Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-catalyzed direct decarboxylative hydrosulfonylation of aryl propiolic acids with sulfonylhydrazides leading to vinylsulfones

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1. General information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. High resolution mass spectra were ensured on a MALDI-FTMS. Dichloromethane, ethyl acetate and hexane were used for column chromatography without further purification. Other solvents were purified according to the standard methods. Reagents were obtained from commercial sources and used without further purification.

2. General procedure

In a clean tube equipped with a stir bar, sulfonylhydrazide (0.2 mmol), aryl propiolic acid or terminal alkyne (0.24 mmol), CuI (0.02 mmol) and 2, 2'-bpy (0.02 mmol) were added in DMF (1 ml). The resulting mixture was heated at 100 ^{o}C for 18 h under air unless otherwise noted. After the reaction was completed and cooled to room temperature, the mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent in vacuo, the residue was purified by column chromatography (ethyl acetate/hexane) to afford the pure product.

3. Optimization of the reaction conditions[a]

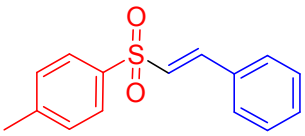
Entry	Catalyst	Solvent	Ligand	Yield[b]
1	CuCl	DMF	-	28%
2	CuBr	DMF	-	51%
3	CuI	DMF	-	57%
4[c]	Cu_2O	DMF	-	25%
5	$Cu(OAc)_2 \cdot H_2O$	DMF	-	36%
6	$CuCl_2$	DMF	-	＜5%
7	$CuBr_2$	DMF	-	＜5%

8	$CuF_2 \cdot 2H_2O$	DMF	-	＜5%
9	CuI	DMA	-	＜5%
10	CuI	THF	-	＜5%
11	CuI	toluene	-	＜5%
12	CuI	DMSO	-	41%
13	CuI	Dioxane	-	25%
14	CuI	p-xylene	-	21%
15	CuI	DMF	pyridine	＜5%
16	CuI	DMF	phen	＜5%
17	CuI	DMF	DMEDA	＜5%
18	**CuI**	**DMF**	**2, 2'-bpy**	**85%**
19	-	DMF	2, 2'-bpy	< 5%
20[d]	CuI	DMF	2, 2'-bpy	87%
21[e]	CuI	DMF	2, 2'-bpy	64%
13[f]	CuI	DMF	2, 2'-bpy	< 5%

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), catalyst (10 mol%) and base (0.4 mmol) in solvent (1 mL) at 100 °C under air for 18 h. [b] Isolated yield. [c] Under 5 mol% of Cu_2O catalyst loading. [d] At 120 °C. [e] At 80 °C. [f] Under a nitrogen atmosphere.

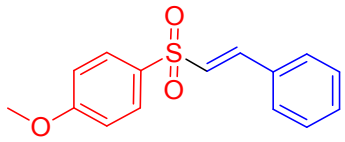
4. Characterizations of Products

(E)-1-methyl-4-(styrylsulfonyl)benzene (3a)[3]



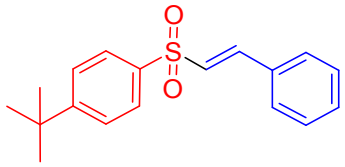
White solid, mp 118–120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 6.84 (d, J = 15.2 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.38–7.40 (m, 3H), 7.46–7.48 (m, 2H), 7.65 (d, J = 15.2 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.6, 127.6, 127.7, 128.5, 129.0, 130.0, 131.1, 132.5, 137.7, 141.9, 144.4.

(E)-1-methoxy-4-(styrylsulfonyl)benzene (3b)[1]



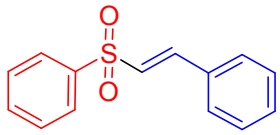
Pale yellow solid, mp 110–112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 6.85 (d, J = 15.2 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 7.38–7.39 (m, 3H), 7.46–7.48 (m, 2H), 7.63 (d, J = 15.2 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 55.6, 114.5, 127.9, 128.4, 129.0, 129.8, 131.0, 132.2, 132.5, 141.3, 163.5.

(E)-1-(tert-butyl)-4-(styrylsulfonyl)benzene (3c)



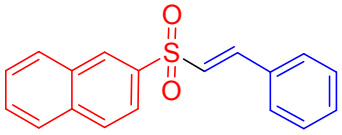
Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.34 (s, 9H), 6.87 (d, J = 15.2 Hz, 1H), 7.38–7.43 (m, 3H), 7.47–7.49 (m, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 15.2 Hz, 1H), 7.87 (d, J = 8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 31.0, 35.2, 126.3, 127.5, 127.6, 128.5, 129.0, 131.1, 132.4, 137.6, 141.9, 157.3.

(E)-(2-(phenylsulfonyl)vinyl)benzene (3d)[1]



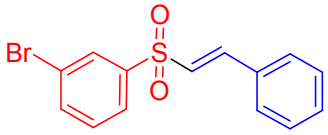
Light yellow solid, mp 69–71 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.87 (d, J = 15.2 Hz, 1H), 7.37–7.42 (m, 3H), 7.48–7.50 (m, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.69 (d, J = 15.2 Hz, 1H), 7.95 (d, J = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 127.3, 127.7, 128.6, 129.1, 129.4, 131.3, 132.4, 133.4, 140.7, 142.5.

(E)-2-(styrylsulfonyl)naphthalene (3e)[1]



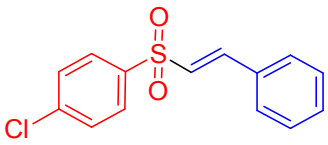
White solid, mp 115–116 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.92 (d, J = 15.2 Hz, 1H), 7.38–7.39 (m, 3H), 7.47–7.49 (m, 2H), 7.60–7.67 (m, 2H), 7.74 (d, J = 15.2 Hz, 1H), 7.87–7.92 (m, 2H), 7.97–8.00 (m, 2H), 8.55 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 122.5, 127.3, 127.6, 127.9, 128.6, 129.1, 129.2, 129.2, 129.4, 129.7, 131.2, 132.3, 132.4, 135.1, 137.5, 142.5.

(E)-1-bromo-3-(styrylsulfonyl)benzene (3f)



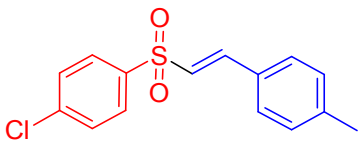
Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.84 (d, J = 15.6 Hz, 1H), 7.41–7.45 (m, 4H), 7.49–7.51 (m, 2H), 7.71 (d, J = 15.6 Hz, 1H), 7.70-7.75 (m, 1H), 7.88 (d, J = 7.6 Hz, 1H), 8.09 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 123.3, 126.2, 126.7, 128.7, 129.2, 130.6, 130.9, 131.5, 132.1, 136.4, 142.7, 143.5.

(E)-1-chloro-4-(styrylsulfonyl)benzene (3g)[3]



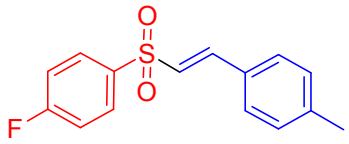
White solid, mp 79–81 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.84 (d, J = 15.2 Hz, 1H), 7.40–7.53 (m, 7H), 7.69 (d, J = 15.2 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 126.8, 128.6, 129.1, 129.7, 131.4, 132.1, 139.2, 140.1, 143.0.

(E)-1-chloro-4-((4-methylstyryl)sulfonyl)benzene (3h)[2]



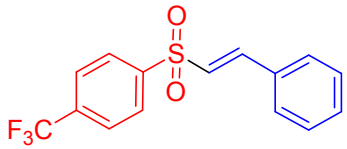
Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.78 (d, J = 15.6 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.50 –7.52 (m, 2H), 7.66 (d, J = 15.6 Hz, 1H), 7.87 –7.89 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.5, 125.6, 128.6, 129.1, 129.4, 129.6, 129.8, 139.4, 139.9, 142.1, 143.1.

(E)-1-fluoro-4-((4-methylstyryl)sulfonyl)benzene (3i)[2].



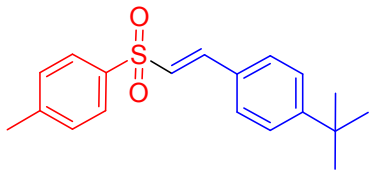
Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 6.79 (d, J = 15.2 Hz, 1H), 7.19 –7.24 (m, 4H), 7.38 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 15.2 Hz, 1H), 7.94 – 7.98 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.5, 116.6 (d, J = 22.5 Hz), 125.8, 128.6, 129.4, 129.8, 130.4 (d, J = 9.4 Hz), 136.9 (d, J= 3.1 Hz), 142.0, 142.7, 165.5 (d, J = 254.7 Hz).

(E)-1-(styrylsulfonyl)-4-(trifluoromethyl)benzene (3*J*)[1]



Light yellow solid, mp 78–80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.86 (d, J = 15.2 Hz, 1H), 7.39–7.45 (m, 3H), 7.50–7.51 (m, 2H), 7.75 (d, J = 15.2 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 123.1 (q, J = 271.4 Hz), 126.2, 126.5 (q, J = 3.6 Hz), 128.2, 128.7, 129.2, 131.6, 132.0, 135.0 (q, J = 32.9 Hz), 144.1, 144.3.

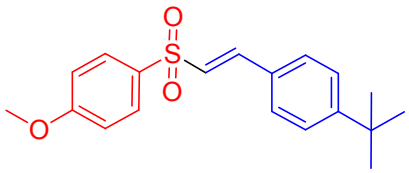
(E)-1-(tert-butyl)-4-(2-tosylvinyl)benzene (3k)[2]



Light yellow solid, mp 77–79 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.30 (s, 9H), 2.43 (s, 3H), 6.80 (d, J = 15.2 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.39–7.43 (m, 4H), 7.64 (d, J

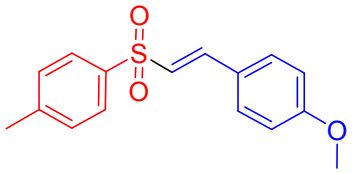
= 15.2 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.6, 31.1, 34.9, 126.0, 126.6, 127.6, 128.4, 129.7, 129.9, 137.9, 141.9, 144.2, 154.8.

(E)-1-(tert-butyl)-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (3l)



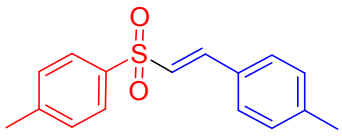
White solid, mp 134–136 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.30 (s, 9H), 3.86 (s, 3H), 6.81 (d, *J* = 15.2 Hz, 1H), 6.99 (d, *J* = 9.2 Hz, 2H), 7.39–7.43 (m, 4H), 7.62 (d, *J* = 15.2 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 31.0, 34.9, 55.6, 114.4, 126.0, 126.9, 128.3, 129.7, 129.7, 132.3, 141.3, 154.7, 163.4; **HRMS-ESI** (m/z): calcd for $C_{19}H_{22}O_3S$ $[M+H]^+$ 331.1362, found 331.1366.

(E)-1-methoxy-4-(2-tosylvinyl)benzene (3m)[3]



White solid, mp 96-98 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.83 (s, 3H), 6.69 (d, *J* = 15.2 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 15.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.6, 55.4, 114.5, 124.8, 125.1, 127.6, 129.9, 130.3, 138.2, 141.7, 144.1, 162.0.

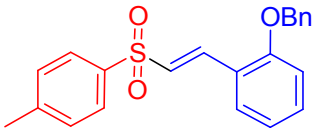
(E)-1-methyl-4-((4-methylstyryl)sulfonyl)benzene (3n)[2]



Light yellow solid, mp 152–155 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.43 (s, 3H), 6.79 (d, *J* = 15.2 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 15.2 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H); **^{13}C**

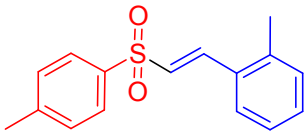
NMR (100 MHz, $CDCl_3$): δ 21.5, 21.6, 126.4, 127.1, 127.6, 128.5, 129.8, 129.9, 138.0, 141.7, 142.0, 144.2.

(E)-1-(benzyloxy)-2-(2-tosylvinyl)benzene (3o)



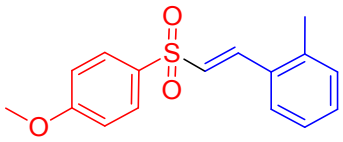
Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 5.13 (s, 2H), 6.94–6.98 (m, 2H), 7.10 (d, J = 15.2 Hz, 1H), 7.28–7.36 (m, 9H), 7.76 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 15.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.6, 70.4, 112.7, 121.1, 121.6, 127.2, 127.6, 128.1, 128.7, 128.7, 129.8, 130.9, 132.2, 136.1, 137.7, 138.1, 144.0, 157.8; **HRMS-ESI** (m/z): calcd for $C_{22}H_{20}O_3S$ $[M+H]^+$ 365.1206, found 365.1205.

