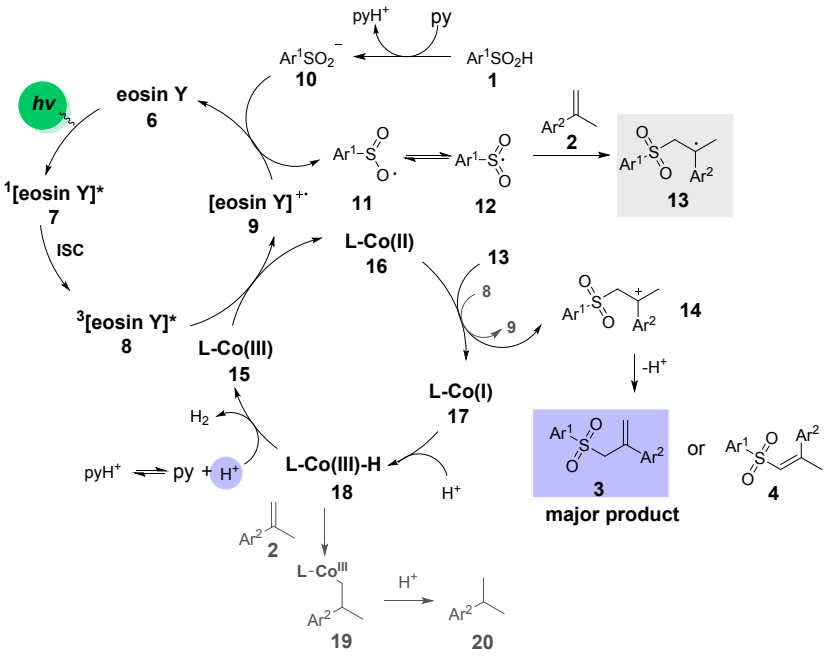


Figure S5. An alternative mechanism in oxidative quenching pathway.

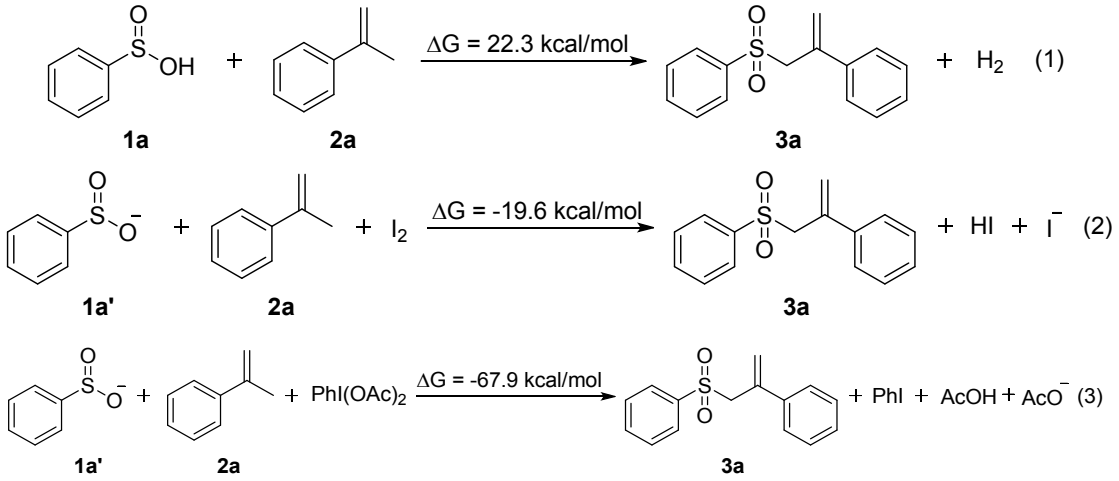
DFT Calculation Study

1. Complete Reference for Gaussian 09

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2013**.

2. Computational Details

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs. DFT method B3-LYP[1] with a standard 6-31G(d) basis set was used for geometry optimizations. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition structures and to derive the thermochemical corrections for the enthalpies and free energies.



1. (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785. (b)

Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

3. Absolute Calculation Energies, Enthalpies, and Free Energies

Geometry	$E_{(elec\text{-}B3LYP)}$[1]	$G_{(corr\text{-}B3LYP)}$[2]	$H_{(corr\text{-}B3LYP)}$[3]	IF[4]
1a	-820.134962	0.099887	0.148078	-
1a'	-780.260501	0.063874	0.106038	-
2a	-348.957193	0.129435	0.171240	-
3a	-1128.565687	0.209135	0.270798	-
H_2	-1.175482	-0.001342	0.013450	-
I_2	-22.834162	-0.025521	0.004310	-
HI	-12.007706	-0.015228	0.008239	-
I^-	-11.518910	-0.016848	0.002360	-
$PhI(OAc)_2$	-699.921704	0.145291	0.211379	-
PhI	-243.053411	0.058488	0.097115	-
AcOH	-229.077610	0.034589	0.067548	-
AcO^-	-228.493171	0.020747	0.053702	-

[1]The electronic energy calculated by B3LYP in gas phase. [2]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase. [3]The thermal correction to enthalpy calculated by B3LYP in gas phase. [4]The B3LYP calculated imaginary frequencies for the transition states.

4. B3LYP geometries for all the optimized compounds and transition states

1a

C	-2.22300700	-1.15597200	-0.14107400
C	-0.83720600	-1.20456600	-0.29154400
C	-0.09883400	-0.02388300	-0.16726300
C	-0.71958600	1.19811000	0.08745800
C	-2.10759300	1.23574600	0.23964500
C	-2.85648300	0.06256500	0.12397000
H	-2.80868600	-2.06687700	-0.22883400
H	-0.33414400	-2.14776700	-0.48650700
H	-0.11040300	2.09312100	0.17077200
H	-2.60340700	2.18043900	0.44531300
S	1.70450700	-0.05136800	-0.42807400
O	2.05514800	-1.19351200	0.76022800
H	1.71787100	-0.86435100	1.61820800
O	2.17729300	1.30092000	-0.01202300
H	-3.93662400	0.09604700	0.23743300

1a'

C	2.18216200	1.20957500	0.03396500
C	0.78665000	1.20588100	-0.04928500
C	0.08407200	-0.00000300	-0.09535600
C	0.78666000	-1.20588500	-0.04932600
C	2.18217000	-1.20956600	0.03393000
C	2.88419600	0.00000800	0.07100100
H	2.72673900	2.15284500	0.07889300
H	0.21367400	2.13084000	-0.05534700
H	0.21368800	-2.13084300	-0.05544100
H	2.72676600	-2.15282600	0.07882600
S	-1.77962600	-0.00001700	-0.35080200
O	-2.17589400	1.29055400	0.36002600
O	-2.17587300	-1.29053200	0.36012900
H	3.97181800	0.00001200	0.13509100

2a

C	1.86231500	-1.22513600	-0.20723400
C	0.46830100	-1.16332500	-0.20596400
C	-0.20659000	0.05498900	-0.01204000
C	0.57344800	1.20554700	0.20965500
C	1.96500200	1.14566000	0.21023200
C	2.61853300	-0.07098500	-0.00175700
H	2.35676600	-2.17959400	-0.36882500
H	-0.09814900	-2.07427200	-0.37259800
H	0.08016800	2.15195200	0.40990200
H	2.54120000	2.04976000	0.38971800
H	3.70412100	-0.11916300	0.00344900
C	-1.69391400	0.12259500	-0.02844900
C	-2.46036800	-1.12039100	0.36874100
H	-2.33008000	-1.92755500	-0.36397800
H	-2.11961000	-1.51043400	1.33576300
H	-3.53187300	-0.91161400	0.43772100
C	-2.34901100	1.23628300	-0.39276500
H	-3.43457500	1.27992000	-0.38037800
H	-1.83425400	2.12956500	-0.73329100

3a

C	-4.30918400	-0.77628700	-0.53526800
C	-3.31101800	0.18360400	-0.70580100
C	-2.23173800	0.20082700	0.18106500
C	-2.13705600	-0.70691300	1.23774000
C	-3.14386000	-1.65978800	1.39955100
C	-4.22311000	-1.69698500	0.51299000

H	-5.15797800	-0.79837300	-1.21277600
H	-3.37375600	0.92512900	-1.49580400
H	-1.29765600	-0.64959400	1.92191300
H	-3.08662700	-2.37001200	2.21941400
S	-0.94294300	1.43839000	-0.03563900
O	-1.54040700	2.60509100	-0.70774700
O	-0.24690000	1.58522400	1.25546800
C	0.22422500	0.71366400	-1.27151000
H	0.89527400	1.55241700	-1.48060400
H	-0.39827600	0.54915200	-2.15519700
C	0.96762600	-0.54044600	-0.87208100
C	0.38117600	-1.73654500	-1.05097000
H	-0.60800800	-1.82794500	-1.49015400
H	0.86614400	-2.66003300	-0.75058400
C	2.35460900	-0.41431300	-0.34486700
C	2.73634900	0.65189300	0.48835700
C	3.32646300	-1.37043000	-0.69204900
C	4.04196600	0.74232800	0.97206400
C	4.62987500	-1.27695000	-0.20801700
H	3.06257300	-2.17593000	-1.37129000
C	4.99348400	-0.21915200	0.62836400
H	4.31263500	1.56795400	1.62484600
H	5.36551800	-2.02328500	-0.49637800
H	6.01104800	-0.14166900	1.00186700
H	-5.00451800	-2.44054100	0.64381300
H	2.00033900	1.38892900	0.79198800

$PhI(OAc)_2$

I	-0.00053900	-0.62244100	-0.00003900
C	0.00124400	1.54329600	-0.00003300
C	0.89833800	2.21055000	-0.82691700
C	-0.89474500	2.21199200	0.82688800
C	0.89352400	3.60801800	-0.81801000
H	1.59834200	1.66376400	-1.44673100
C	-0.88761500	3.60945100	0.81805800
H	-1.59564700	1.66633300	1.44667900
C	0.00353500	4.30575300	0.00004300
H	1.58861200	4.14596000	-1.45645000
H	-1.58180400	4.14851300	1.45653300
H	0.00444000	5.39201600	0.00007700
O	2.20724200	-0.29419400	0.10206900
O	-2.20779800	-0.29066600	-0.10215400
C	2.76111100	-1.48728300	0.12076500
C	-2.76348500	-1.48289600	-0.12071200
C	4.27705000	-1.45532100	0.20214100

H	4.68547800	-0.86493000	-0.62390800
H	4.58571600	-0.97296500	1.13534400
H	4.66824300	-2.47296700	0.16467200
C	-4.27938000	-1.44866500	-0.20196000
H	-4.68685300	-0.85730800	0.62386300
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H	-4.67211600	-2.46569900	-0.16405300
O	2.11038300	-2.52905400	0.08265600
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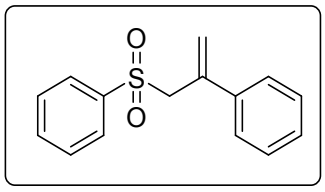
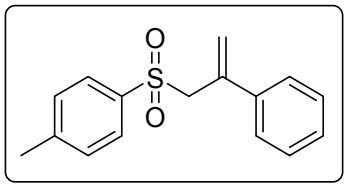
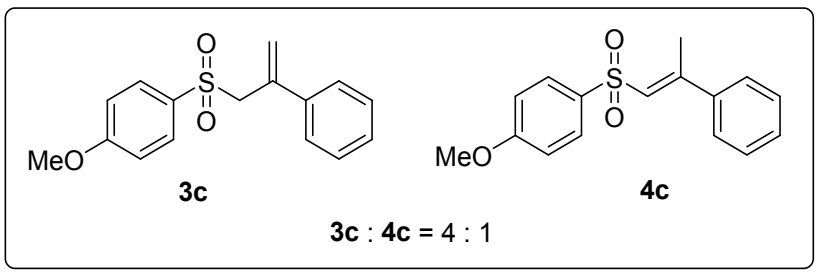
Characterization of Products



((2-phenylallyl)sulfonyl)benzene (**3a**);[6] 36.6 mg (yield: 71%, 0.2 mmol scale), white solid, yield of H_2: 66%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79 – 7.74 (m, 2H), 7.69 – 7.63 (m, 1H), 7.57 – 7.53 (m, 2H), 7.43 – 7.41 (m, 2H), 7.27 – 7.24 (m, 3H), 5.60 (d, J = 0.7 Hz, 1H), 5.15 (s, 1H), 4.62 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 139.0, 138.9, 136.9, 134.2, 129.5, 128.8, 128.6, 128.3, 126.7, 122.3, 60.6.

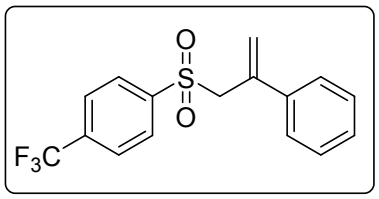


1-methyl-4-((2-phenylallyl)sulfonyl)benzene (**3b**);[6] 39.2mg, (yield: 72%, 0.2 mmol scale), white solid, yield of H_2: 58%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (d, J = 8.2 Hz, 2H), 7.43 – 7.41 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.30 – 7.11 (m, 3H), 5.59 (s, 1H), 5.13 (s, 1H), 4.57 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.3, 138.6, 136.7, 135.8, 129.6, 128.3, 128.3, 127.8, 126.4, 121.8, 60.4, 21.2.

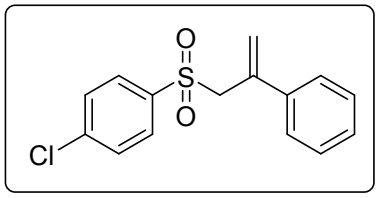


1-methoxy-4-((2-phenylallyl)sulfonyl)benzene (**3c**) and (E)-1-methoxy-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene (**4c**); 43.7 mg (mixture yield: 76%, 0.2 mmol scale, **3c** : **4c** = 4 : 1), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) **3c isomer** δ 7.69 (d, J = 8.8 Hz, 2H), 7.31 – 7.21 (m, 5H), 6.87 (d, J = 8.8 Hz, 2H), 5.59 (s, 1H), 5.21 (s, 1H), 4.25 (s, 2H), 3.84 (s, 3H); **4c isomer** δ 7.44 (d, J = 8.8 Hz,

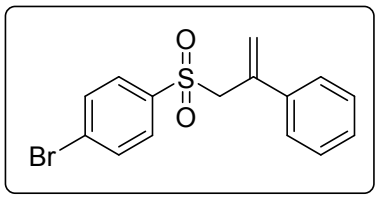
2H), 7.31 – 7.26 (m, 3H), 7.13 – 7.06 (m, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.54 (s, 1H), 3.82 (s, 3H), 2.13 (s, 3H); **3c** and **4c** ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 138.8, 136.7, 130.8, 129.9, 129.7, 129.5, 128.4, 127.9, 127.9, 127.3, 126.2, 121.7, 114.0, 113.8, 77.3, 77.0, 76.7, 62.3, 55.6, 27.7; HRMS (ESI) calcd for $C_{16}H_{17}O_3S^+$, $[M+H]^+$, 289.0893 found 289.0892.



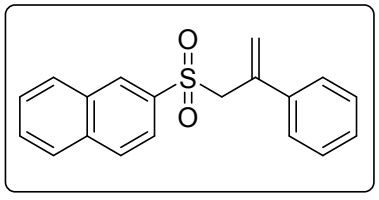
1-((2-phenylallyl)sulfonyl)-4-(trifluoromethyl)benzene (**3d**); 43.7 mg, (yield: 67%, 0.2 mmol scale), white solid, yield of H_2: 53%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, J = 8.3 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.40 (dd, J = 6.7, 2.9 Hz, 2H), 7.27 – 7.21 (m, 3H), 5.66 (s, 1H), 5.29 (s, 1H), 4.79 (s, 2H); ^{13}C NMR (101 MHz, DMSO) δ 142.3, 138.1, 136.3, 133.2 (q, J = 32.3 Hz), 129.3, 128.6, 128.1, 127.8, 127.0, 126.2, 126.1 (q, J = 3.7 Hz), 124.7, 122.3, 122.0, 60.0; HRMS (ESI) calcd for $C_{16}H_{14}F_3O_2S^+$, $[M+H]^+$, 327.0661 found 327.0661.



1-chloro-4-((2-phenylallyl)sulfonyl)benzene (**3e**);[7] 46.7 mg (yield: 80%, 0.2 mmol scale), white solid, yield of H_2: 59%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 – 7.73 (m, 2H), 7.69 – 7.59 (m, 2H), 7.43 (dd, J = 6.4, 3.3 Hz, 2H), 7.36 – 7.24 (m, 3H), 5.65 (d, J = 0.7 Hz, 1H), 5.24 (s, 1H), 4.71 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.9, 138.4, 137.4, 136.6, 130.3, 129.2, 128.2, 127.9, 126.4, 122.2, 60.3.

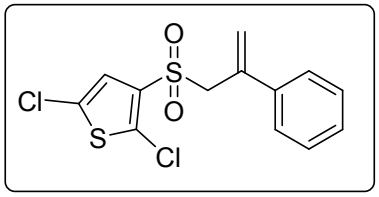


1-bromo-4-((2-phenylallyl)sulfonyl)benzene (**3f**);[6] 49.2 mg (yield: 73%, 0.2 mmol scale), white solid, yield of H_2: 45%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77 – 7.71 (m, 2H), 7.70 – 7.64 (m, 2H), 7.44 – 7.34 (m, 2H), 7.31 – 7.19 (m, 3H), 5.61 (s, 1H), 5.20 (s, 1H), 4.66 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.4, 137.8, 136.5, 132.1, 130.3, 128.2, 128.0, 127.8, 126.3, 122.2, 60.3.

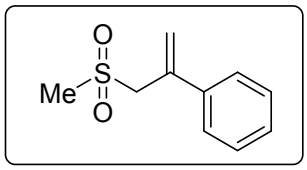


2-((2-phenylallyl)sulfonyl)naphthalene (**3g**);[8] 41.3 mg (yield: 67%, 0.2 mmol scale), white solid, yield of H_2: 59%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (d, J = 1.4 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.83 (dd, J = 8.6, 1.9 Hz, 1H), 7.72 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.51 – 7.37 (m, 2H), 7.27 – 7.10 (m, 3H), 5.58 (d, J = 0.7 Hz, 1H), 5.17 (s, 1H), 4.70 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.5, 136.6, 135.8,

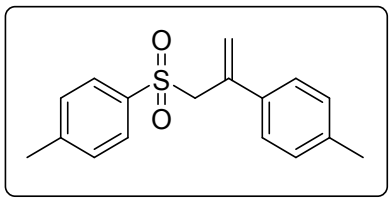
134.8, 131.6, 129.9, 129.6, 129.4, 129.1, 128.2, 127.9, 127.8, 127.7, 126.3, 123.2, 122.0, 60.3.



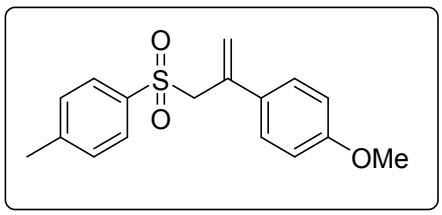
2,5-dichloro-3-((2-phenylallyl)sulfonyl)thiophene (**3h**); 41.8 mg (yield: 63%, 0.2 mmol scale), yelloew liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 – 7.37 (m, 2H), 7.32 – 7.24 (m, 3H), 7.13 (s, 1H), 5.69 (d, J = 0.4 Hz, 1H), 5.40 (s, 1H), 4.72 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 138.1, 136.0, 135.0, 132.5, 128.2, 128.1, 127.4, 126.6, 126.2, 122.7, 60.3; HRMS (ESI) calcd for $C_{13}H_{11}Cl_2O_2S_2^+$, $[M+H]^+$, 332.9572 found 332.9572.