(E)-1-methyl-2-(2-tosylvinyl)benzene (3p)[2]



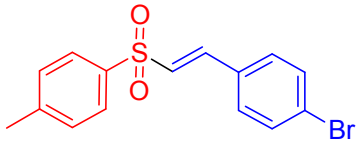
Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.44 (d, J = 4.8 Hz, 6H), 6.77 (d, J = 15.2 Hz, 1H), 7.18–7.22 (m, 2H), 7.27 –7.29 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 7.6 Hz, 1H), 7.82 –7.84 (m, 2H), 7.94 (d, J = 15.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.7, 21.6, 126.4, 126.8, 127.7, 128.5, 130.0, 130.8, 131.0, 131.4, 137.8, 138.1, 139.6, 144.3.

(E)-1-(2-((4-methoxyphenyl)sulfonyl)vinyl)-2-methylbenzene (3q)



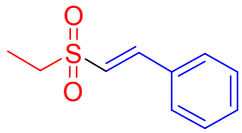
Light yellow solid, mp 106–108 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 3.87 (s, 3H), 6.77 (d, J = 15.2 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 7.16–7.22 (m, 2H), 7.27–7.29 (m, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.86–7.89 (m, 2H), 7.91 (d, J = 15.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.7, 55.7, 114.5, 126.4, 126.8, 128.8, 129.9, 130.7, 131.0, 131.4, 132.2, 138.0, 139.0, 163.5; **HRMS-ESI** (m/z): calcd for $C_{16}H_{16}O_3S$ $[M+H]^+$ 289.0893, found 289.0894.

(E)-1-Bromo-4-((4-methylstyryl)sulfonyl)benzene (3r)[2]



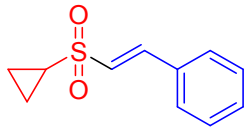
Light yellow solid, mp 160–162 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 6.84 (d, J = 15.2 Hz, 1H), 7.32-7.36 (m, 4H), 7.52 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 15.2Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.6, 125.5, 127.7, 128.2, 129.8, 130.0, 131.3, 132.3, 137.3, 140.4, 144.6.

(E)-(2-(ethylsulfonyl)vinyl)benzene (3s)[4]



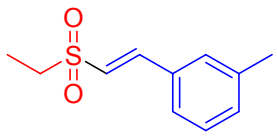
Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): 1.37 (t, J=7.2 Hz, 3H), 3.08 (q, J=7.2 Hz, 2H), 6.82 (d, J=15.6 Hz, 1H), 7.39–7.45 (m, 3H), 7.50–7.53 (m, 2H), 7.59 (d, J=15.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 7.2, 49.3, 124.0, 128.5, 129.1, 131.3, 132.2, 145.1.

(E)-(2-(cyclopropylsulfonyl)vinyl)benzene (3t)[5]



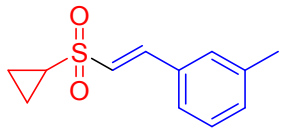
Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): 1.04-1.10 (m, 2H), 1.28-1.33 (m, 2H), 2.42-2.49 (m, 1H), 6.91 (d, J = 15.6 Hz, 1H), 7.40-7.44 (m, 3H), 7.51-7.58 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 5.2, 31.2, 125.5, 128.4, 129.0, 131.0, 132.3, 143.0.

(E)-1-(2-(ethylsulfonyl)vinyl)-3-methylbenzene (3u)



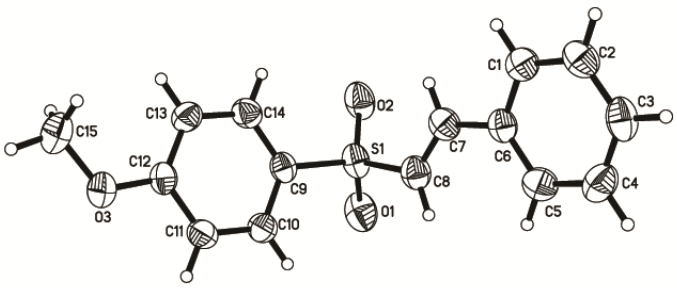
Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): 1.38 (t, J=7.2 Hz, 3H), 2.38 (s, 3H), 3.09 (q, J=7.2 Hz, 2H), 6.80 (d, J=15.6 Hz, 1H), 7.25-7.27 (m, 1H), 7.31–7.33 (m, 3H), 7.57 (d, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 7.2, 21.2, 49.4, 123.8, 125.7, 129.0, 129.1, 132.1, 138.9, 145.3; **HRMS-ESI** (m/z): calcd for $C_{11}H_{14}O_2S$ $[M+H]^+$ 211.0787, found 211.0784.

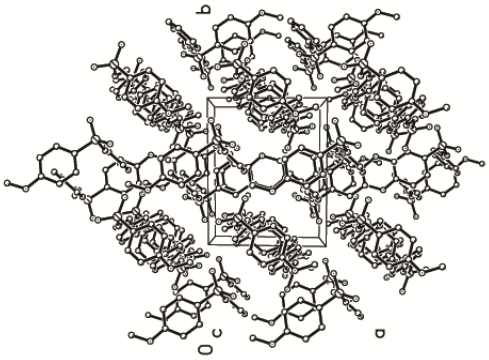
(E)-1-(2-(cyclopropylsulfonyl)vinyl)-3-methylbenzene (3v)



Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): 1.06-1.08 (m, 2H), 1.26-1.31 (m, 2H), 2.37 (s, 3H), 2.41-2.47 (m, 1H), 6.88 (d, J = 15.6 Hz, 1H), 7.23-7.25 (m, 1H), 7.29-7.33 (m, 3H), 7.52 (d, J = 15.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 5.2, 21.2, 31.3, 125.4, 125.6, 128.9, 129.0, 131.9, 132.4, 138.8, 143.3; **HRMS-ESI** (m/z): calcd for $C_{12}H_{14}O_2S$ $[M+H]^+$ 223.0787, found 223.0783.

The single crystal X-ray diffraction study: CCDC 1059933 (**3b**).† Crystal data for compound **3b**: $C_{15}H_{14}O_3S$, M = 274.32, Triclinic, a = 8.5030(6) Å, α = 76.750(5)°, b = 10.6762(5) Å, β = 81.107(5)°, c = 15.8607(10) Å, γ = 88.437(5)°, V = 1384.60(15) Å^3, T = 291.15 K, space group = P1, Z = 4, number of reflections = 9993, Independent reflections = 4932, [R(int) = 0.0186], Final R indices [I>2σ (I)] R1 = 0.0630, wR2 = 0.1737, R indices (all data) R1 = 0.0743, wR2 = 0.1857.





5. References

(1) X.-W. Li, Y.-L. Xu, W.-Q. Wu, C. Jiang, C.-R. Qi and H.-F. Jiang, *Chem.–Eur. J.,* 2014*,* **20***,* 7911.

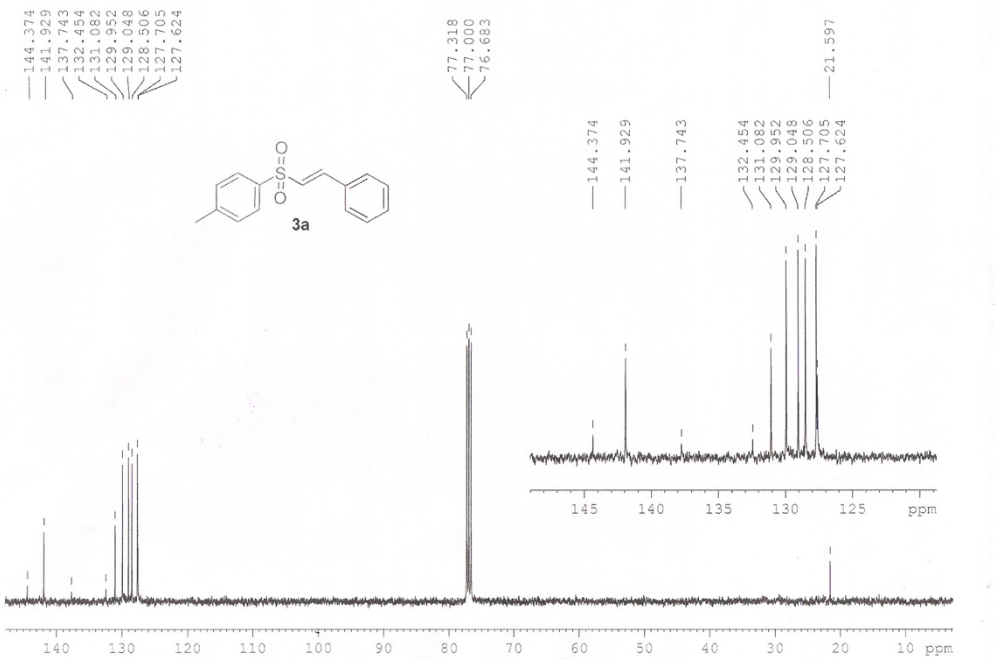
(2) S. Tang, Y. Wu, W.-Q. Liao, R.-P. Bai, C. Liu and A.-W. Lei, *Chem. Commun.*, 2014, **50**, 4496.

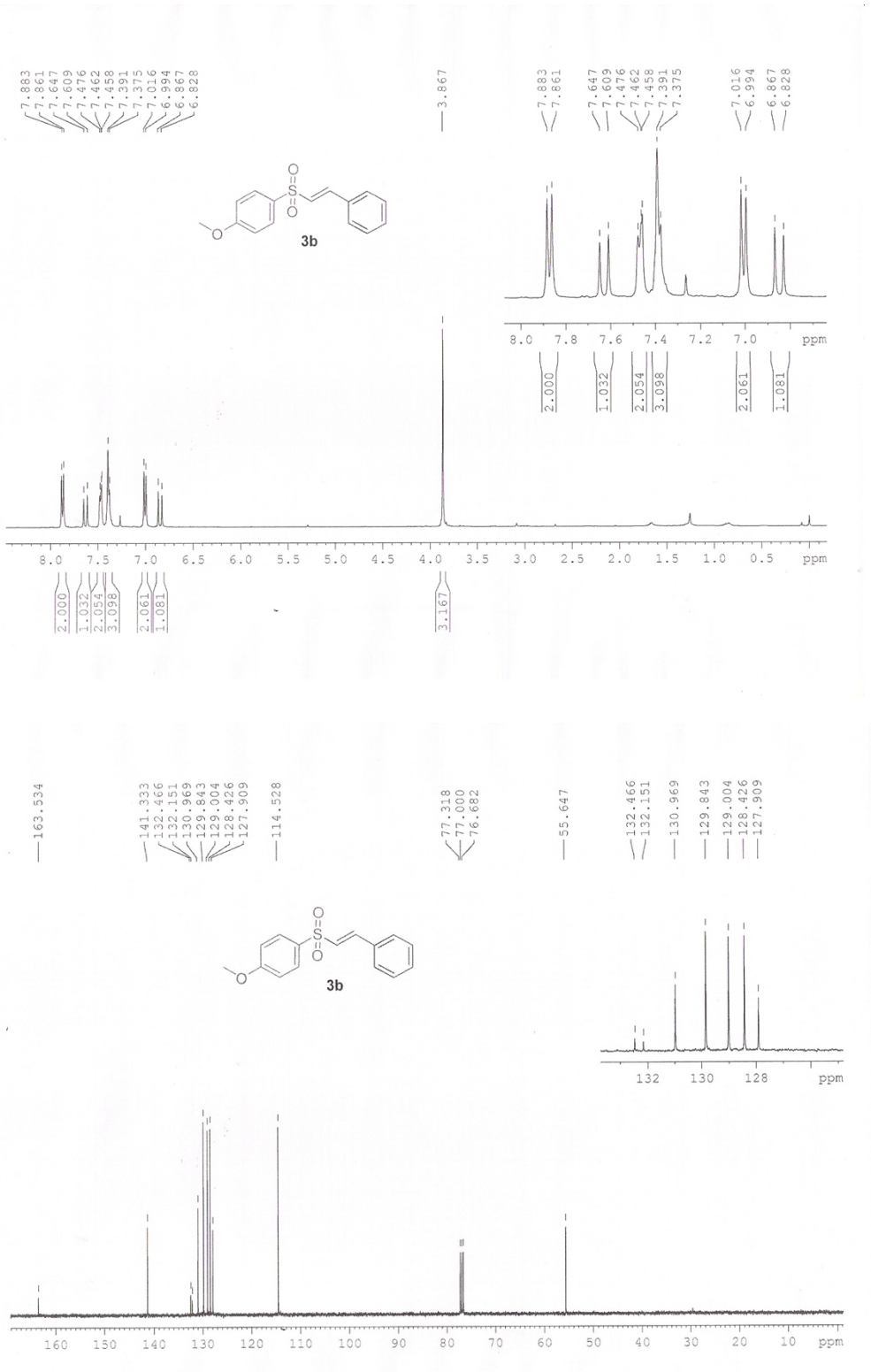
(3) S. Liang, R.-Y. Zhang, G. Wang, S.-Y. Chen and X.-Q. Yu, *Eur. J. Org. Chem.,* 2013, 7050.

(4) Y. Yasutaka, O. Orie, T. Akira and T. Takeshi, *Tetrahedron*, 2006, **62,** 9981.

(5) Y.-L. Xu, J.-W. Zhao, X.-D. Tang, W.-Q. Wu and H.-F. Jiang, *Adv. Synth. Catal.*, 2014, **356,** 2029.

6. Copies of ^{1}H and ^{13}C NMR spectra for the products

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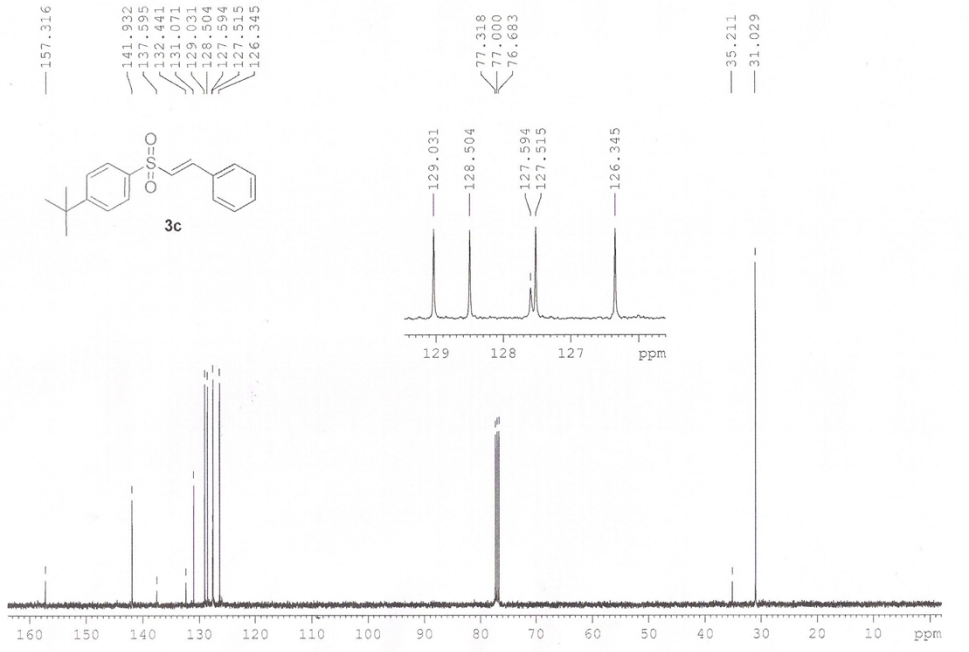
7.861
7.647
7.609
7.476
7.462
7.458
7.391
7.375
7.016
6.994
6.867
6.828
3.867
3b
8.0
7.8
7.6
7.4
7.2
7.0
ppm
2.000
1.032
2.054
3.098
2.061
1.081
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.000
1.032
2.054
3.098
2.061
1.081
3.167
163.534
141.333
132.466
132.151
130.969
129.843
129.004
128.426
127.909
114.528
77.318
77.000
76.682
55.647
132.466
132.151
130.969
129.843
129.004
128.426
127.909
3b
132
130
128
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.880
7.860
7.693
7.655
7.566
7.545
7.490
7.475
7.471
7.426
7.398
7.382
6.887
6.848
1.337
3c
7.8 7.7 7.6 7.5 7.4 7.3 ppm
2.000
1.043
2.181
2.044
3.080
1.010
9.045
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 ppm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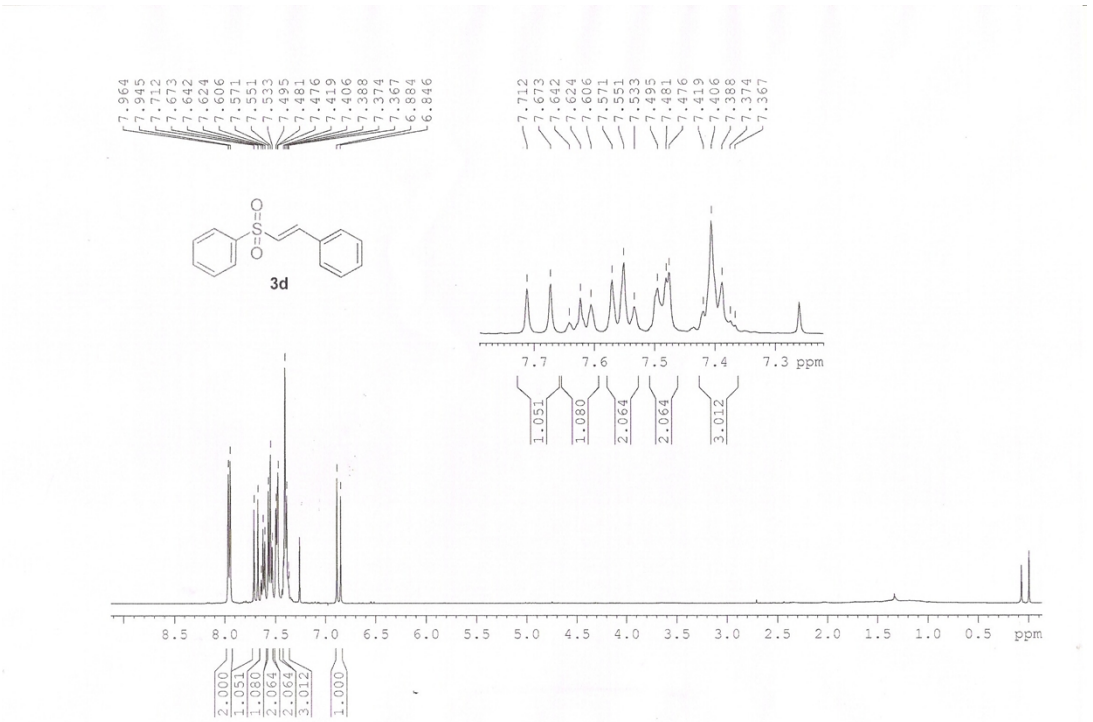
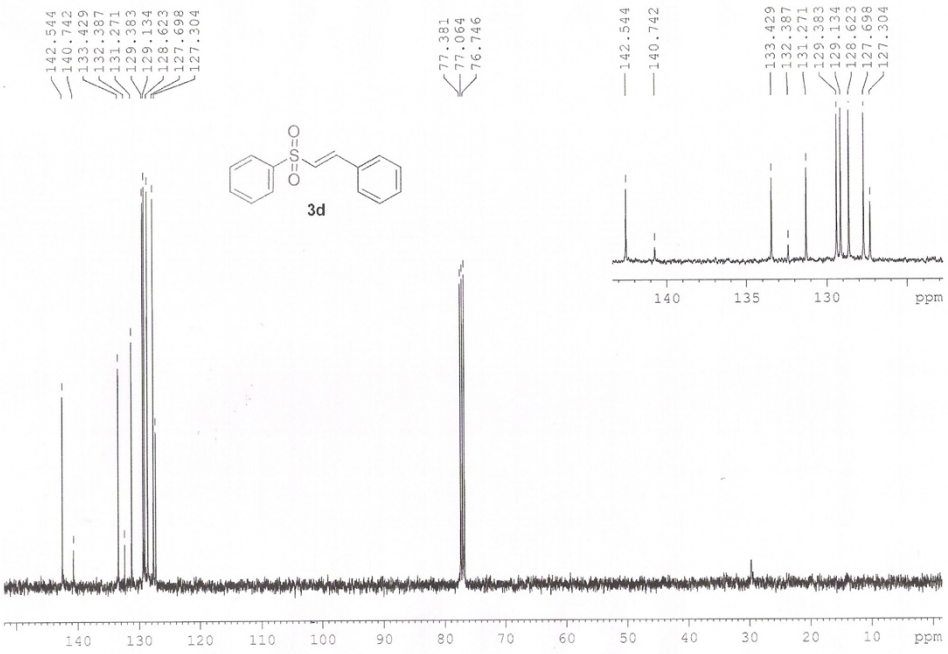
141.932
137.595
132.441
131.071
129.031
128.504
127.594
127.515
126.345
77.318
77.000
76.683
35.211
31.029
3c
129.031
128.504
127.594
127.515
126.345
129 128 127 ppm
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.964
7.945
7.712
7.673
7.642
7.624
7.606
7.571
7.551
7.533
7.495
7.481
7.476
7.419
7.406
7.388
7.374
7.367
6.884
6.846
7.712
7.673
7.642
7.624
7.606
7.571
7.551
7.533
7.495
7.481
7.476
7.419
7.406
7.388
7.374
7.367
3d
7.7
7.6
7.5
7.4
7.3 ppm
1.051
1.080
2.064
2.064
3.012
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
ppm
2.000
1.051
1.080
2.064
2.064
3.012
1.000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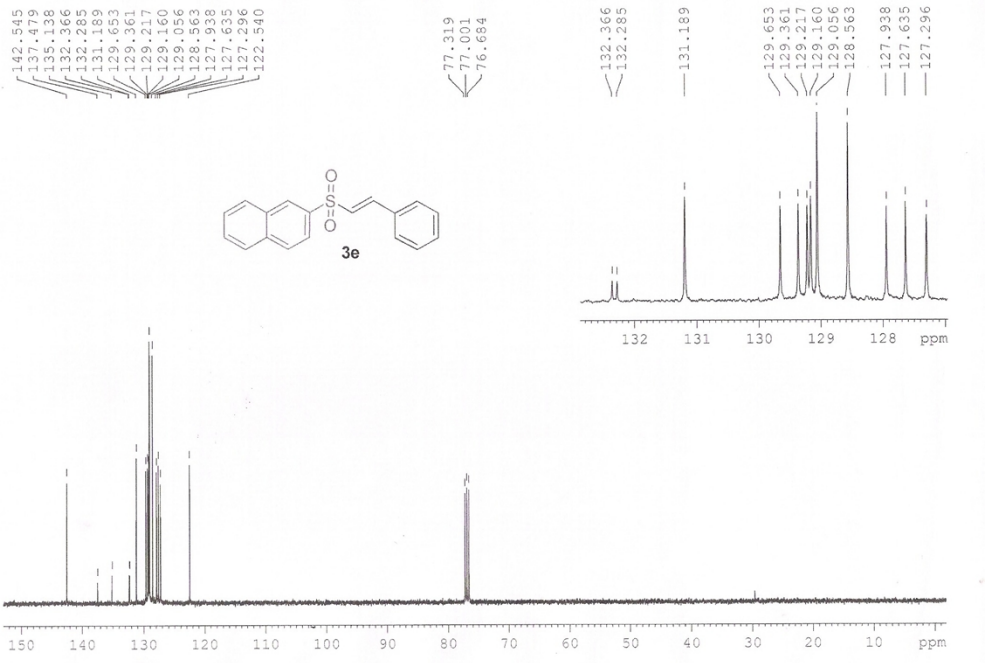
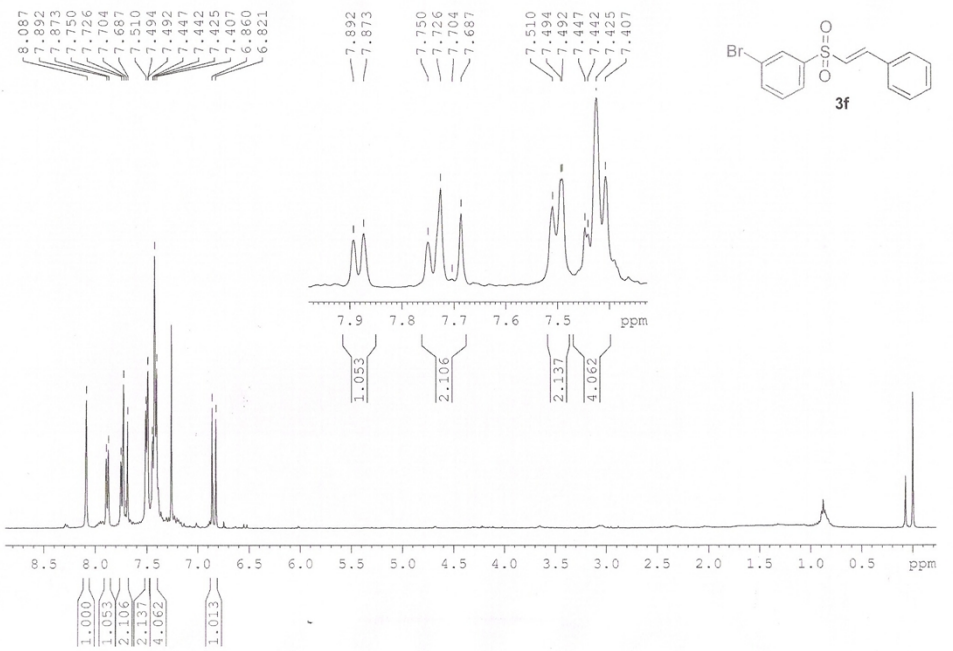
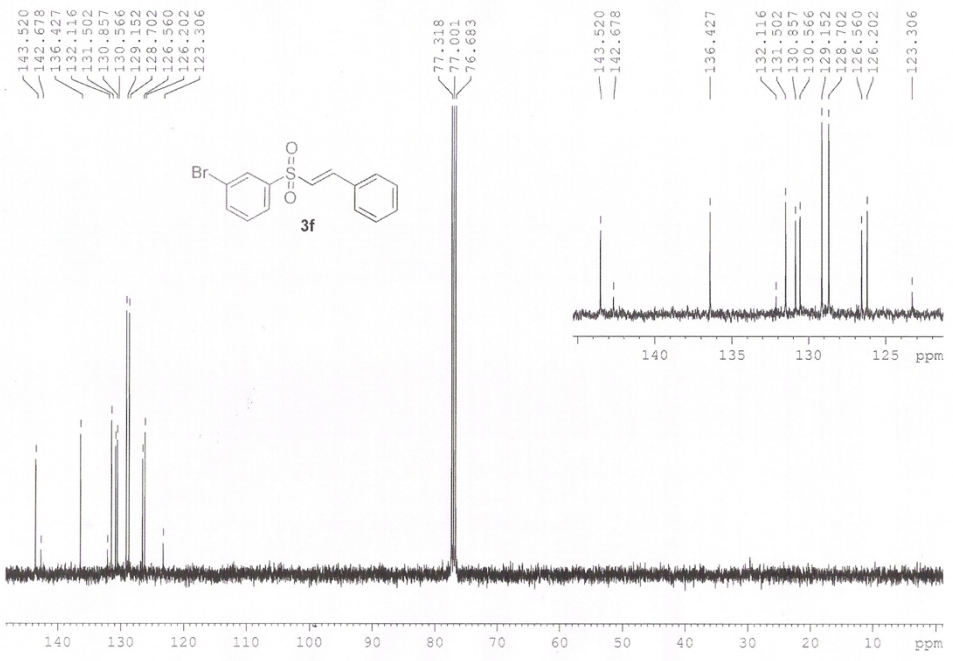
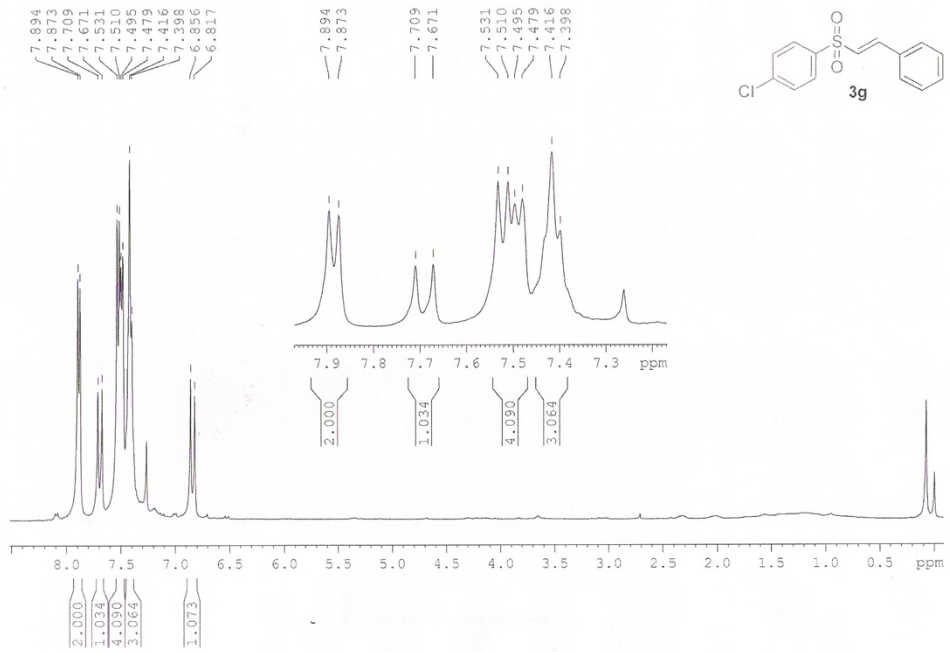
140.742
133.429
132.387
131.271
129.383
129.134
128.623
127.698
127.304
77.381
77.064
76.746
3d
142.544
140.742
133.429
132.387
131.271
129.383
129.134
128.623
127.698
127.304
140
135
130
ppm
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.552
7.998
7.990
7.980
7.969
7.917
7.897
7.875
7.873
7.763
7.725
7.672
7.655
7.634
7.613
7.596
7.493
7.478
7.474
7.392
7.375
6.942
6.904
3e
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 ppm
1.000
2.128
2.121
1.107
2.213
2.080
2.988
1.011
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
2.128
2.121
1.107
2.213
2.080
2.988