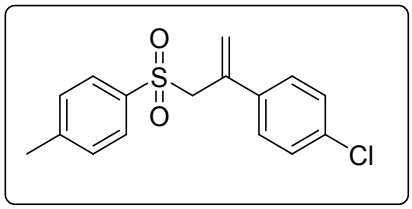
(3-(methylsulfonyl)prop-1-en-2-yl)benzene (**3i**);[9] 21.4 mg (yield: 55%, 0.2 mmol scale), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.43 – 7.31 (m, 3H), 5.77 (s, 1H), 5.57 (s, 1H), 4.20 (s, 2H), 2.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 136.6, 128.8, 128.6, 126.3, 122.2, 60.7, 40.2.



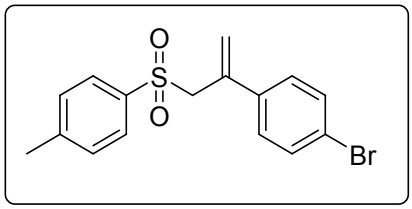
1-methyl-4-((2-(p-tolyl)allyl)sulfonyl)benzene (**3j**);[6] 40.7 mg (yield: 71%, 0.2 mmol scale), white solid, yield of H_2: 69%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 5.53 (s, 1H), 5.06 (s, 1H), 4.53 (s, 2H), 2.37 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.2, 137.2, 136.5, 135.8, 135.7, 129.5, 128.8, 128.3, 126.2, 120.8, 60.5, 21.2, 20.8.



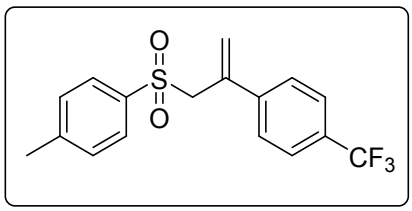
1-methoxy-4-(3-tosylprop-1-en-2-yl)benzene (**3k**);[6] 36.2 mg (yield: 60%, 0.2 mmol scale), yellow oil, yield of H_2: 57%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.63 (d, J = 8.3 Hz, 2H), 7.38 – 7.32 (m, 4H), 6.82 (d, J = 8.9 Hz, 2H), 5.49 (d, J = 0.8 Hz, 1H), 5.01 (s, 1H), 4.52 (s, 2H), 3.74 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.0, 144.1, 136.0, 135.8, 130.9, 129.5, 128.2, 127.6, 119.7, 113.6, 60.6, 55.2, 21.1.



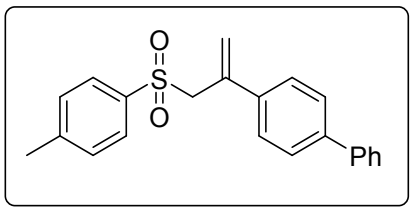
1-chloro-4-(3-tosylprop-1-en-2-yl)benzene (**3l**);[6] 40.4 mg (yield: 66%, 0.2 mmol scale), white solid, yield of H_2: 39%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.32 (dd, J = 13.4, 8.3 Hz, 4H), 5.61 (s, 1H), 5.17 (s, 1H), 4.59 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.4, 137.4, 135.8, 135.6, 132.5, 129.6, 128.3, 128.3, 128.2, 122.6, 60.3, 21.2.



1-bromo-4-(3-tosylprop-1-en-2-yl)benzene (**3m**);[6] 48.4 mg (yield: 69%, 0.2 mmol scale), white solid, yield of H_2: 30%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.35 (t, J = 7.7 Hz, 4H), 5.61 (s, 1H), 5.17 (s, 1H), 4.59 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.4, 137.8, 135.9, 135.6, 131.1, 129.6, 128.6, 128.3, 122.6, 121.2, 60.3, 21.2.

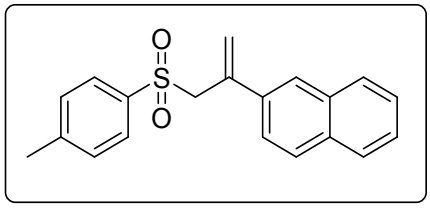


1-methyl-4-((2-(4-(trifluoromethyl)phenyl)allyl)sulfonyl)benzene (**3n**);[6] 55.1 mg (yield: 81%, 0.2 mmol scale), white solid, yield of H_2: 35%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.63 – 7.52 (m, 6H), 7.30 (d, J = 8.0 Hz, 2H), 5.71 (s, 1H), 5.31 (s, 1H), 4.67 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.2, 142.5, 135.9, 135.4, 129.6, 129.5, 128.2, 128.1, 128.0, 127.7, 127.6, 127.2, 125.6, 125.0 (q, J = 3.8 Hz), 124.2, 122.9, 60.2, 21.0.

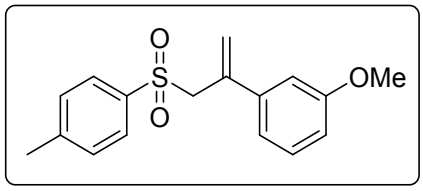


4-(3-tosylprop-1-en-2-yl)-1,1'-biphenyl (**3o**); 34.8 mg (yield: 81%, 0.2 mmol scale), white solid, yield of H_2: 55%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (dd, J = 7.8, 3.4 Hz, 4H), 7.59 – 7.43 (m, 6H), 7.37 (d, J = 7.4 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 5.66 (s, 1H), 5.17 (s, 1H), 4.62 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.3, 139.7, 139.5, 137.6, 136.3, 135.8, 129.6, 129.1, 128.4, 127.7, 127.0, 126.7, 126.5, 121.8, 60.4, 21.2; HRMS (ESI) calcd for $C_{22}H_{21}O_2S^+$, $[M+H]^+$,

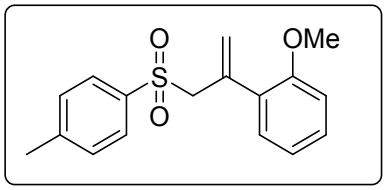
349.1257 found 349.1256.



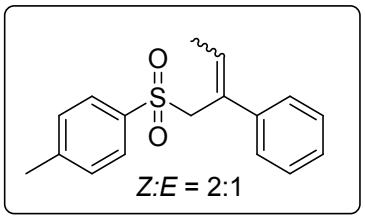
4-(3-tosylprop-1-en-2-yl)-1,1'-biphenyl (**3p**); 54.1 mg (yield: 84%, 0.2 mmol scale), white solid, yield of H_2: 31%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 – 7.85 (m, 2H), 7.84 – 7.78 (m, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.61 (dd, J = 8.6, 1.8 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.26 (d, J = 8.0 Hz, 2H), 5.77 (s, 1H), 5.28 (s, 1H), 4.72 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.3, 136.6, 135.7, 135.7, 132.8, 132.4, 129.5, 128.3, 128.3, 126.3, 126.3, 125.4, 124.5, 122.3, 60.5, 21.0; HRMS (ESI) calcd for $C_{20}H_{19}O_2S^+$, $[M+H]^+$, 323.1100 found 323.1100.



1-methoxy-3-(3-tosylprop-1-en-2-yl)benzene (**3q**);[6] 35.0 mg (yield: 58%, 0.2 mmol scale), white solid, yield of H_2: 30%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.63 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 7.9 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 6.90 (s, 1H), 6.81 (dd, J = 8.2, 2.2 Hz, 1H), 5.59 (s, 1H), 5.15 (s, 1H), 4.56 (s, 2H), 3.72 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.1, 144.2, 140.1, 136.7, 135.8, 129.5, 129.3, 128.3, 122.0, 118.8, 113.3, 112.1, 60.6, 55.1, 21.2.

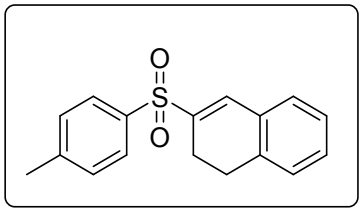


1-methoxy-2-(3-tosylprop-1-en-2-yl)benzene (**3r**); 48.3 mg (yield: 80%, 0.2 mmol scale), yellow oil, yield of H_2: 60%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.20 (ddd, J = 8.2, 7.5, 1.8 Hz, 1H), 6.98 (dd, J = 7.5, 1.7 Hz, 1H), 6.83 (td, J = 7.4, 1.0 Hz, 1H), 6.79 (d, J = 8.3 Hz, 1H), 5.25 (d, J = 1.6 Hz, 1H), 5.20 (d, J = 1.2 Hz, 1H), 4.50 (s, 1H), 3.67 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 155.8, 144.0, 136.7, 135.7, 130.1, 129.3, 129.2, 128.2, 128.0, 124.0, 120.4, 110.8, 61.3, 55.2, 21.1; HRMS (ESI) calcd for $C_{17}H_{19}O_3S^+$, $[M+H]^+$, 303.1049 found 303.1049.

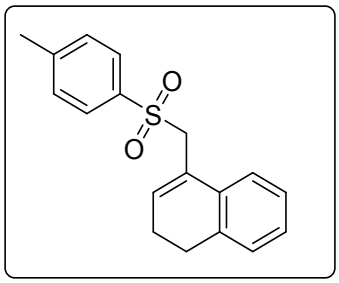


1-methyl-4-((2-phenylbut-2-en-1-yl)sulfonyl)benzene (**3s**);[6] 41.2 mg (yield: 72%, 0.2 mmol scale), colorless oil, yield of H_2: 32%. ^{1}H NMR (400 MHz, DMSO-d_6) ***Z* isomer** δ 7.63 (d, J = 8.3 Hz, 2H),

7.23 – 7.04 (m, 7H), 6.09 (q, *J* = 7.1 Hz, 1H), 4.34 (s, 2H), 2.37 (s, 3H), 1.67 (d, *J* = 7.1 Hz, 3H); ***E* isomer** δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.04 (m, 7H), 5.62 (q, *J* = 7.0 Hz, 1H), 4.35 (s, 2H), 2.37 (s, 3H), 1.53 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.2, 144.0, 141.0, 137.8, 136.1, 135.8, 132.1, 131.9, 129.6, 129.4, 129.3, 129.1, 128.7, 128.2, 128.1, 127.9, 126.8, 126.8, 126.3, 63.8, 56.08, 21.1, 15.1, 14.6.



3-tosyl-1,2-dihydronaphthalene (**4t**);[10] 27.3 mg (yield: 48%, 0.2 mmol scale), white solid, yield of H_2: 21%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78 (d, J = 8.3 Hz, 2H), 7.58 (s, 1H), 7.47 – 7.42 (m, 3H), 7.34 – 7.15 (m, 2H), 2.79 (t, J = 8.3 Hz, 2H), 2.43 – 2.32 (m, 5H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.4, 138.2, 136.3, 135.4, 134.4, 130.6, 130.6, 130.2, 129.2, 127.8, 127.6, 127.1, 26.8, 21.3, 21.1.



4-(tosylmethyl)-1,2-dihydronaphthalene (**3u**);[6] 15.5 mg (yield: 26%, 0.2 mmol scale), colorless oil, yield of H_2: 10%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.01 (m, 4H), 5.90 (t, *J* = 4.7 Hz, 2H), 4.20 (s, 1H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 135.9, 135.4, 134.8, 132.7, 129.4, 128.7, 127.6, 127.3, 126.4, 123.2, 60.0, 27.8, 23.3, 21.6.

Reference

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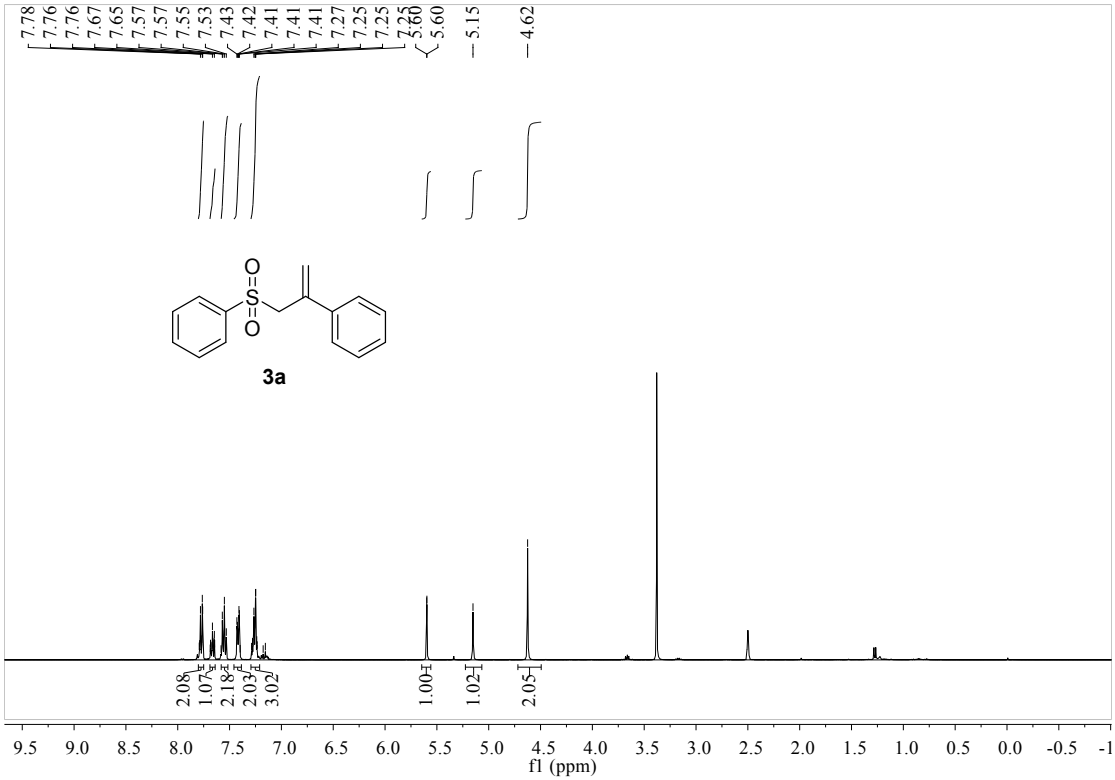
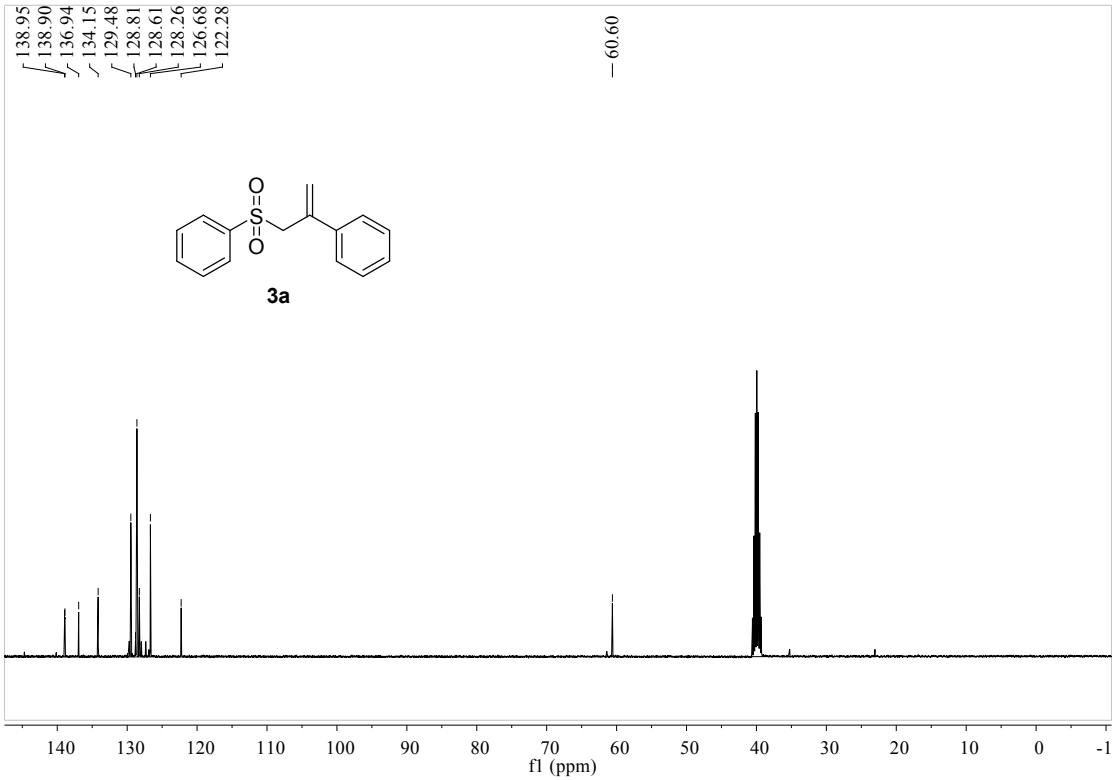
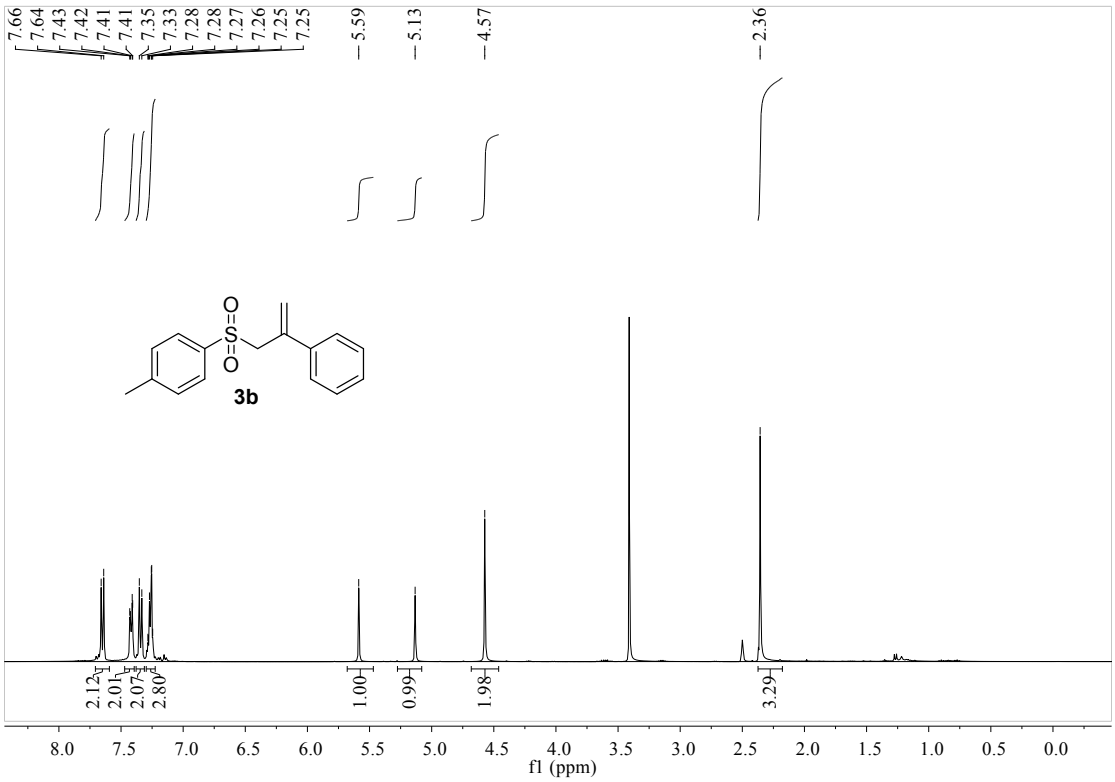
NMR Spectra of Products