142.545
137.479
135.138
132.366
132.285
131.189
129.653
129.361
129.217
129.160
129.056
128.563
127.938
127.635
127.296
122.540
77.319
77.001
76.684
3e
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
132.366
132.285
131.189
129.653
129.361
129.217
129.160
129.056
128.563
127.938
127.635
127.296
132 131 130 129 128 ppm


8.087
7.892
7.873
7.750
7.726
7.704
7.687
7.510
7.494
7.492
7.447
7.442
7.425
7.407
6.860
6.821
Br
O
O
3f
ppm
1.000
1.053
2.106
2.137
4.062
1.013


143.520
142.678
136.427
132.116
131.502
130.857
130.566
129.152
128.702
126.560
126.202
123.306
77.318
77.001
76.683
Br
O
O
3f
ppm


7.894
7.873
7.709
7.671
7.531
7.510
7.495
7.479
7.416
7.398
6.856
6.817
Cl
3g
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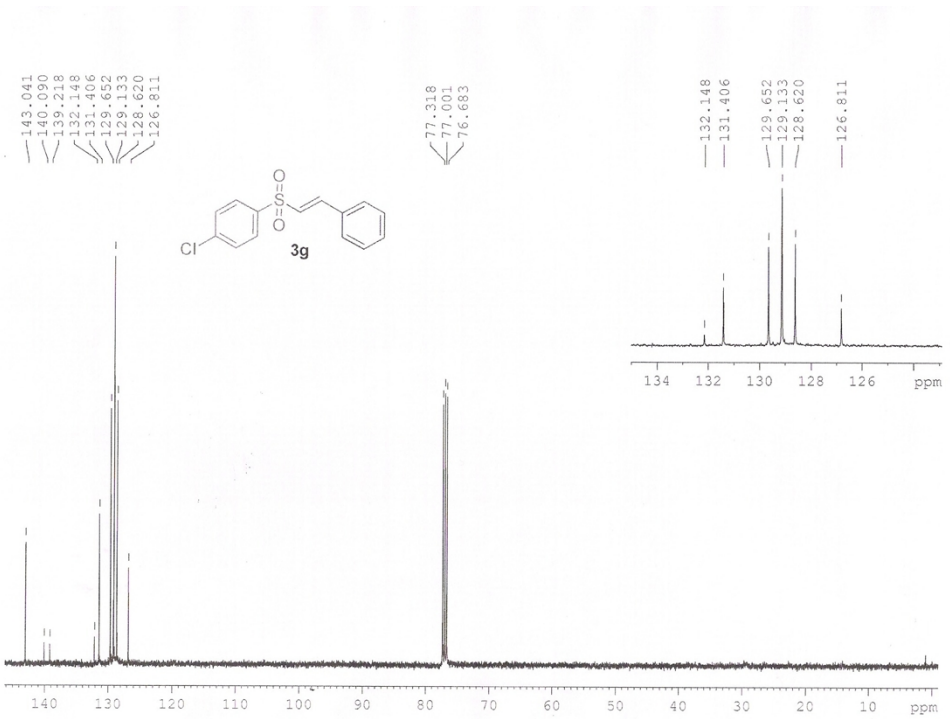
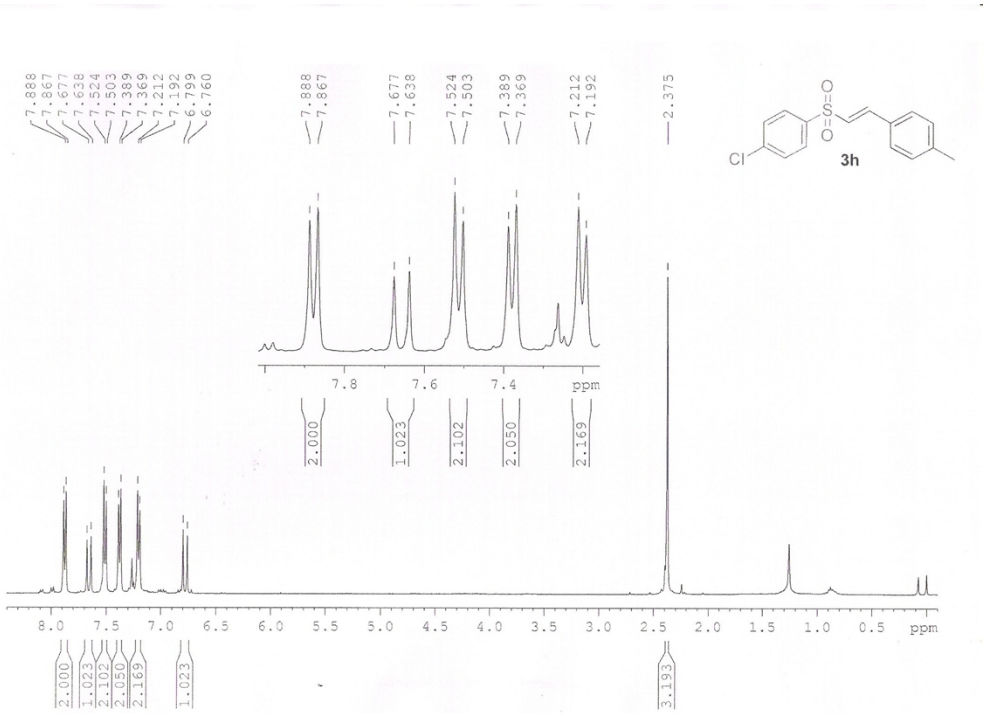
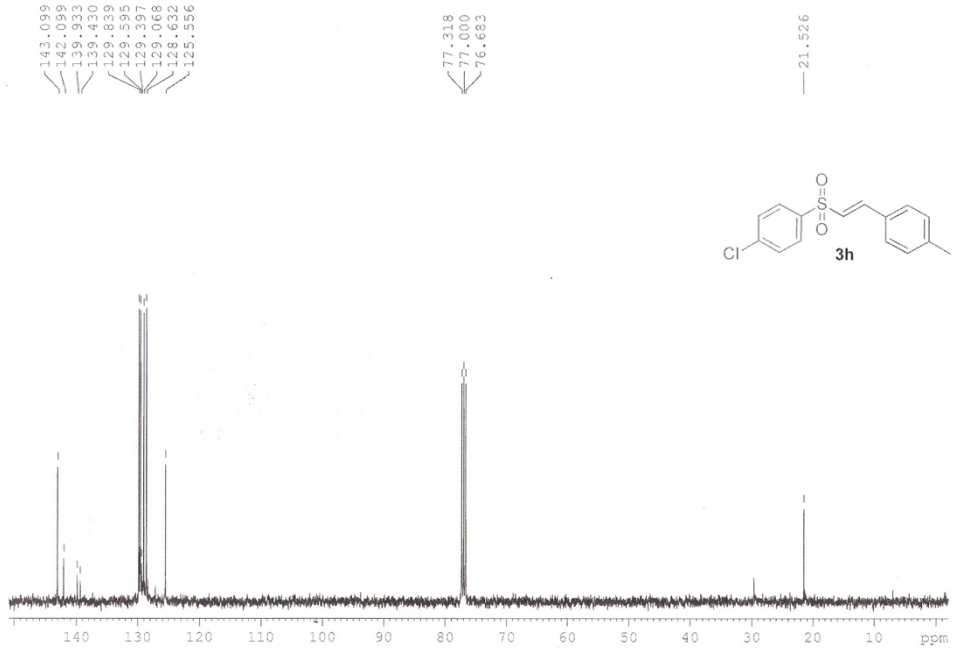
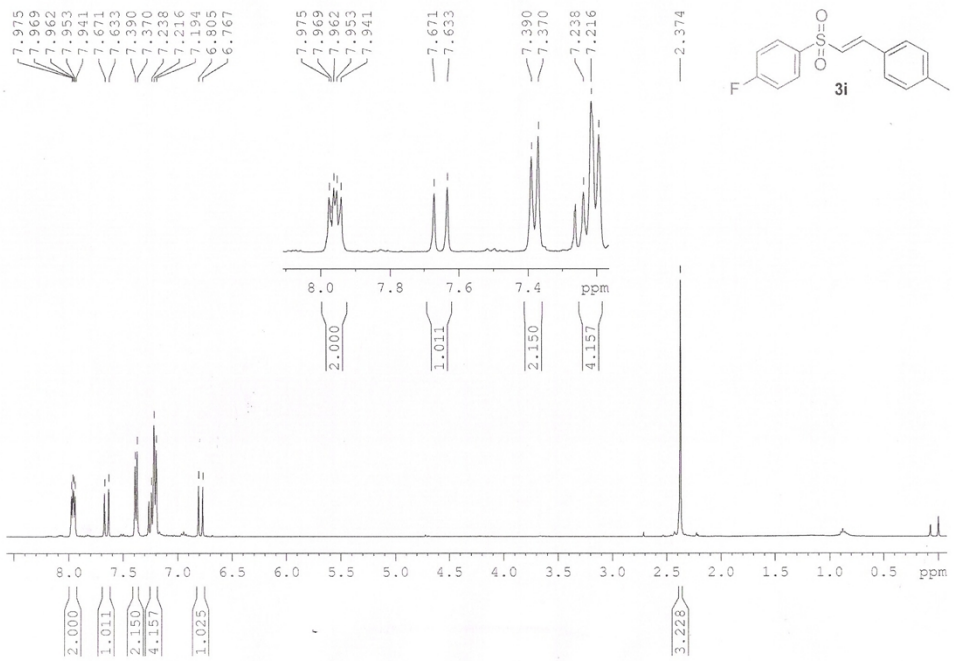
4.090
3.064
1.073
ppm


143.041
140.090
139.218
132.148
131.406
129.652
129.133
128.620
126.811
77.318
77.001
76.683
Cl
3g
ppm


7.888
7.867
7.677
7.638
7.524
7.503
7.389
7.369
7.212
7.192
6.799
6.760
2.375
3h
7.8
7.6
7.4
ppm
2.000
1.023
2.102
2.050
2.169
1.023
3.193


143.099
142.099
139.933
139.430
128.839
129.595
129.397
129.068
128.632
125.556
77.318
77.000
76.683
21.526
3h
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.975
7.969
7.962
7.953
7.941
7.671
7.633
7.390
7.370
7.238
7.216
7.194
6.805
6.767
2.374
3i
8.0
7.8
7.6
7.4
ppm
2.000
1.011
2.150
4.157
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
ppm
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1.011
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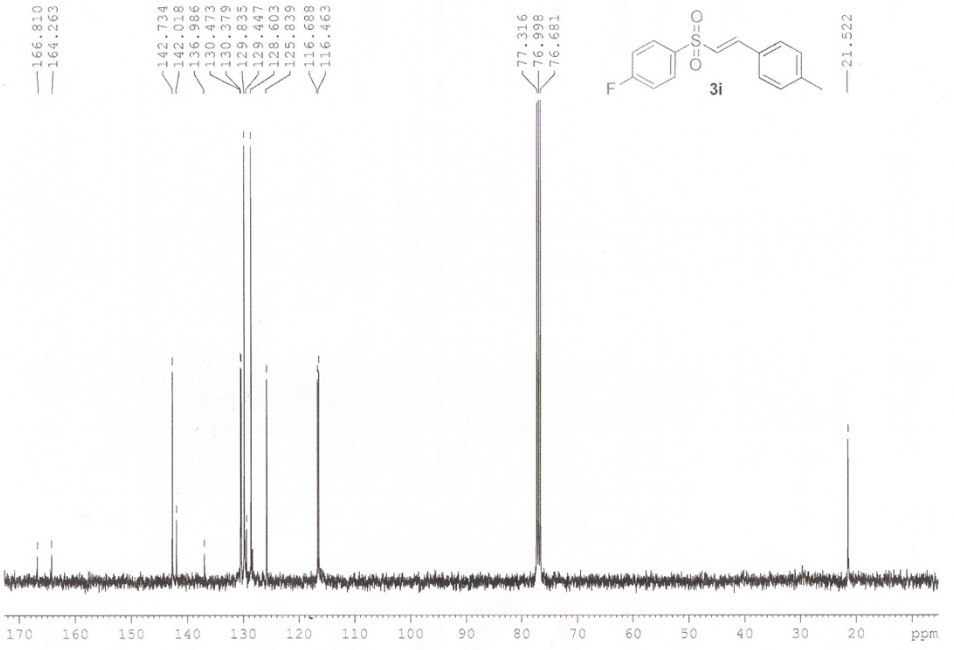
4.157
1.025
3.228


166.810
164.263
142.734
142.018
136.986
130.473
130.379
129.835
129.447
128.603
125.839
116.688
116.463
77.316
76.998
76.681
21.522
3i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.100
8.079
7.829
7.809
7.765
7.726
7.510
7.493
7.447
7.425
7.407
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6.836
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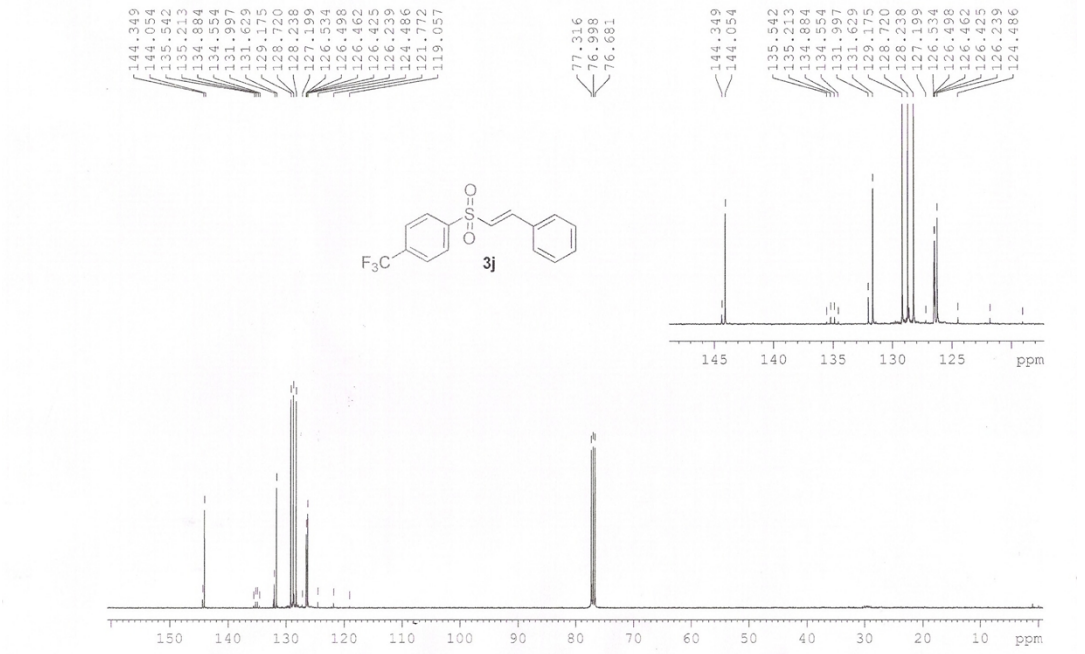
3.079
1.049
ppm
3j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131.629
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128.720
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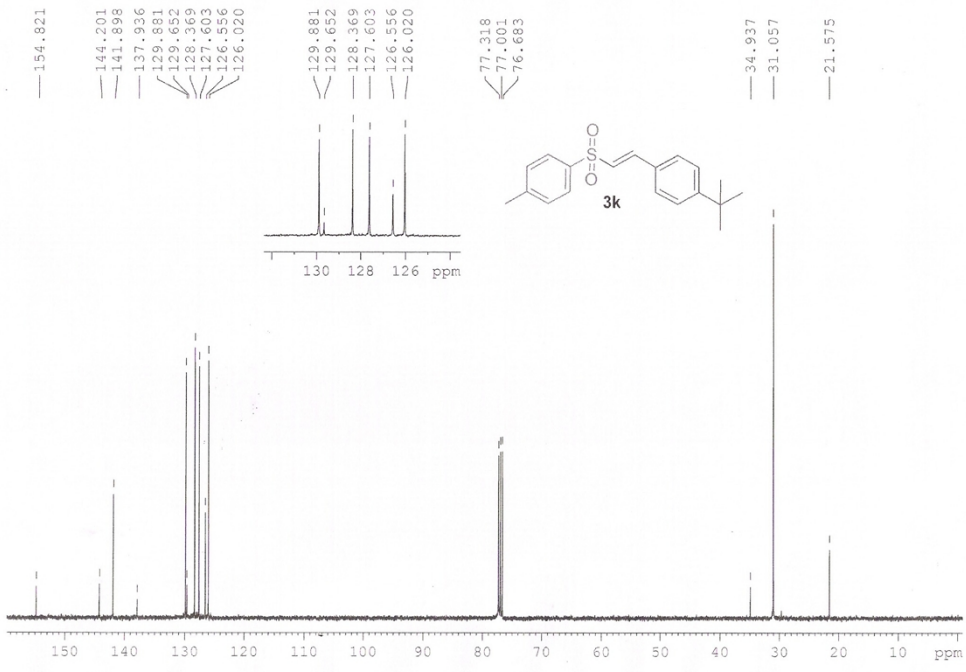
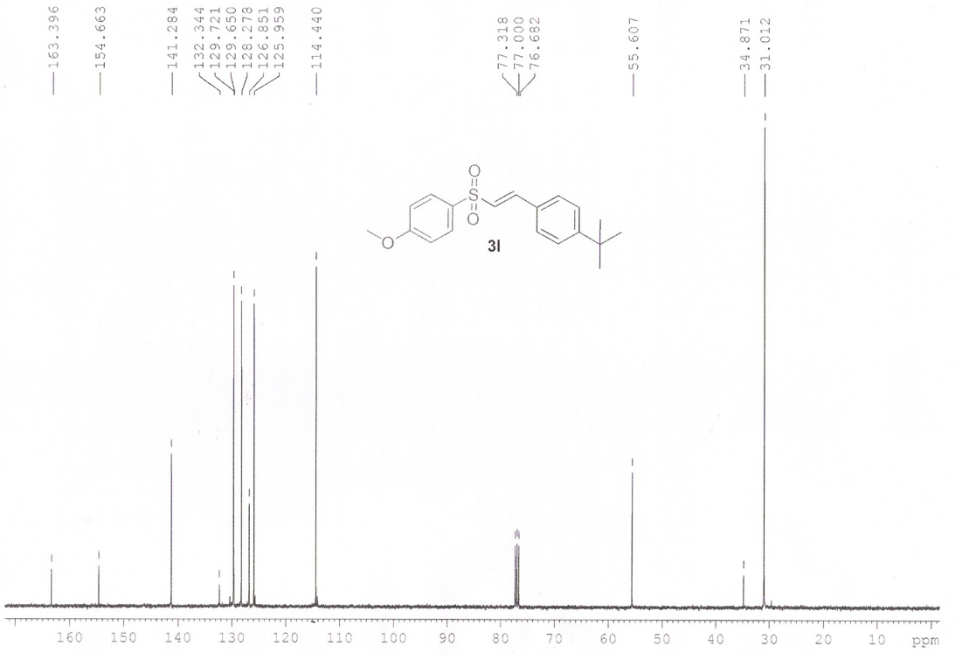
127.199
126.534
126.498
126.462
126.425
126.239
124.486
121.772
119.057
77.316
76.998
76.681
ppm
3j


7.827
7.806
7.663
7.625
7.431
7.410
7.388
7.339
7.319
6.821
6.783
2.428
1.307
3k
8.0 7.8 7.6 7.4 7.2 7.0 ppm
2.000
1.031
4.098
2.096
1.030
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 ppm
2.000
1.031
4.098
2.096
1.030
3.040
9.143