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3b
2.12
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2.80
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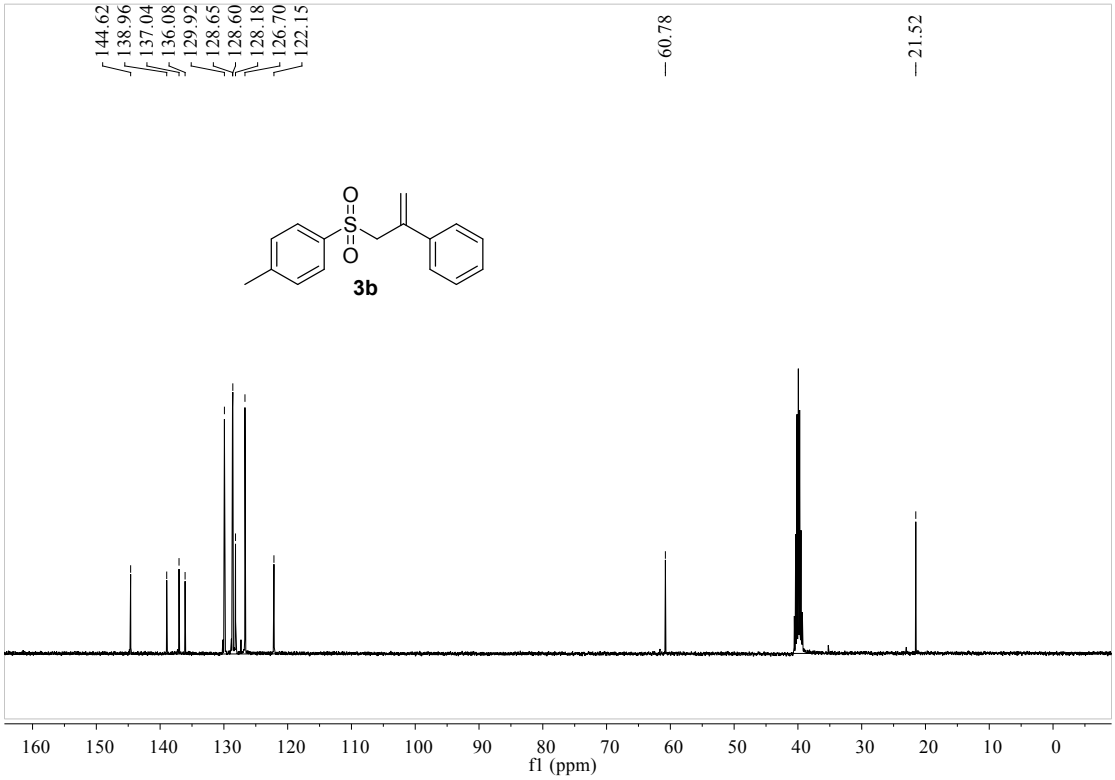
3.29
f1 (ppm)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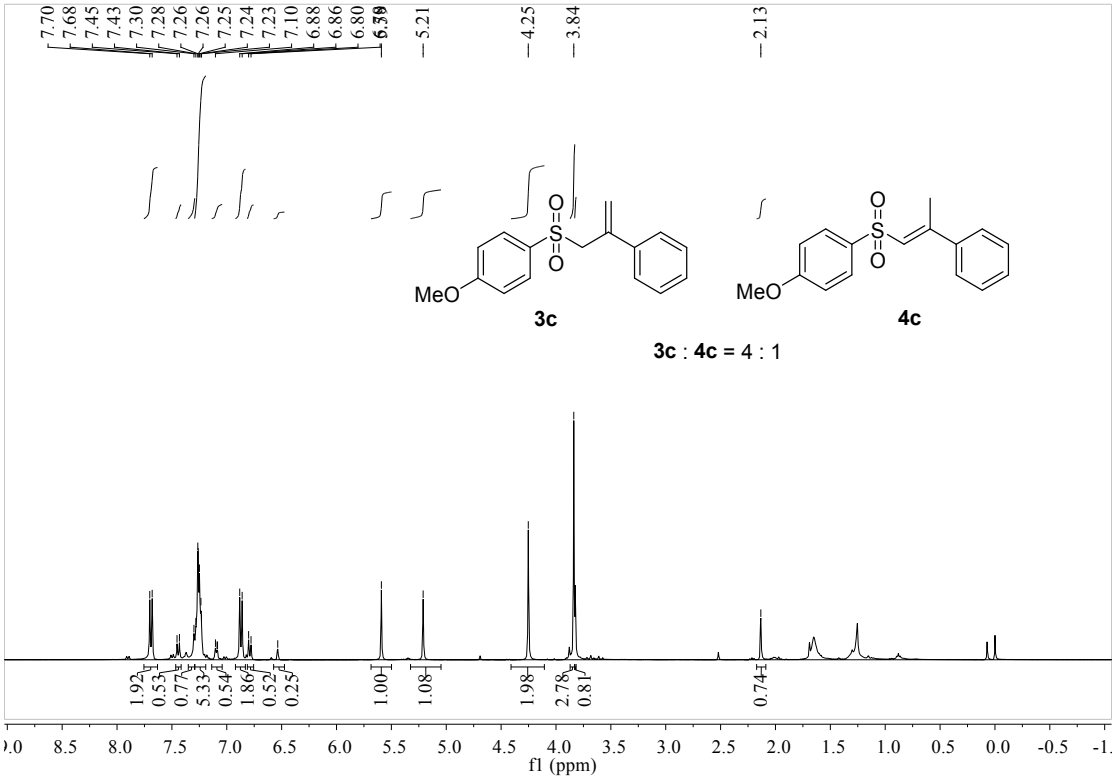
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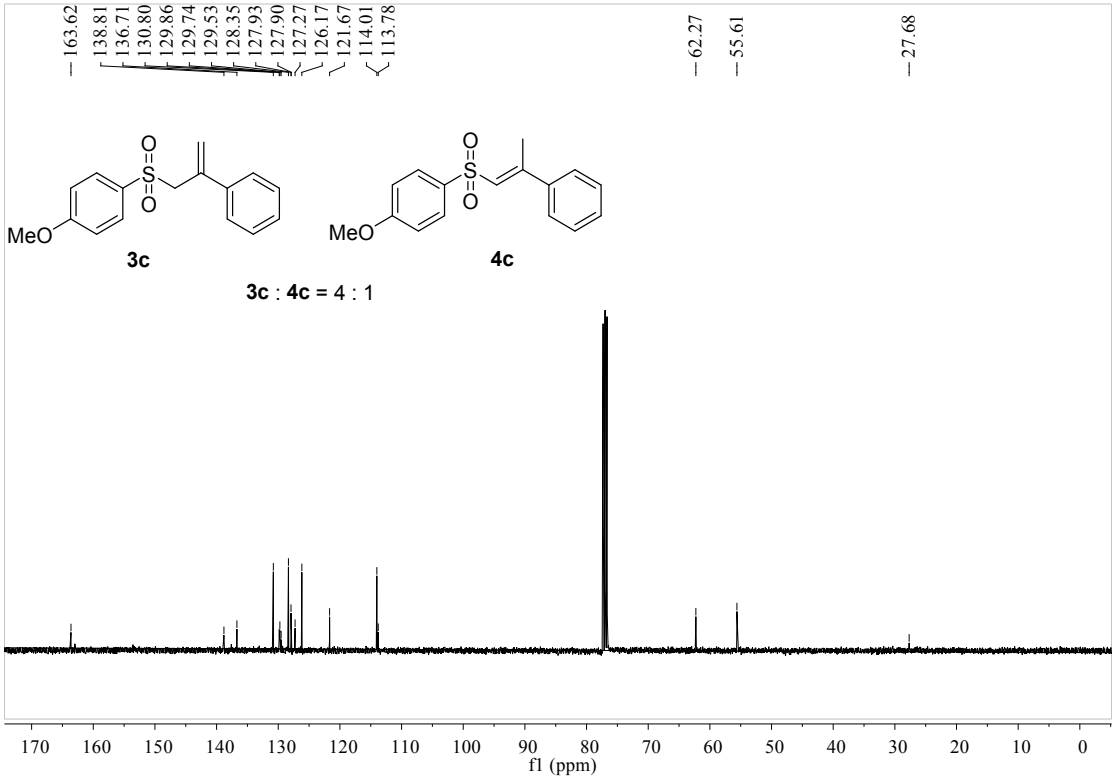
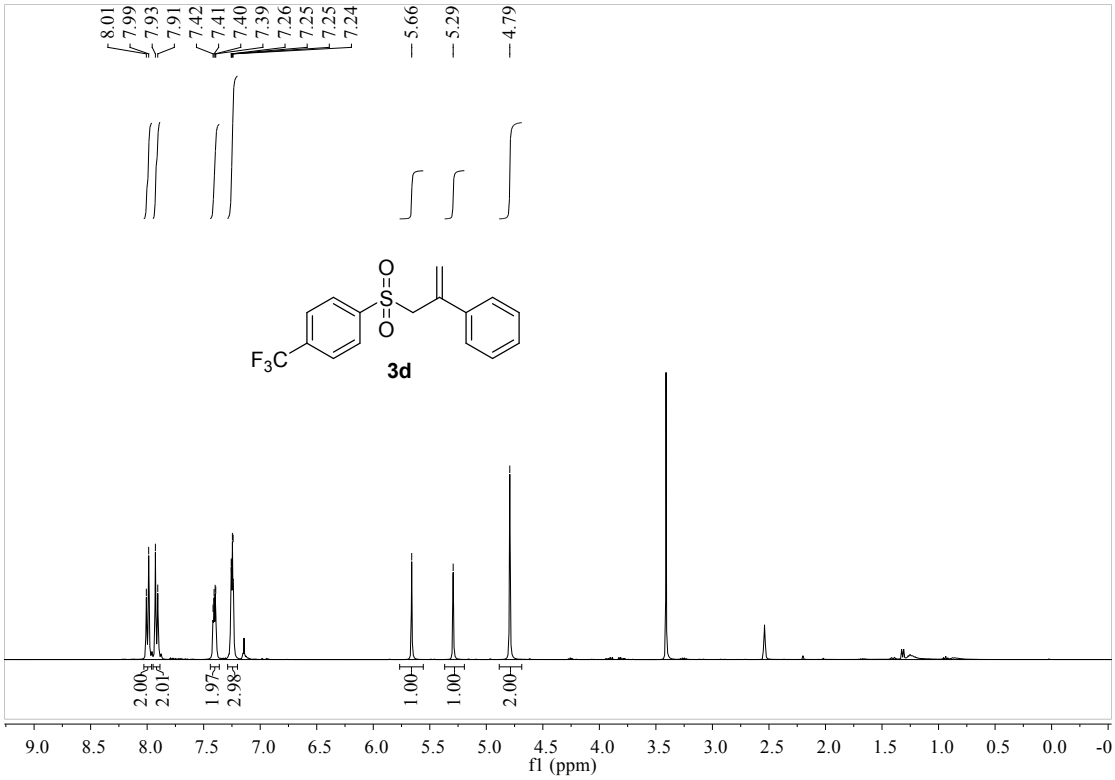
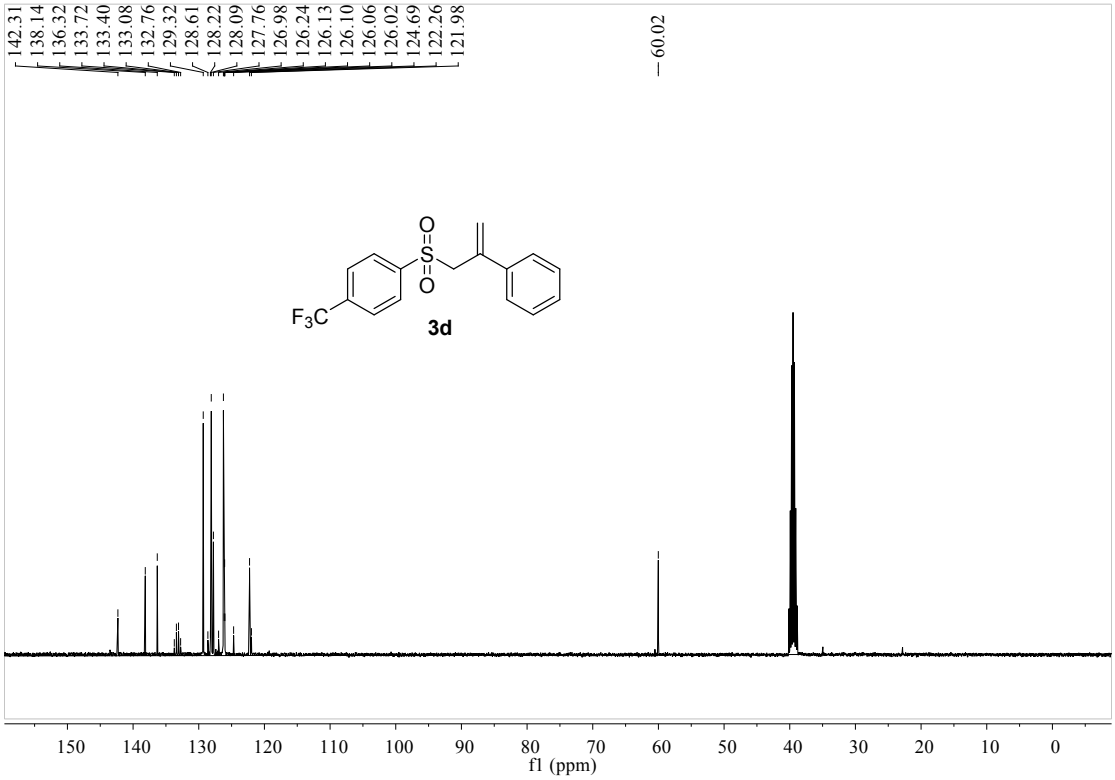
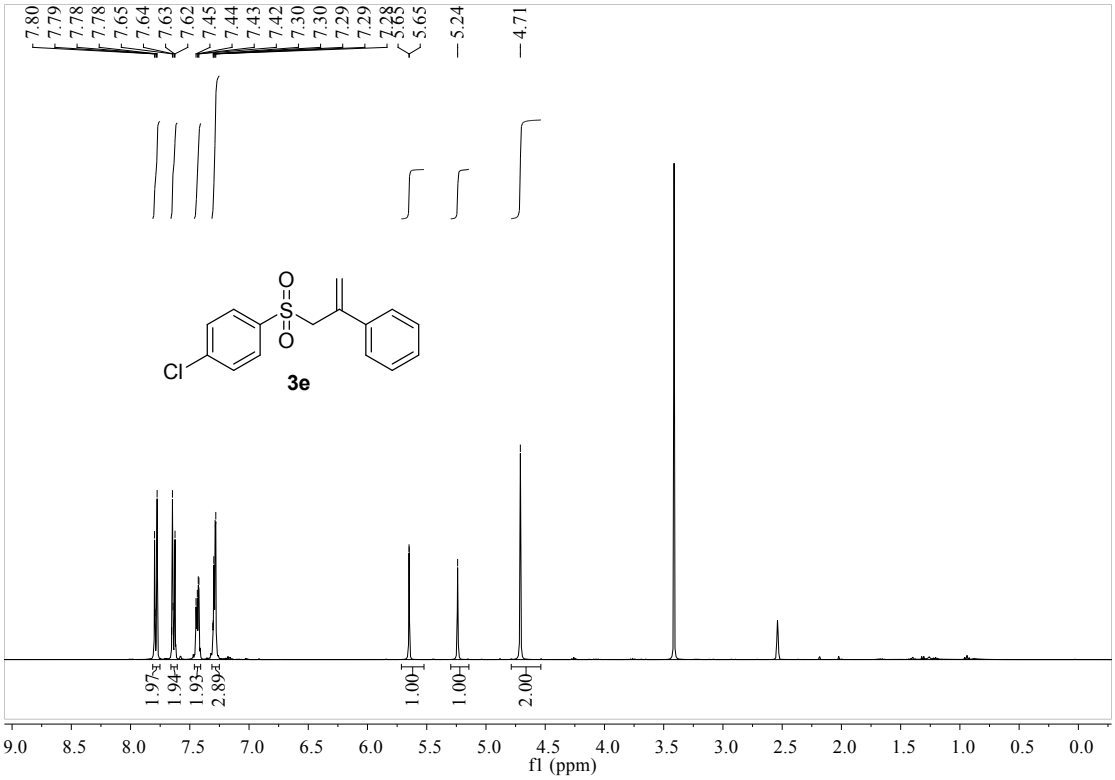
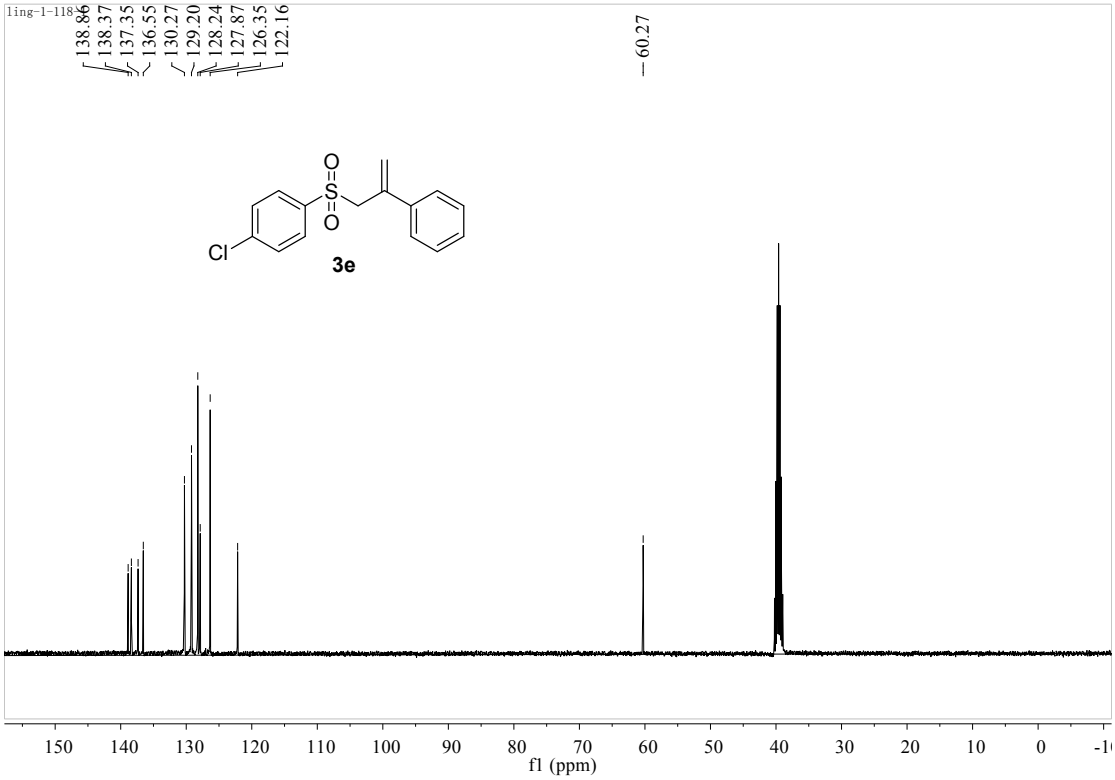
6.86
6.80
5.21
4.25
3.84
2.13
MeO
3c
MeO
4c
3c : 4c = 4 : 1
1.92
0.53
0.77
5.33
0.54
1.86
0.52
0.25
1.00
1.08
1.98
2.78
0.81
0.74
f1 (ppm)