154.821
144.201
141.998
137.936
129.881
129.652
128.369
127.603
126.556
126.020
77.318
77.001
76.683
34.937
31.057
21.575
3k
130 128 126 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.875
7.853
7.640
7.601
7.430
7.407
7.385
7.006
6.983
6.832
6.794
3.860
1.304
3I
7.8 7.6 7.4 7.2 7.0 ppm
2.000
1.035
4.195
2.090
1.023
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 ppm
2.000
1.035
4.195
2.090
1.023
3.168
9.376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129.650
128.278
126.851
125.959
114.440
77.318
77.000
76.682
55.607
34.871
31.012
3I
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.824
7.803
7.620
7.581
7.430
7.408
7.338
7.318
6.899
6.878
6.710
6.672
3.827
2.425
3m
7.5
7.0
ppm
2.000
1.079
2.034
2.043
2.072
1.002
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
ppm
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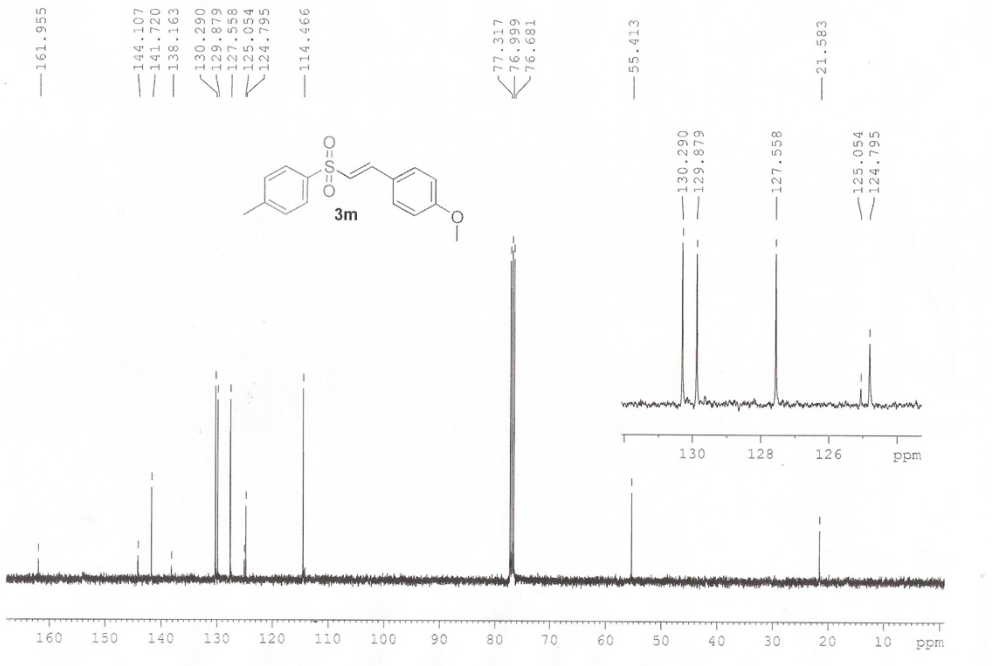
2.043
2.072
1.002
3.160
3.008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129.879
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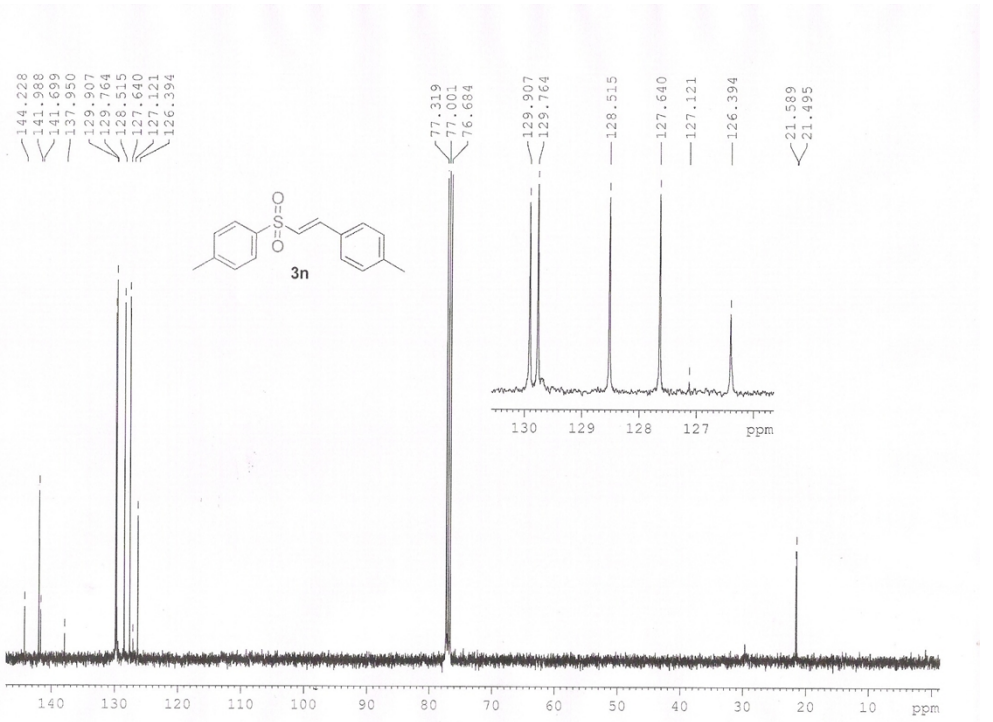
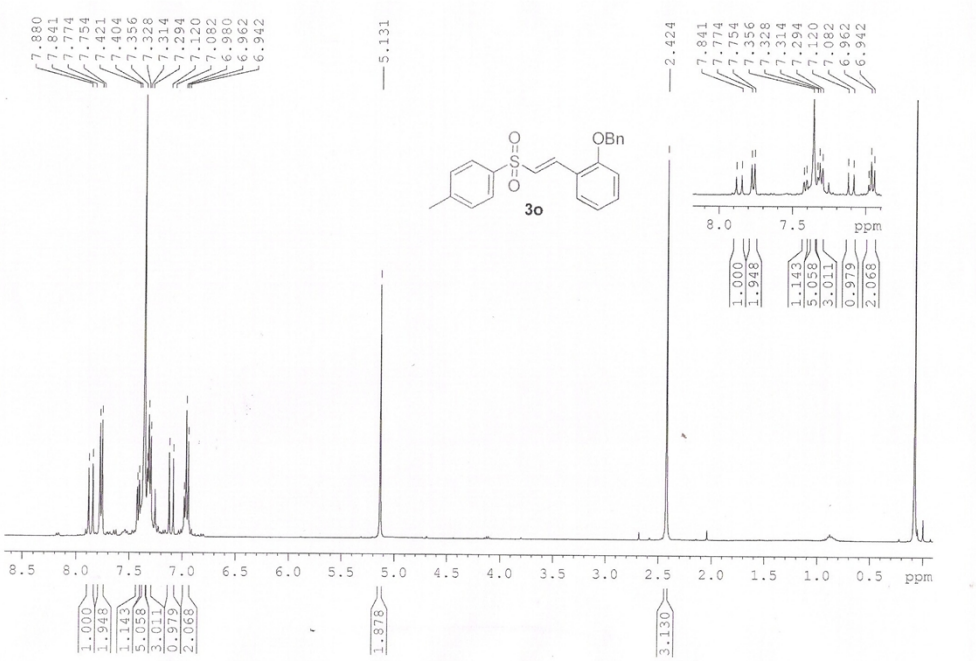
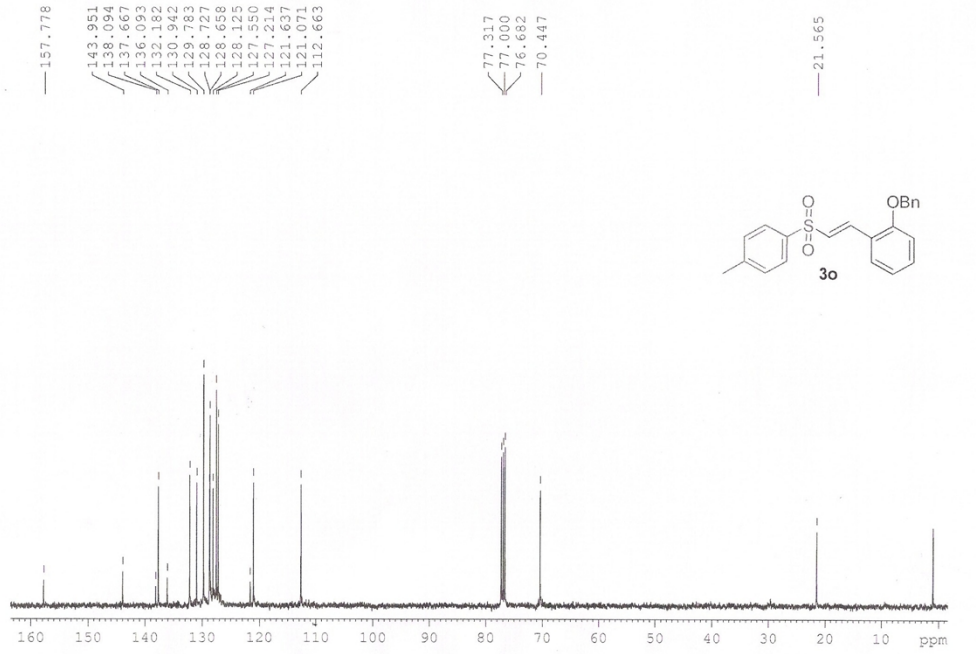
125.054
124.795
114.466
77.317
76.999
76.681
55.413
21.583
3m
130.290
129.879
127.558
125.054
124.795
130
128
126
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

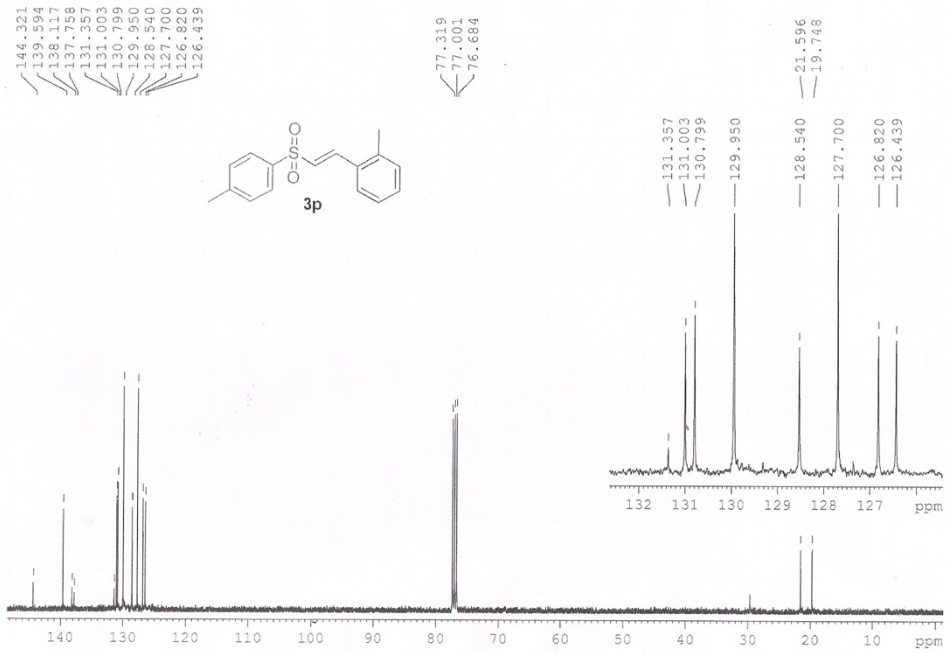

7.839
7.808
7.641
7.603
7.373
7.353
7.343
7.322
7.194
7.174
6.805
6.767
2.429
2.364
3n
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.013
1.011
4.036
2.077
1.009
3.000
3.100
7.5 7.0 ppm

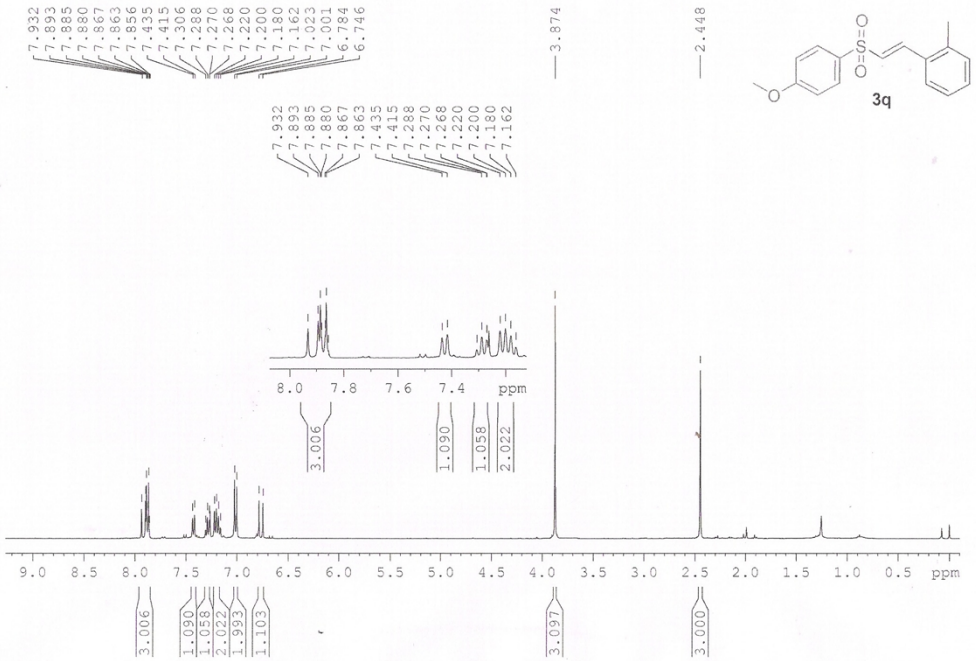

144.228
141.988
141.699
137.950
129.907
129.764
128.515
127.640
127.121
126.394
77.319
77.001
76.684
21.589
21.495
3n
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
130 129 128 127 ppm

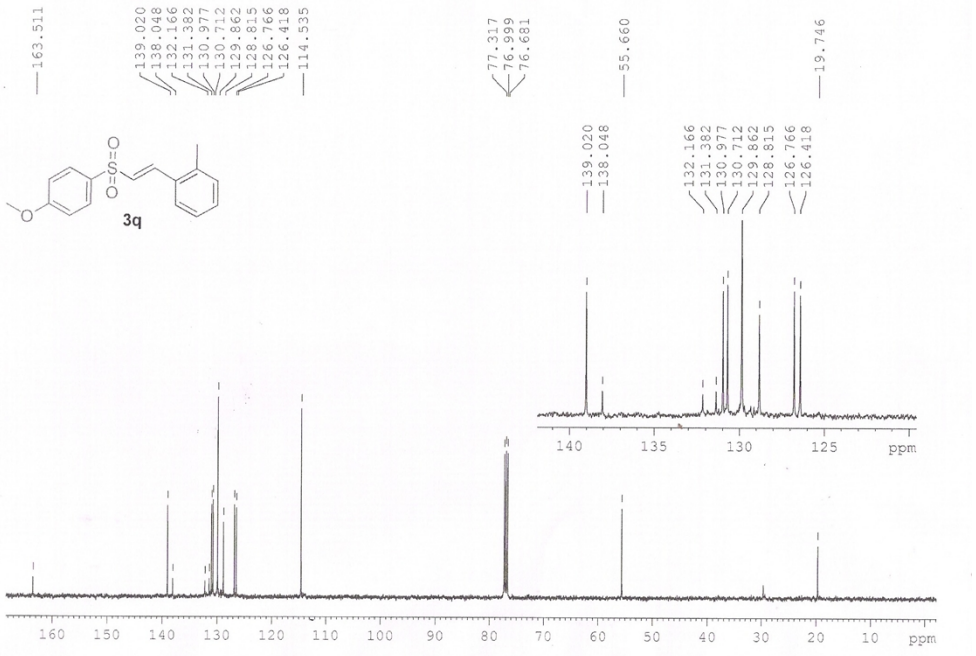

7.880
7.841
7.774
7.754
7.421
7.404
7.356
7.328
7.314
7.294
7.120
7.082
6.980
6.962
6.942
5.131
2.424
OBn
3o
8.0
7.5
ppm
1.000
1.948
1.143
5.058
3.011
0.979
2.068
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.948
1.143
5.058
3.011
0.979
2.068
1.878
3.130

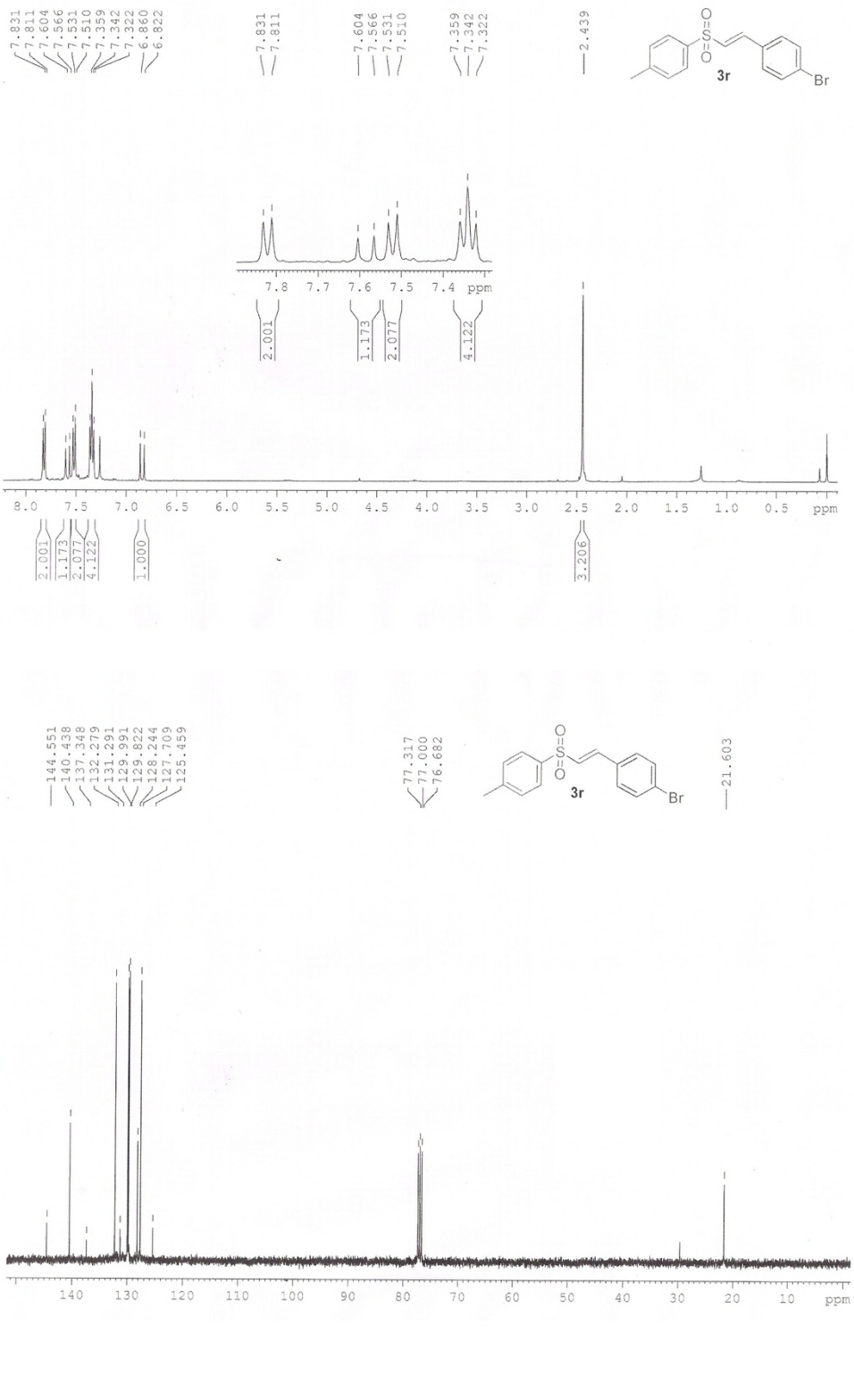

157.778
143.951
138.084
137.667
136.093
132.182
130.942
129.783
128.727
128.658
128.125
127.550
127.214
121.637
121.071
112.663
77.317
77.000
76.682
70.447
21.565
OBn
3o
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

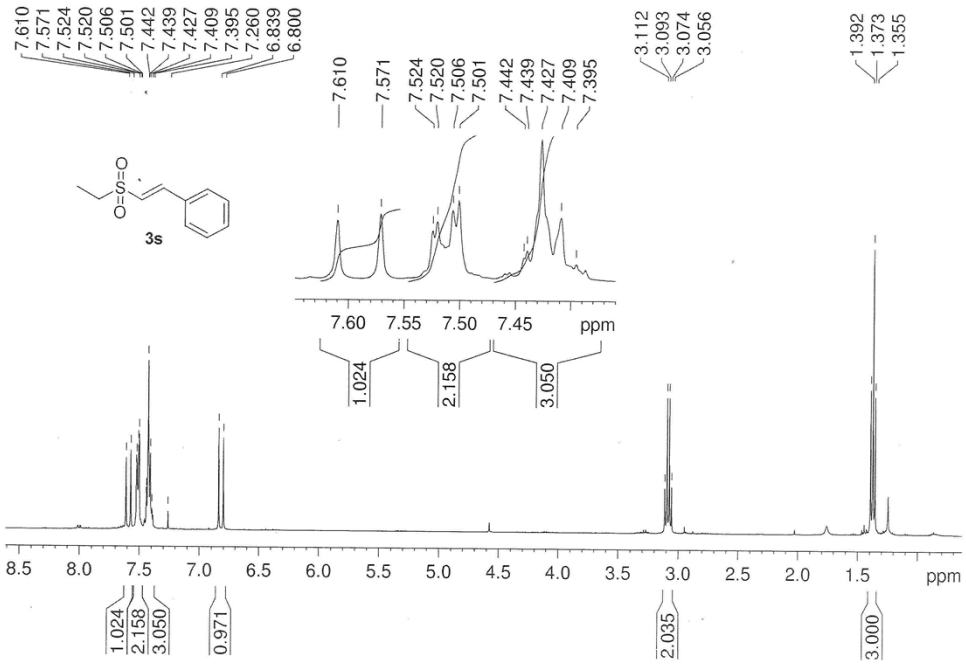

7.956
7.918
7.838
7.818
7.431
7.412
7.354
7.334
7.288
7.270
7.220
7.199
7.178
6.785
6.747
2.449
2.437
3p
8.0
7.8
7.6
7.4
ppm
1.000
1.909
1.114
2.048
0.919
2.171
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.909
1.114
2.048
0.919
2.171
1.011
6.145

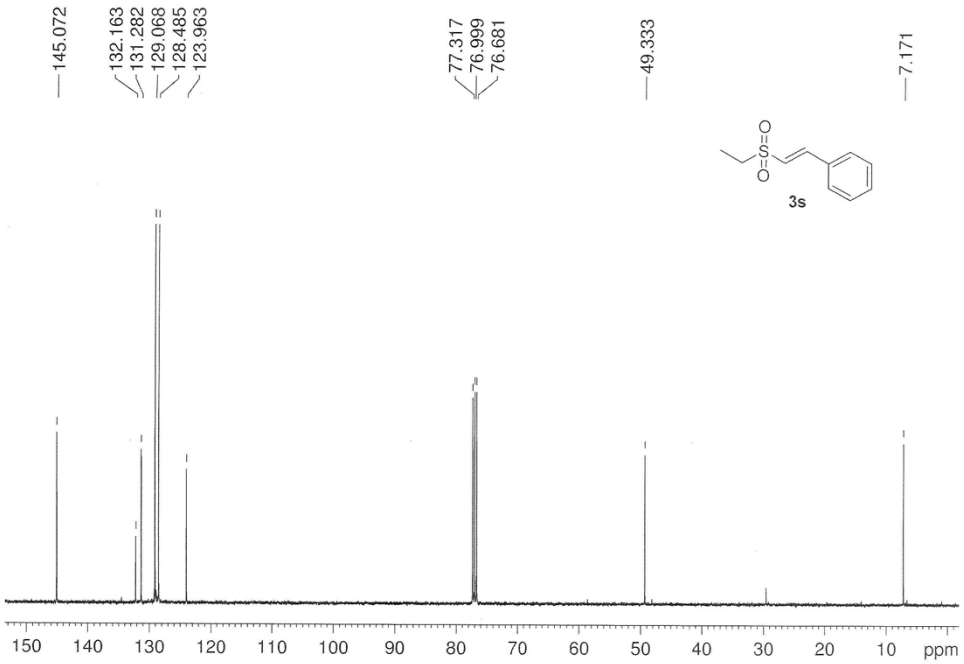

144.321
139.594
138.117
137.758
131.357
131.003
130.799
129.950
128.540
127.700
126.820
126.439
77.319
77.001
76.684
21.596
19.748
3p
131.357
131.003
130.799
129.950
128.540
127.700
126.820
126.439
132
131
130
129
128
127
ppm
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

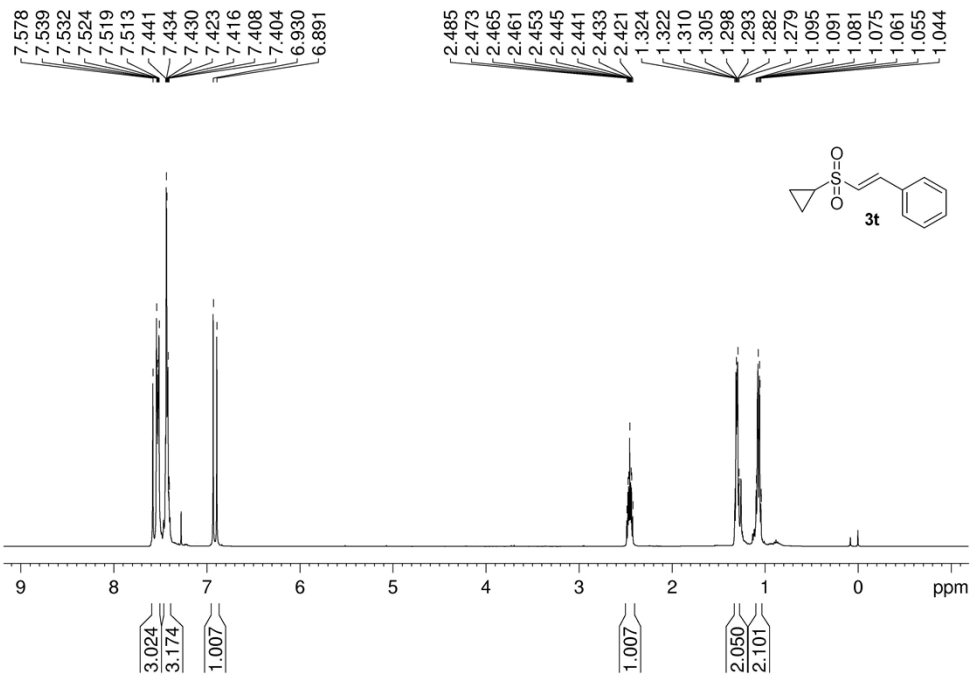

7.932
7.893
7.885
7.880
7.867
7.863
7.856
7.435
7.415
7.306
7.288
7.270
7.268
7.220
7.200
7.180
7.162
7.023
7.001
6.784
6.746
3.874
2.448
3q
8.0
7.8
7.6
7.4
ppm
3.006
1.090
1.058
2.022
1.993
1.103
3.097
3.000