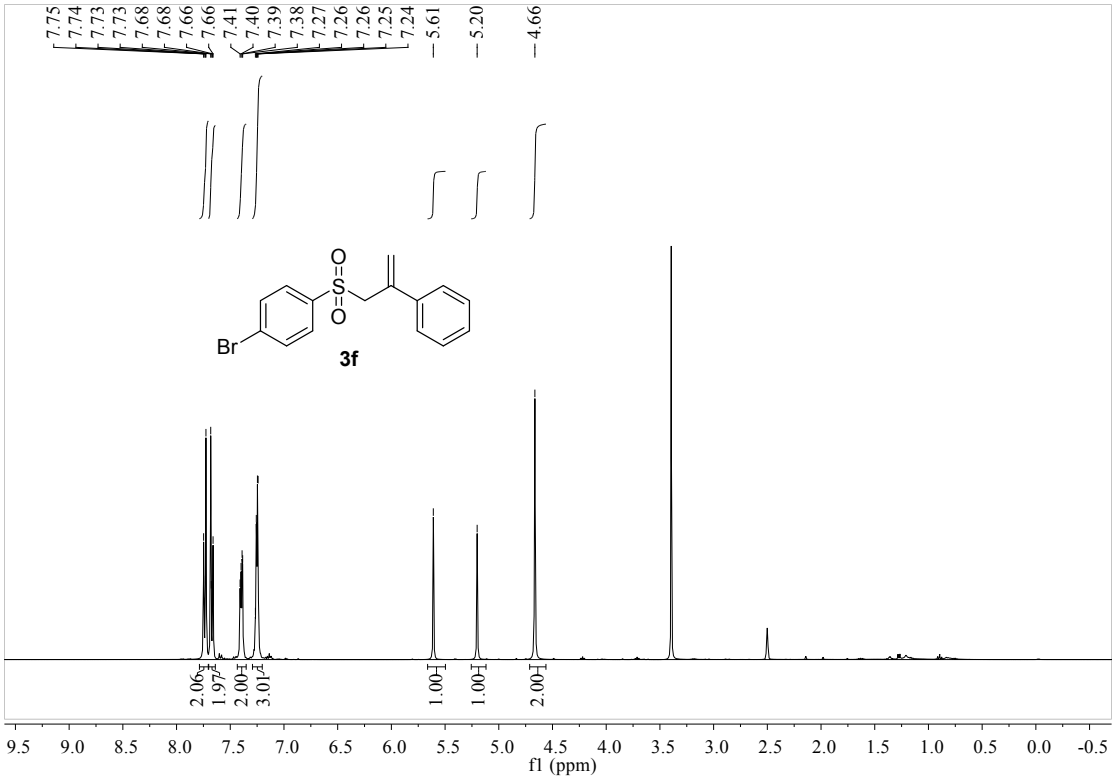

163.62
138.81
136.71
130.80
129.86
129.74
129.53
128.35
127.93
127.90
127.27
126.17
121.67
114.01
113.78
62.27
55.61
27.68
MeO
3c
MeO
4c
3c : 4c = 4 : 1
f1 (ppm)

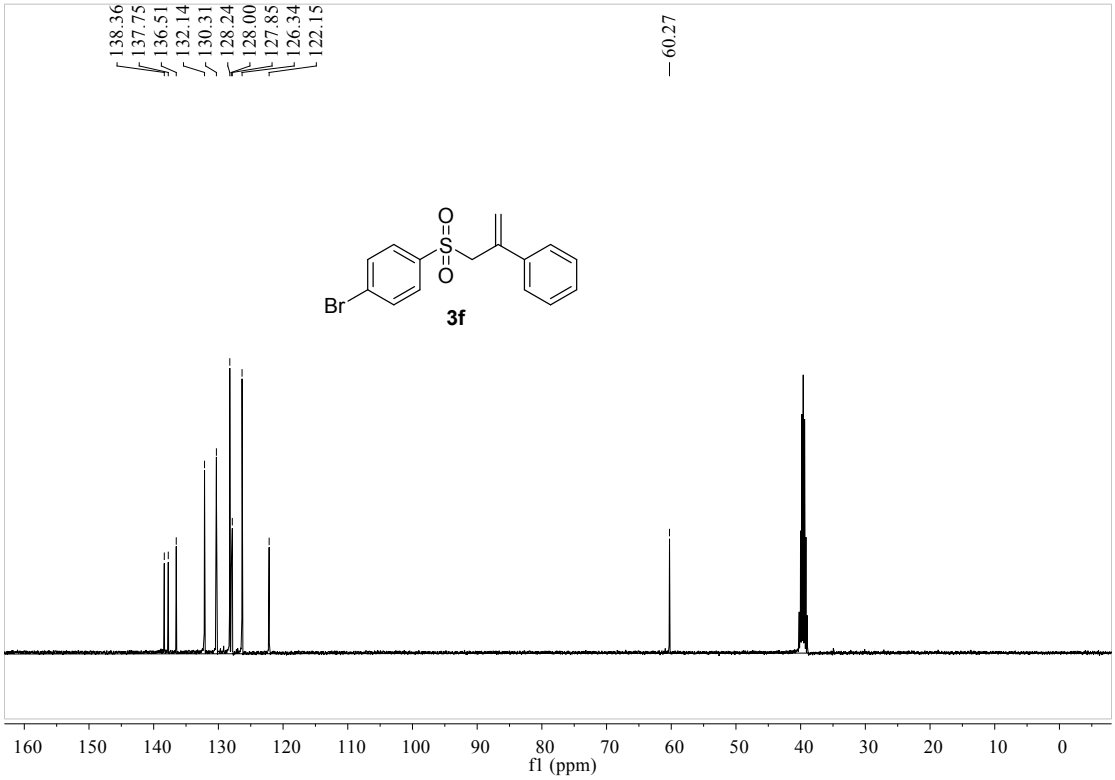

8.01
7.99
7.93
7.91
7.42
7.41
7.40
7.39
7.26
7.25
7.25
7.24
5.66
5.29
4.79
O
S
O
F3C
3d
2.00
2.01
1.97
2.98
1.00
1.00
2.00
f1 (ppm)

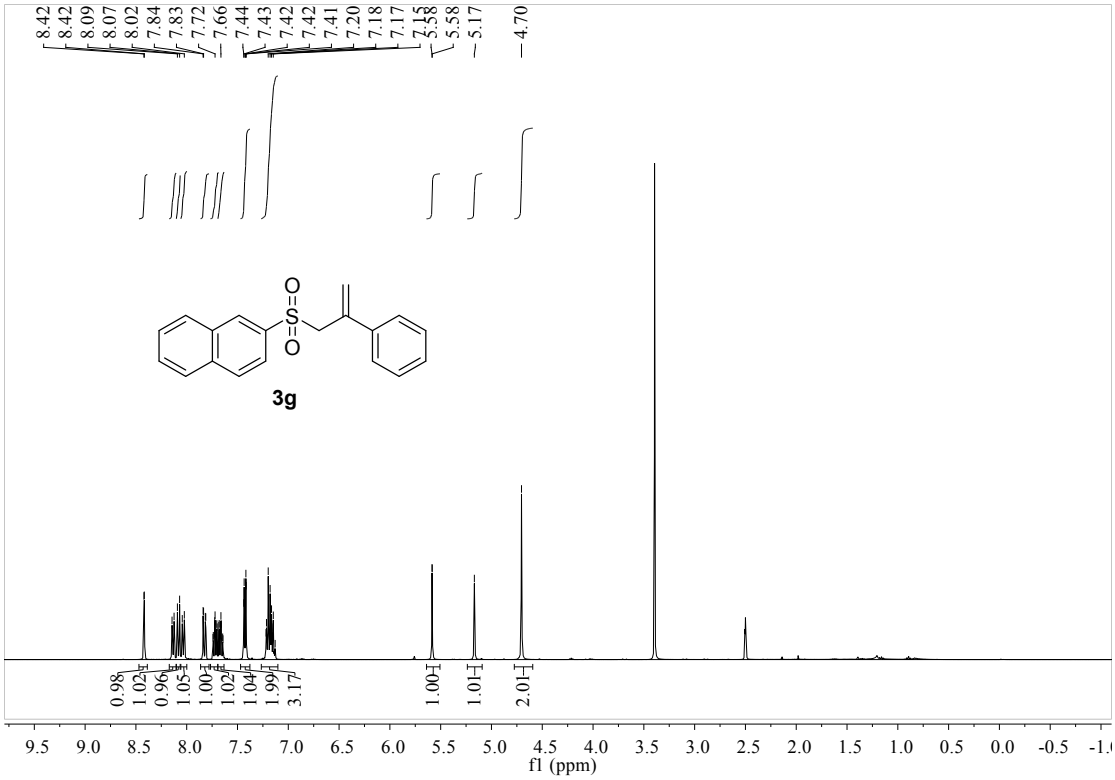

142.31
138.14
136.32
133.72
133.40
133.08
132.76
129.32
128.61
128.22
128.09
127.76
126.98
126.24
126.13
126.10
126.06
126.02
124.69
122.26
121.98
60.02
O
S
O
F3C
3d
f1 (ppm)

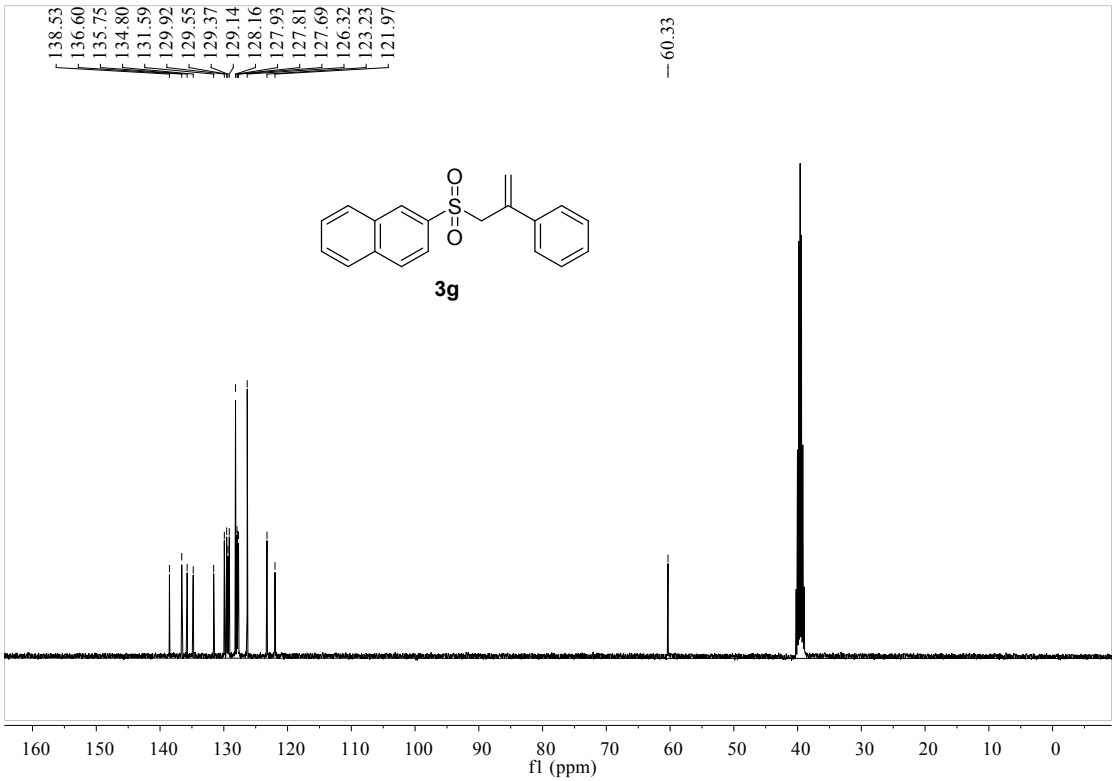

7.80
7.79
7.78
7.78
7.65
7.64
7.63
7.62
7.45
7.44
7.43
7.42
7.30
7.30
7.29
7.29
5.65
5.65
5.24
4.71
O
S
O
Cl
3e
1.97
1.94
1.93
2.89
1.00
1.00
2.00
f1 (ppm)

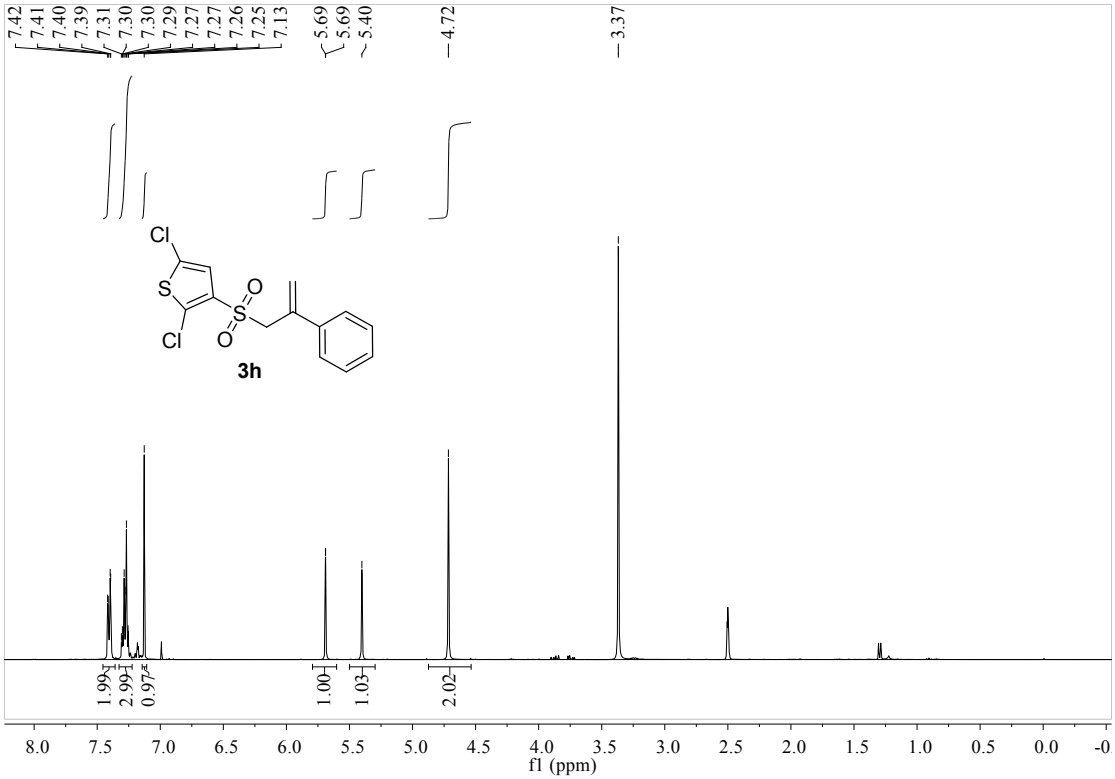

ling-1-118
138.86
138.37
137.35
136.55
130.27
129.20
128.24
127.87
126.35
122.16
60.27
O
S
O
Cl
3e
f1 (ppm)

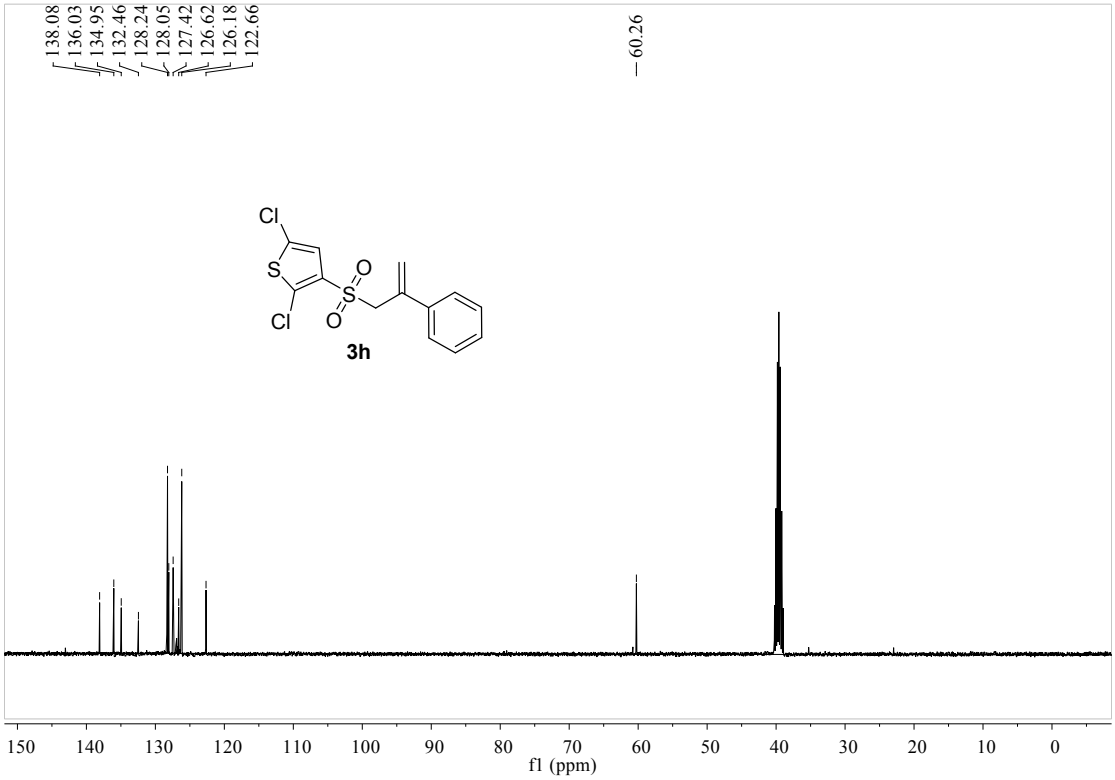

7.75
7.74
7.73
7.73
7.68
7.68
7.66
7.66
7.41
7.40
7.39
7.38
7.27
7.26
7.26
7.25
7.24
5.61
5.20
4.66
Br
3f
2.06
1.97
2.00
3.01
1.00
1.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

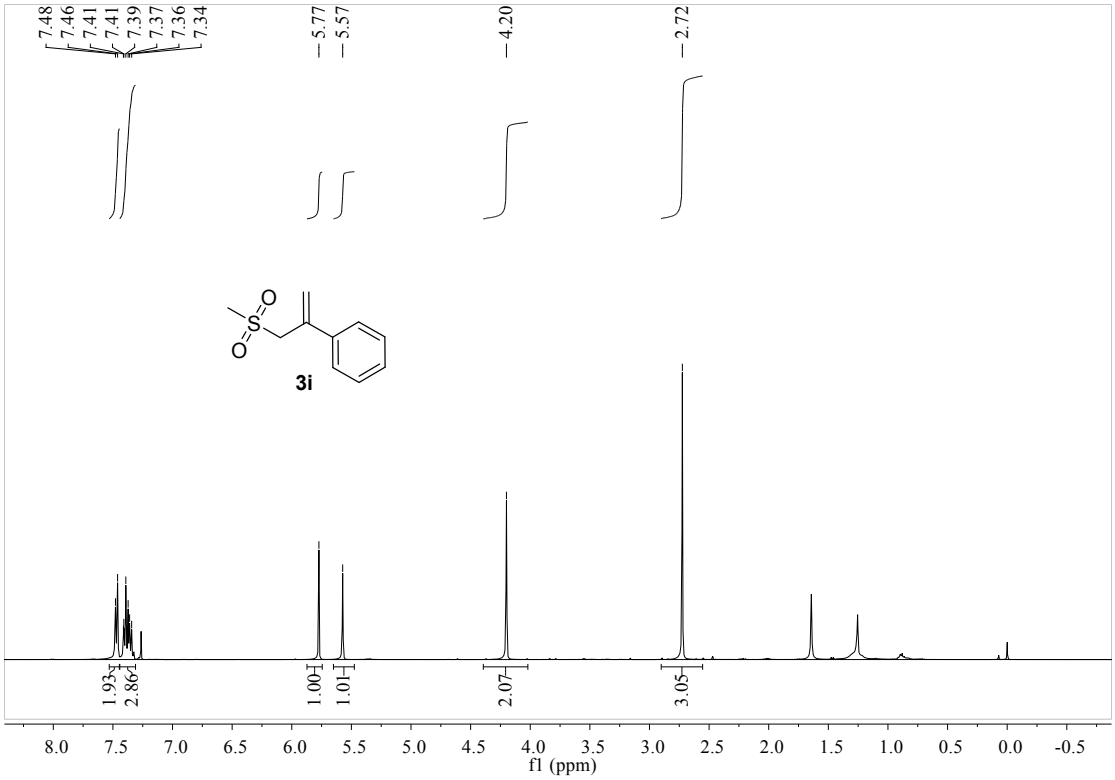

138.36
137.75
136.51
132.14
130.31
128.24
128.00
127.85
126.34
122.15
60.27
Br
3f
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.42
8.42
8.09
8.07
8.02
7.84
7.83
7.72
7.66
7.44
7.43
7.42
7.42
7.41
7.20
7.18
7.17
7.15
5.58
5.58
5.17
4.70
O
S
O
3g
0.98
1.02
0.96
1.05
1.00
1.02
1.04
1.99
3.17
1.00
1.01
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


138.53
136.60
135.75
134.80
131.59
129.92
129.55
129.37
129.14
128.16
127.93
127.81
127.69
126.32
123.23
121.97
60.33
O
S
O
3g
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.42
7.41
7.40
7.39
7.31
7.30
7.30
7.29
7.27
7.27
7.26
7.25
7.13
5.69
5.69
5.40
4.72
3.37
Cl
S
Cl
O
O
3h
1.99
2.99
0.97
1.00
1.03
2.02
f1 (ppm)


138.08
136.03
134.95
132.46
128.24
128.05
127.42
126.62
126.18
122.66
60.26
Cl
S
Cl
O
O
3h
f1 (ppm)


7.48
7.46
7.41
7.41
7.39
7.37
7.36
7.34
5.77
5.57
4.20
2.72
3i
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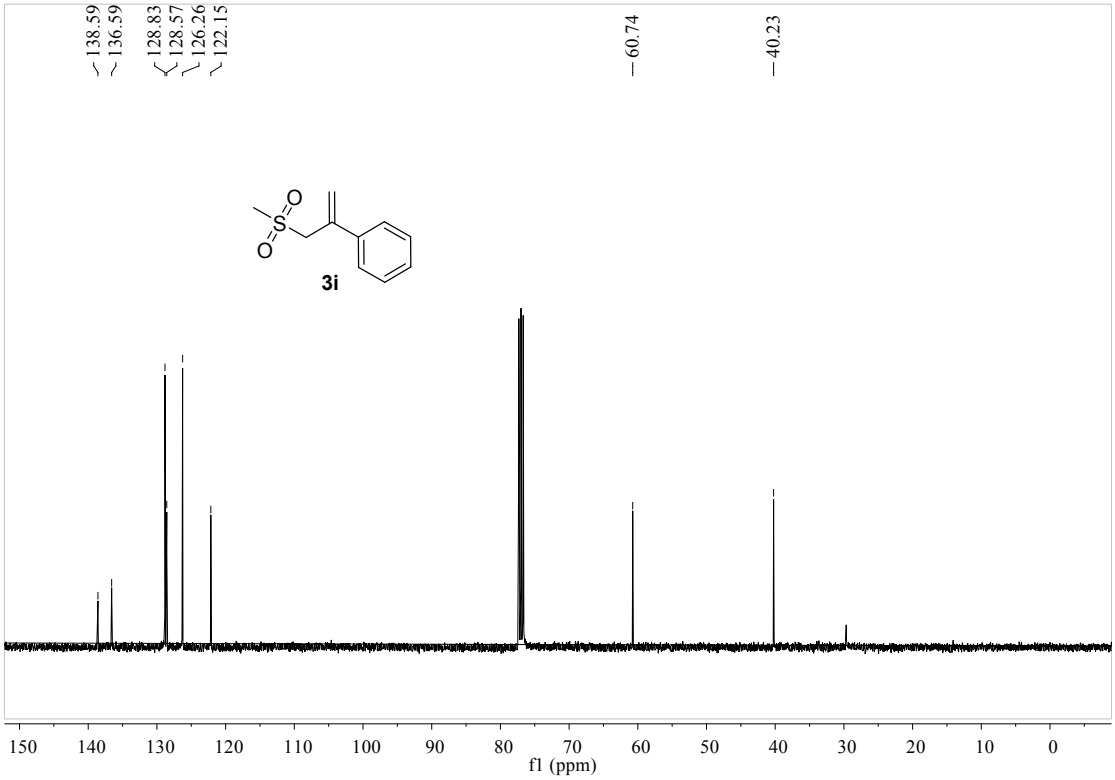
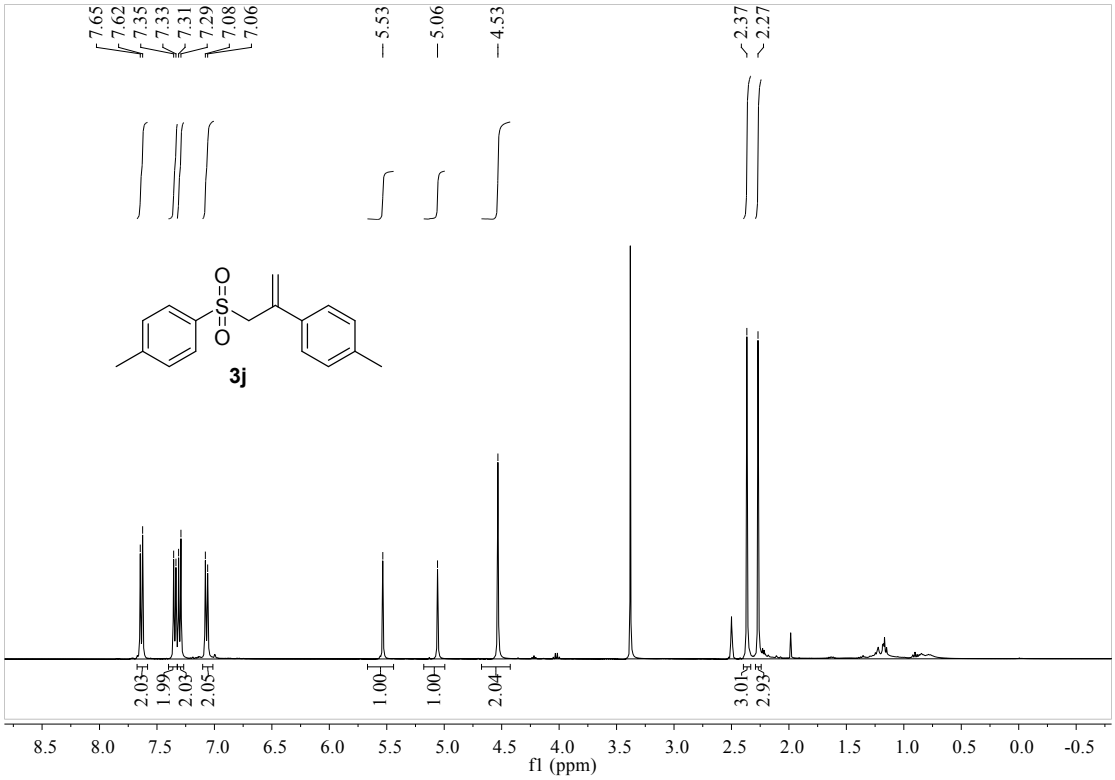
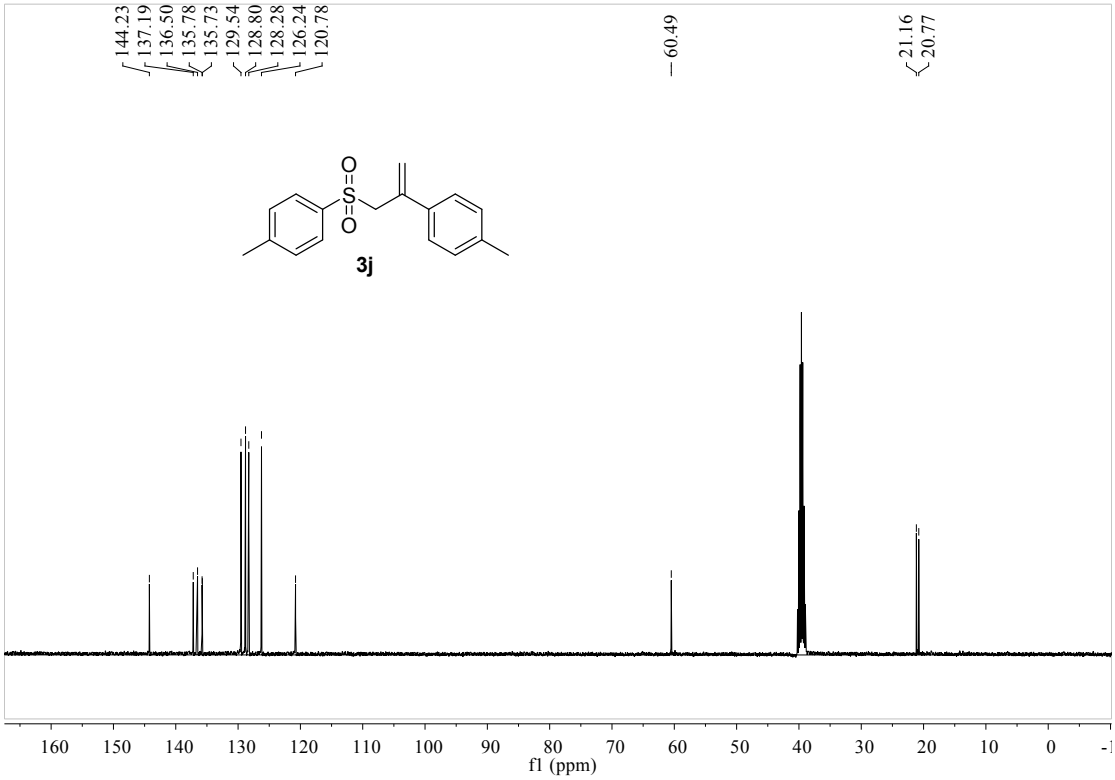
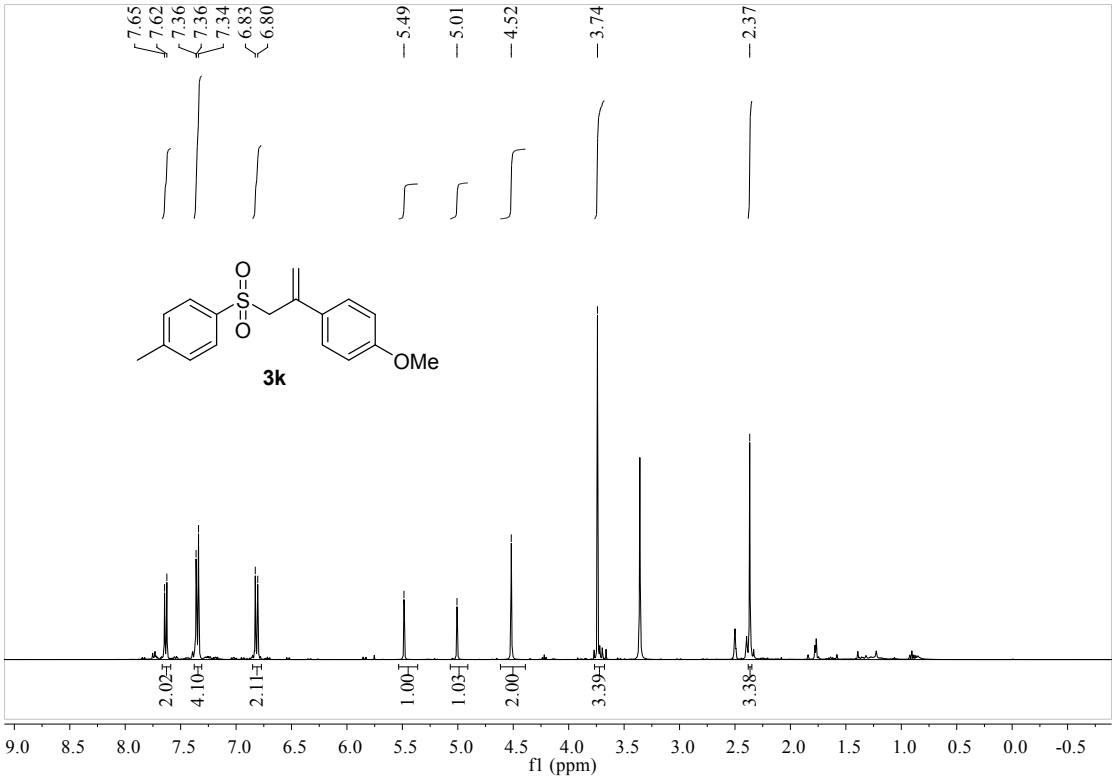
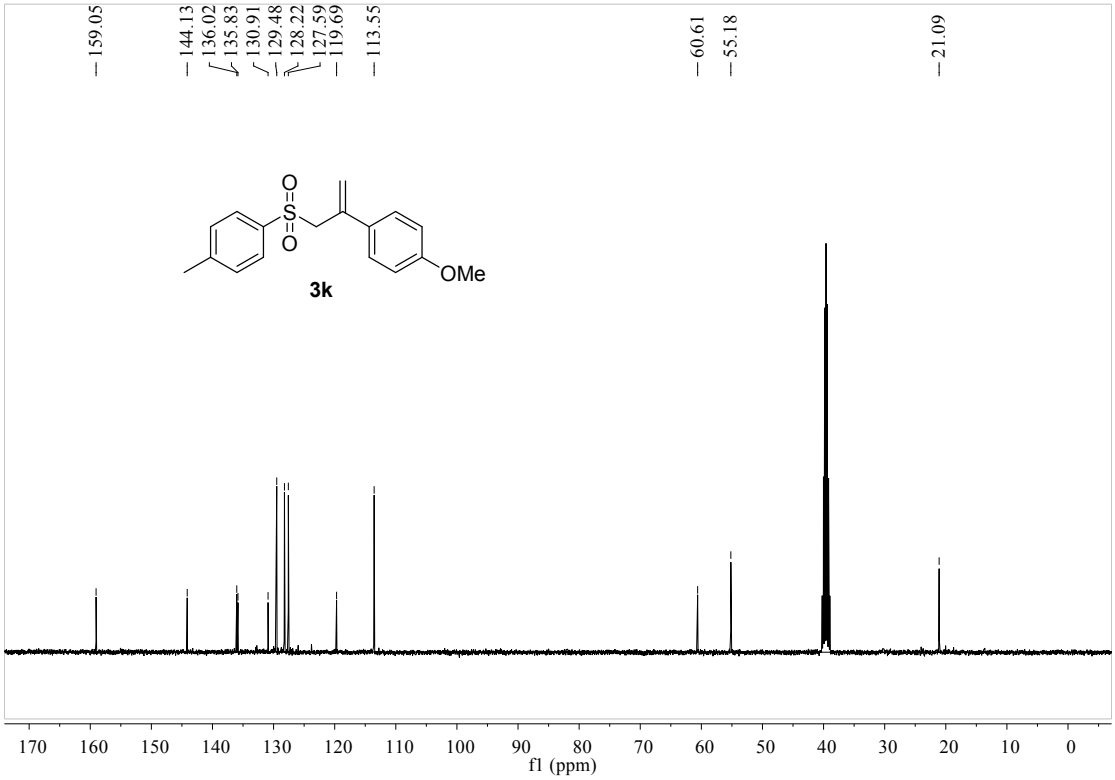
1.00
1.01
2.07
3.05
f1 (ppm)

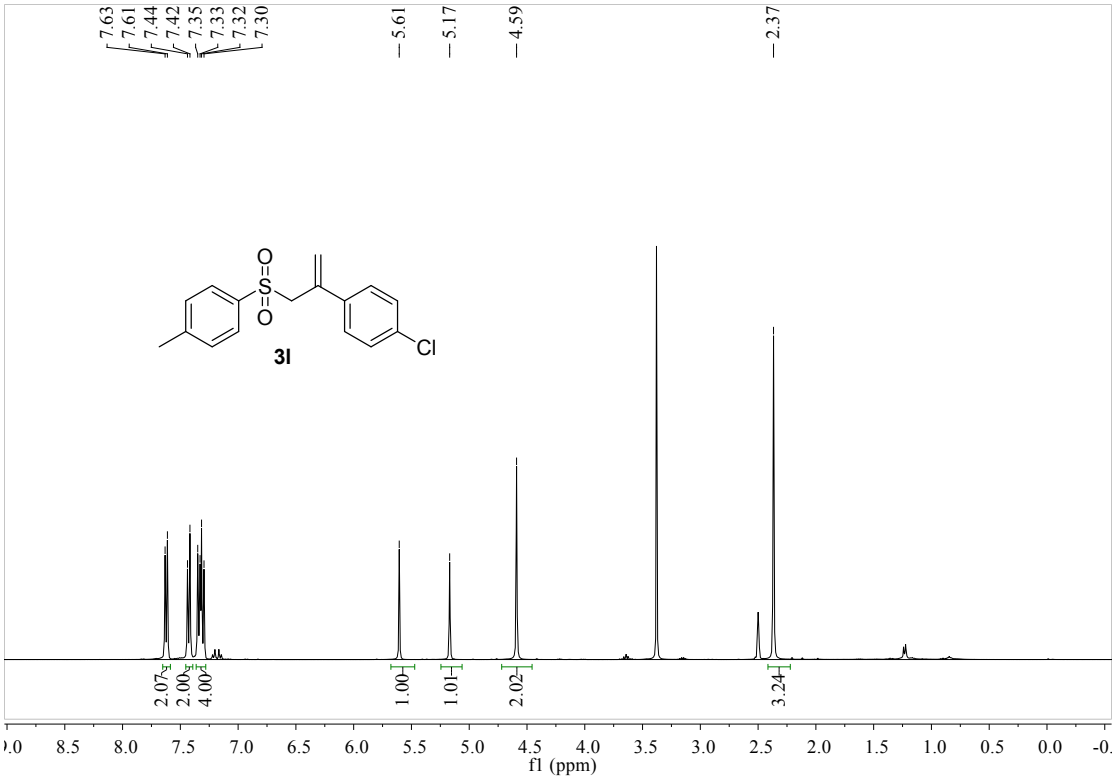

138.59
136.59
128.83
128.57
126.26
122.15
60.74
40.23
3i
f1 (ppm)

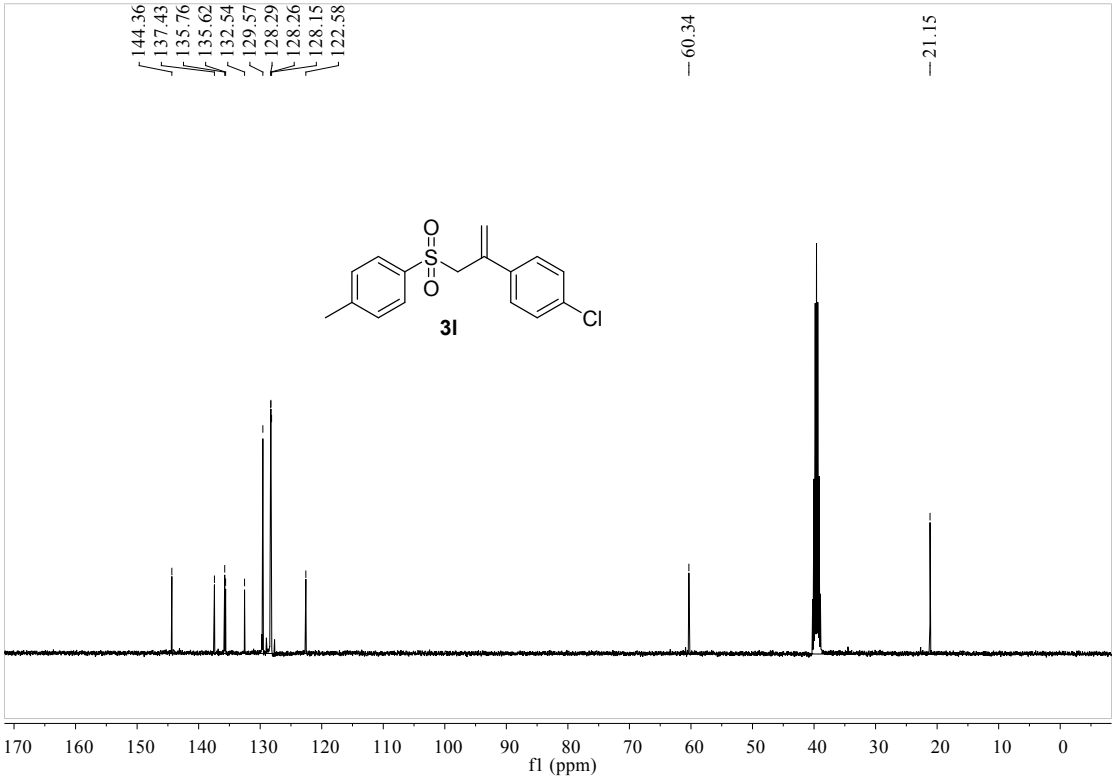

7.65
7.62
7.35
7.33
7.31
7.29
7.08
7.06
5.53
5.06
4.53
2.37
2.27
3j
2.03
1.99
2.03
2.05
1.00
1.00
2.04
3.01
2.93
f1 (ppm)

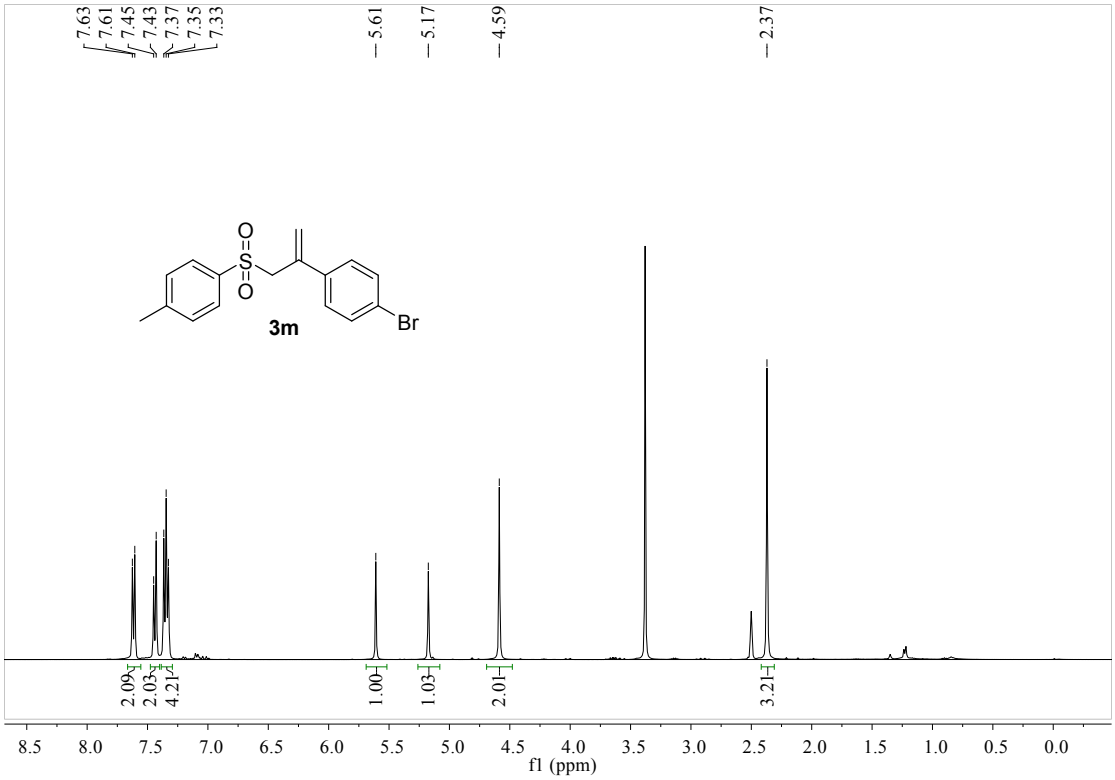

144.23
137.19
136.50
135.78
135.73
129.54
128.80
128.28
126.24
120.78
60.49
21.16
20.77
3j
f1 (ppm)

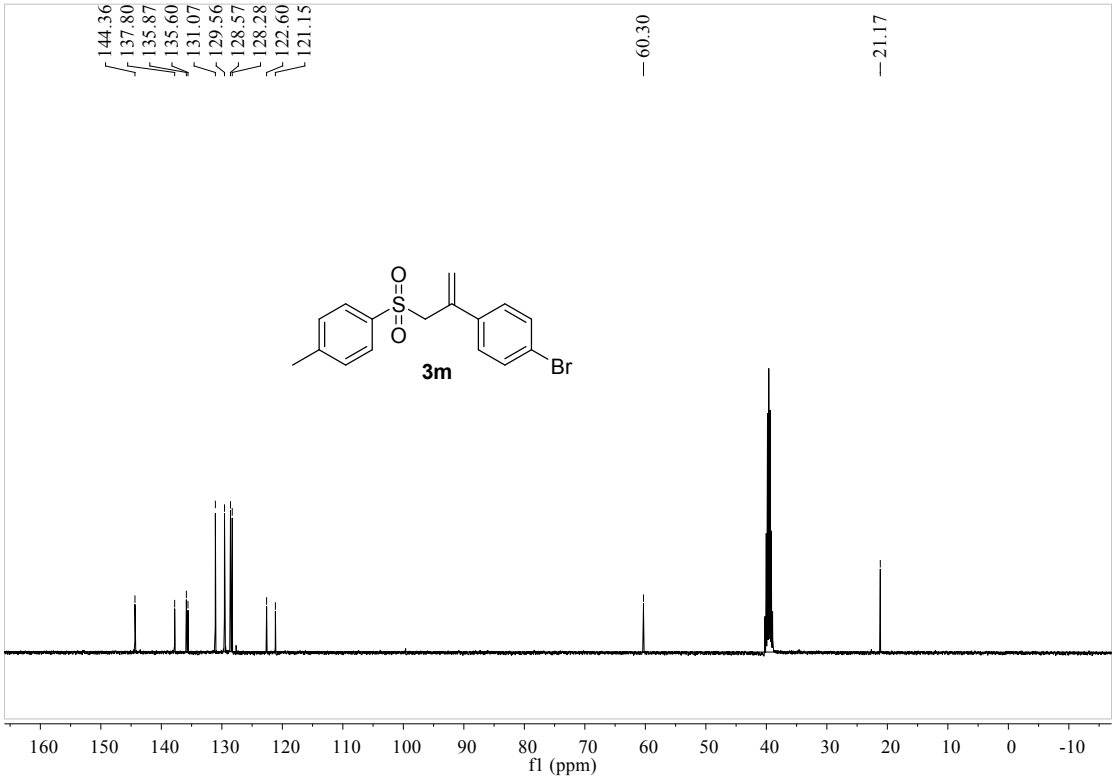

7.65
7.62
7.36
7.36
7.34
6.83
6.80
5.49
5.01
4.52
3.74
2.37
O
S
O
OMe
3k
2.02
4.10
2.11
1.00
1.03
2.00
3.39
3.38
f1 (ppm)

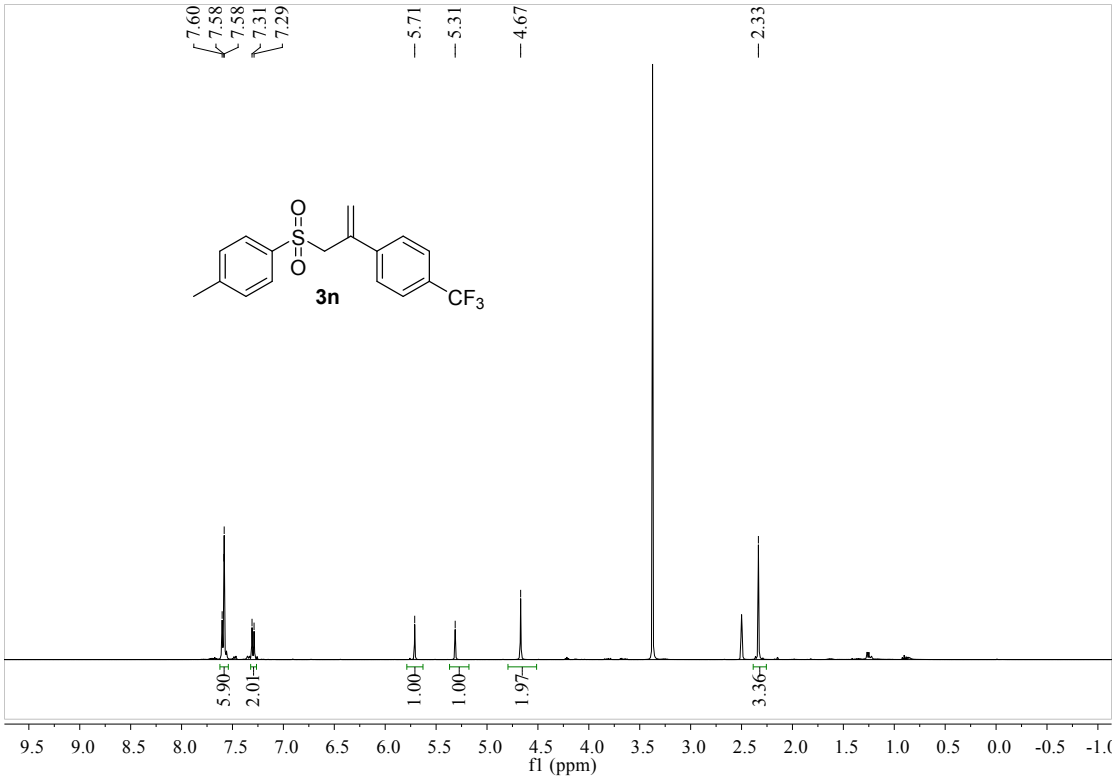

159.05
144.13
136.02
135.83
130.91
129.48
128.22
127.59
119.69
113.55
60.61
55.18
21.09
O
S
O
OMe
3k
f1 (ppm)

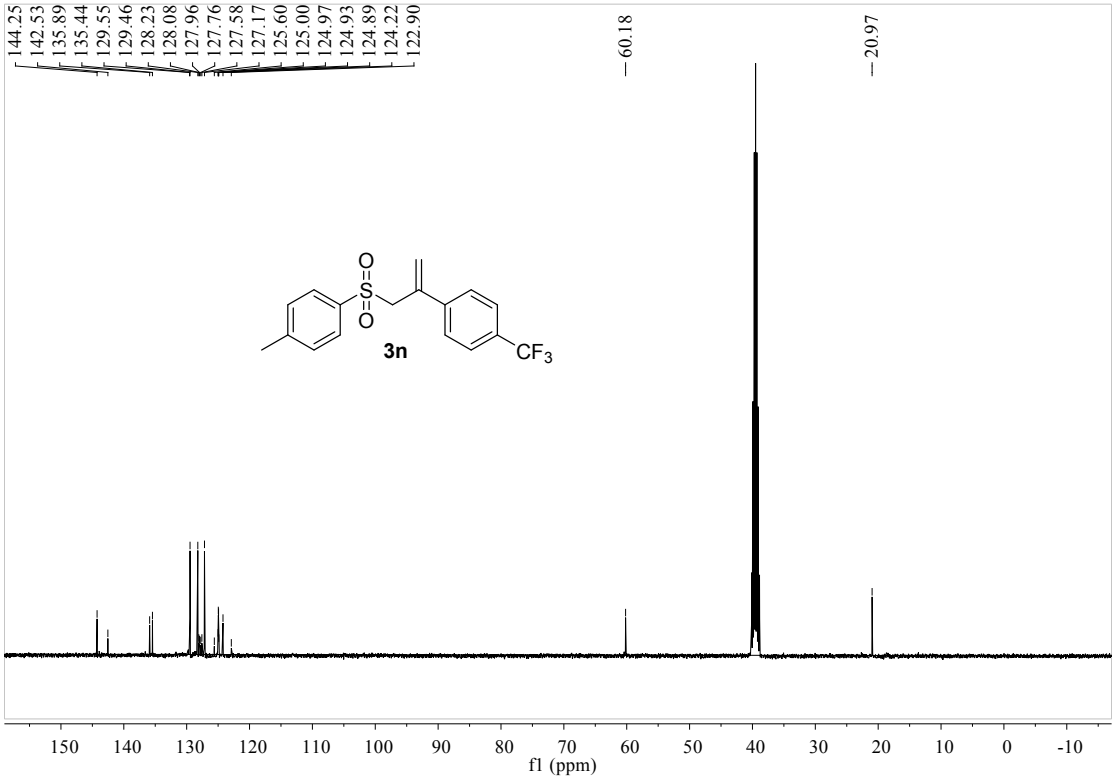

7.63
7.61
7.44
7.42
7.35
7.33
7.32
7.30
5.61
5.17
4.59
2.37
O
S
O
Cl
3l
2.07
2.00
4.00
1.00
1.01
2.02
3.24
f1 (ppm)


144.36
137.43
135.76
135.62
132.54
129.57
128.29
128.26
128.15
122.58
60.34
21.15
O
S
O
Cl
3l
f1 (ppm)


7.63
7.61
7.45
7.43
7.37
7.35
7.33
5.61
5.17
4.59
2.37
O
S
O
Br
3m
2.09
2.03
4.21
1.00
1.03
2.01
3.21
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.36
137.80
135.87
135.60
131.07
129.56
128.57
128.28
122.60
121.15
60.30
21.17
O
S
O
Br
3m
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.60
7.58
7.58
7.31
7.29
5.71
5.31
4.67
2.33
3n
CF3
5.90
2.01
1.00
1.00
1.97
3.36
f1 (ppm)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135.44
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129.46
128.23
128.08
127.96
127.76
127.58
127.17
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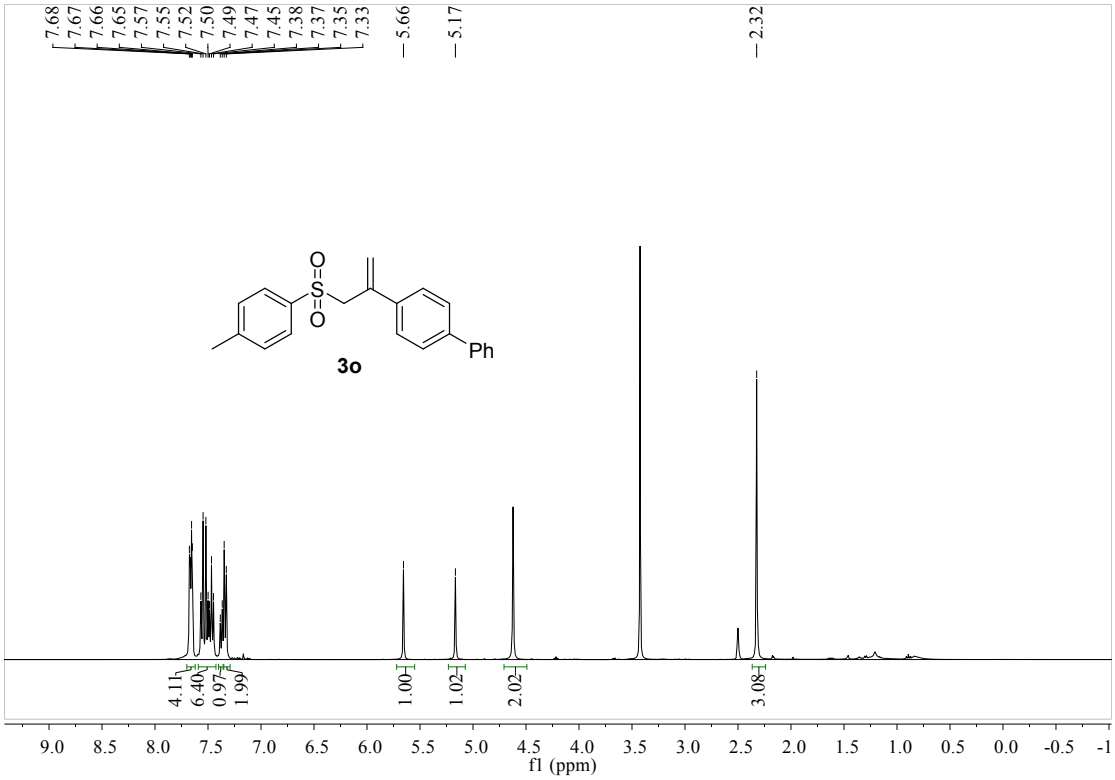
122.90
60.18
20.97
3n
CF3
f1 (ppm)


7.68
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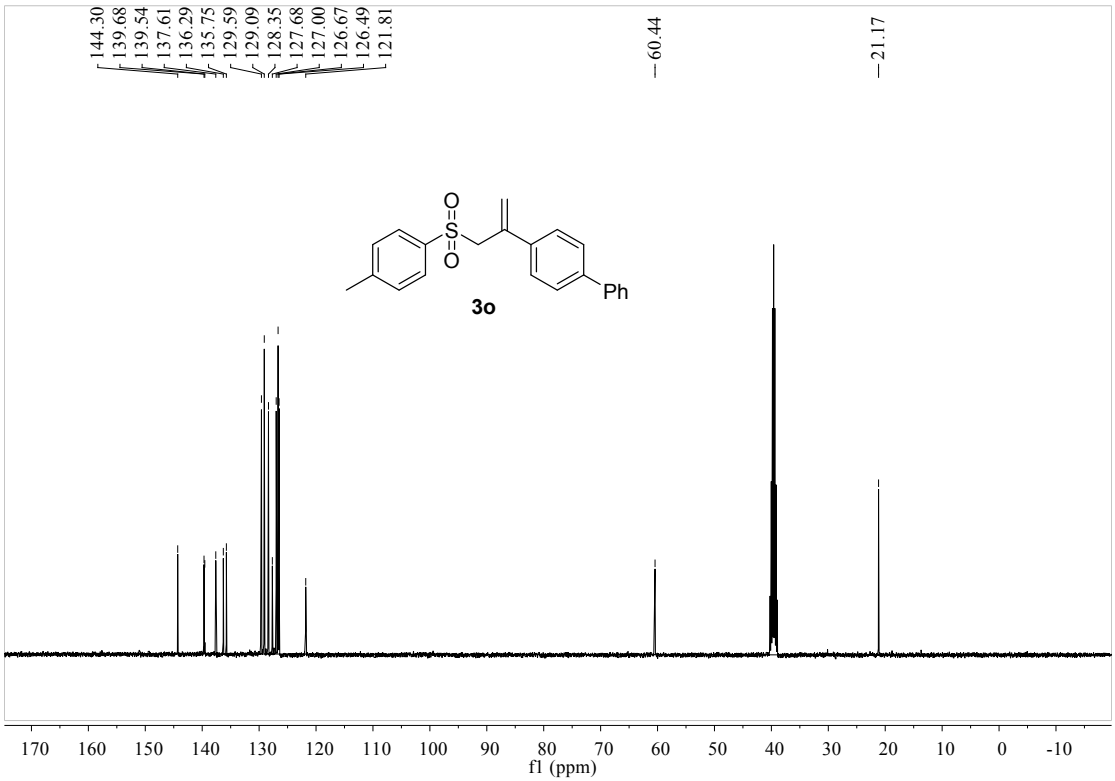
7.57
7.55
7.52
7.50
7.49
7.47
7.45
7.38
7.37
7.35
7.33
5.66
5.17
2.32
O
S
O
Ph
3o
4.11
6.40
0.97
1.99
1.00
1.02
2.02
3.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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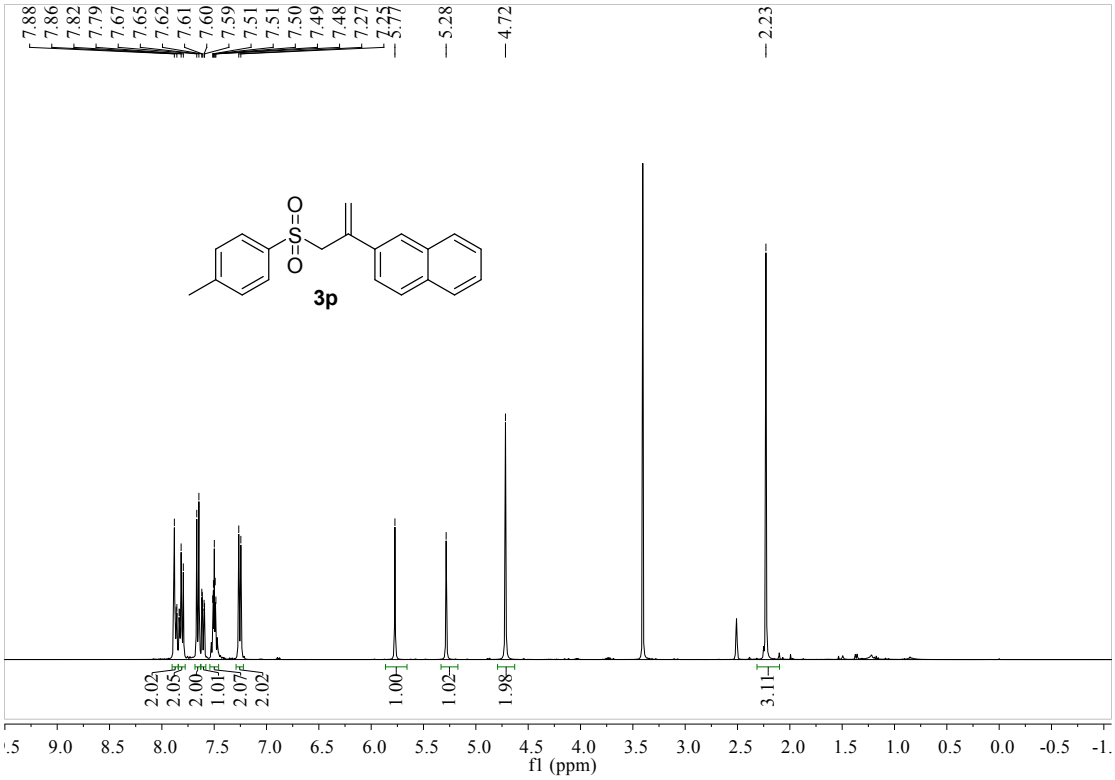
139.68
139.54
137.61
136.29
135.75
129.59
129.09
128.35
127.68
127.00
126.67
126.49
121.81
60.44
21.17
O
S
O
Ph
3o
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.88
7.86
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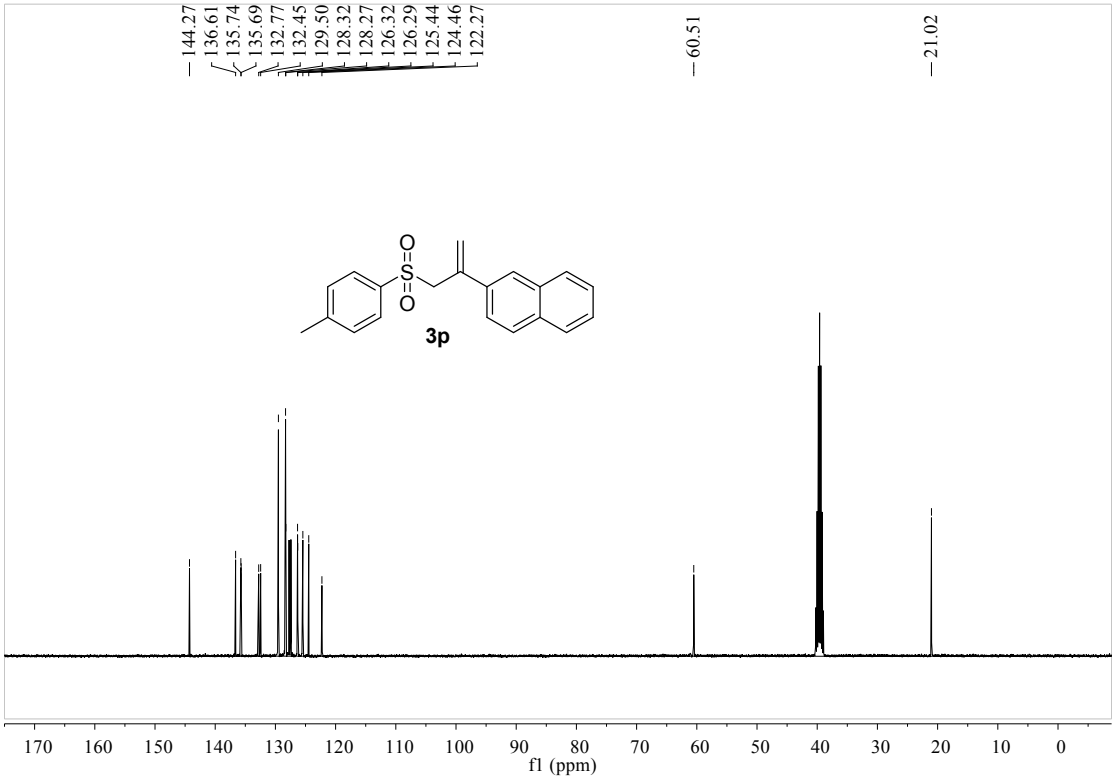
7.79
7.67
7.65
7.62
7.61
7.60
7.59
7.51
7.51
7.50
7.49
7.48
7.27
5.28
4.72
2.23
3p
2.02
2.05
2.00
1.01
2.07
2.02
1.00
1.02
1.98
3.11
f1 (ppm)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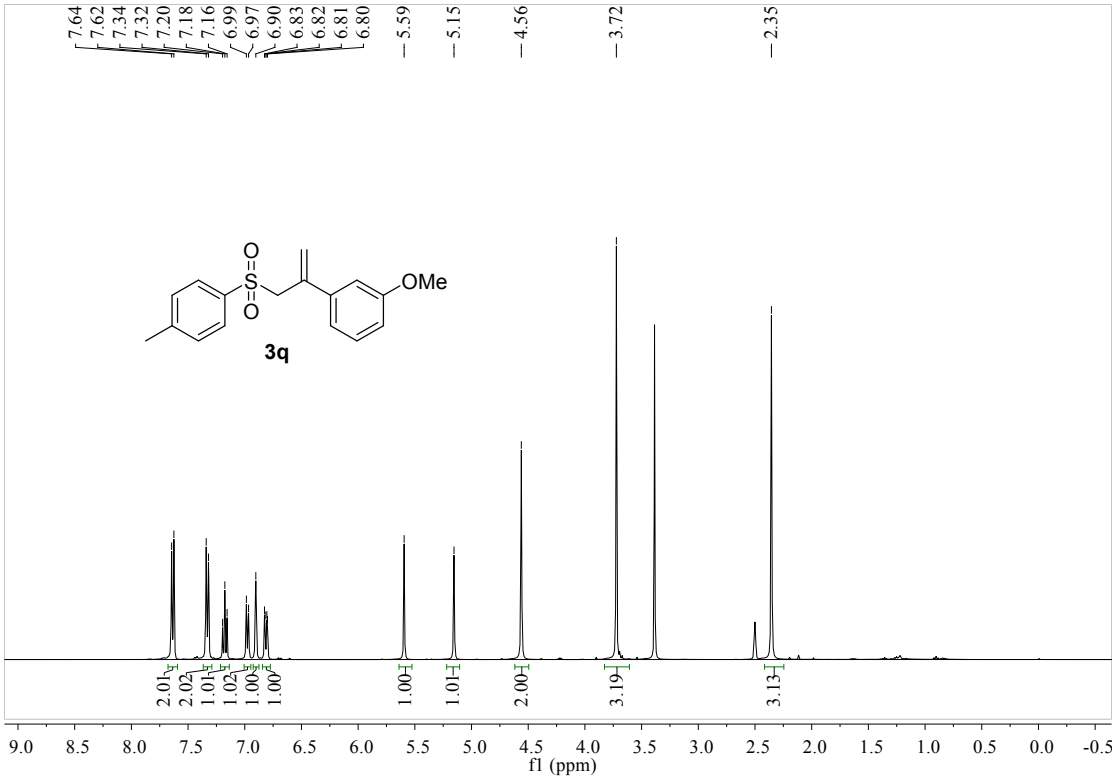
136.61
135.74
135.69
132.77
132.45
129.50
128.32
128.27
126.32
126.29
125.44
124.46
122.27
60.51
21.02
3p
f1 (ppm)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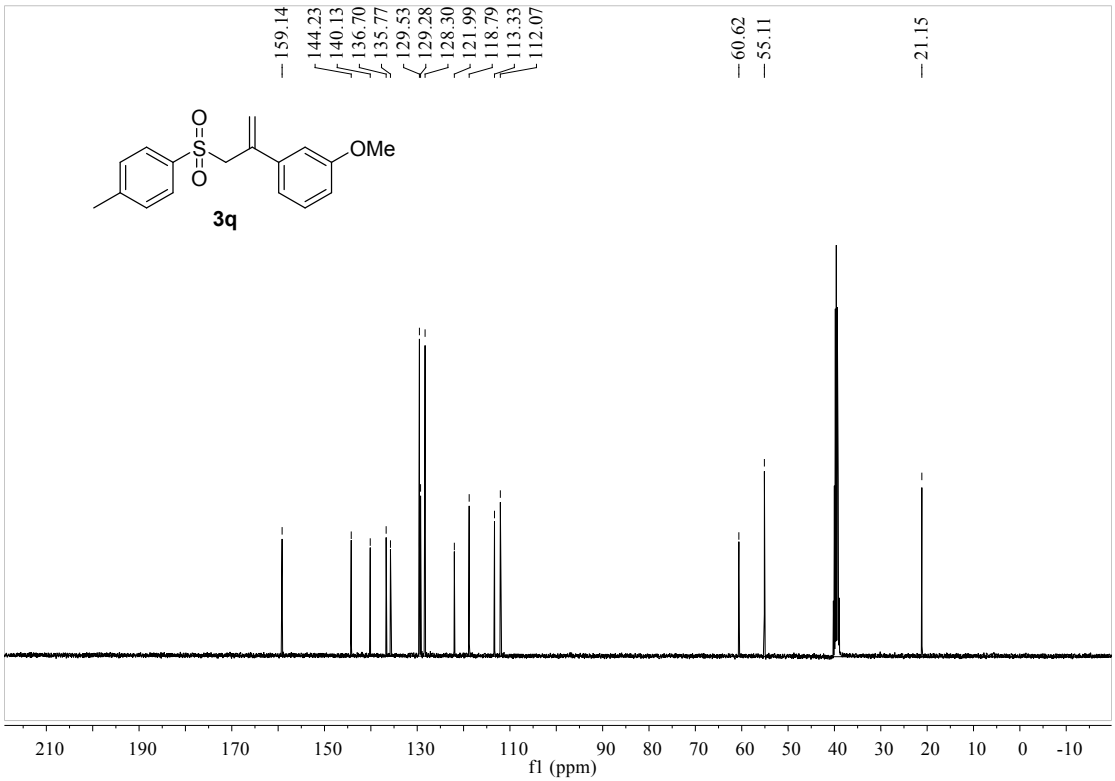
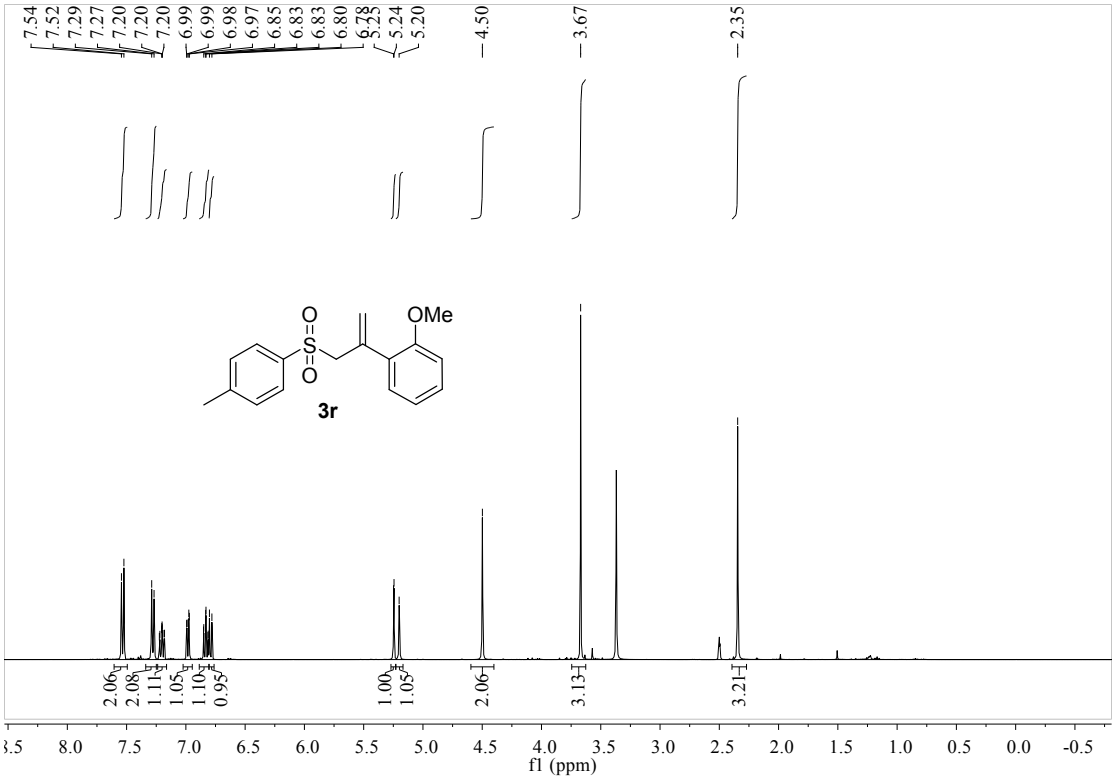
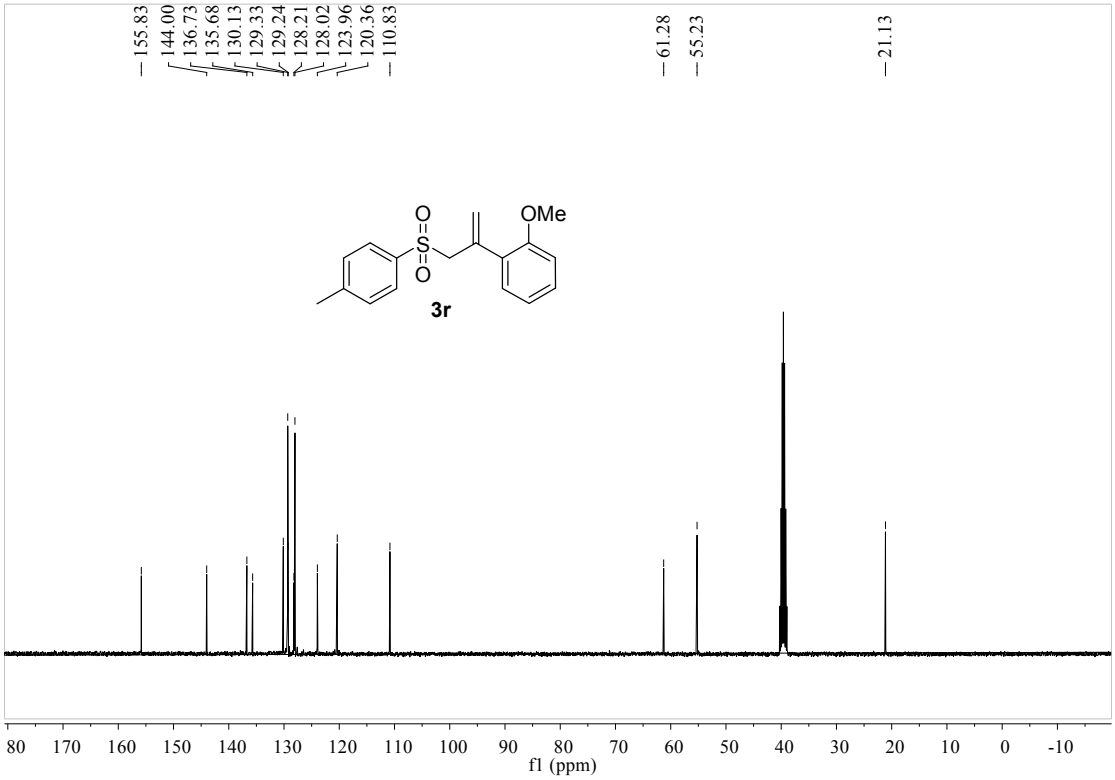
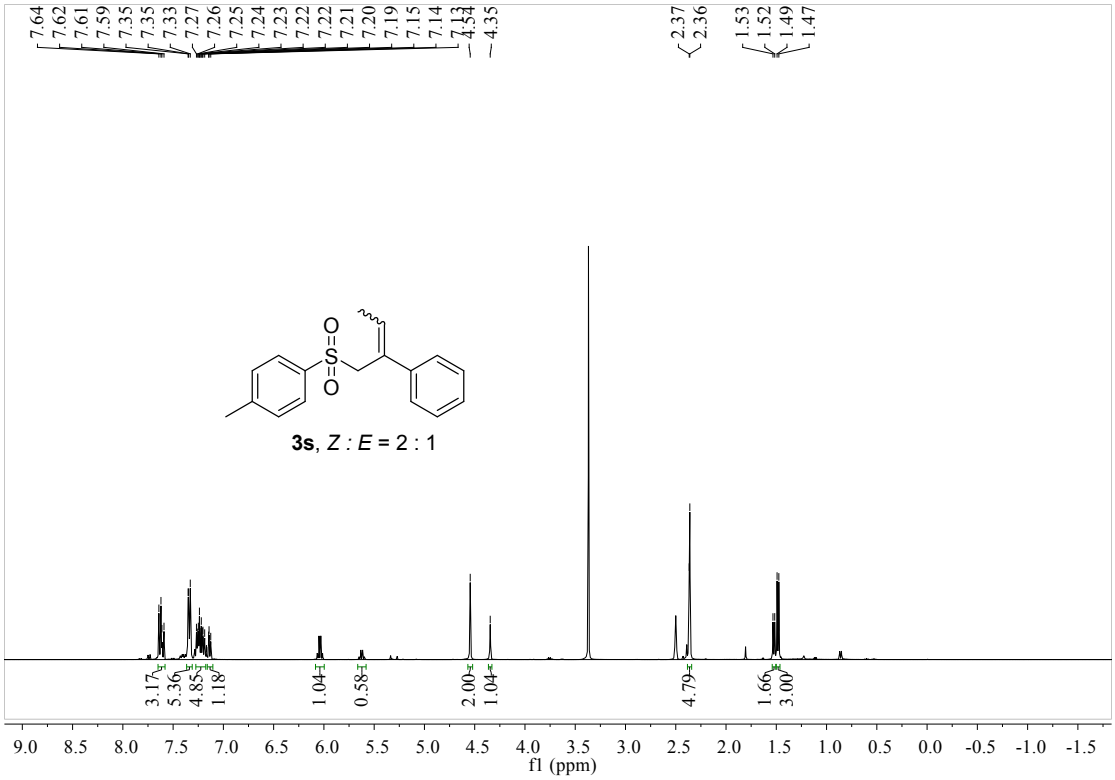
7.62
7.34
7.32
7.20
7.18
7.16
6.99
6.97
6.90
6.83
6.82
6.81
6.80
5.59
5.15
4.56
3.72
2.35
O
O=S=O
OMe
3q
2.01
2.02
1.01
1.02
1.00
1.00
1.00
1.01
2.00
3.19
3.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

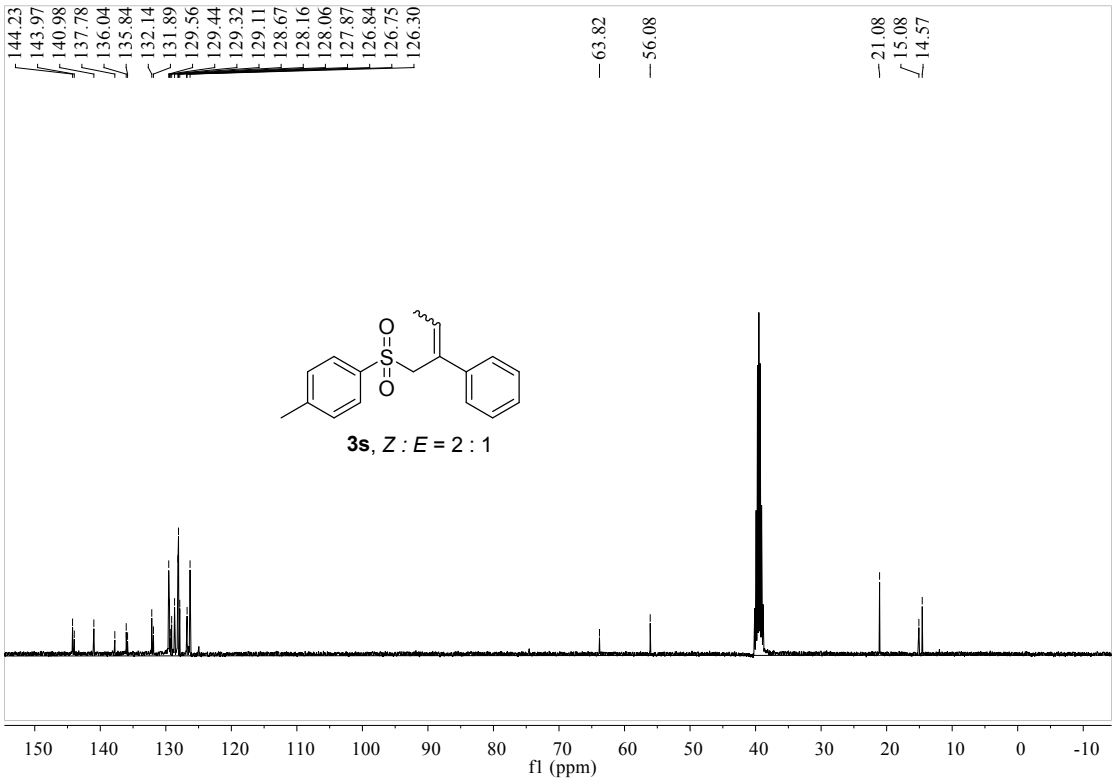

159.14
144.23
140.13
136.70
135.77
129.53
129.28
128.30
121.99
118.79
113.33
112.07
60.62
55.11
21.15
O
O=S=O
OMe
3q
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.54
7.52
7.29
7.27
7.20
7.20
7.20
6.99
6.99
6.98
6.97
6.85
6.83
6.83
6.80
6.78
5.24
5.20
4.50
3.67
2.35
O
S
O
OMe
3r
2.06
2.08
1.11
1.05
1.10
0.95
1.00
1.05
2.06
3.13
3.21
f1 (ppm)

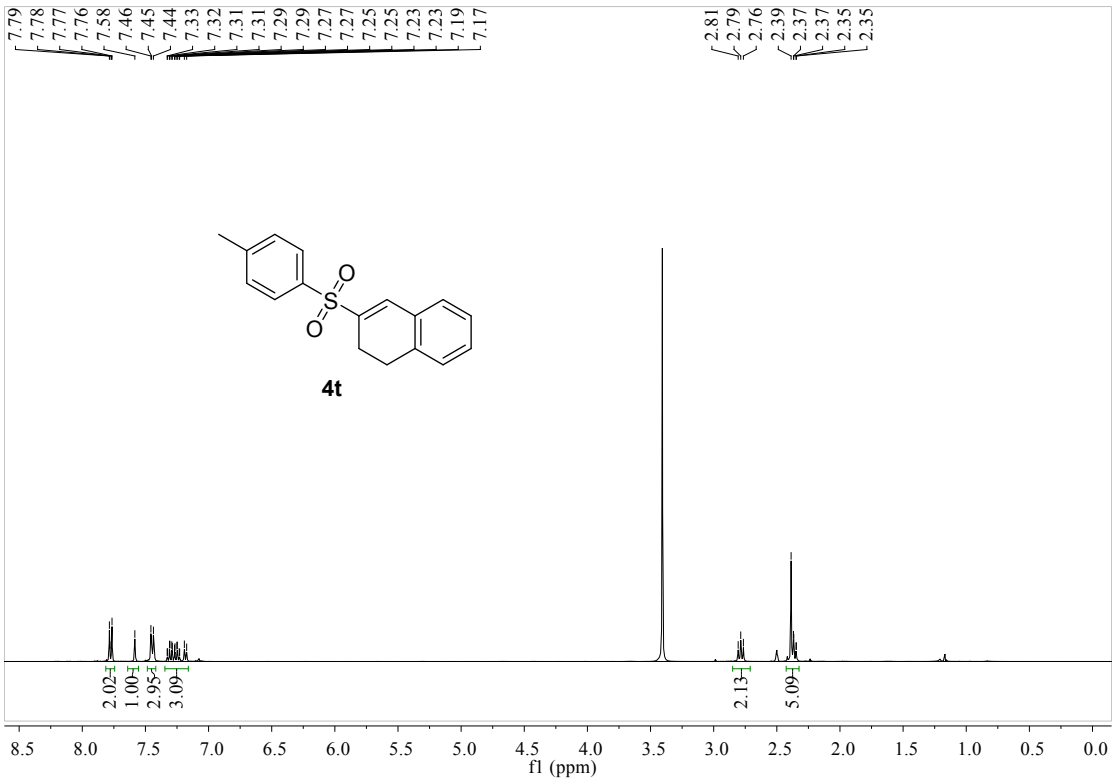

155.83
144.00
136.73
135.68
130.13
129.33
129.24
128.21
128.02
123.96
120.36
110.83
61.28
55.23
21.13
O
S
O
OMe
3r
f1 (ppm)

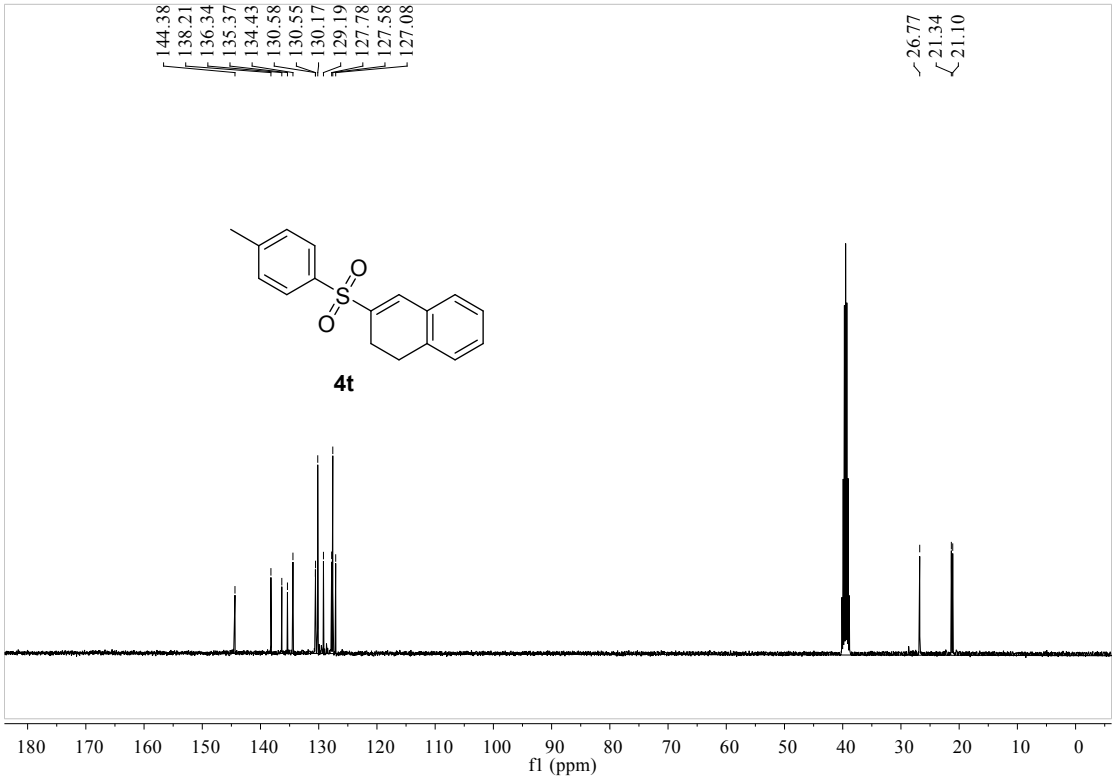


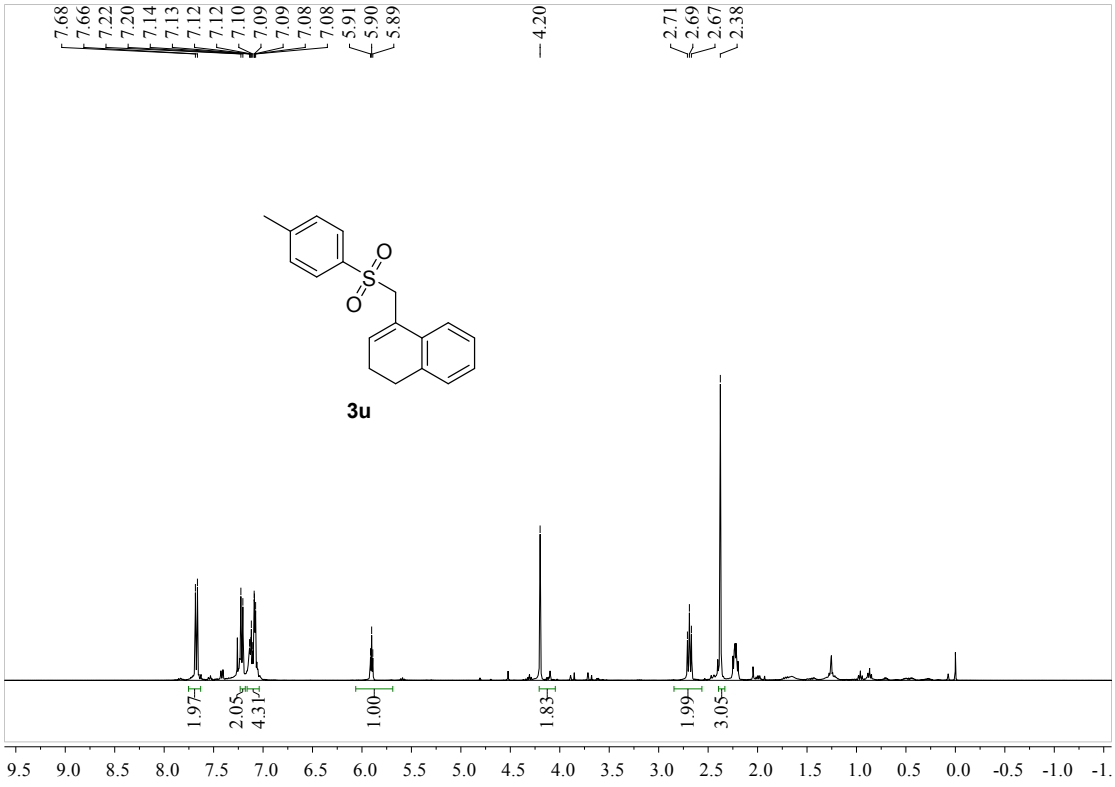
3s, *Z* : *E* = 2 : 1

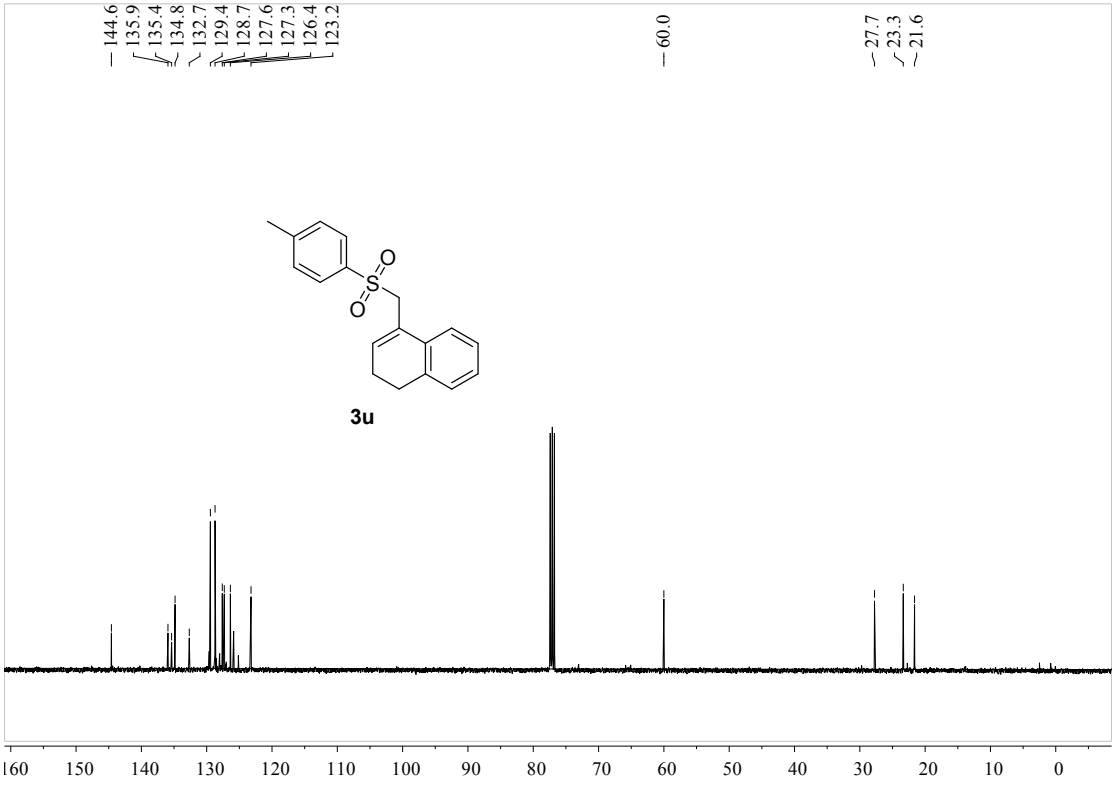


3s, *Z* : *E* = 2 : 1


7.79
7.78
7.77
7.76
7.58
7.46
7.45
7.44
7.33
7.32
7.31
7.31
7.29
7.29
7.27
7.27
7.25
7.25
7.23
7.23
7.19
7.17
2.81
2.79
2.76
2.39
2.37
2.37
2.35
2.35
4t
2.02
1.00
2.95
3.09
2.13
5.09
f1 (ppm)


144.38
138.21
136.34
135.37
134.43
130.58
130.55
130.17
129.19
127.78
127.58
127.08
26.77
21.34
21.10
4t
f1 (ppm)


7.68
7.66
7.22
7.20
7.14
7.13
7.12
7.12
7.10
7.09
7.09
7.08
7.08
5.91
5.90
5.89
4.20
2.71
2.69
2.67
2.38
3u
1.97
2.05
4.31
1.00
1.83
1.99
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.


144.6
135.9
135.4
134.8
132.7
129.4
128.7
127.6
127.3
126.4
123.2
60.0
27.7
23.3
21.6
3u
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0