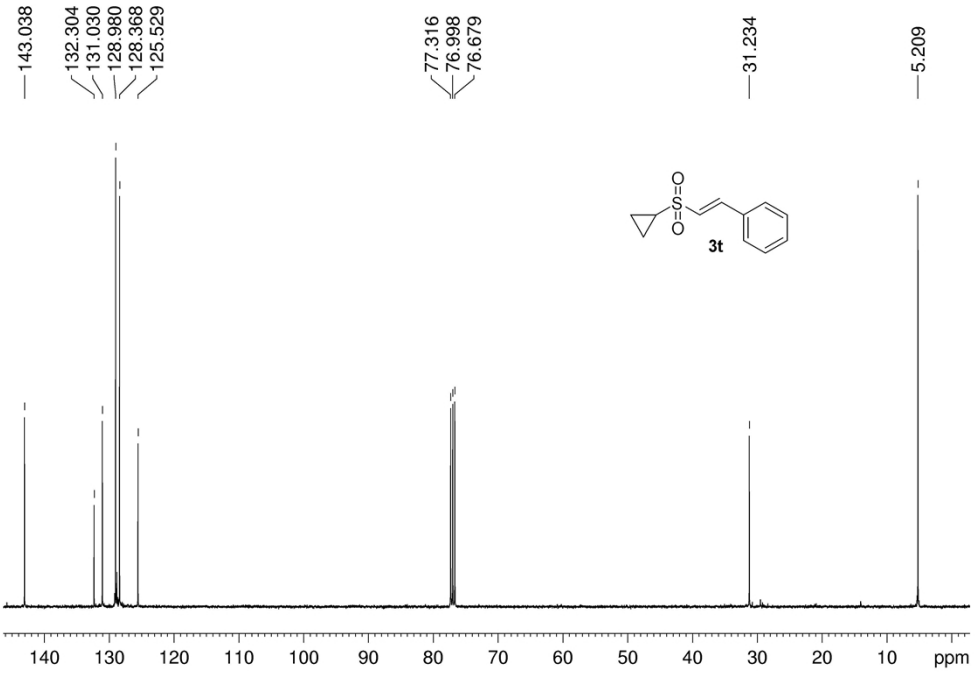

163.511
139.020
138.048
132.166
131.382
130.977
130.712
129.862
128.815
126.766
126.418
114.535
77.317
76.999
76.681
55.660
19.746
3q
140
135
130
125
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

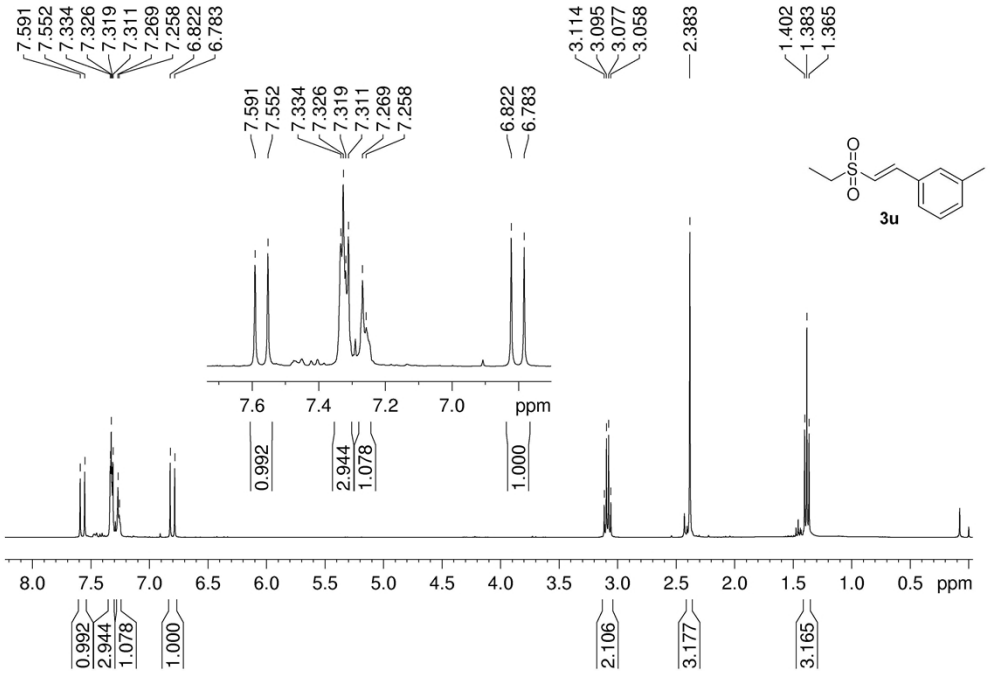

7.831
7.811
7.604
7.566
7.531
7.510
7.359
7.342
7.322
6.860
6.822
2.439
3r
Br
7.8 7.7 7.6 7.5 7.4 ppm
2.001
1.173
2.077
4.122
1.000
3.206
144.551
140.438
137.348
132.279
131.291
129.991
129.822
128.244
127.709
125.459
77.317
77.000
76.682
21.603
ppm

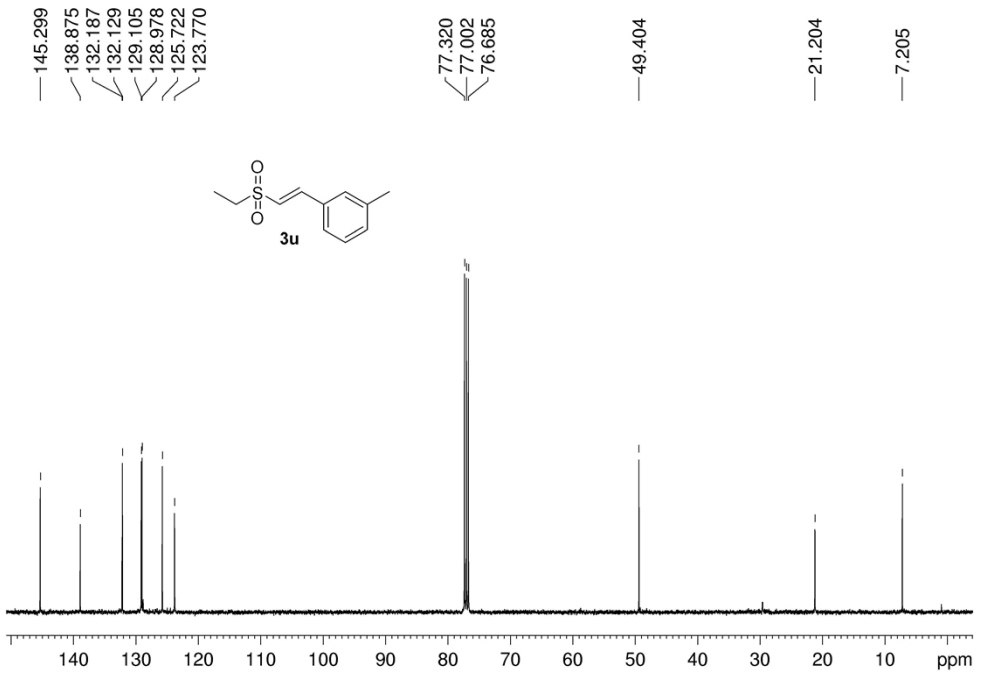

7.610
7.571
7.524
7.520
7.506
7.501
7.442
7.439
7.427
7.409
7.395
7.260
6.839
6.800
3.112
3.093
3.074
3.056
1.392
1.373
1.355
3s
7.60 7.55 7.50 7.45 ppm
1.024
2.158
3.050
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.024
2.158
3.050
0.971
2.035
3.000

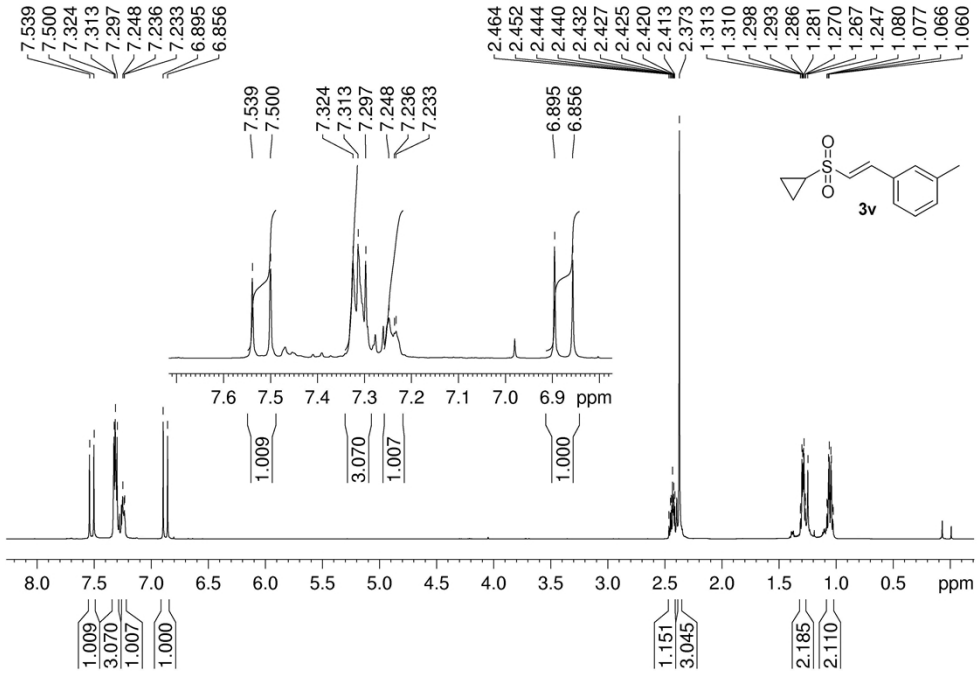

145.072
132.163
131.282
129.068
128.485
123.963
77.317
76.999
76.681
49.333
7.171
3s
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

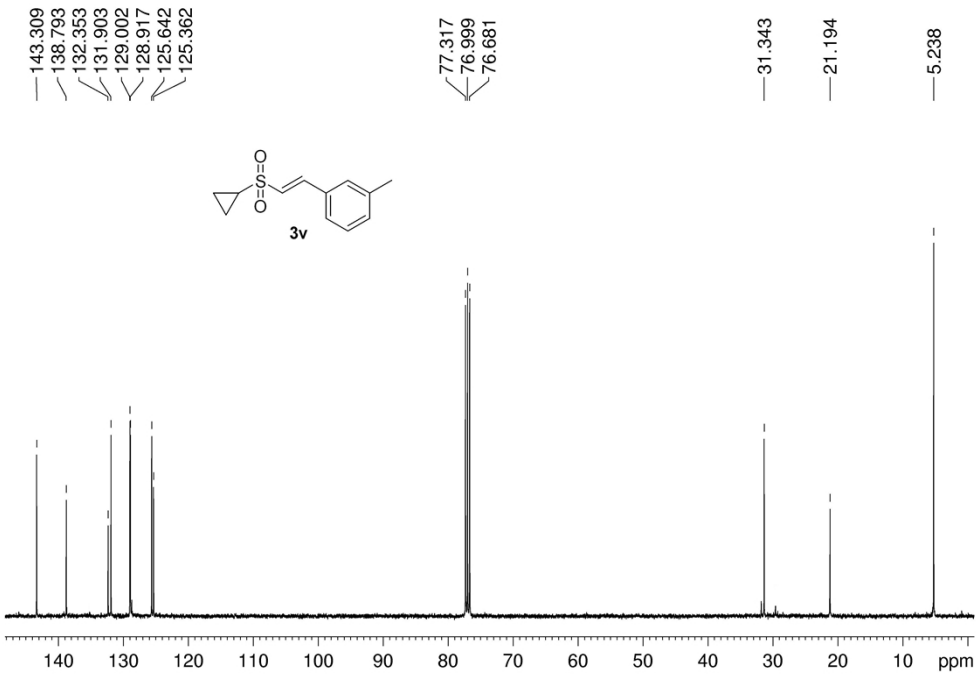

7.578
7.539
7.532
7.524
7.519
7.513
7.441
7.434
7.430
7.423
7.416
7.408
7.404
6.930
6.891
2.485
2.473
2.465
2.461
2.453
2.445
2.441
2.433
2.421
1.324
1.322
1.310
1.305
1.298
1.293
1.282
1.279
1.095
1.091
1.081
1.075
1.061
1.055
1.044
3t
9
8
7
6
5
4
3
2
1
0
ppm
3.024
3.174
1.007
1.007
2.050
2.101


143.038
132.304
131.030
128.980
128.368
125.529
77.316
76.998
76.679
31.234
5.209
3t
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.591
7.552
7.334
7.326
7.319
7.311
7.269
7.258
6.822
6.783
3.114
3.095
3.077
3.058
2.383
1.402
1.383
1.365
3u
7.6
7.4
7.2
7.0
ppm
0.992
2.944
1.078
1.000
2.106
3.177
3.165
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
ppm


145.299
138.875
132.187
132.129
129.105
128.978
125.722
123.770
77.320
77.002
76.685
49.404
21.204
7.205
3u
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.539
7.500
7.324
7.313
7.297
7.248
7.236
7.233
6.895
6.856
2.464
2.452
2.444
2.440
2.432
2.427
2.425
2.420
2.413
2.373
1.313
1.310
1.298
1.293
1.286
1.281
1.270
1.267
1.247
1.080
1.077
1.066
1.060
3v
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 ppm
1.009
3.070
1.007
1.000
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 ppm
1.009
3.070
1.007
1.000
1.151
3.045
2.185
2.110


143.309
138.793
132.353
131.903
129.002
128.917
125.642
125.362
77.317
76.999
76.681
31.343
21.194
5.238
3v
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm