

Supporting Information for

Base-controlled divergent synthesis of vinyl sulfones from (benzylsulfonyl)benzenes and paraformaldehyde

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Table of Contents

1. General information	2
2. General procedures for the synthesis of vinyl sulfone	2
3. Characterization data of products	3-22
4. ¹ H NMR and ¹³ C NMR spectra of products	23-76
5. ¹⁹ F NMR spectra of products	77-81

General information

The reactions of 2a was carried out under an atmosphere of argo. other reactions were carried out under an atmosphere of air. Column chromatography was performed using silica gel (200-300 mesh). ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker-AV (400, 100, 376 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at the Keeloud (shanghai) Biotechnology co. LTD. HRMS was conducted using electrospraying ionization (ESI) and was performed on a Thermo Scientific LTQ Orbitrap XL. The structures of known compounds were further corroborated by comparing their ^1H NMR, ^{13}C NMR, ^{19}F NMR data and MS data with those of literature. Most reagents were obtained from commercial suppliers (such as Energy Chemical, Aladdin and Tansoole) and used without further purification. The obtain of (benzylsulfonyl)benzene was according to the reported literature unless otherwise noted.

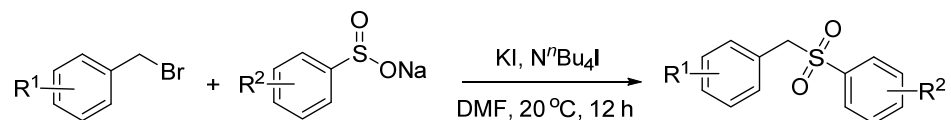
General procedure (2a)

A flat bottom reaction tube (10 mL) equipped with a stir bar was charged with paraformaldehyde(1.8 mmol, 54 mg), Et_3N (0.18 mmol, 23 μL), (benzylsulfonyl)benzene (0.2 mmol, 46.4 mg), and DMF (0.4 mL) under an atmosphere of argo. The sealed reaction vessel was stirred at 140 $^\circ\text{C}$ for 18 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (15 mL). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product.

General procedure (3a)

A flat bottom reaction tube (10 mL) equipped with a stir bar was charged with paraformaldehyde(1 mmol, 30 mg), pyridine(0.2 mmol, 16 μL), (benzylsulfonyl)benzene (0.2 mmol, 46.4 mg), and DMF (1 mL) under air. The sealed reaction vessel was stirred at 120 $^\circ\text{C}$ for 18 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (10 mL). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product.

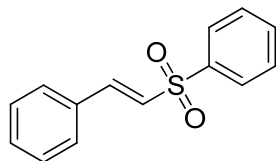
Preparation of aryl benzyl sulfone ^[1]



Sodium benzenesulfinate 6 (0.80 g, 5 mmol) was dissolved in DMF (30 mL), in which N₄I (0.18 g, 0.5 mmol), KI (1.0 g, 6 mmol) and benzyl bromide (1.02g, 6 mmol) were added. The mixture was stirred at room temperature for 12 h. After which, the DMF was removed by vacuum distillation and a residual yellow oil was obtained. The oil was purified by CC (25% EtOAc in hexanes) to give aryl benzyl sulfone.

Characterization data of products

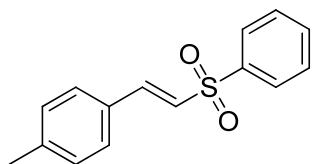
(*E*)-2-(phenylsulfonyl)vinylbenzene (**2a**)^[2]



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and (benzylsulfonyl)benzene (46.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2a** as white solid (40.5 mg, 83% yield), mp 69-70 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.56 – 7.52 (m, 2H), 7.47 – 7.46 (m, 2H), 7.39 – 7.37 (m, 3H), 6.88 (d, *J* = 15.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 142.4, 140.5, 133.3, 132.1, 131.1, 129.2, 129.0, 128.5, 127.5, 127.0.

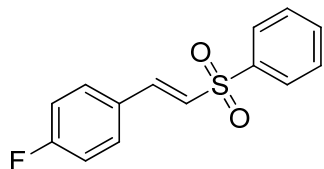
(*E*)-1-Methyl-4-[2-(phenylsulfonyl)vinyl]benzene (**2b**)^[3]



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-methyl-4-((phenylsulfonyl)methyl)benzene (49.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2b** as white solid. (35.6 mg, 69% yield), mp 131-132 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.52 (m, 4H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 15.4 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.6, 141.8, 140.9, 133.2, 129.8, 129.7, 129.3, 128.6, 127.6, 126.0, 21.5.

(*E*)-1-Fluoro-4-[2-(phenylsulfonyl)vinyl]benzene (**2c**)^[3]

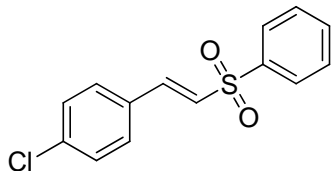


The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-fluoro-4-((phenylsulfonyl)methyl)benzene (50.0 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2c** as white solid (44.6 mg, 85% yield), mp 92-93 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.68 – 7.62 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 15.4 Hz, 1H). ¹³C NMR (100 MHz,

CDCl₃) δ 164.3(d, J = 251.5 Hz), 141.1, 140.5, 133.4, 130.6(d, J = 87.1 Hz), 129.4, 128.5(d, J = 3.3 Hz), 127.6, 127.0(d, J = 1.9 Hz), 116.3(d, J = 21.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -107.7.

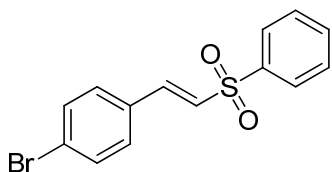
(E)-1-Chloro-4-[2-(phenylsulfonyl)vinyl]benzene (2d)^[3]



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-chloro-4-((phenylsulfonyl)methyl)benzene (53.3 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2d** as white solid. (47.1 mg, 82% yield), mp 128-130 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 7.0 Hz, 2H), 7.67 – 7.62 (m, 2H), 7.56 (t, J = 7.4 Hz, 2H), 7.43 – 7.36 (m, 4H), 6.84 (d, J = 15.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 141.0, 140.5, 137.3, 133.5, 130.8, 129.7, 129.4, 129.4, 127.9, 127.7.

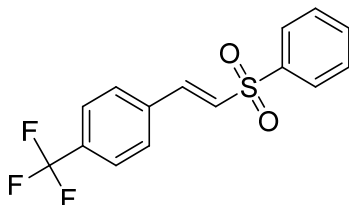
(E)-1-Bromo-4-[2-(phenylsulfonyl)vinyl]benzene (2e)^[3]



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-bromo-4-((phenylsulfonyl)methyl)benzene (62.3 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2e** as white solid. (42.0 mg, 65% yield), mp 150-151 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 7.0 Hz, 2H), 7.64 – 7.52 (m, 6H), 7.35 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 15.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 141.0, 140.4, 133.5, 132.3, 131.2, 129.9, 129.4, 127.9, 127.7, 125.6.

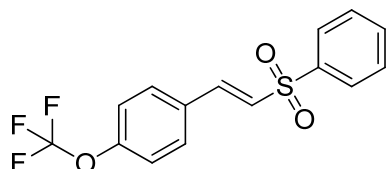
(E)-1-(Trifluoromethyl)-4-[2-(phenylsulfonyl)vinyl]benzene (2f)^[3]



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-((phenylsulfonyl)methyl)-4-(trifluoromethyl)benzene (60.0 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2f** as white solid (18.7 mg, 30% yield), mp 132-133 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.4$ Hz, 2H), 7.73 – 7.65 (m, 4H), 7.61 – 7.56 (m, 4H), 6.95 (d, $J = 15.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.4, 140.1, 135.7, 133.7, 132.6 (q, $J = 32.7$ Hz), 130.0, 129.5, 128.7, 127.8, 126.0 (q, $J = 3.6$ Hz), 123.6 (q, $J = 270.8$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -63.0.

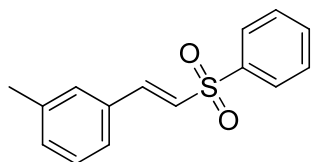
(E)-1-(2-(phenylsulfonyl)vinyl)-4-(trifluoromethoxy)benzene(2g)



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-((phenylsulfonyl)methyl)-4-(trifluoromethoxy)benzene (63.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2g** as white solid (24.3 mg, 37% yield), mp 90-92 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 7.2$ Hz, 2H), 7.69 – 7.62 (m, 2H), 7.58 – 7.52 (m, 4H), 7.24 (d, $J = 8.2$ Hz, 2H), 6.85 (d, $J = 15.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 140.7, 140.4, 133.6, 130.9, 130.2, 129.5, 128.3, 127.7, 121.3, 117.7 (q, $J = 254.1$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -57.7. HRMS m/z calcd for: $\text{C}_{15}\text{H}_{12}\text{F}_3\text{O}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 329.0454, found 329.0451.

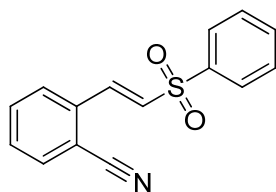
(E)-1-Methyl-3-[2-(phenylsulfonyl)vinyl]benzene (2h)^[3]



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-methyl-3-((phenylsulfonyl)methyl)benzene (49.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2h** as white solid (29.0 mg, 56% yield), mp 105-106 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 7.4$ Hz, 2H), 7.68 – 7.53 (m, 4H), 7.29 – 7.23 (m, 5H), 6.84 (d, $J = 15.0$ Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.7, 140.8, 138.8, 133.3, 132.3, 132.1, 129.3, 129.1, 129.0, 127.6, 127.0, 125.8, 21.3.

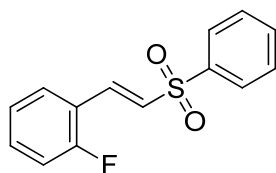
(E)-2-(2-(phenylsulfonyl)vinyl)benzonitrile(2i)



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 2-((phenylsulfonyl)methyl)benzotrile (51.5 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2i** as white solid (11.8 mg, 22% yield), mp 121-122 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.93 (d, *J* = 15.4 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.57 (m, 5H), 7.54 – 7.50 (m, 1H), 7.14 (d, *J* = 15.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 139.8, 137.3, 135.2, 133.8, 133.9, 133.1, 132.5, 130.9, 129.5, 128.1, 128.0, 116.7, 112.9. HRMS calcd for: C₁₅H₁₂NO₂S⁺ (M+H)⁺ 270.0583, found 270.0587.

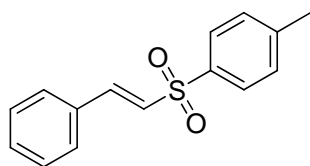
(E)-1-fluoro-2-(2-(phenylsulfonyl)vinyl)benzene (2j)



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-fluoro-2-((phenylsulfonyl)methyl)benzene (50.1 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2j** as white solid (45.6 mg, 87% yield), mp 130-131 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.77 (d, *J* = 15.6 Hz, 1H), 7.66 – 7.54 (m, 3H), 7.49 – 7.38 (m, 2H), 7.20 – 7.09 (m, 2H), 7.03 (d, *J* = 15.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 161.5(d, *J* = 253.8 Hz), 140.4, 135.5, 133.5, 132.8(d, *J* = 8.9 Hz), 130.3(d, *J* = 2.6 Hz), 130.1(d, *J* = 8.6 Hz), 129.4, 127.7, 124.7(d, *J* = 3.6 Hz), 120.5(d, *J* = 11.7 Hz), 116.4(d, *J* = 21.6 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -112.3. HRMS calcd for: C₁₄H₁₂FO₂S⁺ (M+H)⁺ 263.0537, found 263.0532.

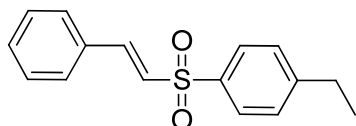
(E)-1-methyl-4-(styrylsulfonyl)benzene (2l)^[2]



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-(benzylsulfonyl)-4-methylbenzene (49.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2l** as white solid (19.6 mg, 38% yield), mp 119-120 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 15.4 Hz, 1H), 7.49 – 7.47 (m, 2H), 7.42 – 7.34 (m, 5H), 6.85 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.4, 142.0, 137.8, 132.5, 131.1, 130.0, 129.1, 128.5, 127.7, 127.6, 21.6.

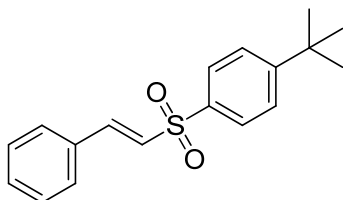
(E)-1-ethyl-4-(styrylsulfonyl)benzene(2m)



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-(benzylsulfonyl)-4-ethylbenzene (52.1 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2m** as white solid (26.7 mg, 49 % yield), mp 71-72 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 15.4 Hz, 1H), 7.49 – 7.48(m, 2H), 7.41 – 7.36 (m, 5H), 6.85 (d, *J* = 15.4 Hz, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.5, 142.0, 137.9, 132.4, 131.1, 129.0, 128.8, 128.5, 127.8, 127.6, 28.9, 15.1. HRMS *m/z* calcd for: C₁₆H₁₇O₂S⁺ (M+H)⁺ 273.0944, found 273.0949.

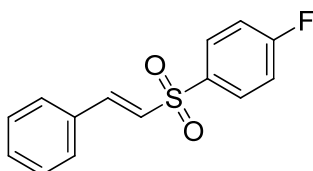
(E)-1-(tert-butyl)-4-(styrylsulfonyl)benzene (2n)



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-(benzylsulfonyl)-4-(tert-butyl)benzene (57.7 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2n** as white solid (46.9 mg, 78% yield), mp 111-112 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 7.0 Hz, 2H), 7.67 (d, *J* = 15.2 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.40 – 7.37 (s, 3H), 6.86 (d, *J* = 15.2 Hz, 1H), 1.34 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 157.3, 141.9, 137.6, 132.4, 131.1, 129.0, 128.5, 127.6, 127.5, 126.4, 35.2, 31.0. HRMS calcd for: C₁₈H₂₁O₂S⁺ (M+H)⁺ 301.1257, found 301.1259.

(E)-1-fluoro-4-(styrylsulfonyl)benzene (2o)^[21]

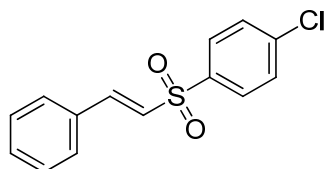


The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-(benzylsulfonyl)-4-fluorobenzene (50.0 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2o** as white solid (38.8 mg, 74% yield), mp 85-86 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.94 (m, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.50 – 7.48 (m, 2H), 7.43 – 7.38 (m, 3H), 7.25 – 7.20 (m, 2H), 6.85 (d, *J* = 15.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃)

δ 165.6(d, $J = 254.4$ Hz) , 142.6, 136.7, 132.1, 131.3, 130.5(d, $J = 9.5$ Hz), 129.1, 128.6, 127.0, 116.6(d, $J = 22.5$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -103.9.

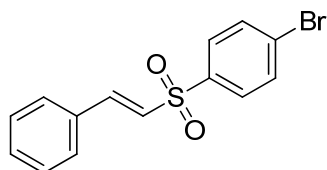
(E)-1-chloro-4-(styrylsulfonyl)benzene (2p)^[2]



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-(benzylsulfonyl)-4-chlorobenzene (53.3 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2p** as white solid (38.5 mg, 69% yield), mp 82-83 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.6$ Hz, 2H), 7.69 (d, $J = 15.4$ Hz, 1H), 7.54 – 7.49 (m, 4H), 7.44 – 7.38 (m, 3H), 6.84 (d, $J = 15.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 140.1, 139.2, 132.2, 131.4, 129.7, 129.2, 128.6, 126.8.

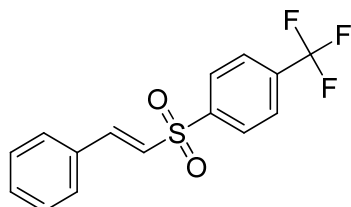
(E)-1-bromo-4-(styrylsulfonyl)benzene (2q)^[2]



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-(benzylsulfonyl)-4-bromobenzene (62.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2q** as white solid (47.8 mg, 74% yield), mp 102-103 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.4$ Hz, 2H), 7.71 – 7.66 (m, 3H), 7.50 – 7.39 (m, 5H), 6.83 (d, $J = 15.4$ Hz, 1H). ^{13}C NMR (100MHz, CDCl_3) δ 143.1, 139.8, 132.7, 132.2, 131.5, 129.4, 129.2, 129.1, 128.7, 126.9.

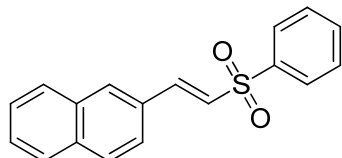
(E)-1-(styrylsulfonyl)-4-(trifluoromethyl)benzene (2r)^[4]



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 1-(benzylsulfonyl)-4-(trifluoromethyl)benzene (60.0 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2r** as white solid (53.1 mg, 85% yield), mp 77-79 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.0$ Hz, 2H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 15.4$ Hz, 1H), 7.50 (d, $J = 7.4$ Hz, 2H), 7.41 – 7.39 (m, 3H), 6.86 (d, $J = 15.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 144.0, 135.0(q, $J = 32.9$ Hz), 131.9, 131.6, 129.1, 128.7, 128.2, 126.4(q, $J = 3.7$ Hz), 126.2, 123.1(q, $J = 271.2$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -63.3.

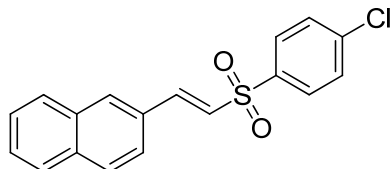
(E)-2-(2-(phenylsulfonyl)vinyl)naphthalene (2t)



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 2-((phenylsulfonyl)methyl)naphthalene (56.5 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2t** as white solid (30.6 mg, 52% yield), mp 98-100 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 7.2$ Hz, 2H), 7.92 (s, 1H), 7.86 – 7.79 (m, 4H), 7.63 – 7.49 (m, 6H), 6.97 (d, $J = 15.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.5, 140.7, 134.4, 133.3, 133.0, 131.0, 130.9, 129.7, 129.3, 128.9, 128.6, 127.8, 127.6, 127.2, 126.9, 123.3. HRMS calcd for: $\text{C}_{18}\text{H}_{15}\text{O}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 295.0787, found 295.0793.

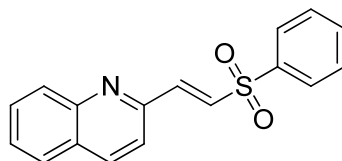
(E)-2-(2-((4-chlorophenyl)sulfonyl)vinyl)naphthalene (2u)



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 2-(((4-chlorophenyl)sulfonyl)methyl)naphthalene (63.3 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2u** as white solid (31.6 mg, 48% yield), mp 182-183 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.95 – 7.84 (m, 7H), 7.57 – 7.52 (m, 5H), 6.94 (d, $J = 15.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 140.0, 139.3, 134.5, 133.0, 131.1, 129.6, 129.7, 129.1, 129.0, 128.7, 127.9, 127.8, 127.0, 126.8, 123.3. HRMS calcd for: $\text{C}_{18}\text{H}_{14}\text{ClO}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 329.0397, found 329.0394.

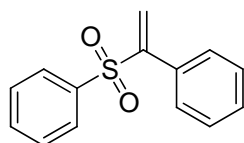
(E)-2-(2-(phenylsulfonyl)vinyl)quinoline (2v)



The reaction was conducted with paraformaldehyde (54 mg, 1.8 mmol), and 2-((phenylsulfonyl)methyl)quinoline (56.7 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1) to yield the desired product **2v** as white solid (13.6 mg, 23% yield), mp 139-140 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 7.4 Hz, 2H), 7.85 (t, *J* = 11.8 Hz, 2H), 7.78–7.74 (m, 1H), 7.67–7.55 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 150.9, 147.9, 140.9, 140.1, 137.4, 133.7, 133.3, 130.6, 129.6, 129.4, 128.4, 128.0, 128.0, 127.6, 121.5. HRMS calcd for: C₁₇H₁₄NO₂S⁺ (M+H)⁺ 296.0739, found 296.0735.

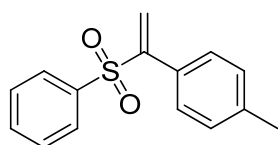
(1-(phenylsulfonyl)vinyl)benzene (**3a**)^[6]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and (benzylsulfonyl)benzene (46.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3a** as white solid (41.9 mg, 86% yield), mp 70-71 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44–7.40 (m, 2H), 7.35–7.28 (m, 5H), 6.65 (s, 1H), 5.98 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 138.5, 133.4, 132.3, 129.3, 129.1, 128.8, 128.3, 128.2, 126.0.

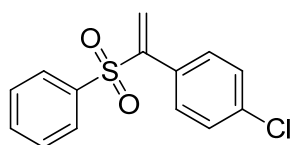
1-methyl-4-(1-(phenylsulfonyl)vinyl)benzene (**3b**)^[6]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-methyl-4-((phenylsulfonyl)methyl)benzene (49.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3b** as white solid (38.7 mg, 75% yield), mp 85-86 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.60 (s, 1H), 5.93 (s, 1H), 2.32 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.7, 139.4, 138.8, 133.3, 129.4, 129.0, 128.9, 128.8, 128.3, 125.5, 21.2.

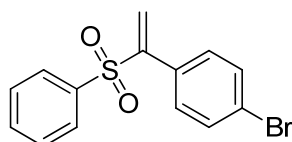
1-chloro-4-(1-(phenylsulfonyl)vinyl)benzene (**3c**)^[7]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-chloro-4-((phenylsulfonyl)methyl)benzene (53.3 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3c** as white solid (44.5 mg, 80% yield), mp 71-73 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.2$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.29 – 7.24 (m, 4H), 6.64 (s, 1H), 5.96 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.7, 138.3, 135.6, 133.6, 130.8, 130.4, 129.0, 128.5, 128.2, 126.4.

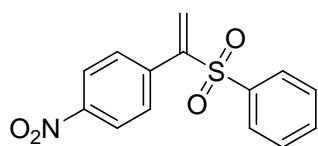
1-bromo-4-(1-(phenylsulfonyl)vinyl)benzene (**3d**)^[7]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-bromo-4-((phenylsulfonyl)methyl)benzene (62.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3d** as yellow solid (45.2 mg, 70% yield), mp 76-77 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.2$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.45 – 7.40 (m, 4H), 7.20 (d, $J = 8.4$ Hz, 2H), 6.64 (s, 1H), 5.96 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 138.4, 133.6, 131.5, 131.4, 130.6, 129.0, 128.3, 126.3, 123.9.

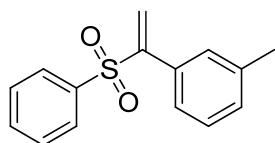
1-nitro-4-(1-(phenylsulfonyl)vinyl)benzene (**3e**)



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-nitro-4-((phenylsulfonyl)methyl)benzene (55.5 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3e** as white solid. (26.0 mg, 45% yield), mp 113-115 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.2$ Hz, 2H), 7.60 – 7.53 (m, 3H), 7.45 (t, $J = 7.6$ Hz, 2H), 6.77 (s, 1H), 6.08 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.4, 148.3, 138.9, 138.0, 133.9, 130.1, 129.2, 128.3, 127.7, 123.5. HRMS (ESI) m/z calcd for: $\text{C}_{14}\text{H}_{12}\text{NO}_4\text{S}^+$ ($\text{M}+\text{H}$)⁺ 290.0481, found 290.0488.

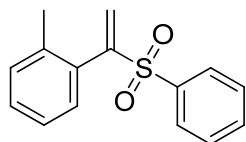
1-methyl-3-(1-(phenylsulfonyl)vinyl)benzene (**3f**)^[7]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-methyl-3-((phenylsulfonyl)methyl)benzene (49.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3f** as white solid (42.3 mg, 82% yield), mp 82-83 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.16 – 7.09 (m, 4H), 6.60 (s, 1H), 5.94 (s, 1H), 2.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 138.6, 137.9, 133.3, 132.2, 130.0, 129.6, 128.8, 128.3, 128.1, 126.1, 125.7, 21.2.

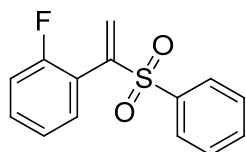
1-methyl-2-(1-(phenylsulfonyl)vinyl)benzene (**3g**)^[6]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-methyl-2-((phenylsulfonyl)methyl)benzene (49.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3g** as white solid (44.9 mg, 87% yield), mp 80-81 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.58 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.13 – 7.07 (m, 2H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 5.84 (s, 1H), 1.95 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.9, 138.2, 137.7, 133.5, 131.4, 130.6, 130.1, 129.2, 128.9, 128.8, 126.9, 125.1, 19.2.

1-fluoro-2-(1-(phenylsulfonyl)vinyl)benzene (**3h**)

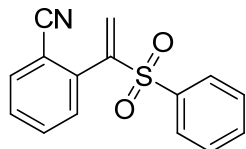


The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-fluoro-2-((phenylsulfonyl)methyl)benzene (50.0 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3h** as white solid (44.5 mg, 85% yield), mp 87-89 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 3H), 7.33 – 7.28 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 9.0 Hz, 1H), 6.85 (s, 1H), 6.03 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 159.8 (d, *J* = 248.9 Hz), 144.1, 138.2, 133.6, 131.7 (d, *J* = 1.7 Hz), 131.3 (d, *J* = 8.0 Hz), 128.9, 128.8, 128.4, 123.7 (d, *J* = 3.8 Hz), 119.8 (d, *J* = 15.0 Hz),

115.5(d, $J = 21.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -115.0. HRMS (ESI) m/z calcd for: $\text{C}_{14}\text{H}_{12}\text{FO}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 263.0537, found 263.0539.

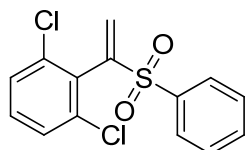
2-(1-(phenylsulfonyl)vinyl)benzonitrile (3i)



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 2-((phenylsulfonyl)methyl)benzonitrile (51.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3i** as white solid (26.9 mg, 49% yield), mp 99-100 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.4$ Hz, 1H), 7.67 (d, $J = 7.4$ Hz, 2H), 7.60 (m, 2H), 7.54 (d, $J = 7.4$ Hz, 1H), 7.48 – 7.43 (m, 3H), 6.93 (s, 1H), 6.13 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.1, 137.5, 135.5, 134.0, 132.9, 132.3, 131.1, 129.7, 129.5, 129.2, 128.7, 116.4, 113.4. HRMS (ESI) m/z calcd for: $\text{C}_{15}\text{H}_{12}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 270.0583, found 270.0588.

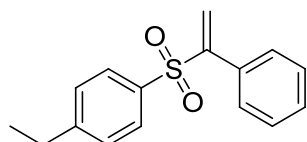
1,3-dichloro-2-(1-(phenylsulfonyl)vinyl)benzene (3j)



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1,3-dichloro-2-((phenylsulfonyl)methyl)benzene (51.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3j** as white solid (54.5 mg, 87% yield), mp 113-114 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 7.8$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.26 – 7.17 (m, 3H), 6.85 (s, 1H), 5.98 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.2, 139.1, 136.4, 133.9, 131.4, 131.0, 130.8, 129.2, 129.1, 128.7, 128.6, 128.2. HRMS (ESI) m/z calcd for: $\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{O}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 312.9851, found 312.9855.

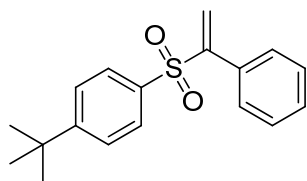
1-ethyl-4-((1-phenylvinyl)sulfonyl)benzene (3k)^[2]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-(benzylsulfonyl)-4-ethylbenzene (52.0 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3k** as pale yellow viscous liquid (45.1 mg, 83% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 8.4$ Hz, 2H), 7.33 – 7.31 (m, 3H), 7.28 – 7.24 (m, 2H), 7.21 (d, $J = 8.2$ Hz, 2H), 6.59 (s, 1H), 5.93 (s, 1H), 2.65 (q, $J = 7.6$ Hz, 2H), 1.20 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 150.4, 135.8, 132.5, 129.2, 129.0, 128.4, 128.3, 128.2, 125.5, 28.7, 14.9.

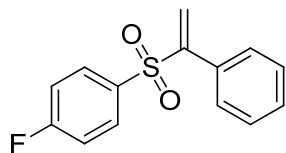
1-(tert-butyl)-4-((1-phenylvinyl)sulfonyl)benzene (**3l**)



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-(benzylsulfonyl)-4-(tert-butyl)benzene (57.7 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3l** as white solid (51.6 mg, 86% yield), mp 85-86 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.35 – 7.31 (m, 3H), 7.28 – 7.24 (m, 2H), 6.58 (s, 1H), 5.93 (s, 1H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.2, 150.9, 135.6, 132.5, 129.2, 129.1, 128.2, 128.1, 125.8, 125.6, 35.1, 30.9. HRMS (ESI) m/z calcd for: $\text{C}_{18}\text{H}_{21}\text{O}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 301.1257, found 301.1255.

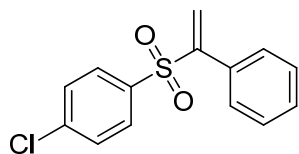
1-fluoro-4-((1-phenylvinyl)sulfonyl)benzene (**3m**)^[8]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-(benzylsulfonyl)-4-fluorobenzene (50.0 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3m** as white solid. (43.4 mg, 83% yield), mp 92-93 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.70 – 7.66 (m, 2H), 7.36 – 7.26 (m, 5H), 7.06 (t, $J = 8.6$ Hz, 2H), 6.63 (s, 1H), 5.96 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.5 (d, $J = 254.5$ Hz), 150.7, 134.5 (d, $J = 3.3$ Hz), 132.1, 131.2 (d, $J = 9.5$ Hz), 129.4, 129.0, 128.3, 126.0, 116.1 (d, $J = 22.8$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -102.3.

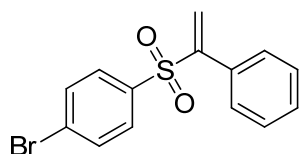
1-chloro-4-((1-phenylvinyl)sulfonyl)benzene (**3n**)^[7]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-(benzylsulfonyl)-4-chlorobenzene (53.3 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3n** as white solid (38.3 mg, 69% yield), mp 87-88 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, J = 8.6 Hz, 2H), 7.37 – 7.28 (m, 7H), 6.65 (s, 1H), 5.98 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 140.0, 137.1, 132.0, 129.7, 129.5, 129.1, 129.0, 128.3, 126.3.

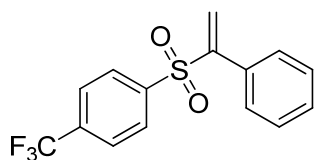
1-bromo-4-((1-phenylvinyl)sulfonyl)benzene (**3o**)^[7]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-(benzylsulfonyl)-4-bromobenzene (62.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3o** as white solid (47.8 mg, 74% yield), mp 80-81 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.53 (s, 4H), 7.38 – 7.27 (m, 5H), 6.65 (s, 1H), 5.99 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 137.7, 132.1, 132.0, 129.8, 129.5, 129.4, 128.7, 128.4, 126.4.

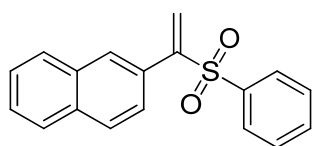
1-((1-phenylvinyl)sulfonyl)-4-(trifluoromethyl)benzene (**3p**)^[7]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-(benzylsulfonyl)-4-(trifluoromethyl)benzene (60.0 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3p** as white solid (44.9 mg, 72% yield), mp 80-82 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, J = 12.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.38 – 7.27 (m, 5H), 6.70 (s, 1H), 6.05 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 142.3, 134.9 (q, J = 32.8 Hz), 131.8, 129.6, 129.1, 128.8, 128.5, 127.2, 125.9 (q, J = 3.8 Hz), 123.0 (q, J = 271.5 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -63.2.

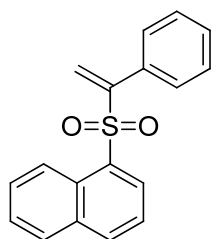
2-(1-(phenylsulfonyl)vinyl)naphthalene (**3q**)^[7]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 2-((phenylsulfonyl)methyl)naphthalene (51.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3q** as white solid (36.5 mg, 62% yield), mp 71-72 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.82 – 7.72 (m, 5H), 7.53 – 7.43 (m, 4H), 7.37 (t, *J* = 7.8 Hz, 2H), 6.74 (s, 1H), 6.08 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 138.6, 133.4, 133.2, 132.6, 129.7, 128.9, 128.8, 128.3, 128.2, 128.0, 127.5, 127.0, 126.5, 126.6, 126.1.

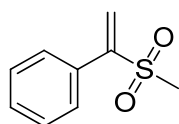
1-((1-phenylvinyl)sulfonyl)naphthalene (**3r**)^[7]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 1-(benzylsulfonyl)naphthalene (56.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3r** as white solid (30.6 mg, 52% yield), mp 99-100 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 8.6 Hz, 1H), 8.12 (d, *J* = 7.4 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.23 – 7.10 (m, 5H), 6.77 (s, 1H), 6.04 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 151.2, 135.0, 133.6, 132.6, 132.0, 131.2, 129.0, 128.9, 128.5, 128.4, 128.1, 127.9, 126.6, 125.6, 123.9, 123.9.

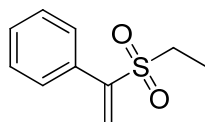
(1-(methylsulfonyl)vinyl)benzene (**3s**)^[8]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and ((methylsulfonyl)methyl)benzene (34 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3s** as pale yellow viscous liquid (26.9 mg, 74% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.62 (m, 2H), 7.48 – 7.41 (m, 3H), 6.54 (s, 1H), 6.03 (s, 1H), 2.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.9, 132.4, 129.8, 128.8, 128.5, 125.9, 40.5.

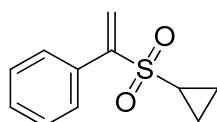
(1-(ethylsulfonyl)vinyl)benzene (**3t**)^[6]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and ((ethylsulfonyl)methyl)benzene (36.8 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3t** as pale yellow viscous liquid (28.2 mg, 72% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.62 (m, 2H), 7.46 – 7.39 (m, 3H), 6.52 (s, 1H), 6.08 (s, 1H), 2.85 (q, $J = 7.4$ Hz, 1H), 1.22 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 132.5, 129.7, 128.8, 128.5, 127.5, 46.2, 6.9.

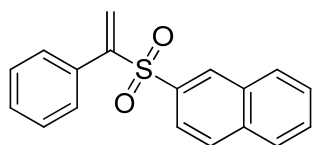
(1-(cyclopropylsulfonyl)vinyl)benzene (**3u**)^[8]



The reaction was conducted with paraformaldehyde (30mg, 1.0 mmol), and ((cyclopropylsulfonyl)methyl)benzene (39.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3u** as pale yellow viscous liquid (32.8 mg, 79 % yield).

^1H NMR (400 MHz, CDCl_3) δ 7.51 (m, 2H), 6.42 (s, 1H), 5.94 (s, 1H), 2.25 – 2.20 (m, 1H), 1.12 – 1.11 (m, 2H), 0.89 – 0.88 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 132.9, 129.5, 128.9, 128.5, 125.2, 29.4, 5.4.

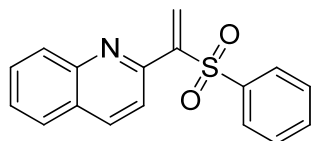
2-((1-phenylvinyl)sulfonyl)naphthalene (**3v**)^[7]



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 2-(benzylsulfonyl)naphthalene (56.4 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3v** as white solid (35.8 mg, 61% yield), mp 90-91 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.29 (s, 1H), 7.88 – 7.84 (m, 3H), 7.65 – 7.55 (m, 3H), 7.35 – 7.22 (m, 5H), 6.70 (s, 1H), 6.01 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.8, 135.5, 135.0, 132.4, 131.9, 130.1, 129.3, 129.3, 129.1, 129.1, 129.0, 128.2, 127.8, 127.4, 126.1, 122.9.

2-(1-(phenylsulfonyl)vinyl)quinoline (**3w**)

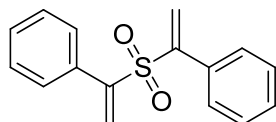


The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and 2-((phenylsulfonyl)methyl)quinoline (56.7 mg, 0.2 mmol). The residue was purified by column

chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3w** as yellow solid (29.5 mg, 50% yield), mp 89-90 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.4$ Hz, 1H), 7.97 – 7.89 (m, 4H), 7.80 (d, $J = 7.4$ Hz, 1H), 7.71 – 7.67 (m, 1H), 7.57 – 7.44 (m, 4H), 6.95 (s, 1H), 6.73 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.6, 150.2, 147.6, 139.7, 136.7, 133.4, 130.0, 129.5, 129.4, 128.8, 128.5, 127.5, 127.4, 127.3, 120.1. HRMS calcd for: $\text{C}_{17}\text{H}_{14}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 296.0739, found 296.0735.

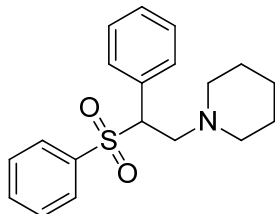
(sulfonylbis(ethene-1,1-diyl)dibenzene (3x)



The reaction was conducted with paraformaldehyde (30 mg, 1.0 mmol), and (sulfonylbis(methylene)dibenzene (49.2 mg, 0.2 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the desired product **3x** as pale yellow viscous liquid (16.2 mg, 30% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.27 (m, 10H), 6.41 (s, 2H), 5.92 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.3, 132.2, 129.4, 128.9, 128.3, 128.0. HRMS calcd for: $\text{C}_{16}\text{H}_{15}\text{O}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 270.0715, found 270.0715.

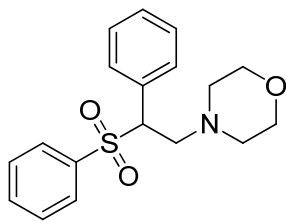
1-(2-phenyl-2-(phenylsulfonyl)ethyl)piperidine (5a)



Prepared α -substituted vinyl sulfones (0.2 mmol) with piperidine (37 μL , 0.4 mmol) reacting. The title compound was obtained as a white solid (48.1 mg, 73%), mp 100-101 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.52 (m, 3H), 7.39 (t, $J = 7.8$ Hz, 2H), 7.31 – 7.23 (m, 3H), 7.18 (d, $J = 6.6$ Hz, 2H), 4.35 – 4.31 (m, 1H), 3.50 – 3.46 (m, 1H), 3.10 – 3.05 (m, 1H), 2.28 – 2.22 (m, 4H), 1.33 – 1.28 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.2, 133.2, 132.7, 129.9, 128.7, 128.5, 128.5, 128.3, 69.0, 57.2, 54.3, 25.6, 23.8. HRMS calcd for: $\text{C}_{19}\text{H}_{24}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 330.1522, found 330.1522.

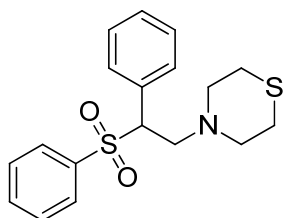
4-(2-phenyl-2-(phenylsulfonyl)ethyl)morpholine (5b)



Prepared α -substituted vinyl sulfones (0.2 mmol) with morpholine (35 μ L, 0.4 mmol) reacting. The title compound was obtained as a white solid (47.7 mg, 72%), mp 108-110 $^{\circ}$ C.

^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.53 (m, 3H), 7.39 (t, J = 7.8 Hz, 2H), 7.31 – 7.22 (m, 3H), 7.16 (d, J = 6.8 Hz, 2H), 4.34 – 4.32 (m, 1H), 3.51 – 3.45 (m, 5H), 3.13 – 3.09 (m, 1H), 2.37 – 2.33 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 133.4, 132.3, 129.8, 128.8, 128.7, 128.5, 128.4, 68.9, 66.5, 56.8, 53.3. HRMS calcd for: $\text{C}_{18}\text{H}_{22}\text{NO}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 332.1315, found 332.1317.

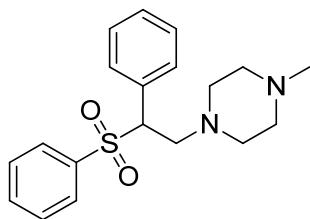
4-(2-phenyl-2-(phenylsulfonyl)ethyl)thiomorpholine (5c)



Prepared α -substituted vinyl sulfones (0.2 mmol) with thiomorpholine (41.3 mg, 0.4 mmol) reacting. The title compound was obtained as a white solid (52.1 mg, 75%), mp 129-130 $^{\circ}$ C.

^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.53 (m, 3H), 7.39 (t, J = 7.6 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.16 (d, J = 7.2 Hz, 2H), 4.32 – 4.29 (m, 1H), 3.57 – 3.52 (m, 1H), 3.20 – 3.14 (m, 1H), 2.68 – 2.60 (m, 4H), 2.43 – 2.39 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 133.4, 132.5, 129.8, 128.7, 128.6, 128.4, 68.8, 57.3, 54.6, 27.6. HRMS calcd for: $\text{C}_{18}\text{H}_{22}\text{NO}_2\text{S}_2^+$ ($\text{M}+\text{H}$) $^+$ 348.1086, found 348.1086.

1-methyl-4-(2-phenyl-2-(phenylsulfonyl)ethyl)piperazine (5d)

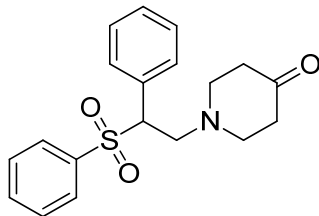


Prepared α -substituted vinyl sulfones (0.2 mmol) with 1-methylpiperazine (45 μ L, 0.4 mmol) reacting. The title compound was obtained as a white solid (63.3 mg, 92%), mp 113-114 $^{\circ}$ C.

^1H NMR (400 MHz, CDCl_3) δ 7.55 (m, 3H), 7.39 (t, J = 7.8 Hz, 2H), 7.31 – 7.22 (m, 3H), 7.16 (d, J = 7.2 Hz, 2H), 4.34 – 4.31 (m, 1H), 3.56 – 3.51 (m, 1H), 3.17 – 3.12 (m, 1H), 2.39 (s, 4H), 2.22 – 2.05 (m, 7H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.9, 133.3, 132.4, 129.8, 128.7, 128.6, 128.5,

128.3, 68.8, 56.2, 54.5, 52.6, 45.7. HRMS calcd for: $C_{19}H_{25}N_2O_2S^+$ (M+H)⁺ 345.1631, found 345.1634.

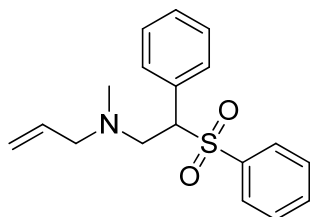
1-(2-phenyl-2-(phenylsulfonyl)ethyl)piperidin-4-one (5e)



Prepared α -substituted vinyl sulfones (0.2 mmol) with reacting piperidin-4-one•HClH₂O (61.5 mg, 0.4 mmol) reacting. The title compound was obtained as a white solid (41.2 mg, 60%), mp 152-153 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.51 (m, 3H), 7.40 (t, J = 7.8 Hz, 2H), 7.35 – 7.22 (m, 4H), 7.18 (d, J = 6.8 Hz, 2H), 4.38 – 4.27 (m, 1H), 3.71 – 3.61 (m, 1H), 3.30 – 3.25 (m, 1H), 2.79 – 2.50 (m, 4H), 2.35 – 2.14 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 208.3, 138.0, 133.5, 132.1, 129.7, 128.8, 128.7, 128.6, 128.5, 128.5, 69.4, 55.4, 52.8, 40.8. HRMS calcd for: $C_{19}H_{22}NO_3S^+$ (M+H)⁺ 344.1315, found 344.1305.

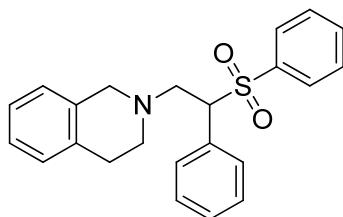
N-methyl-N-(2-phenyl-2-(phenylsulfonyl)ethyl)prop-2-en-1-amine (5f)



Prepared α -substituted vinyl sulfones (0.2 mmol) with N-methylprop-2-en-1-amine (39 μ L, 0.4 mmol) reacting. The title compound was obtained as a white solid (48.5 mg, 77%), mp 80-81 °C.

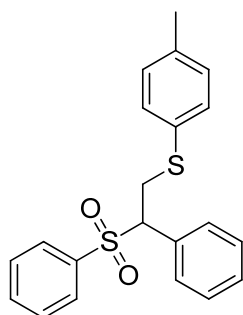
¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 9.6 Hz, 3H), 7.38 (t, J = 7.6 Hz, 2H), 7.29 – 7.22 (m, 3H), 7.14 (d, J = 7.0 Hz, 2H), 5.69 – 5.59 (m, 1H), 5.09 – 5.05 (m, 2H), 4.31 – 4.28 (m, 1H), 3.41 – 3.23 (m, 2H), 3.02 – 2.91 (m, 2H), 2.13 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 137.6, 134.8, 133.4, 132.2, 129.9, 128.8, 128.6, 128.5, 128.3, 118.0, 69.7, 60.8, 54.3, 42.3. HRMS calcd for: $C_{18}H_{22}NO_2S^+$ (M+H)⁺ 316.1366, found 316.1364.

2-(2-phenyl-2-(phenylsulfonyl)ethyl)-1,2,3,4-tetrahydroisoquinoline (5g)



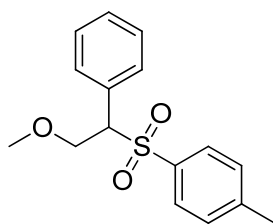
Prepared α -substituted vinyl sulfones (0.2 mmol) with 1,2,3,4-tetrahydroisoquinoline (51 μ L, 0.4 mmol) reacting. The title compound was obtained as a white solid (65 mg, 86%), mp 124-125 $^{\circ}$ C. ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, J = 4.2 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.37 – 7.20(m, 7H), 7.11 – 7.00 (m, 3H), 6.90 (d, J = 8.4 Hz, 1H), 4.44 – 4.40 (m, 1H), 3.69 – 3.52 (m, 3H), 3.37 – 3.31 (m, 1H), 2.74 – 2.63 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.8, 134.1, 133.9, 133.3, 132.5, 129.9, 128.8, 128.7, 128.5, 128.4, 126.4, 126.1, 125.5, 69.6, 55.9, 55.6, 50.6, 28.7. HRMS calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 378.1522, found 378.1528.

(2-phenyl-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (5h)



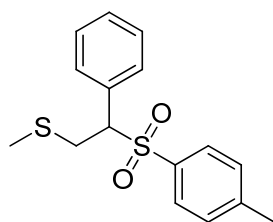
Prepared α -substituted vinyl sulfones (0.2 mmol) with 4-methylbenzenethiol (49.6 mg, 0.4 mmol) reacting. The title compound was obtained as a white solid (63.3 mg, 86%), mp 133-134 $^{\circ}$ C. ^1H NMR (400 MHz, CDCl_3) δ 7.55 (t, J = 7.4 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.24 (t, J = 8.6 Hz, 3H), 7.12 (d, J = 8.0 Hz, 2H), 7.07 – 7.05 (m, 4H), 4.16 – 4.12 (m, 1H), 3.95 – 3.91 (m, 1H), 3.47 (t, J = 12.8 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.3, 136.9, 133.7, 131.1, 130.8, 130.1, 130.0, 129.9, 129.1, 129.0, 128.7, 128.4, 70.3, 32.6, 21.1. HRMS calcd for: $\text{C}_{21}\text{H}_{21}\text{O}_2\text{S}_2^+$ ($\text{M}+\text{H}$) $^+$ 369.0977, found 369.0973.

1-((2-methoxy-1-phenylethyl)sulfonyl)-4-methylbenzen (5i)



Prepared (benzylsulfonyl)benzene (0.2 mmol), $(\text{HCHO})_n$ (1 mmol), CH_3OH (0.8 mL).reacting. The title compound was obtained as a white solid (39.8 mg, 72%), mp 119-120 $^{\circ}$ C. ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, J = 8.2 Hz, 2H), 7.33 – 7.25 (m, 3H), 7.19 (d, J = 7.8 Hz, 4H), 4.40 – 4.37 (m, 1H), 4.28 – 4.26 (m, 1H), 4.07 – 4.03 (m, 1H), 3.30 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 134.8, 131.2, 129.8, 129.2, 128.9, 128.9, 128.5, 70.7, 69.8, 59.1, 21.6. HRMS calcd for: $\text{C}_{16}\text{H}_{19}\text{O}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 291.1049, found 291.1051.

methyl(2-phenyl-2-tosylethyl)sulfane (5j)



Prepared (benzylsulfonyl)benzene (0.2 mmol), (HCHO)_n (1 mmol), DMSO (1.5 mL).reacting. The title compound was obtained as a white solid (43.4 mg, 71%), mp 110-111 °C.

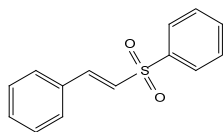
¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.24 (m, 4H), 7.19 – 7.13 (m, 3H), 4.23 (d, *J* = 14.2 Hz, 1H), 3.52 – 3.48 (m, 1H), 3.24 (t, *J* = 12.6, 1H), 2.39 (s, 3H), 1.97 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 144.8, 134.0, 131.5, 130.8, 129.9, 129.4, 129.0, 128.4, 32.1, 21.6, 16.2. HRMS calcd for: C₁₆H₁₉O₂S₂⁺ (M+H)⁺ 306.0748, found 306.0750.

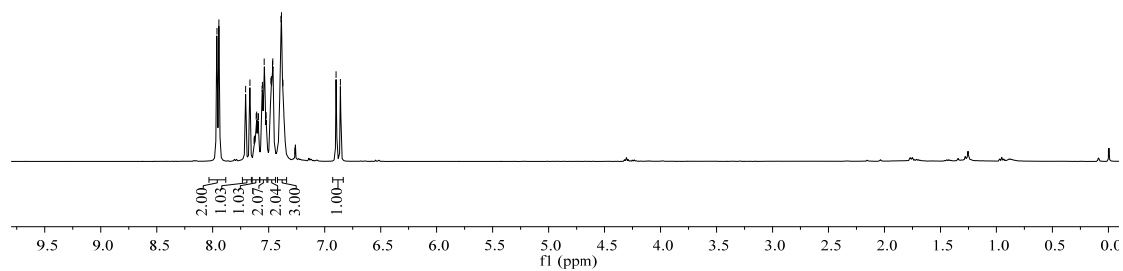
Reference:

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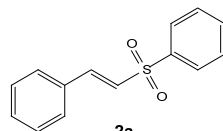


2a

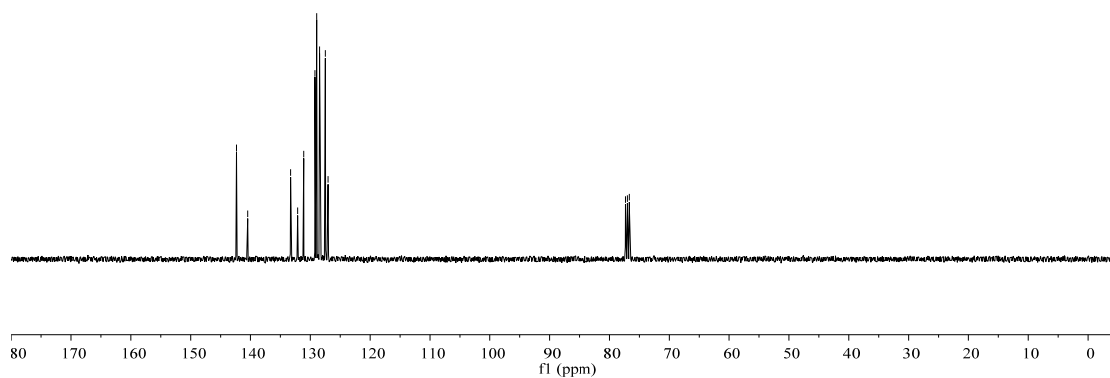


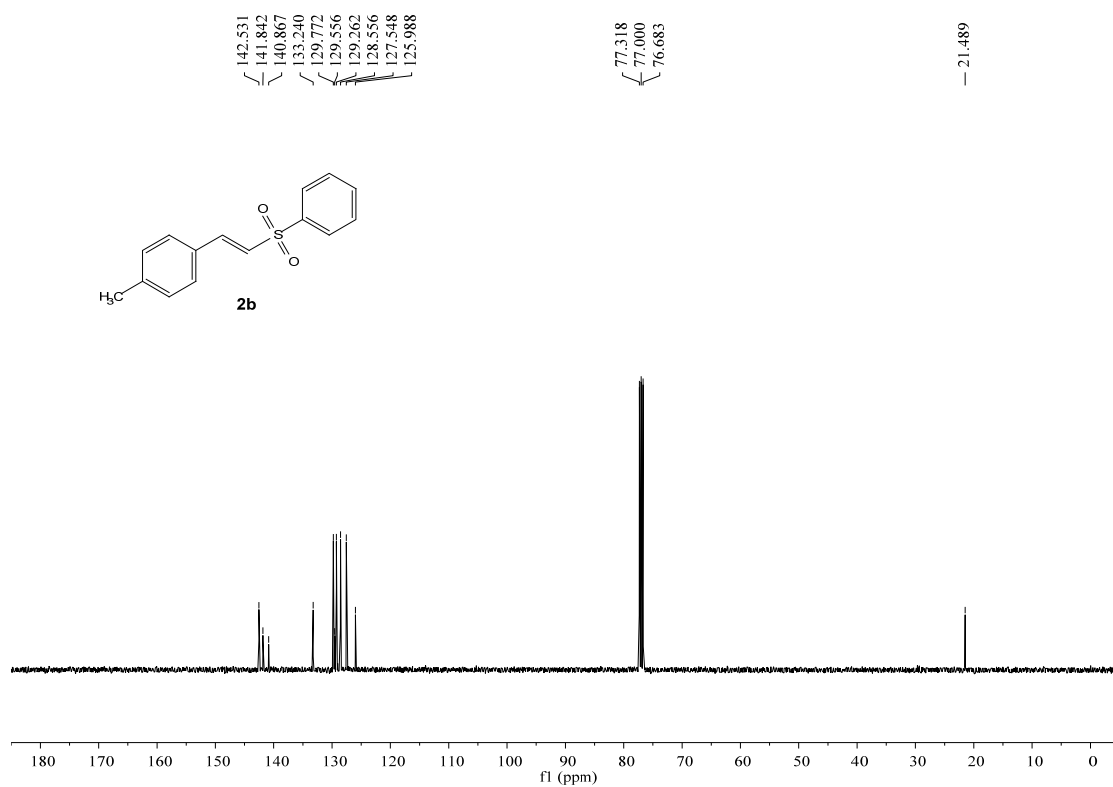
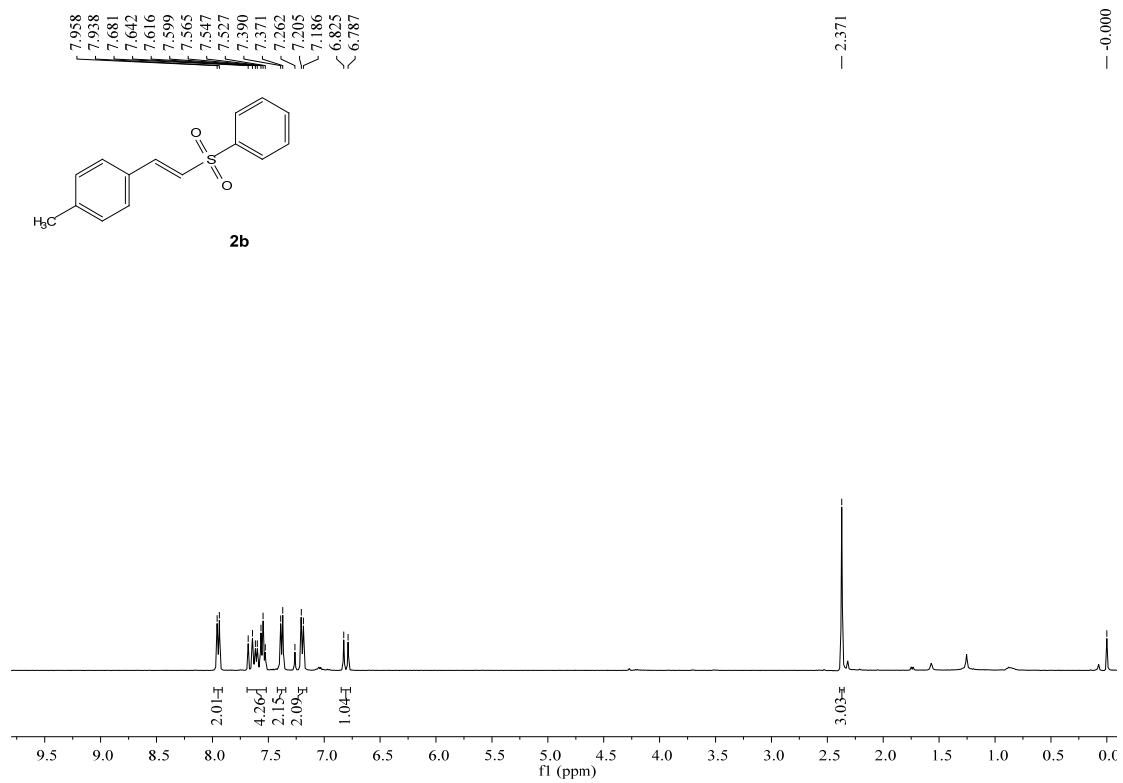
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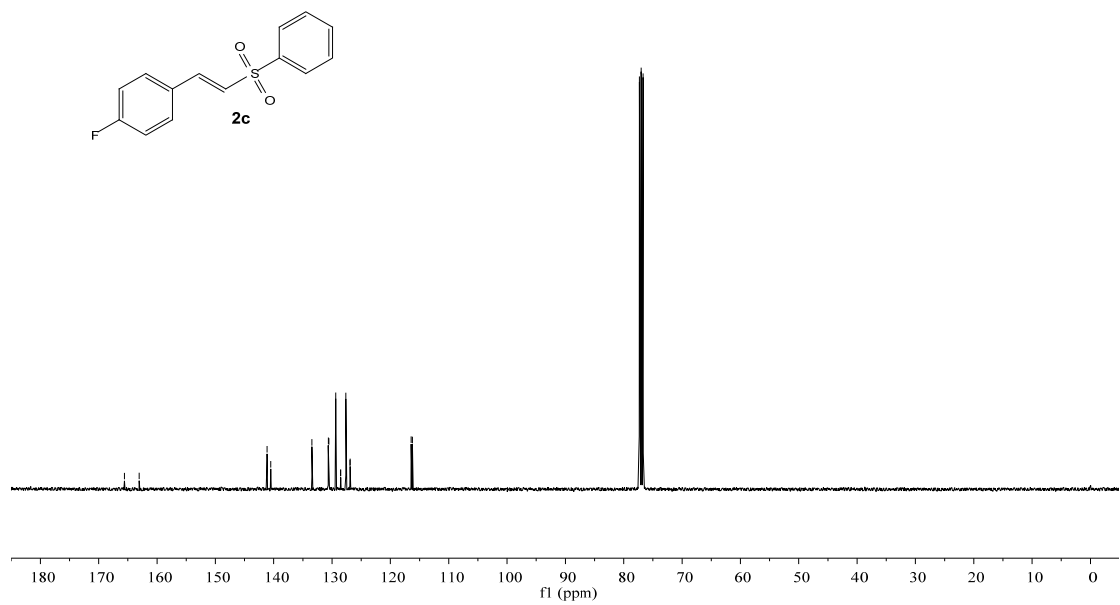
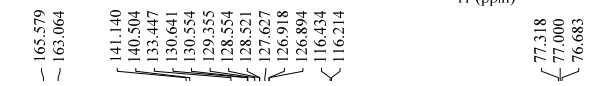
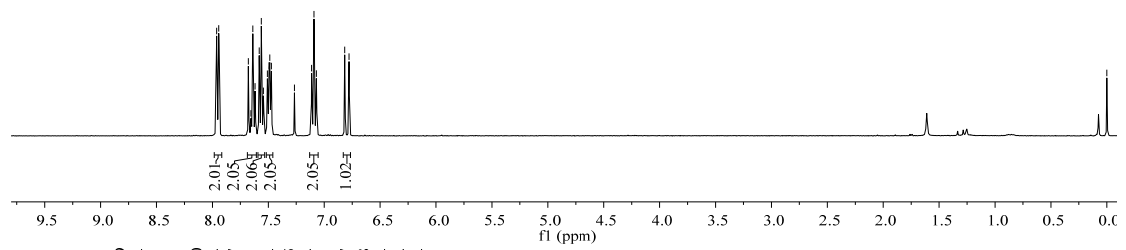
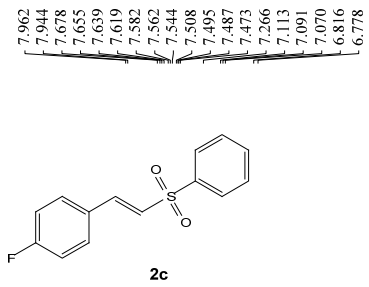
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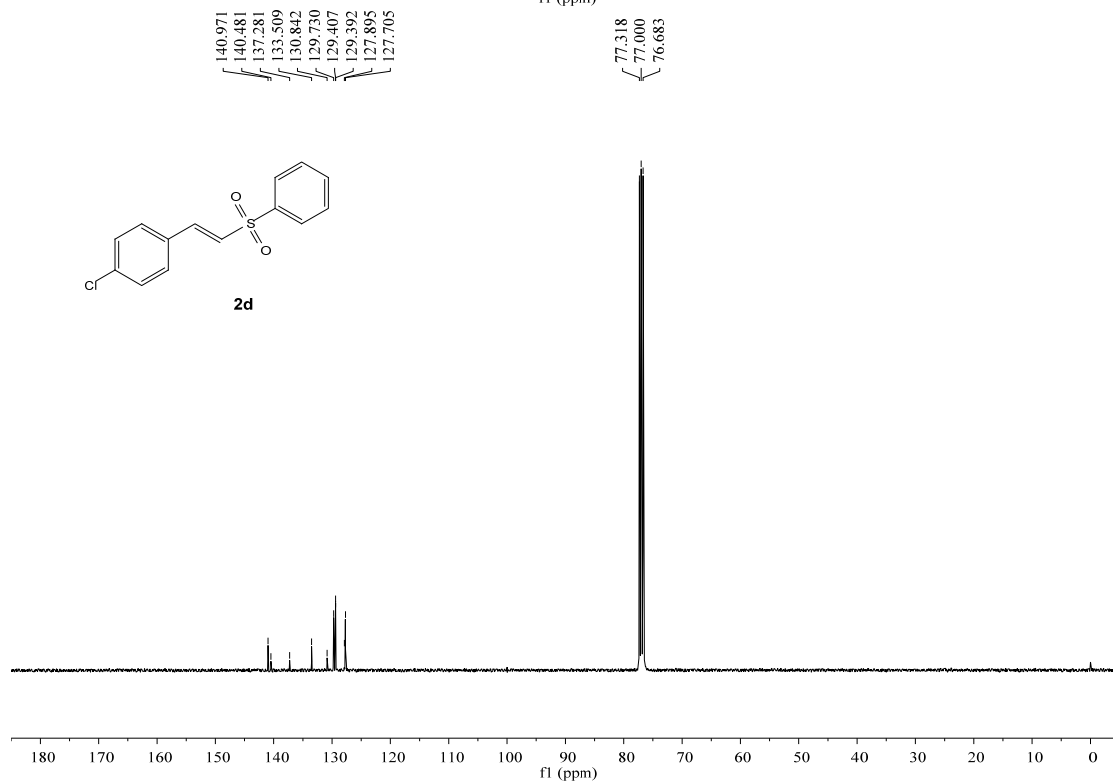
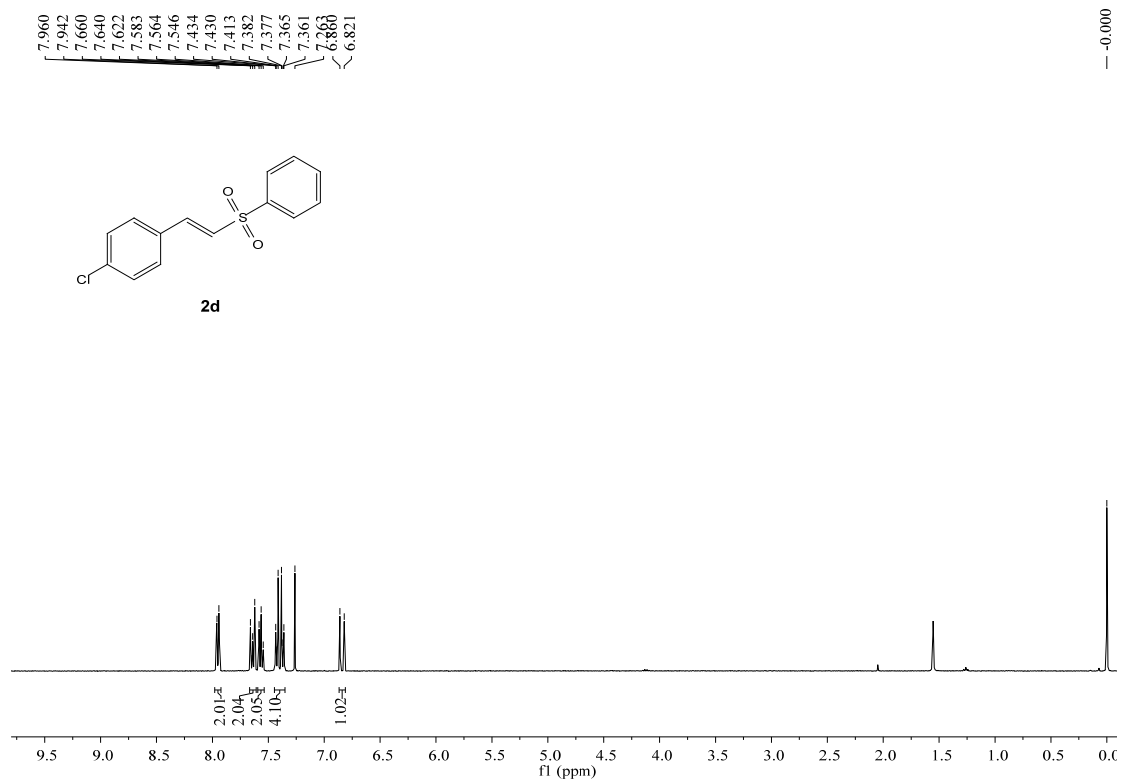
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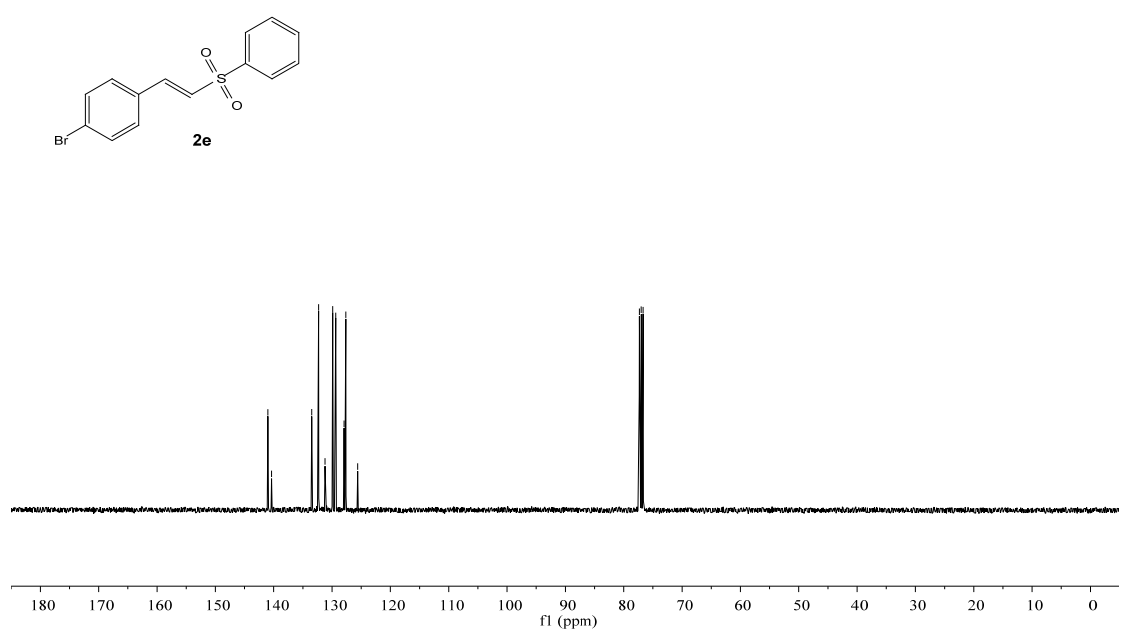
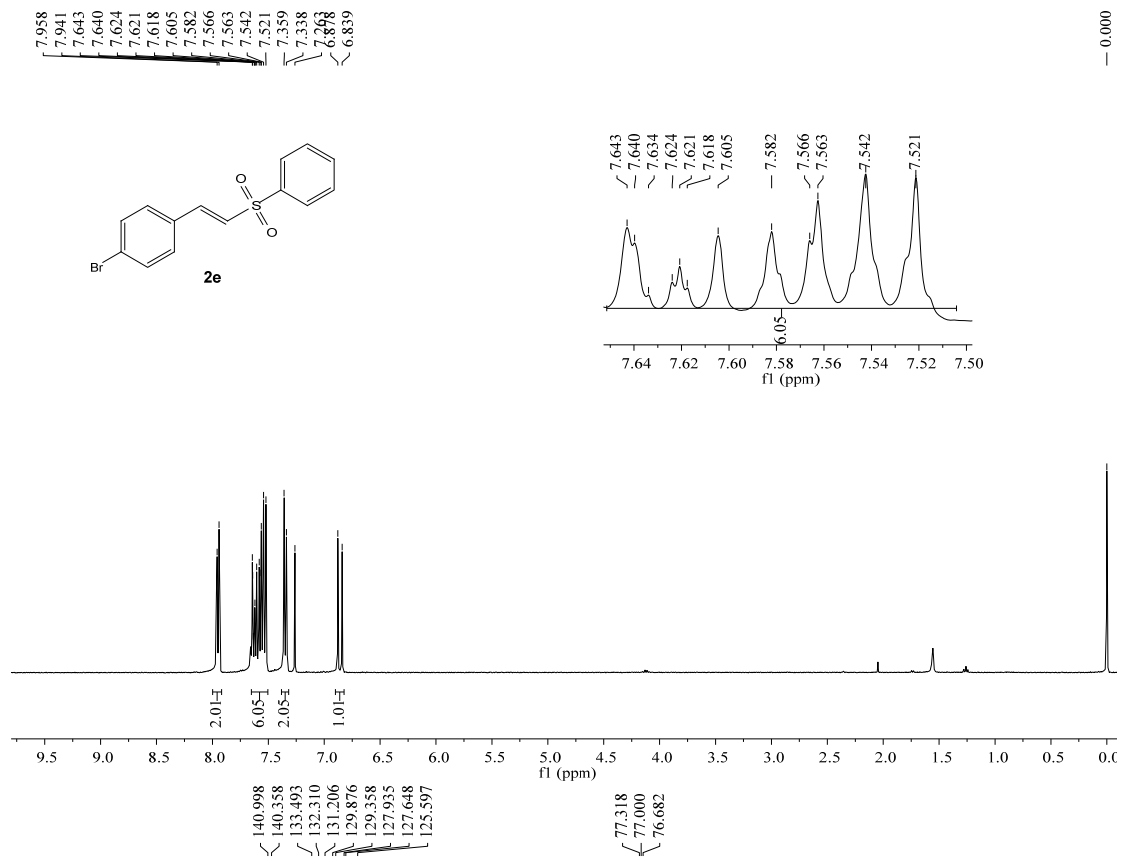


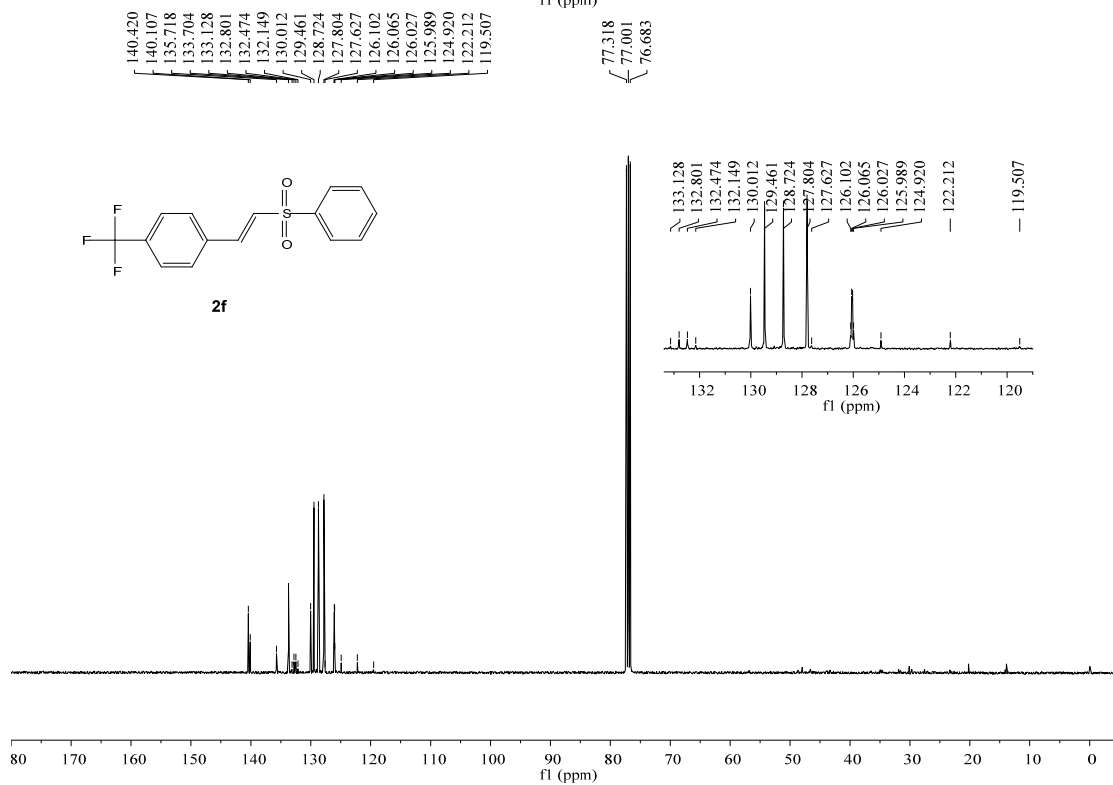
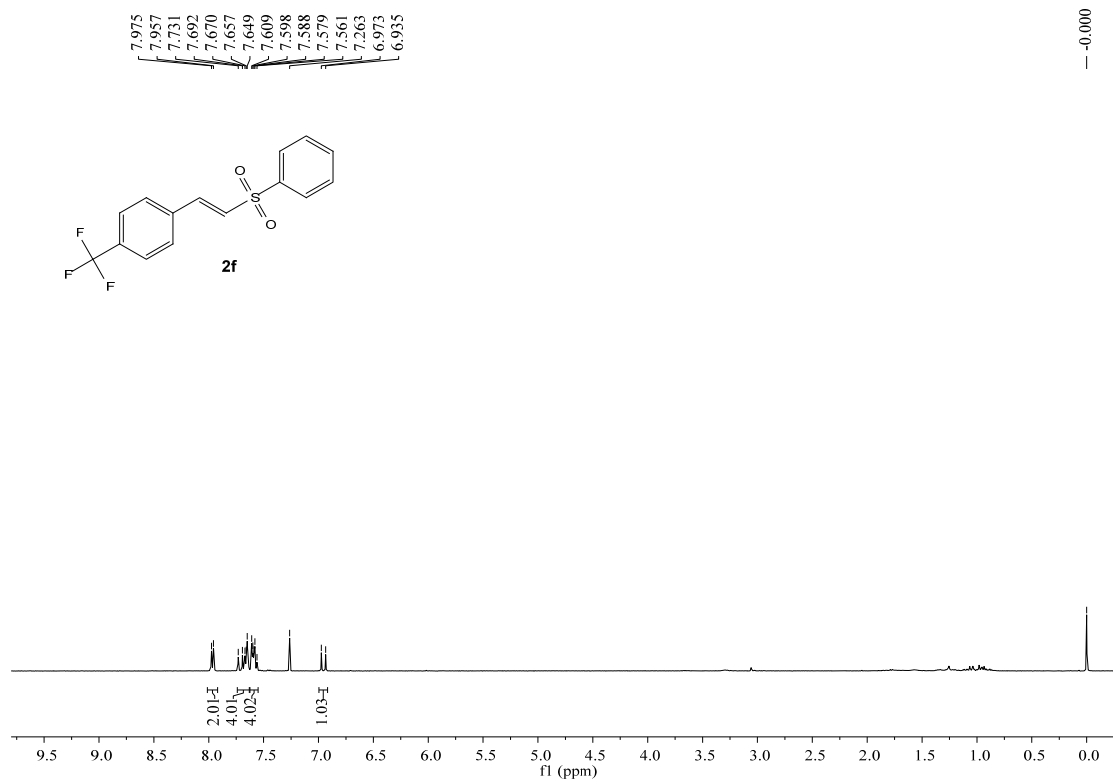


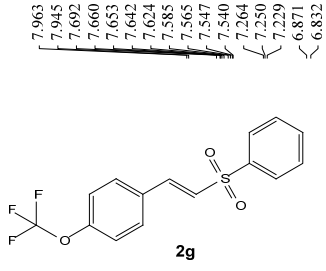


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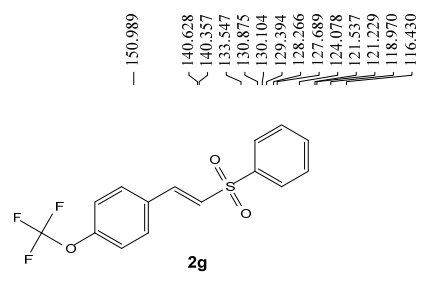
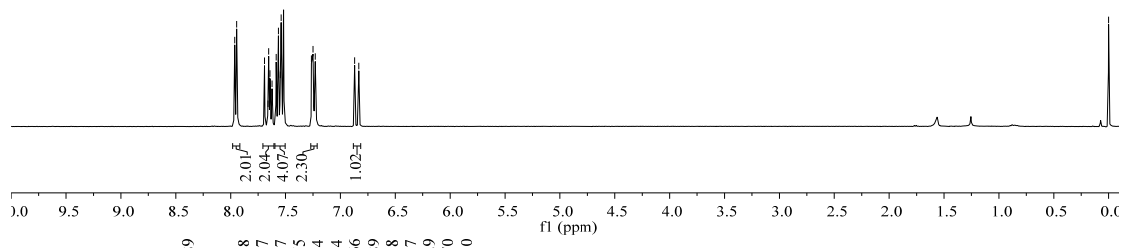




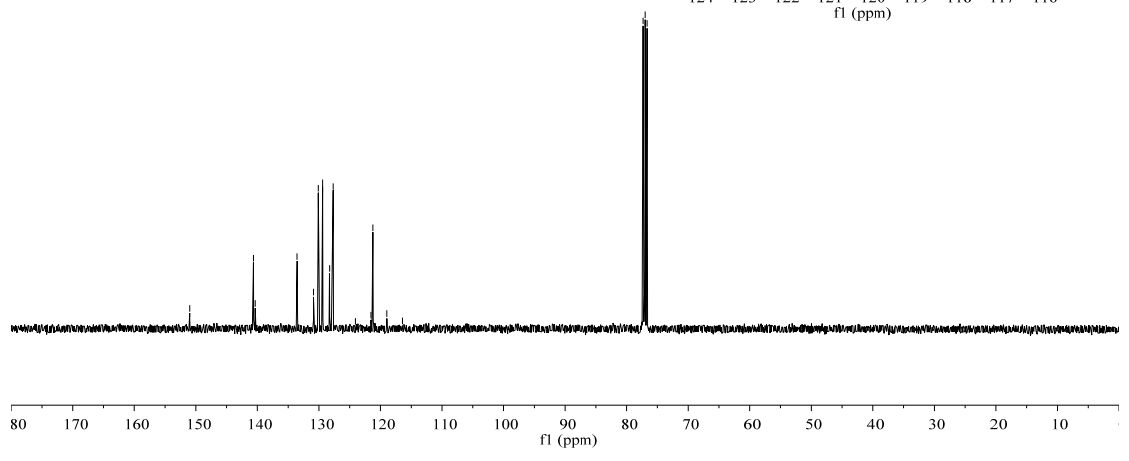
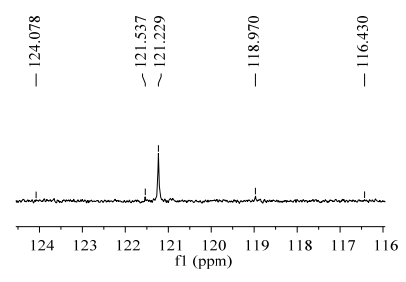


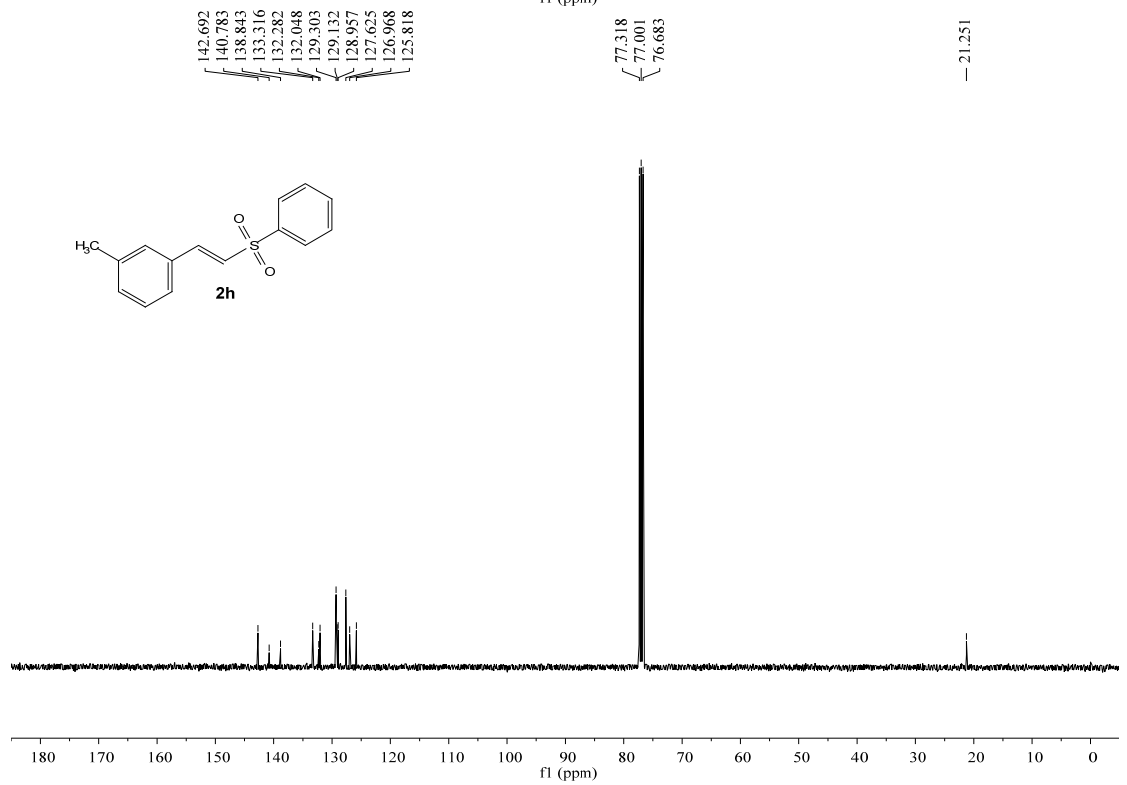
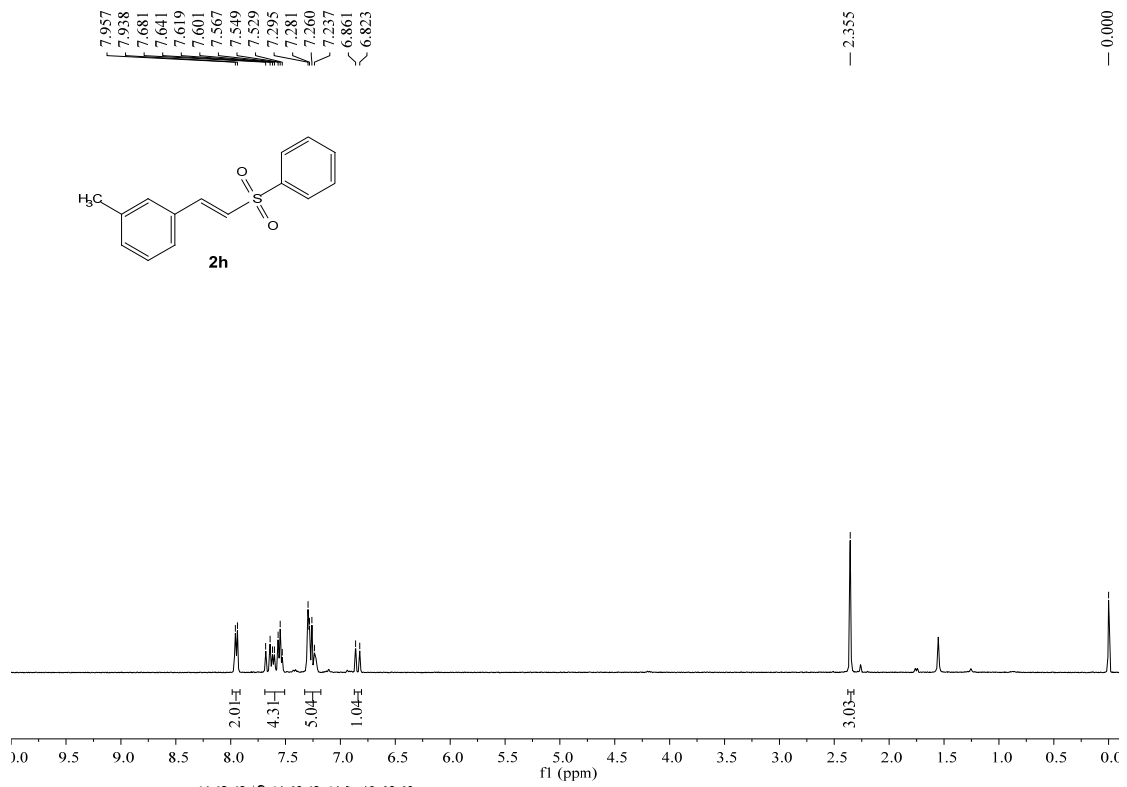


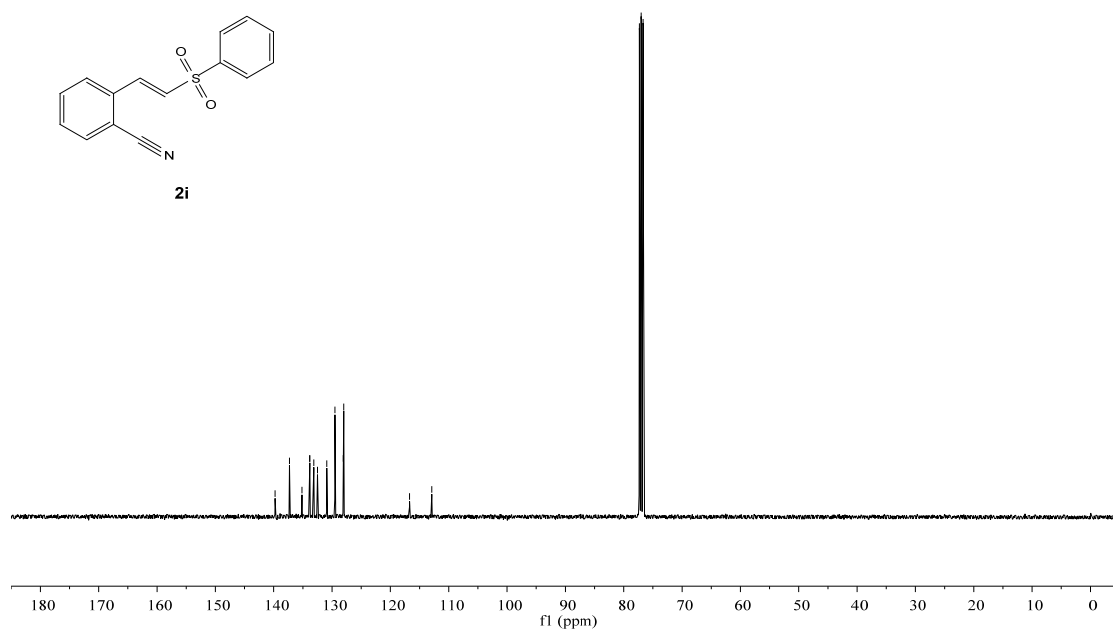
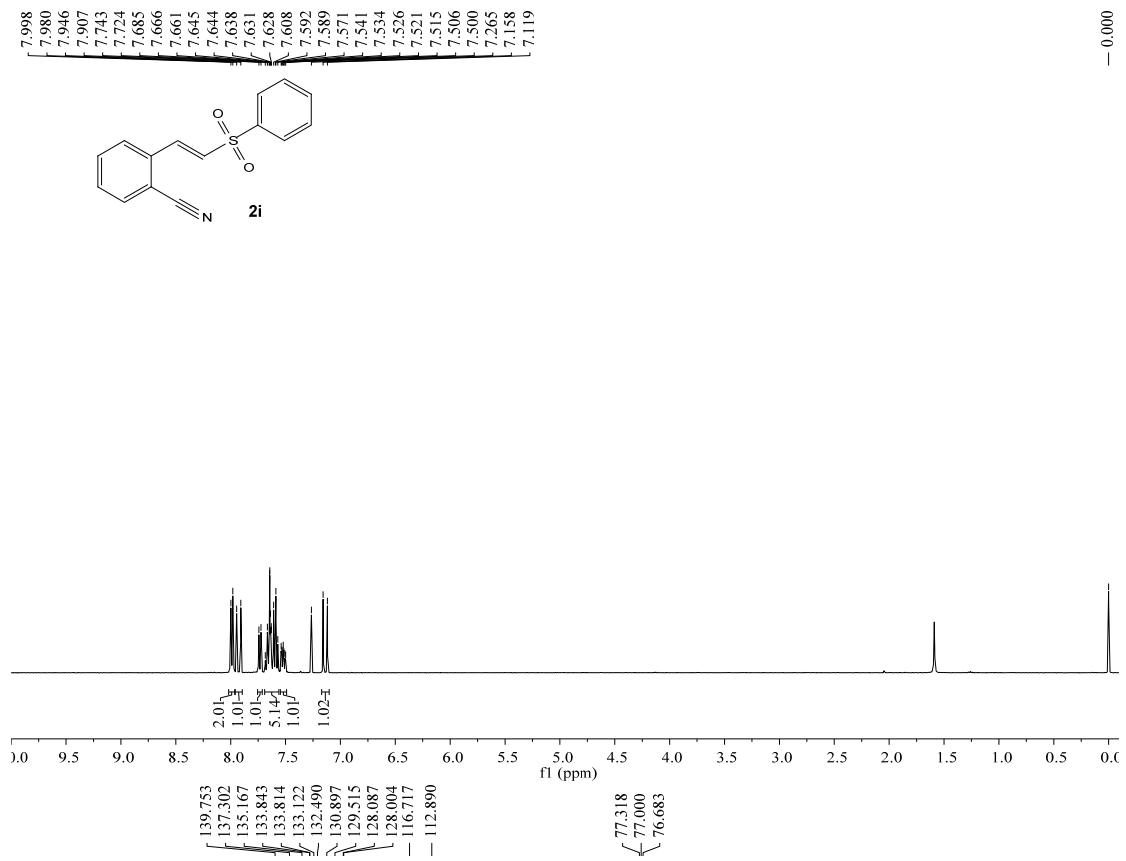
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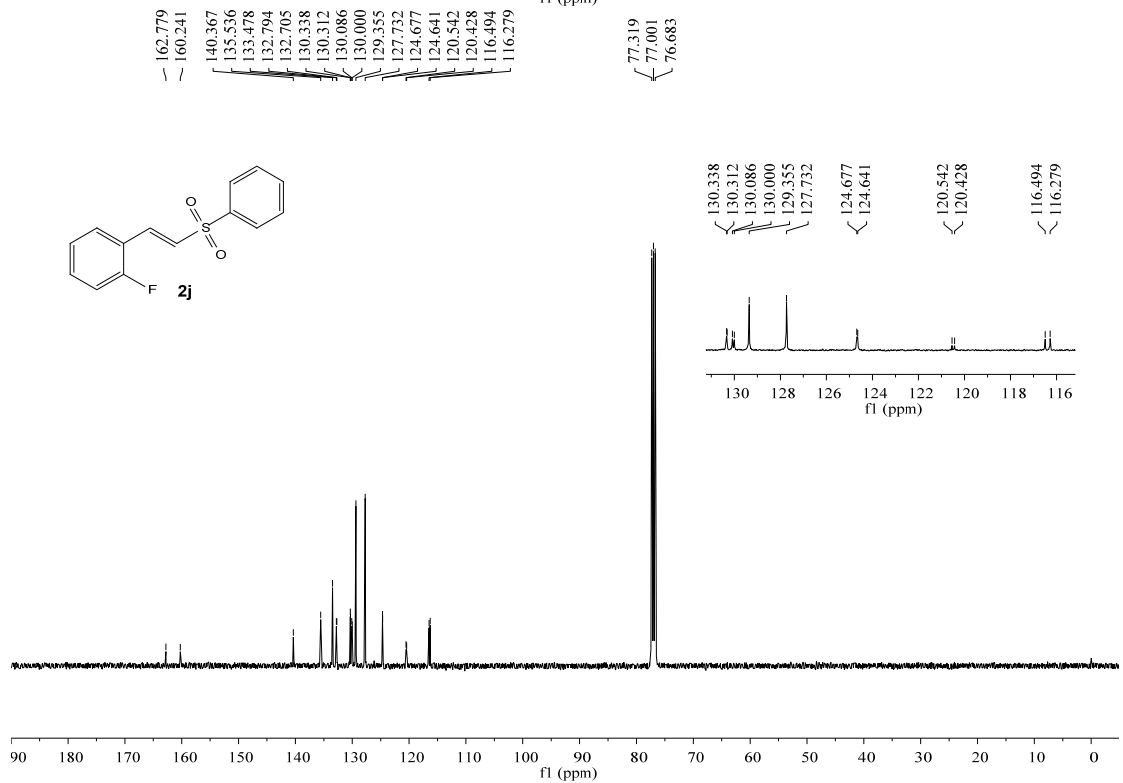
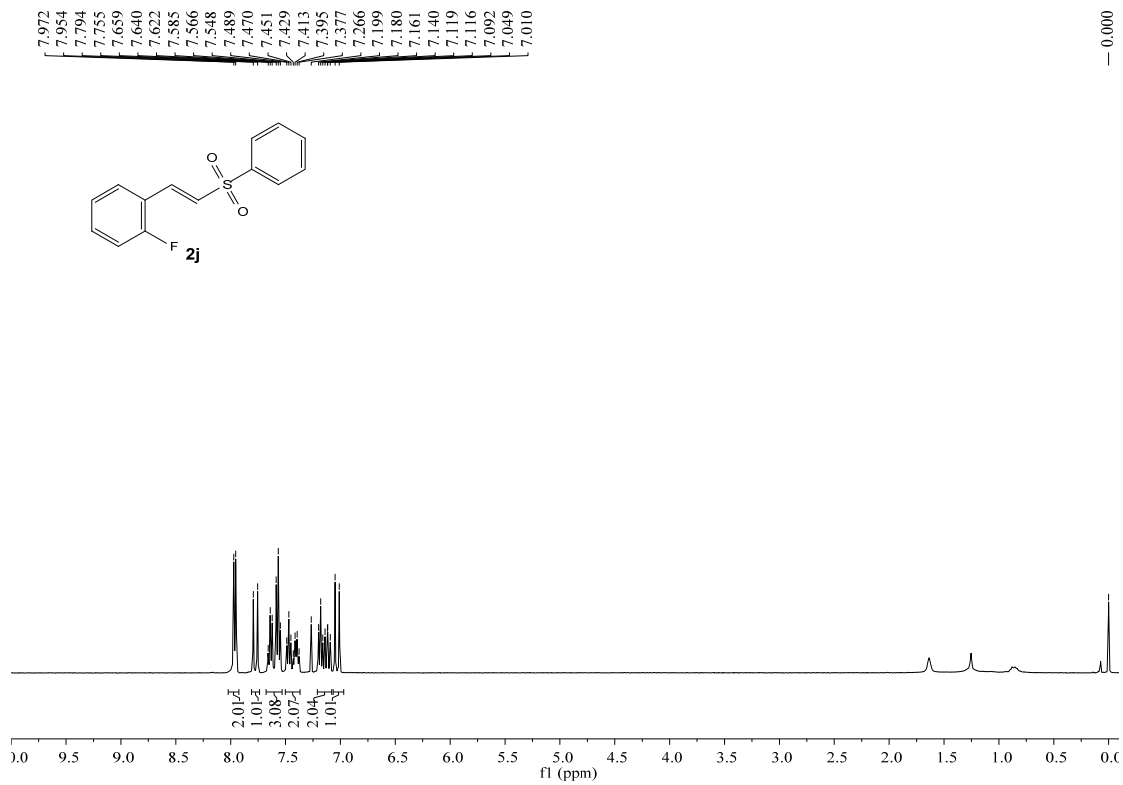


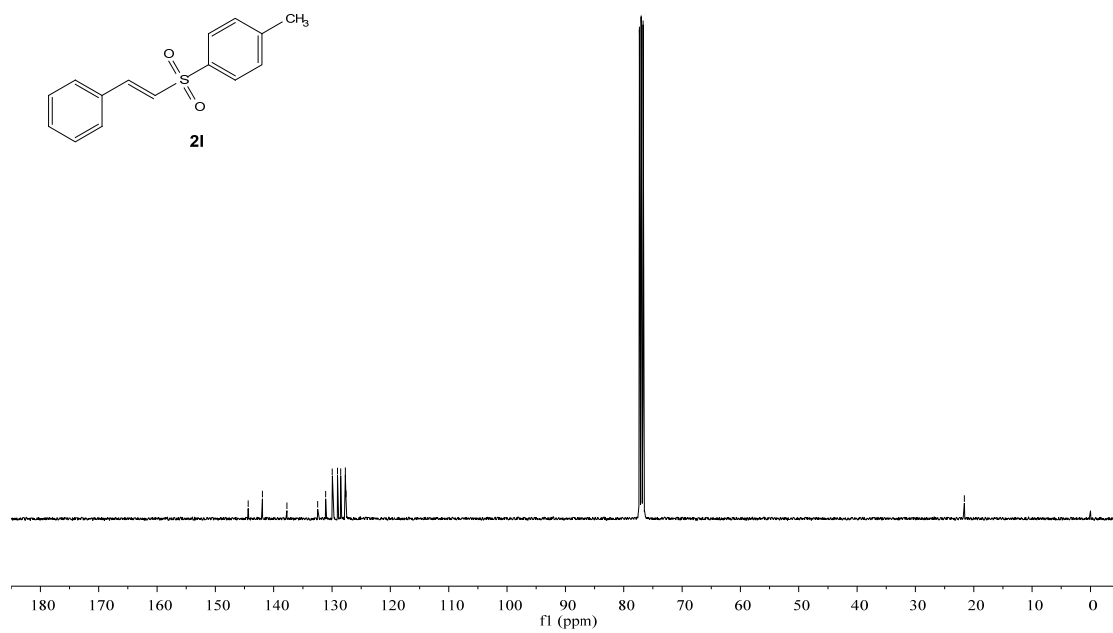
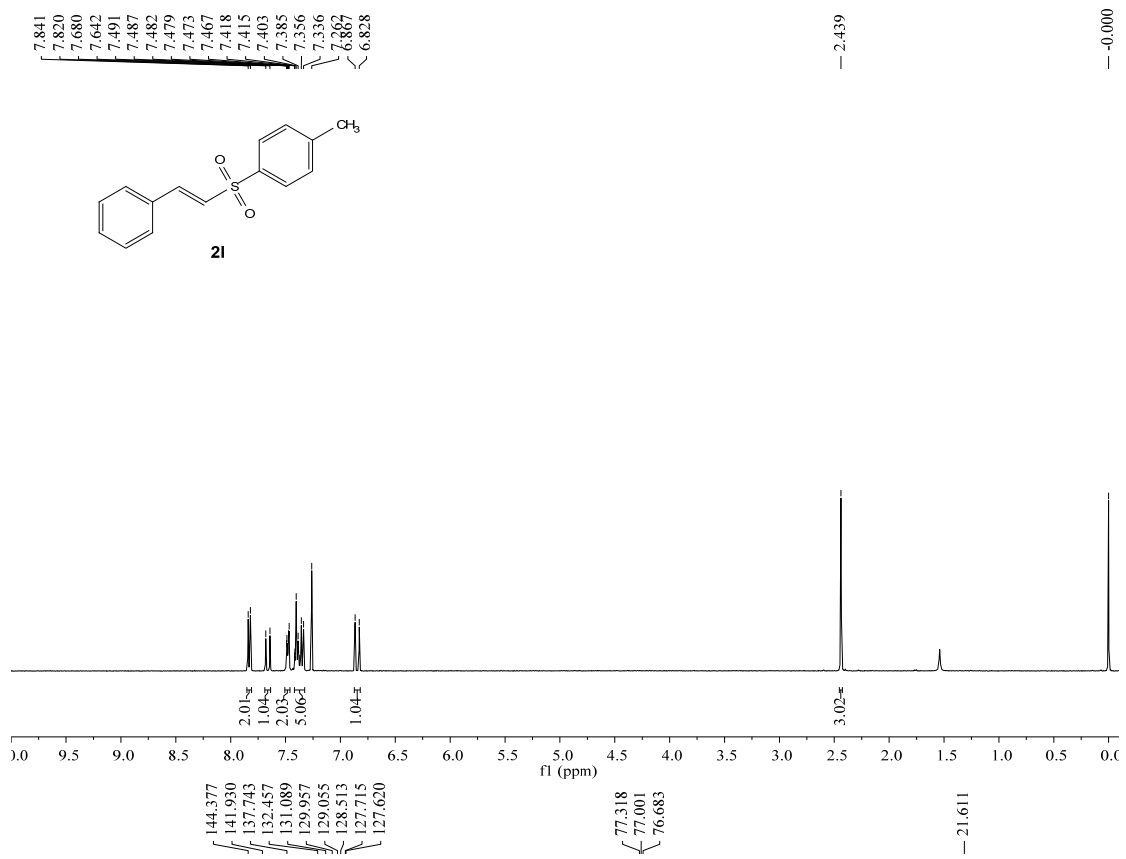
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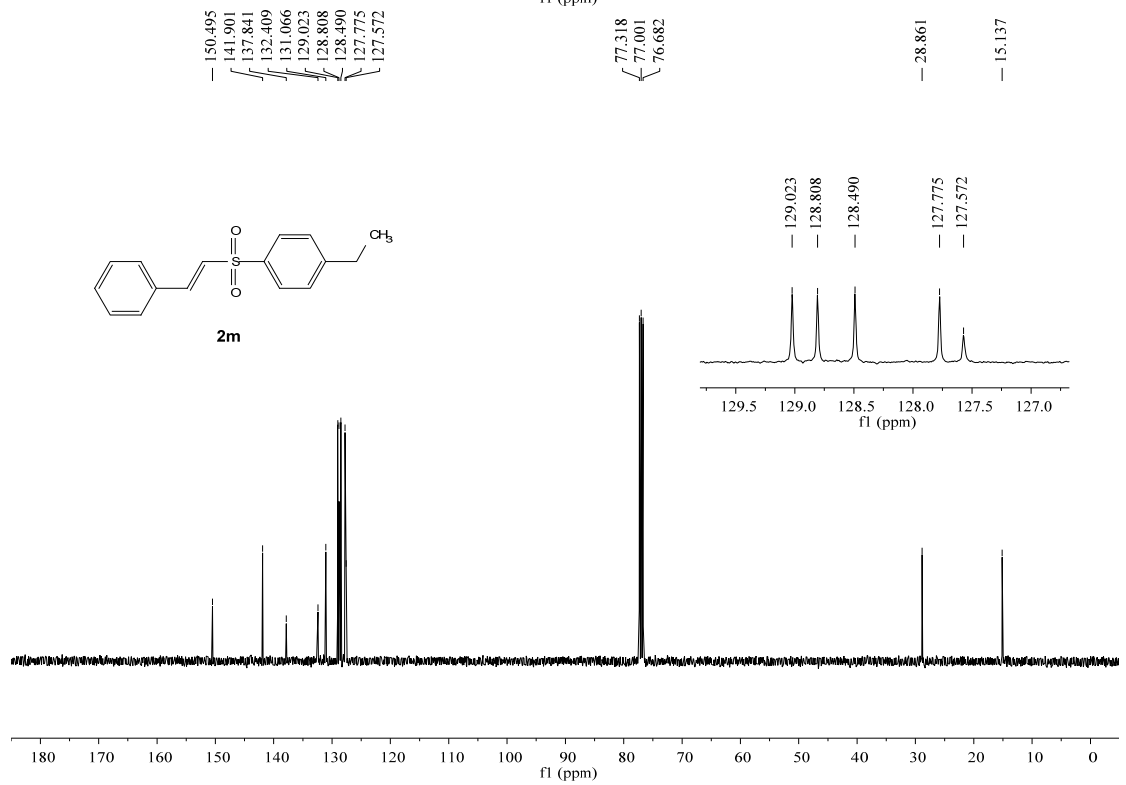
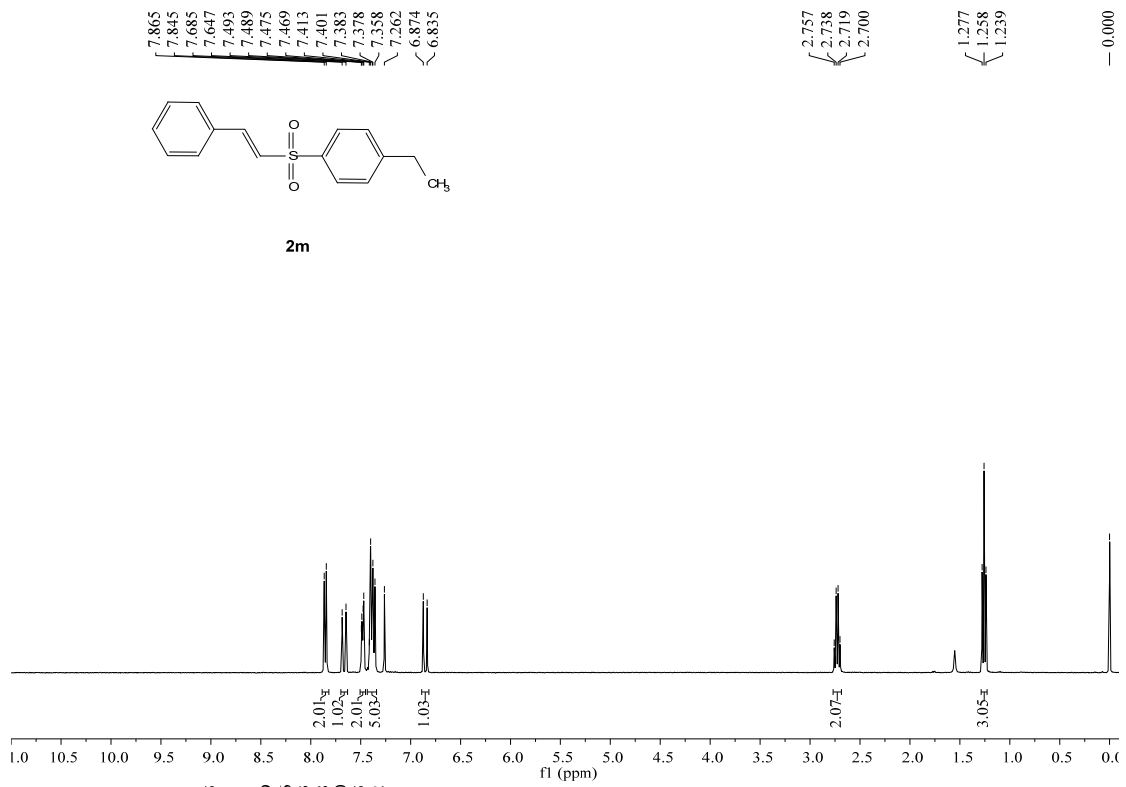


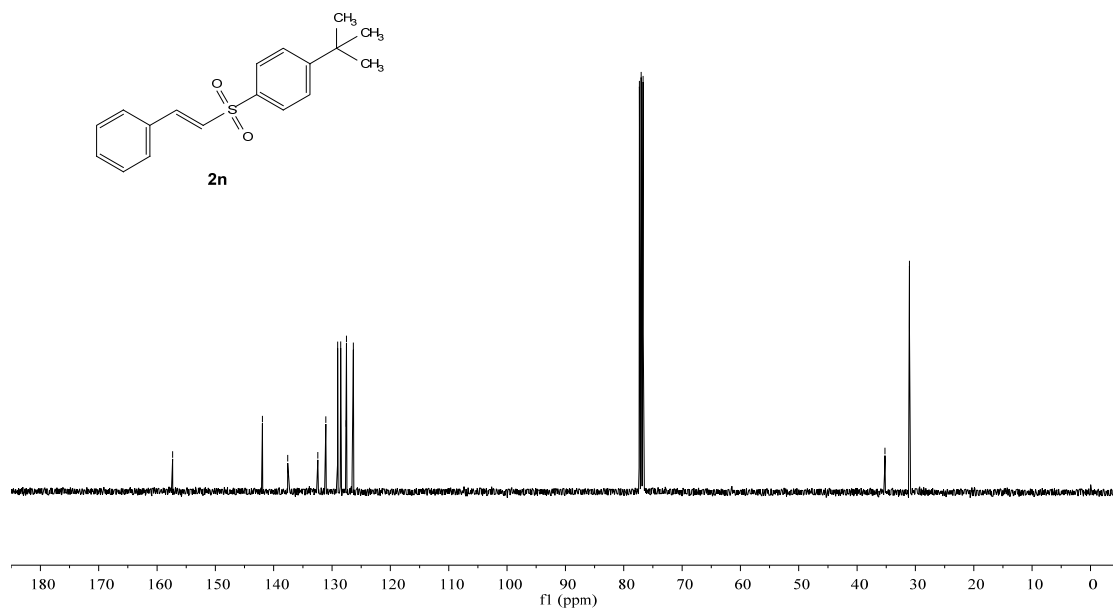
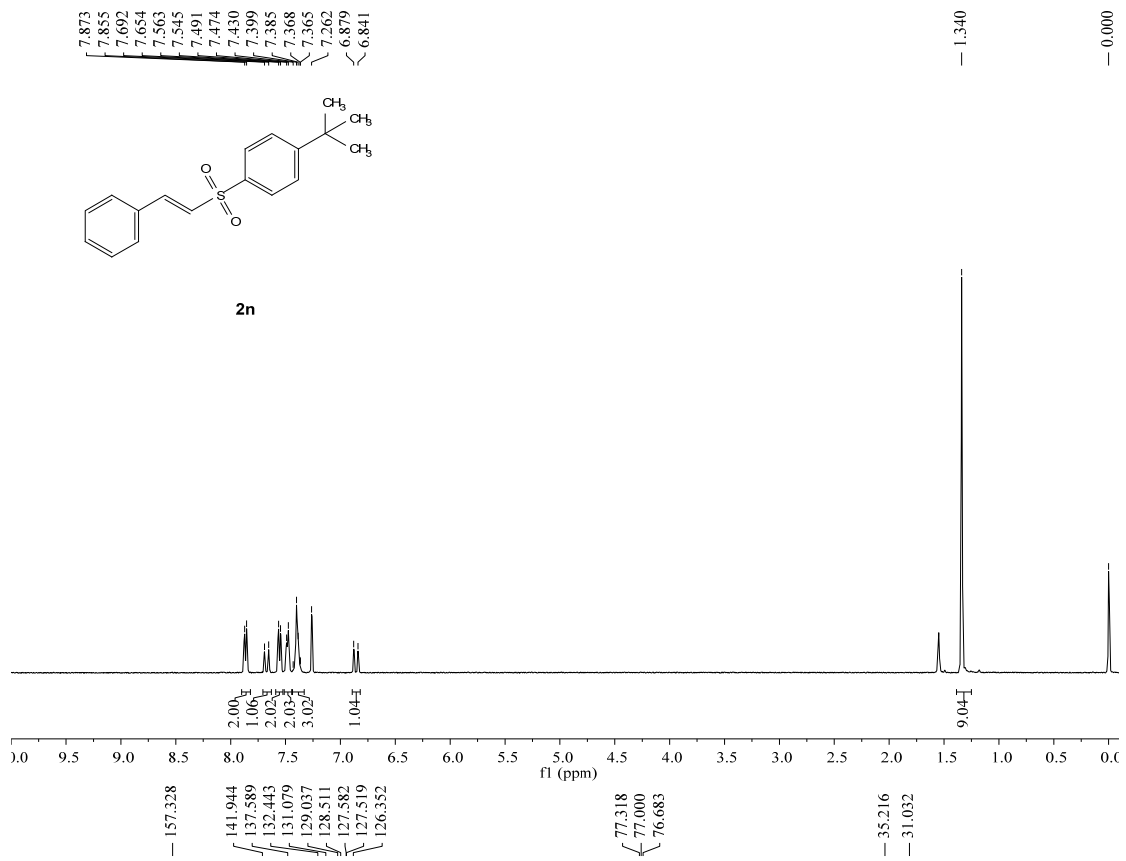


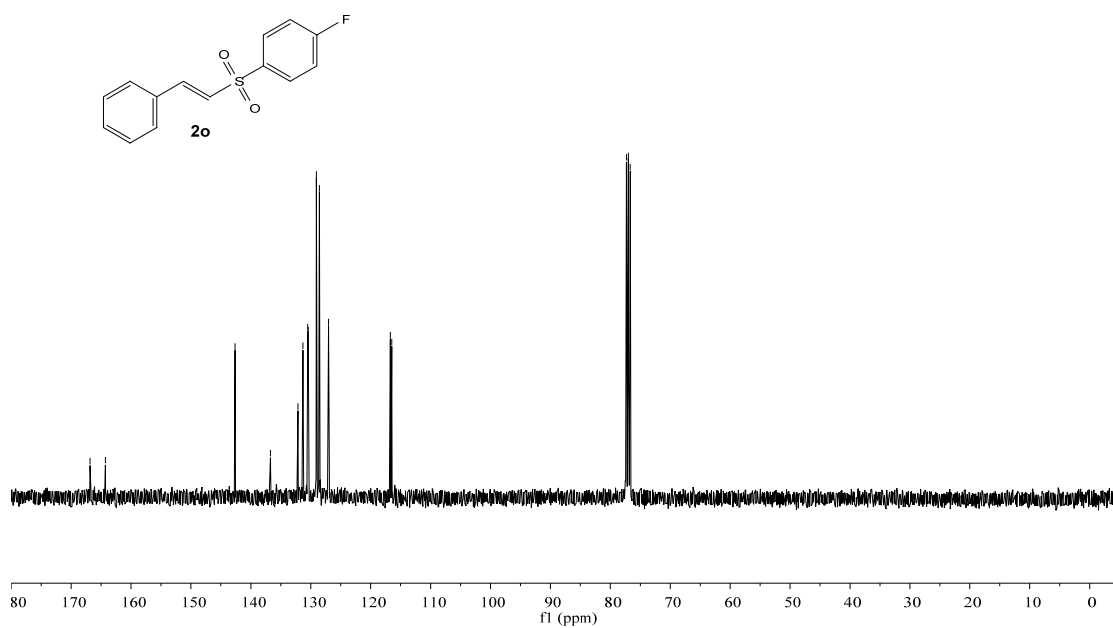
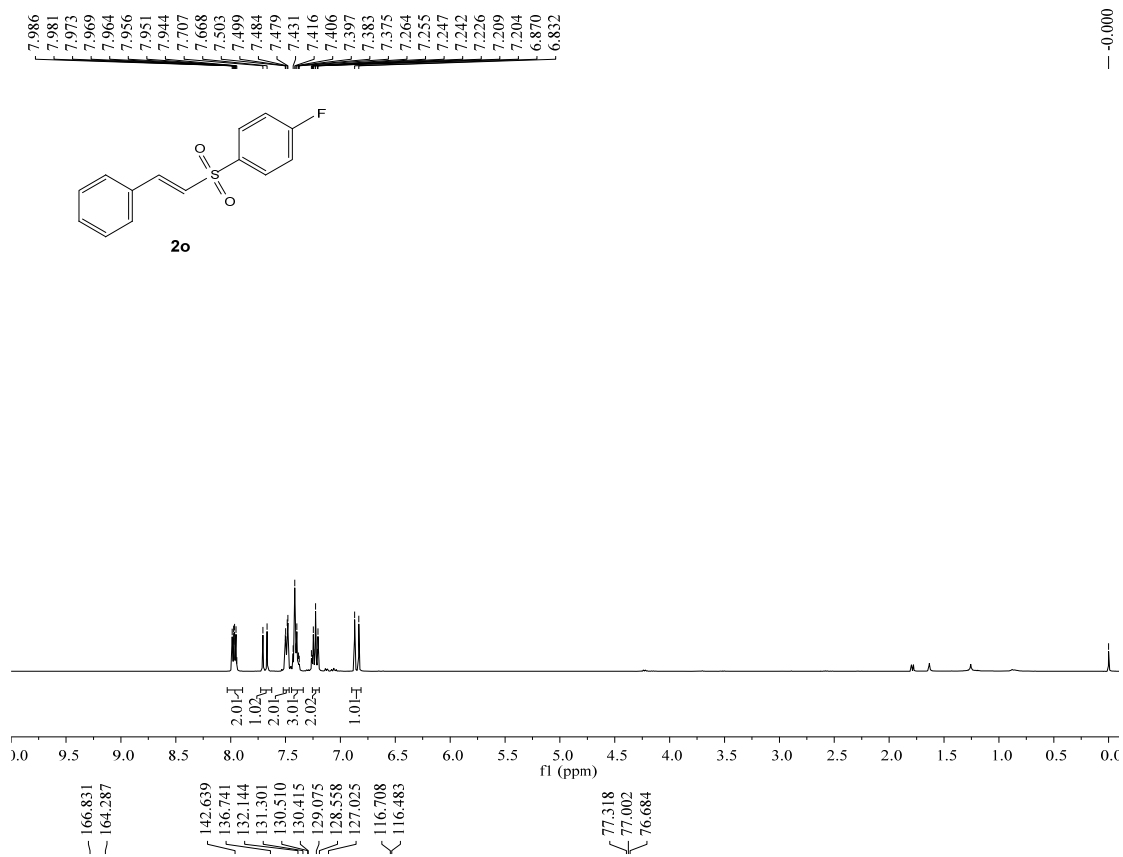


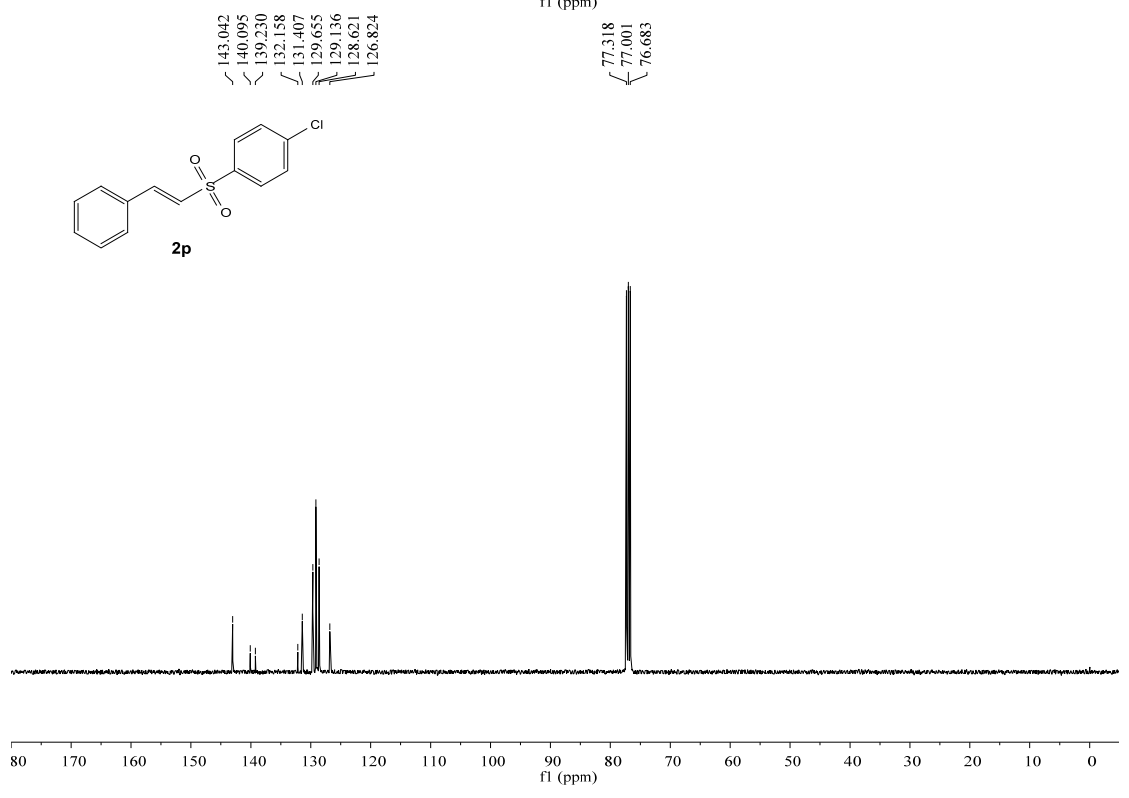
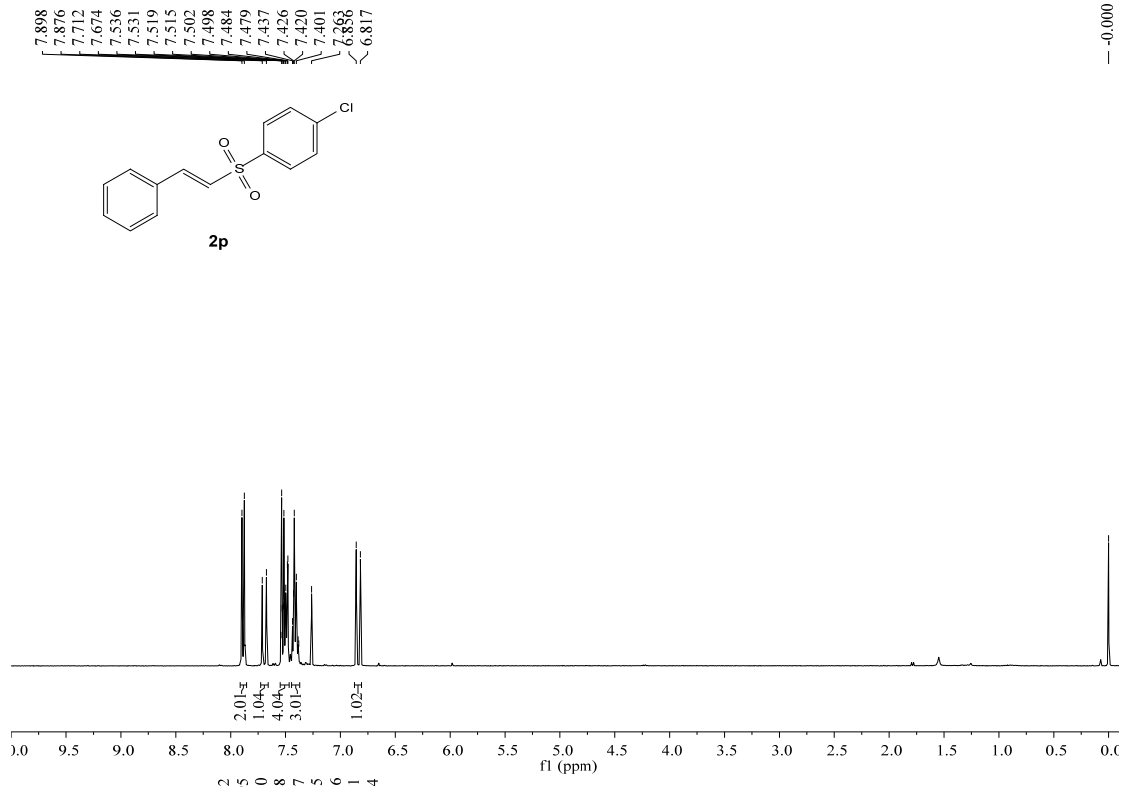


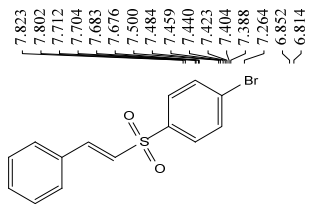




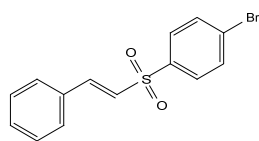
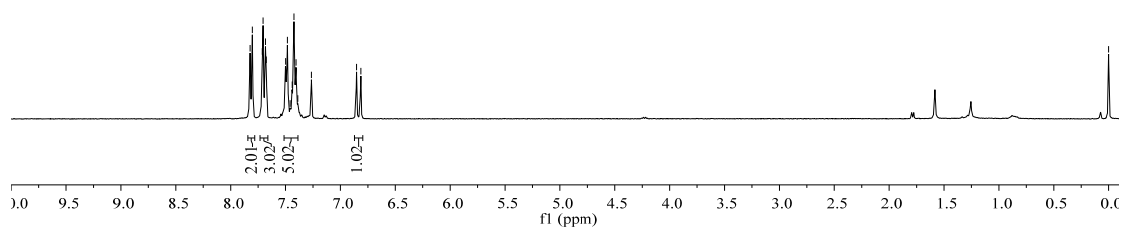




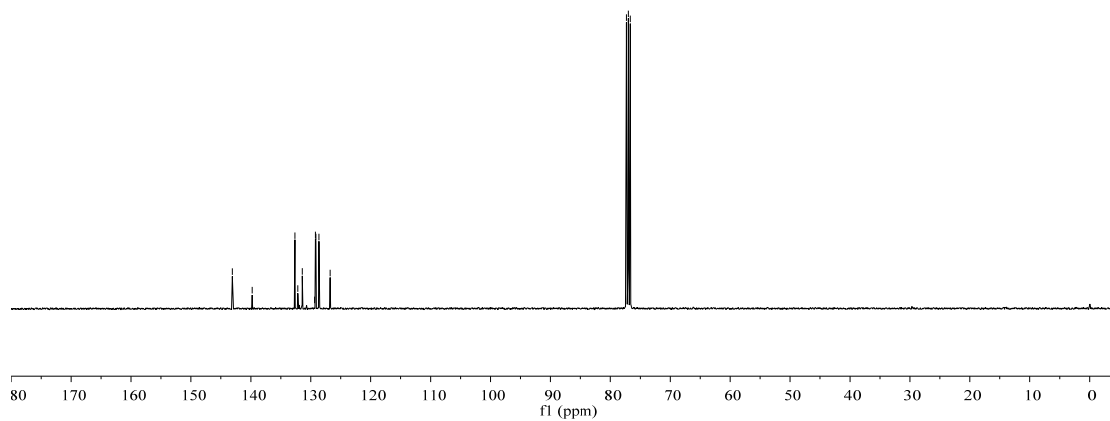


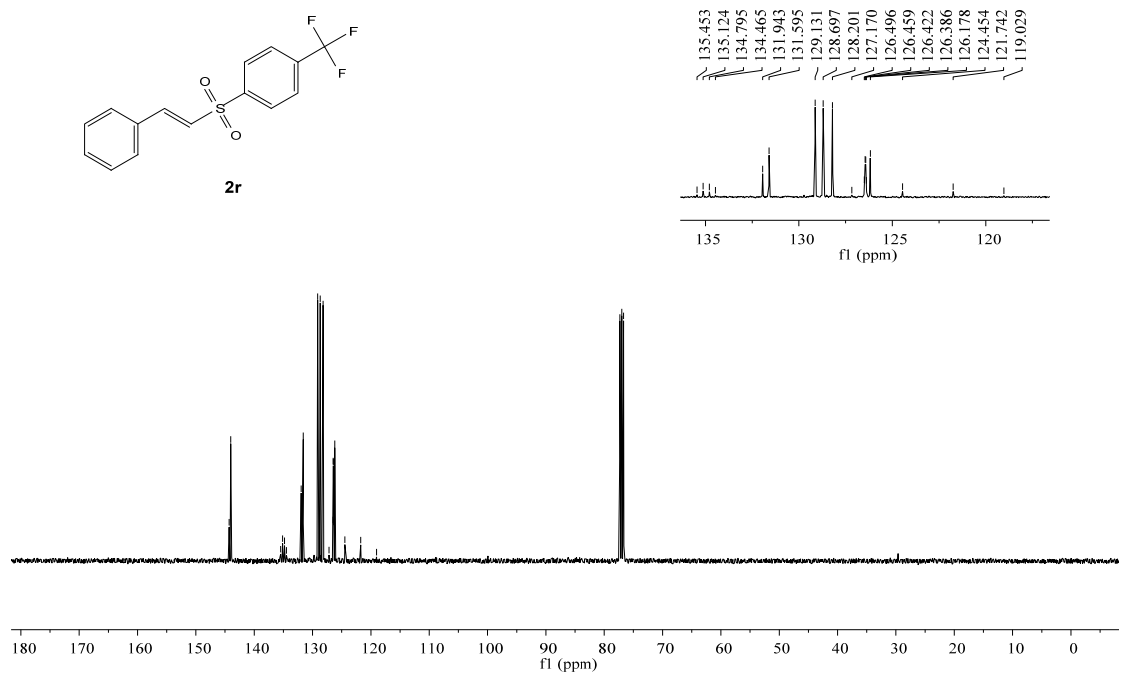
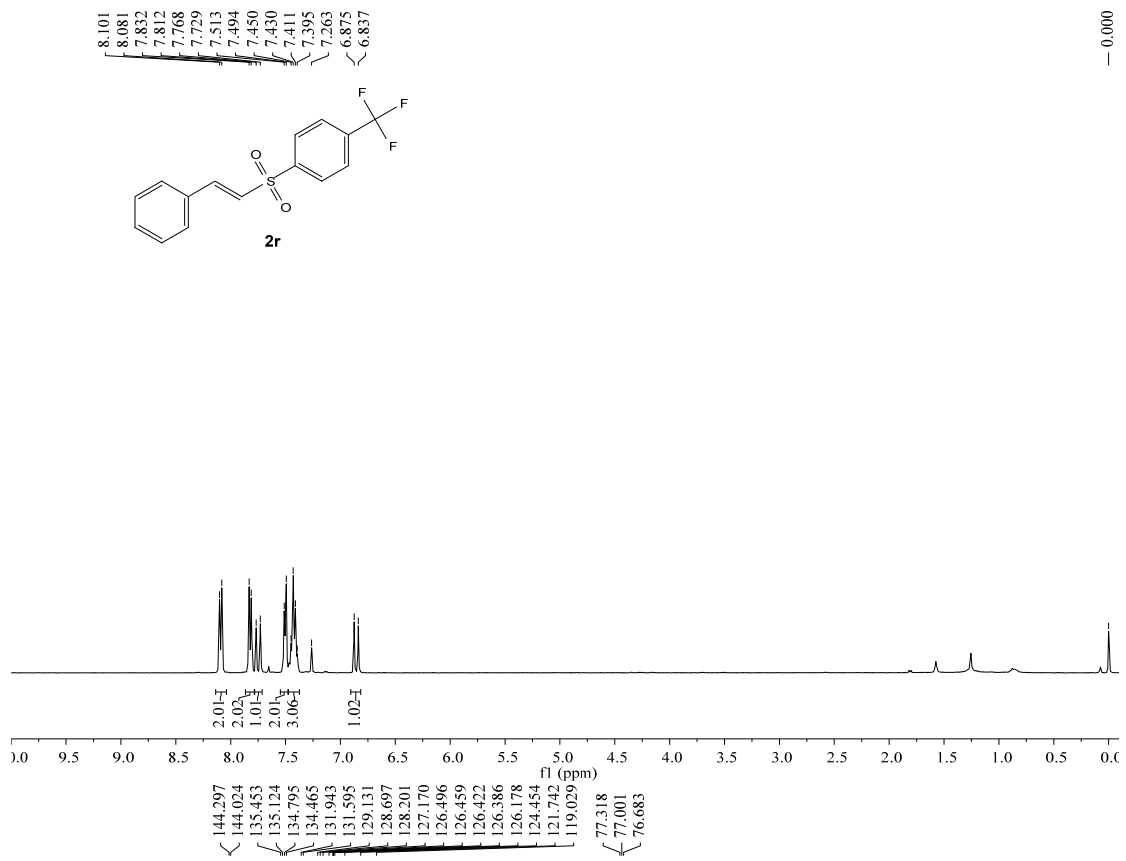


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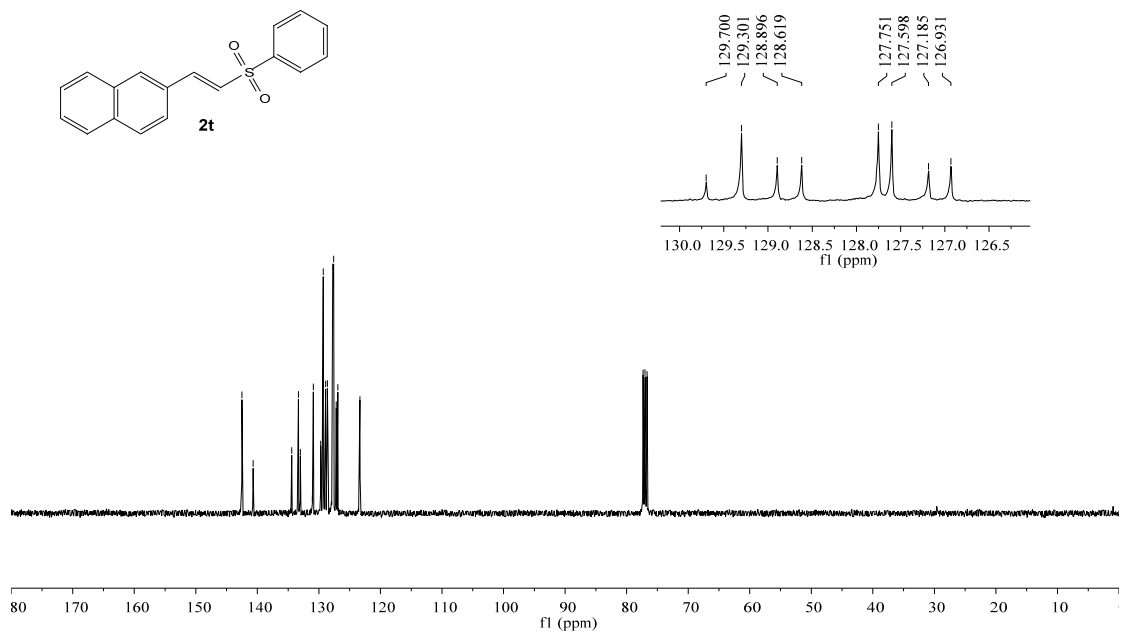
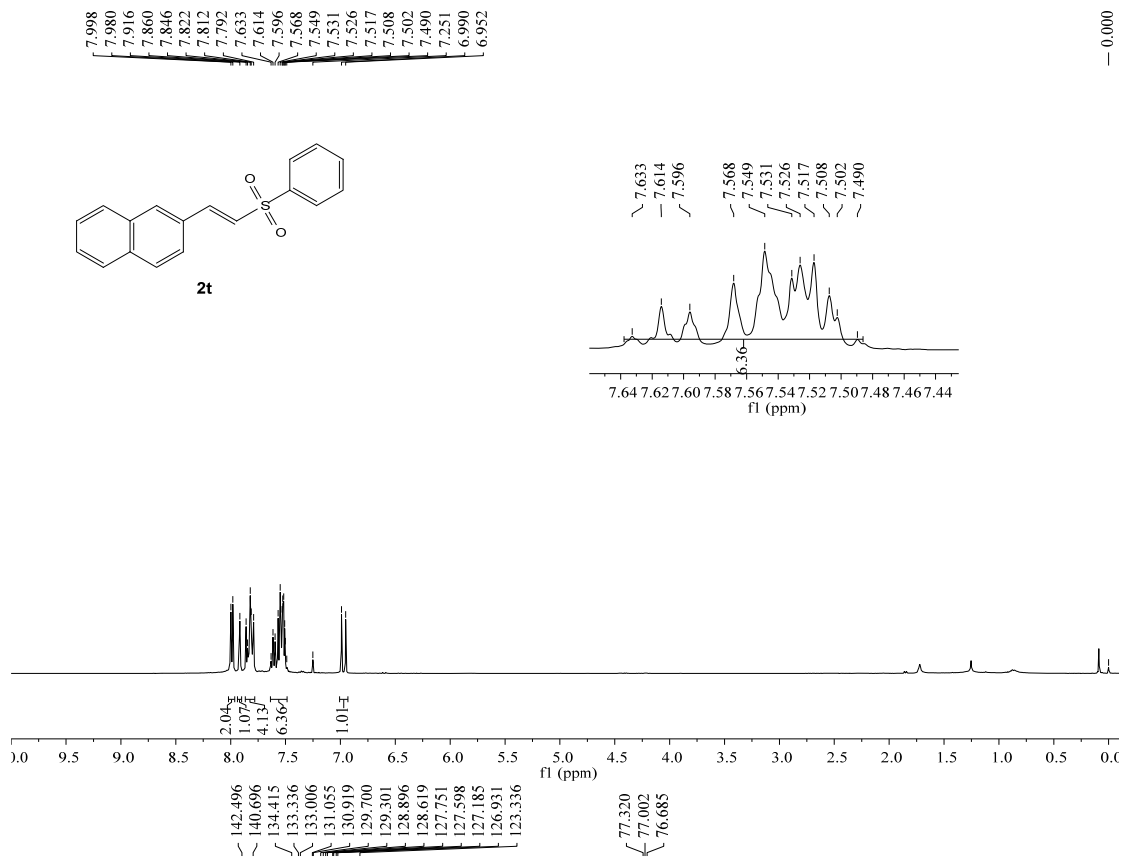


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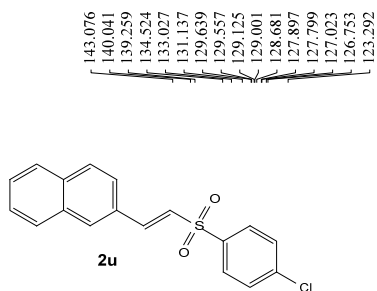
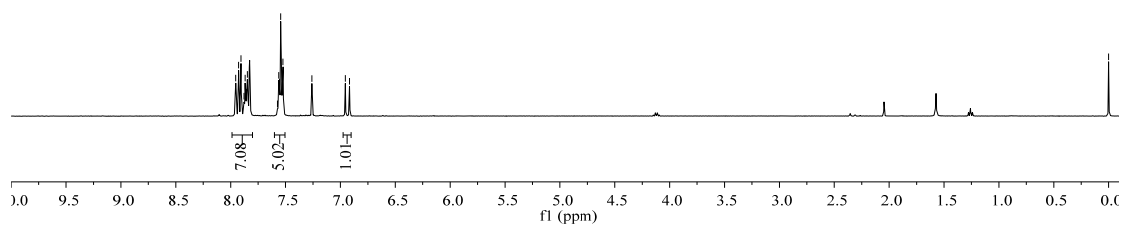
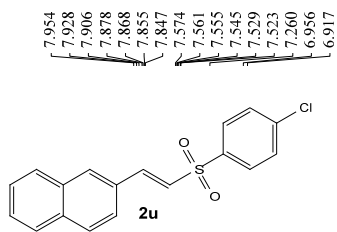




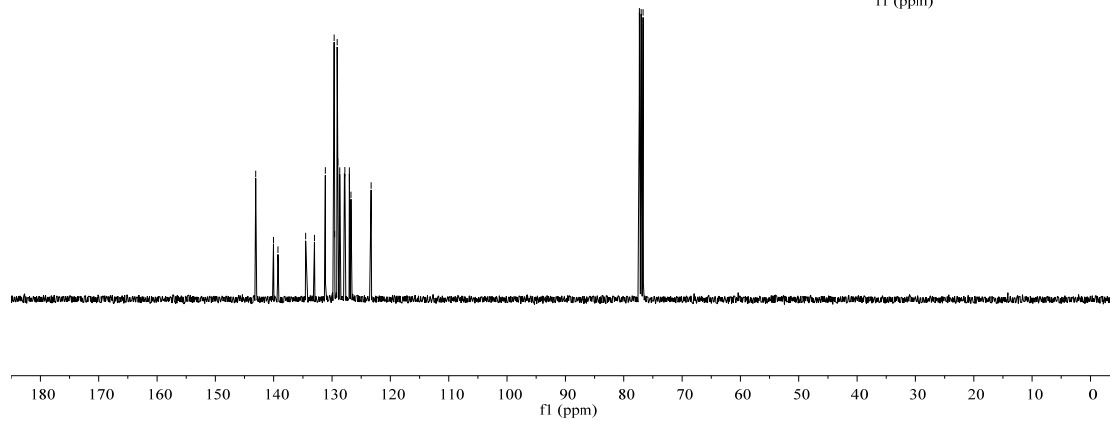
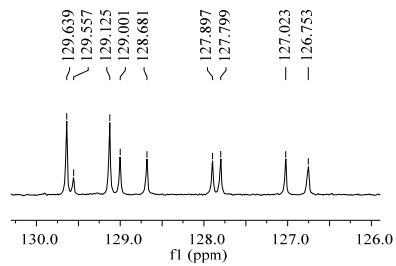
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-0.000

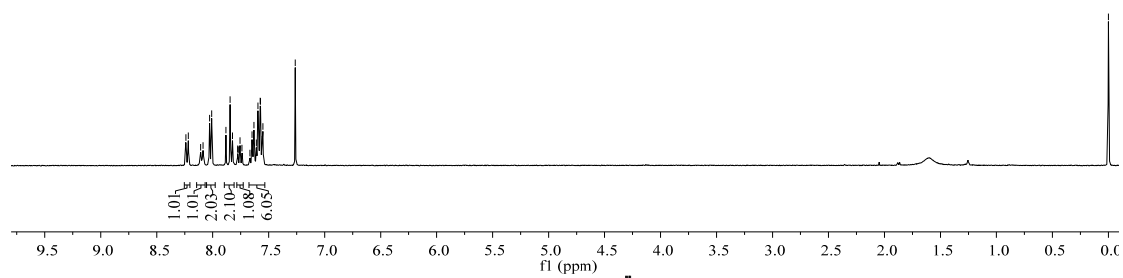
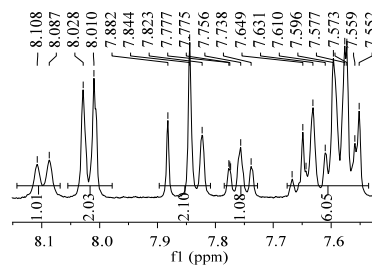
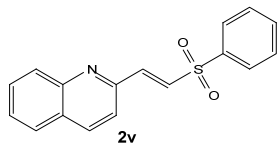


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77.002
76.684

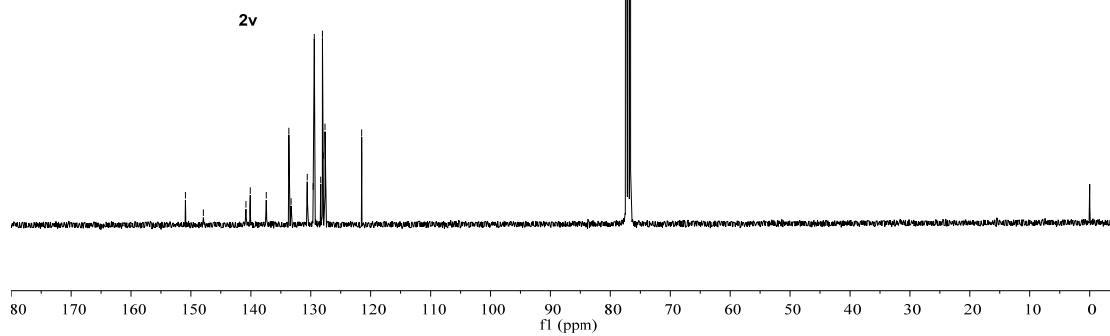
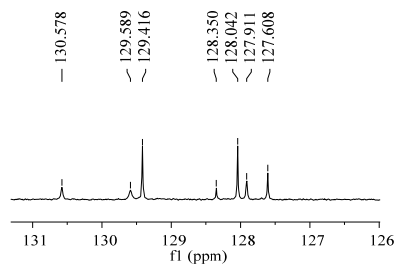
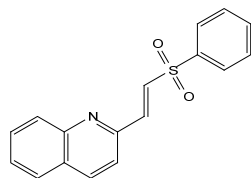


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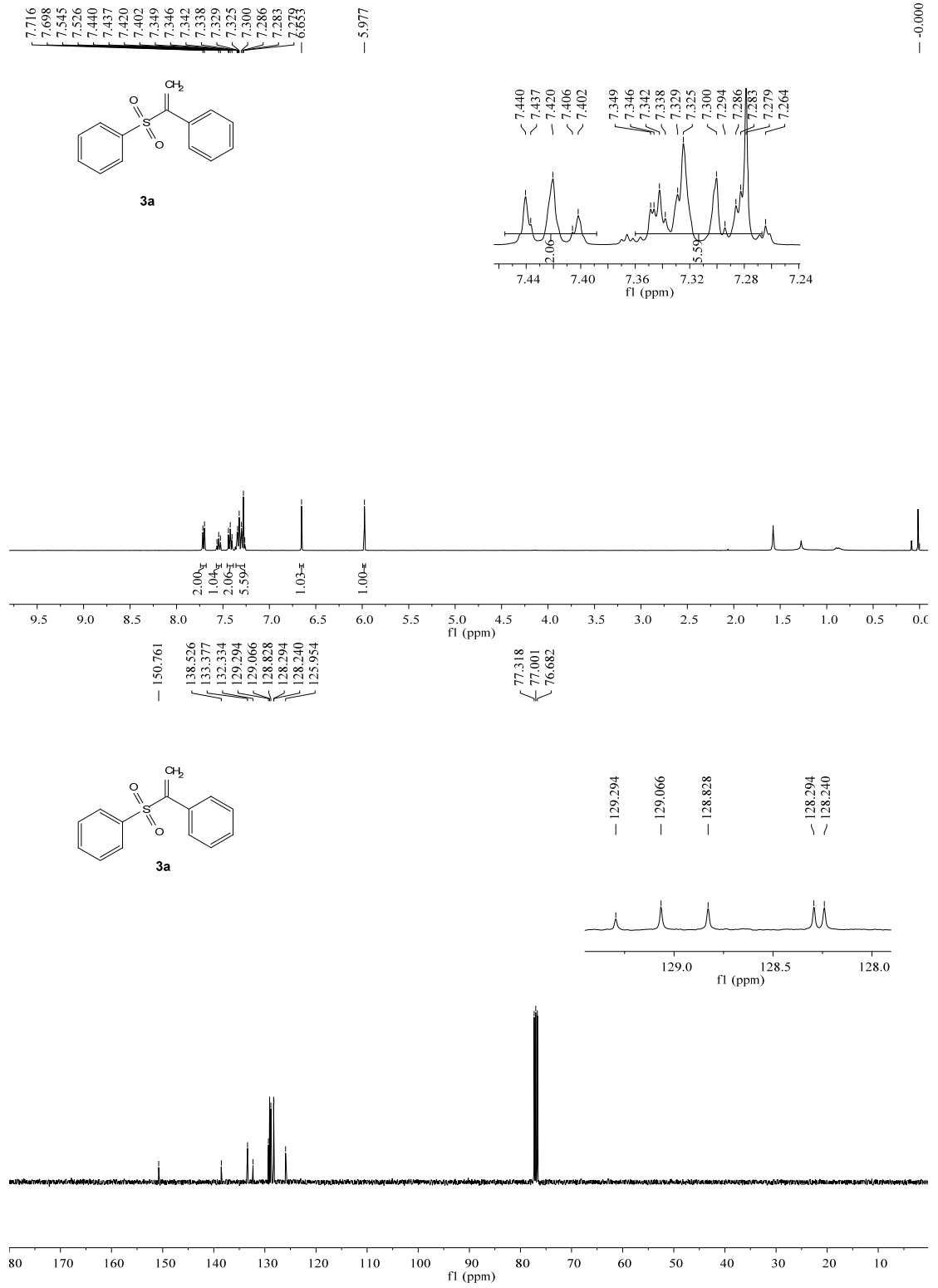
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7.552
7.263

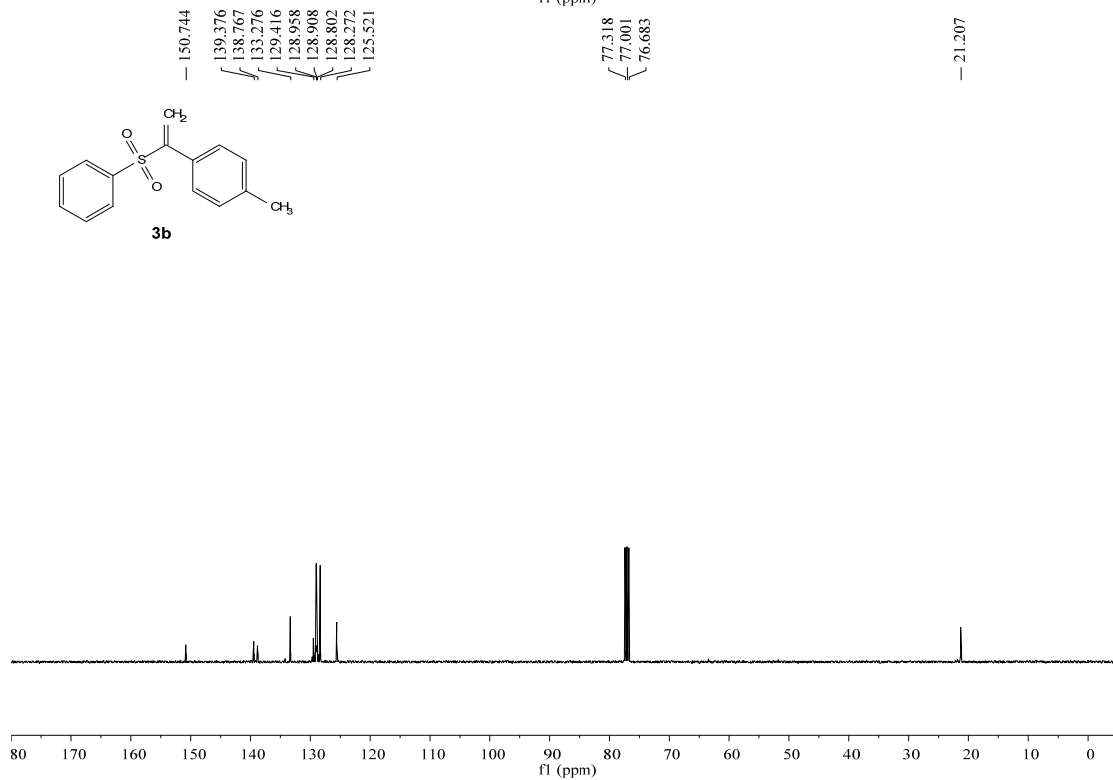
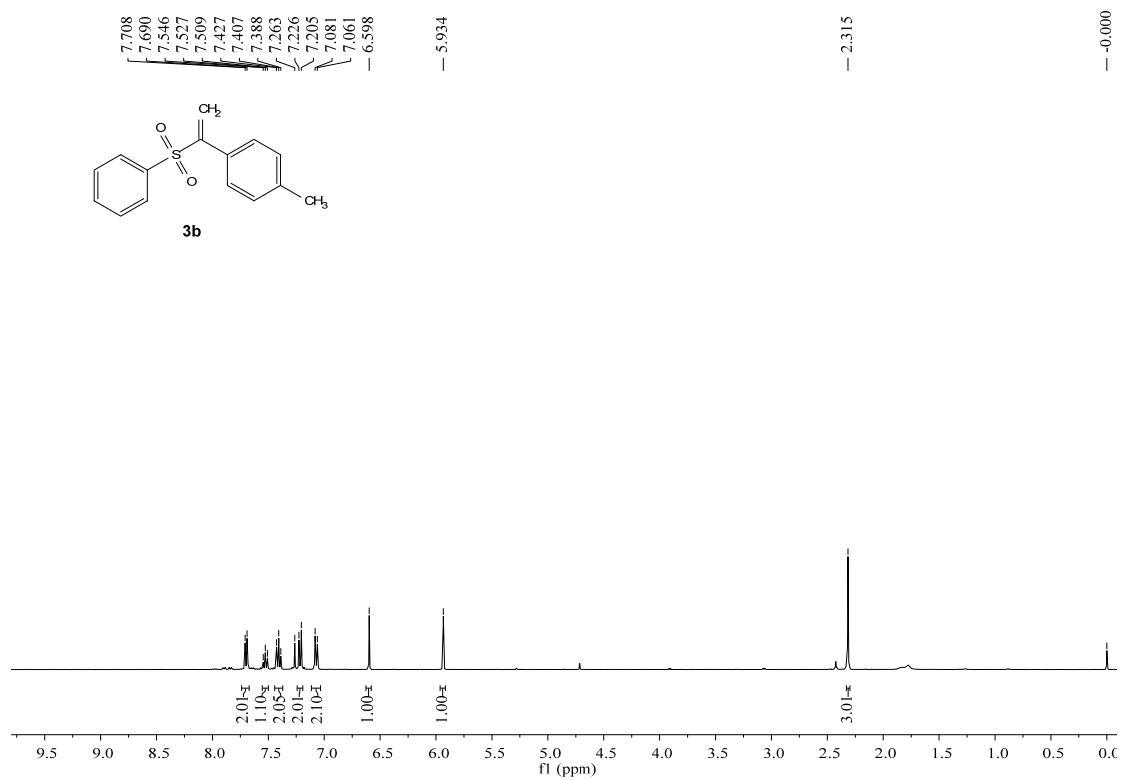


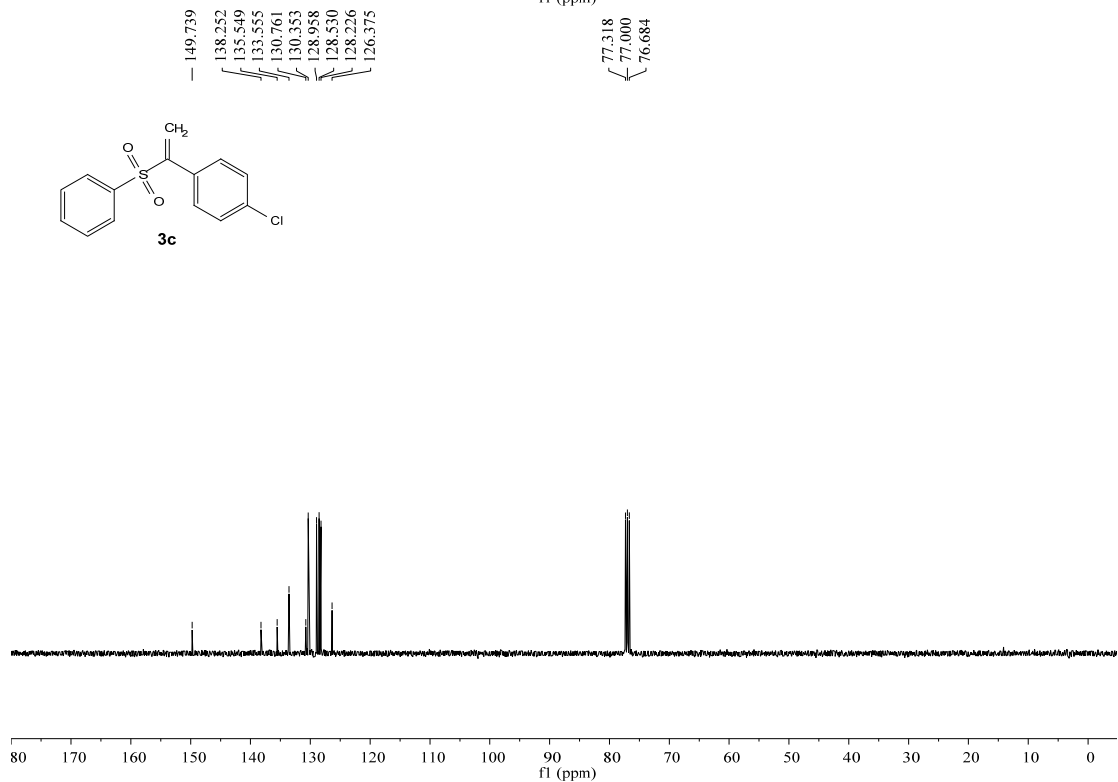
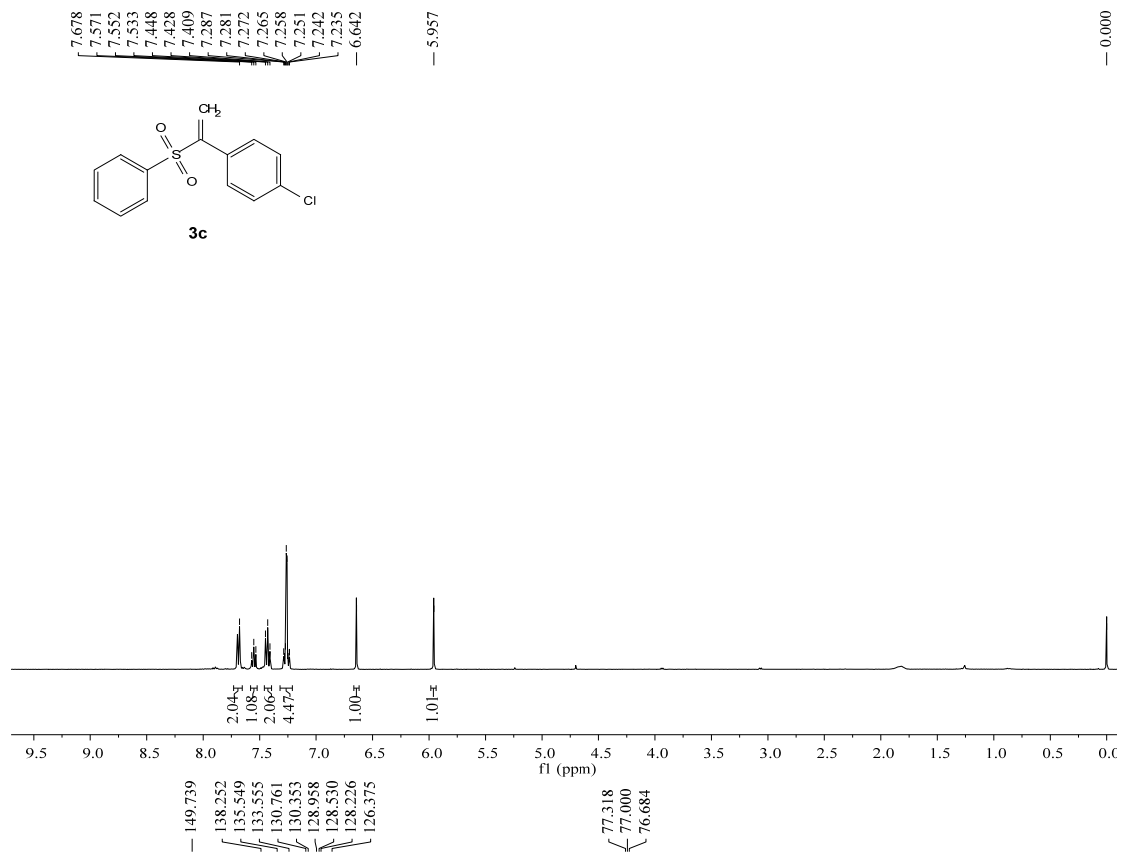
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127.608
121.494

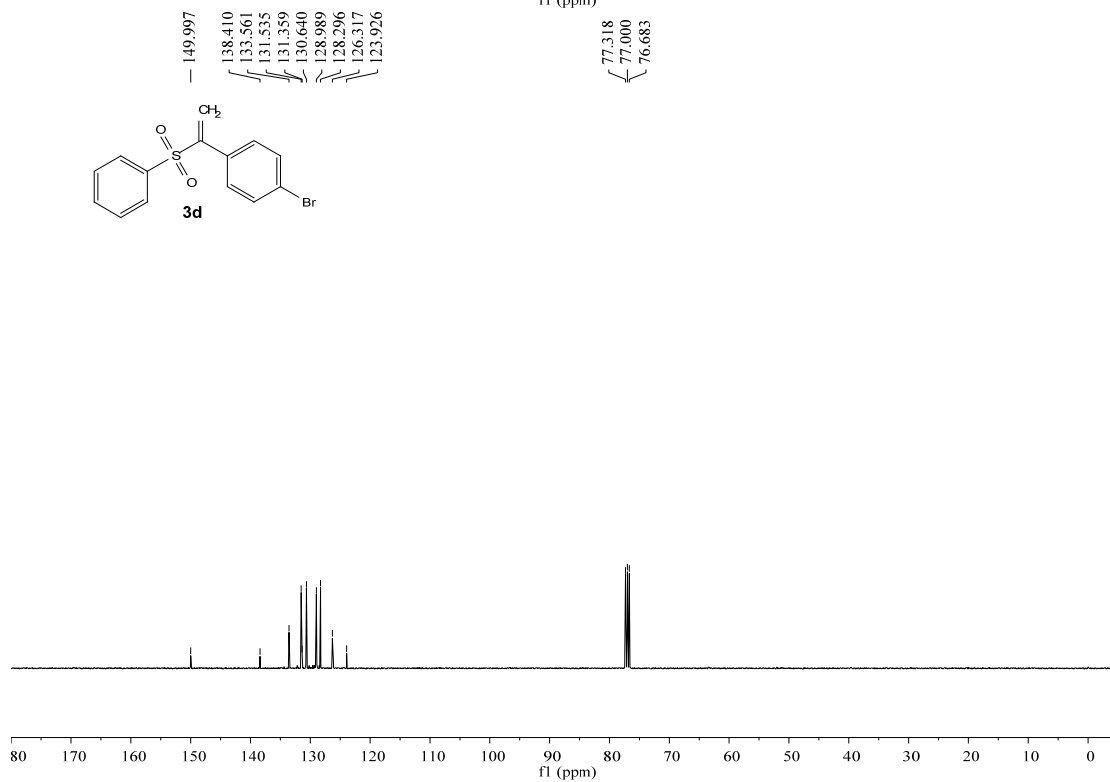
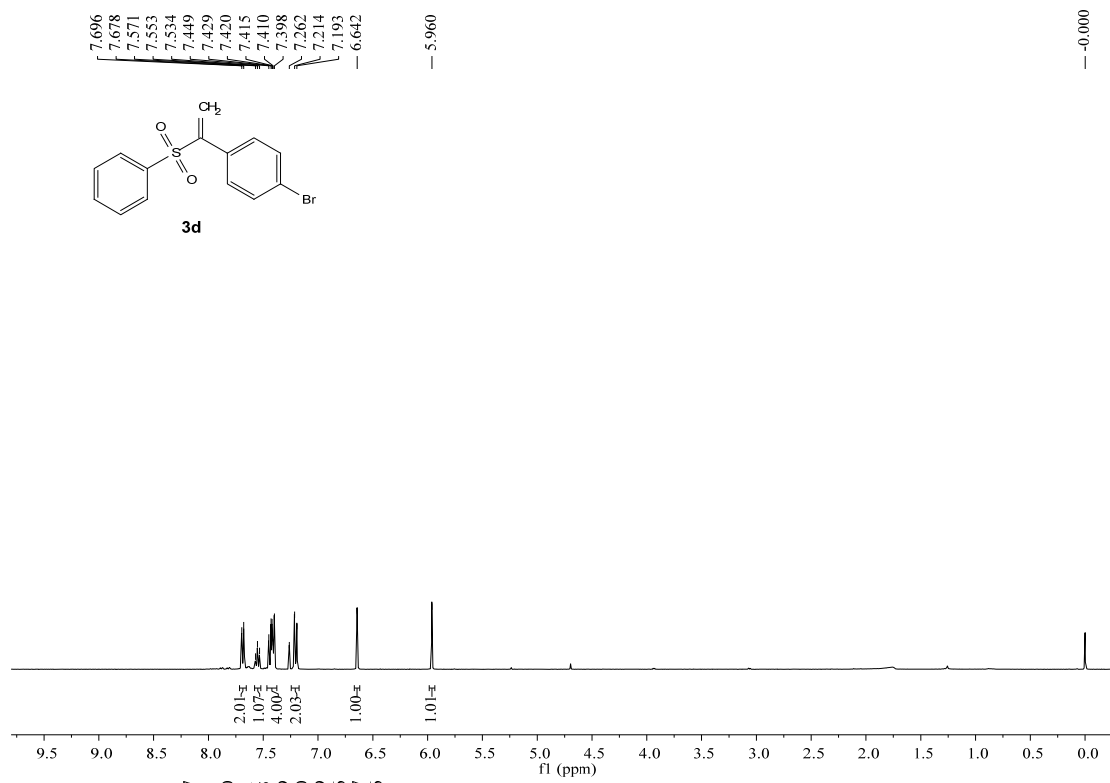


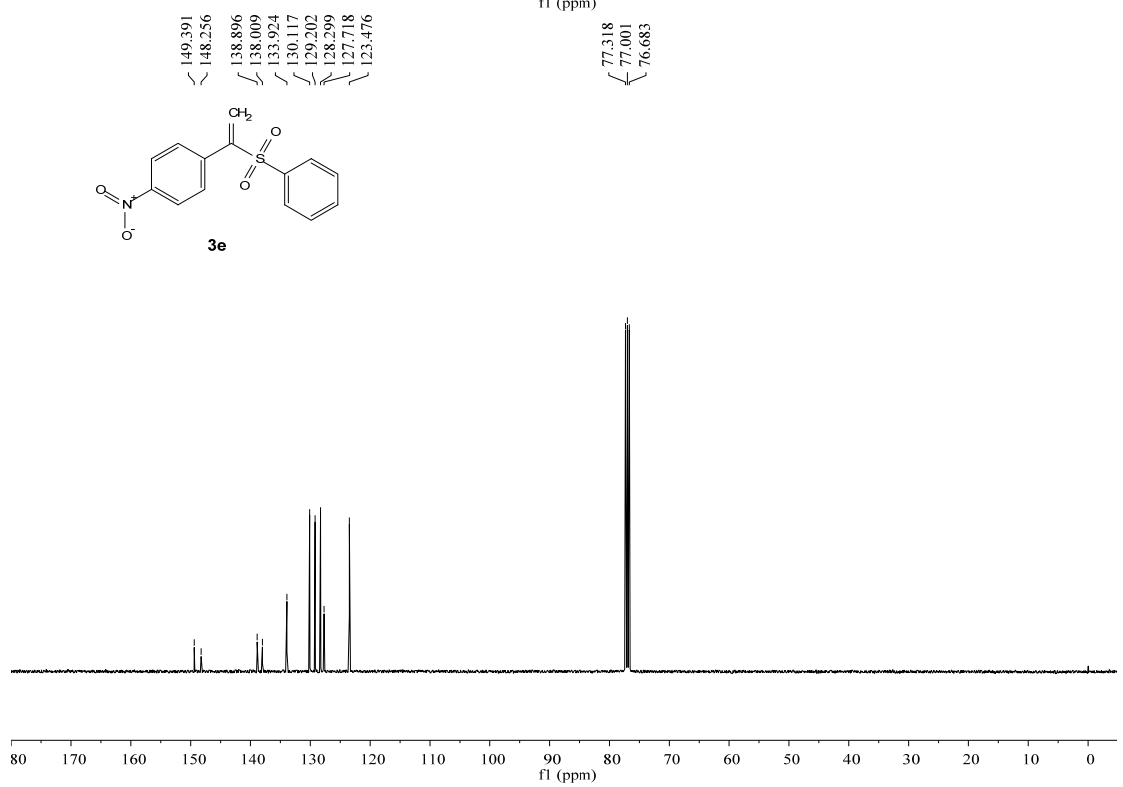
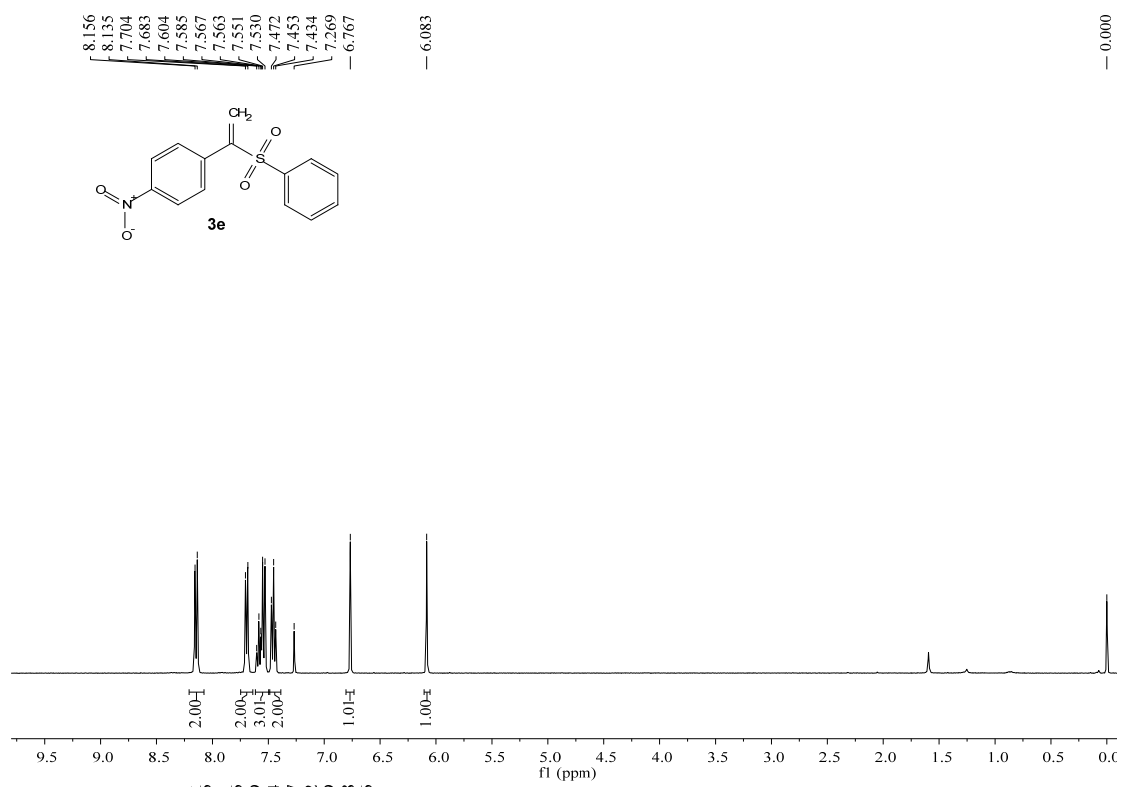
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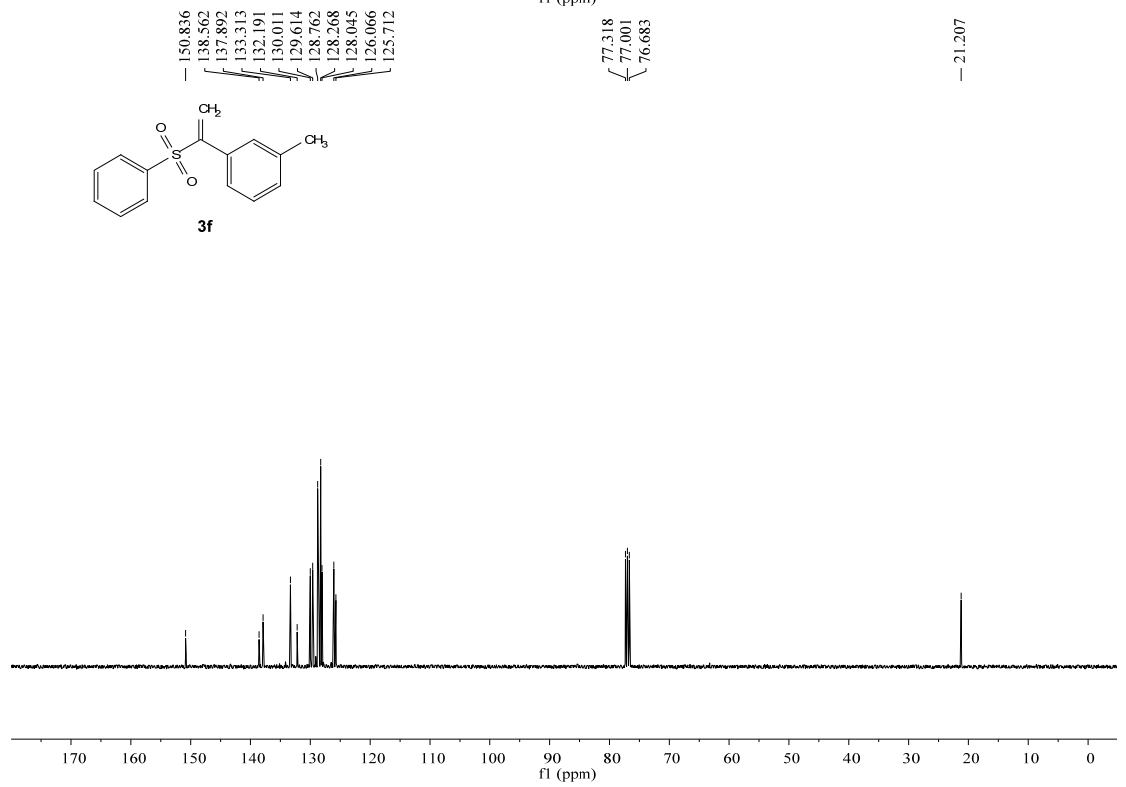
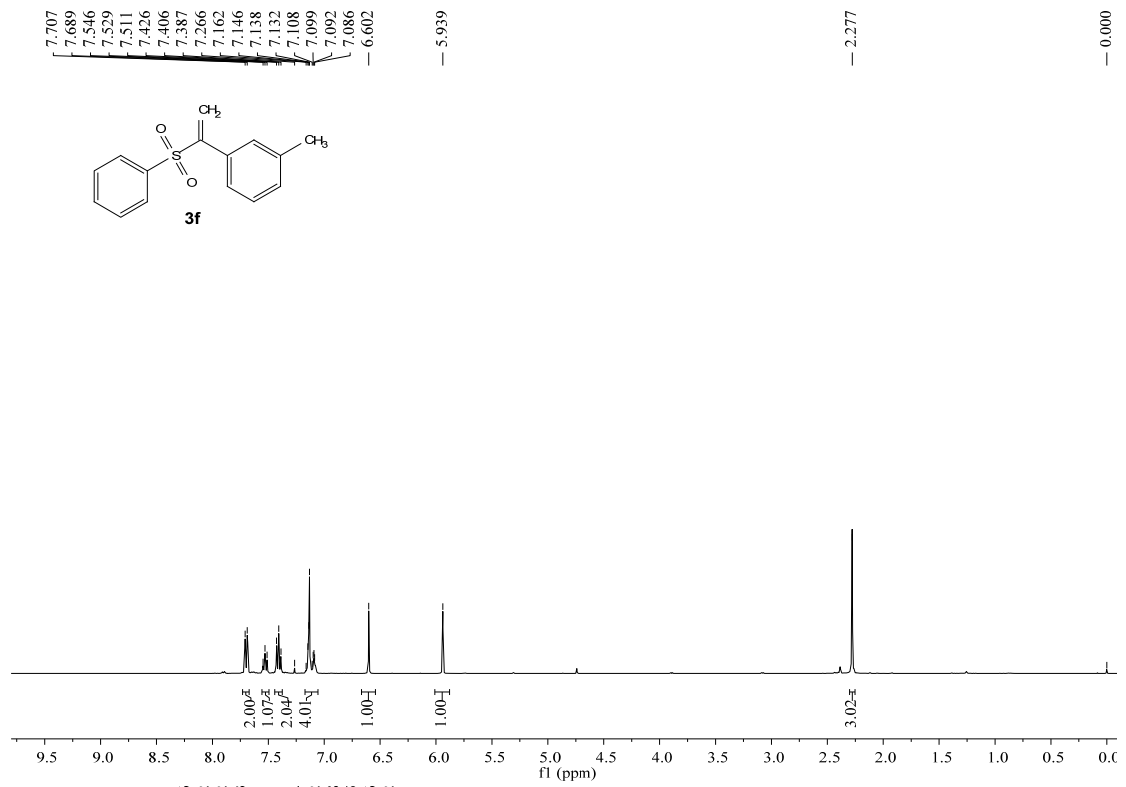


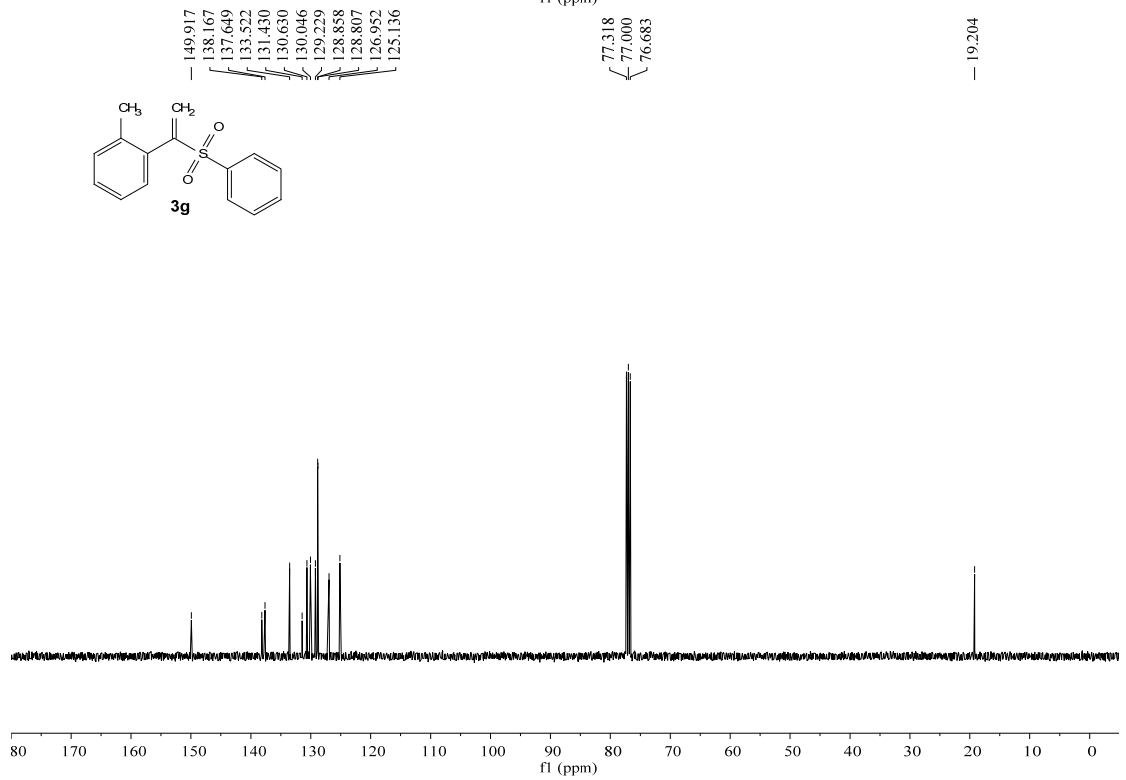
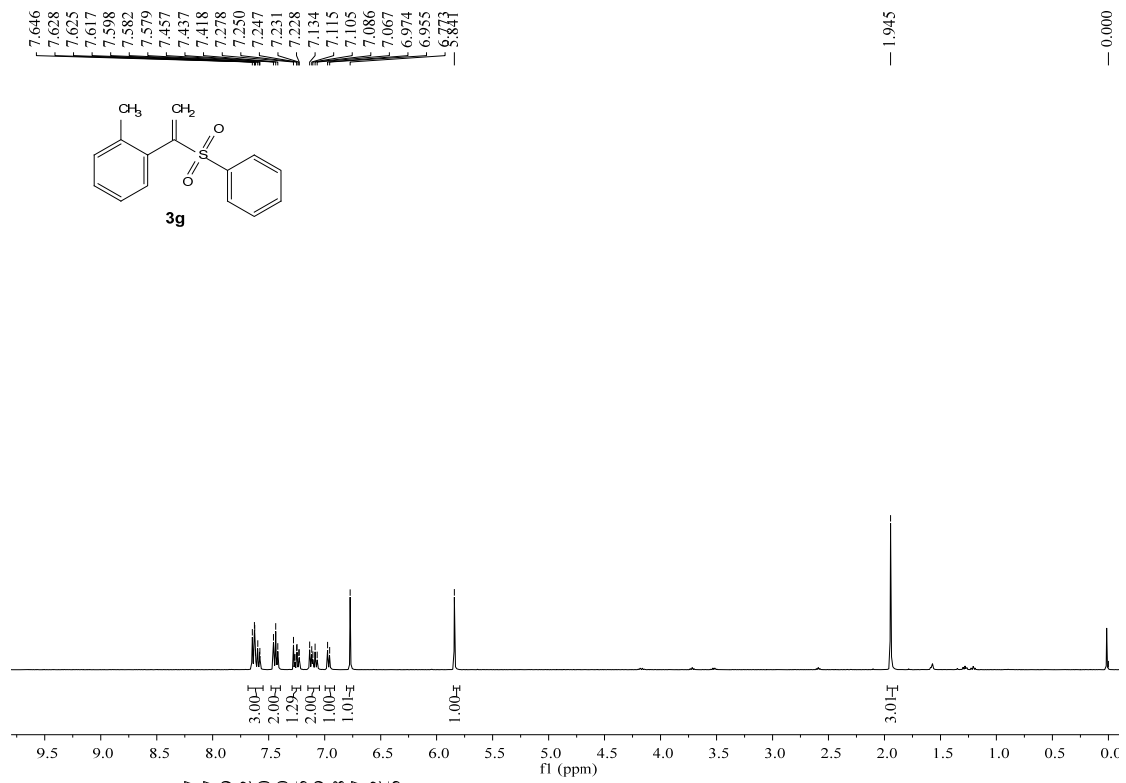


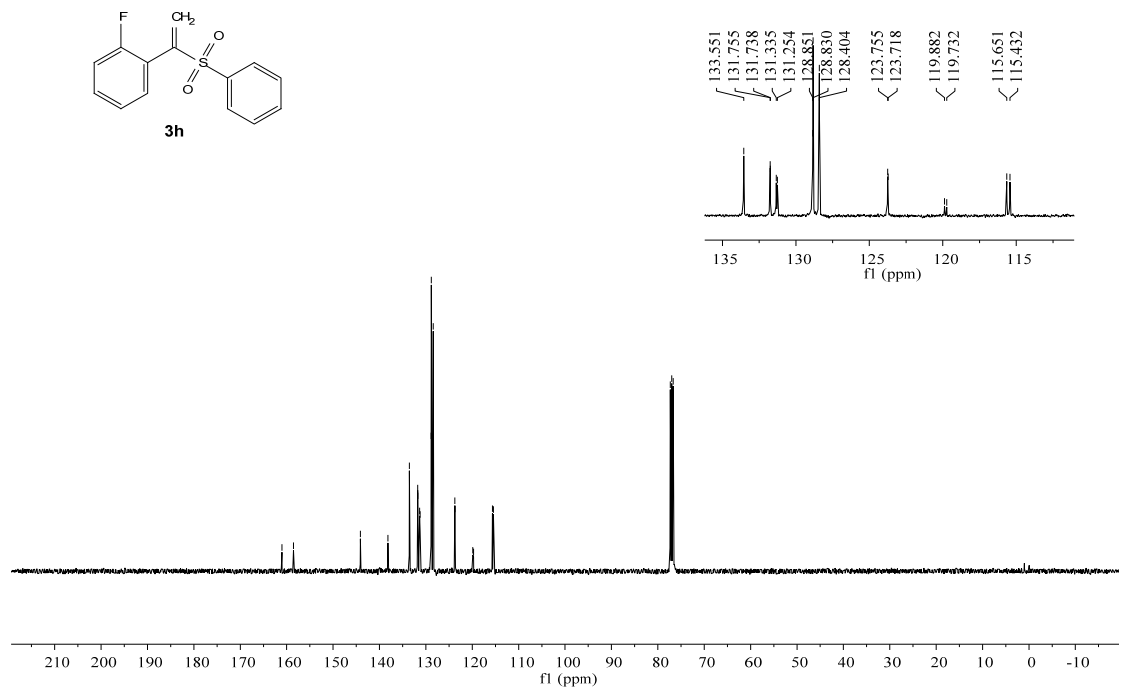
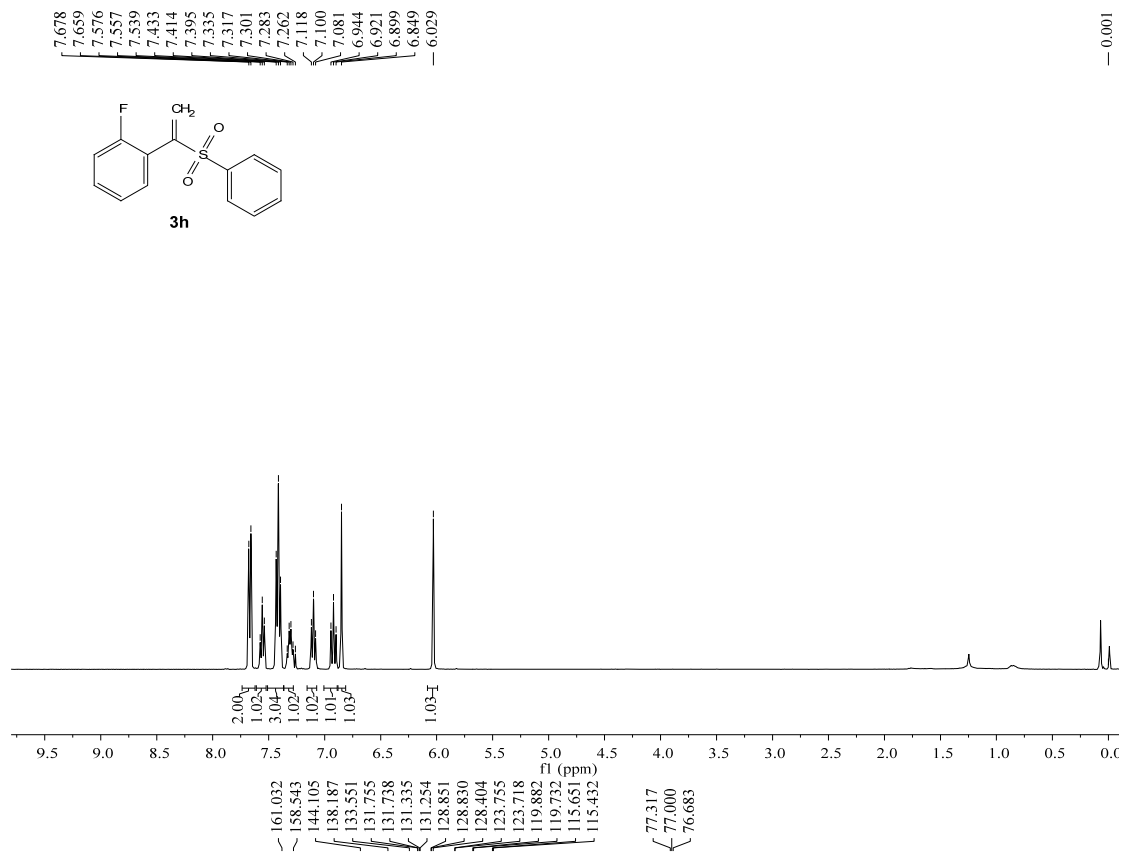




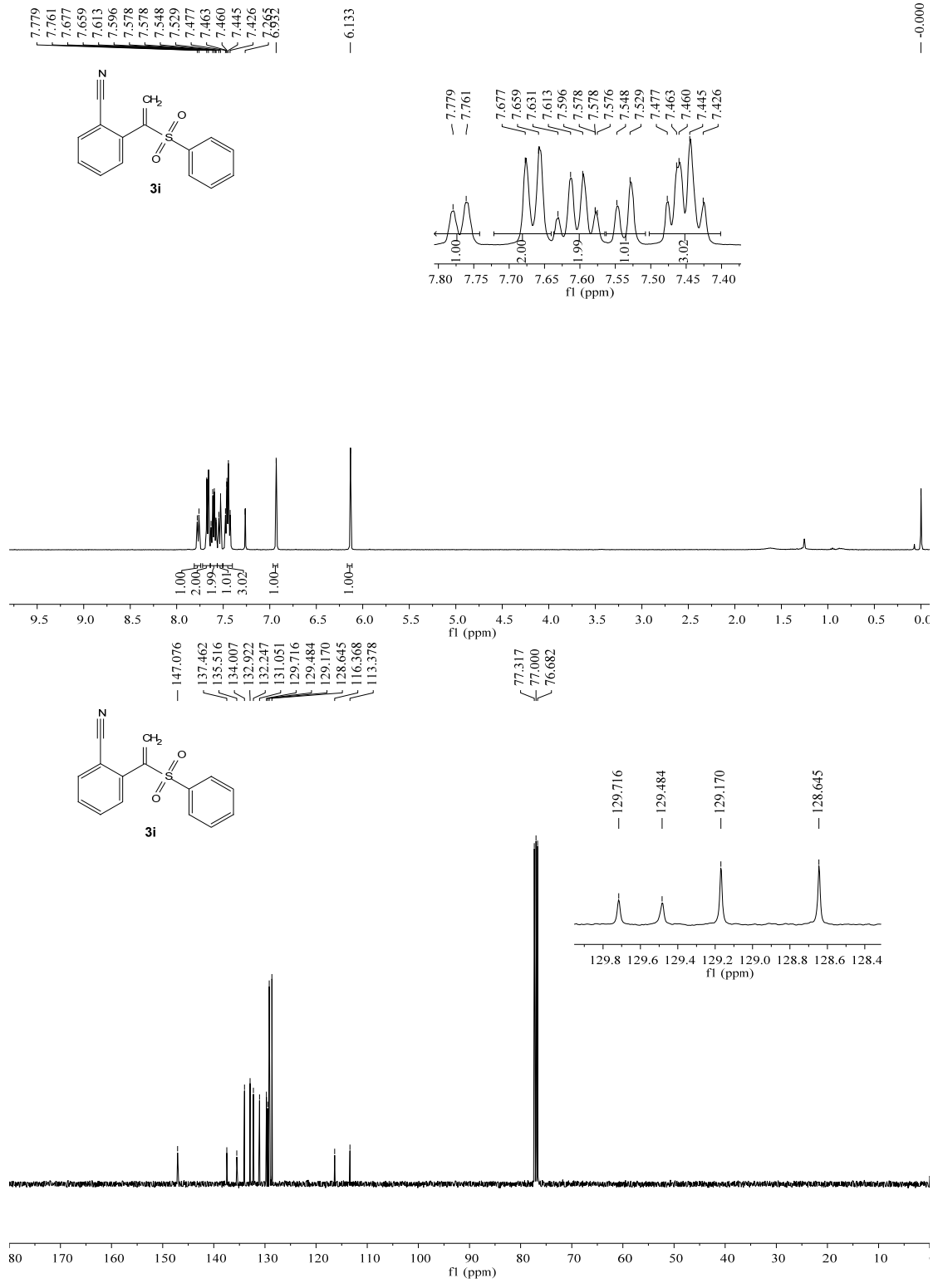


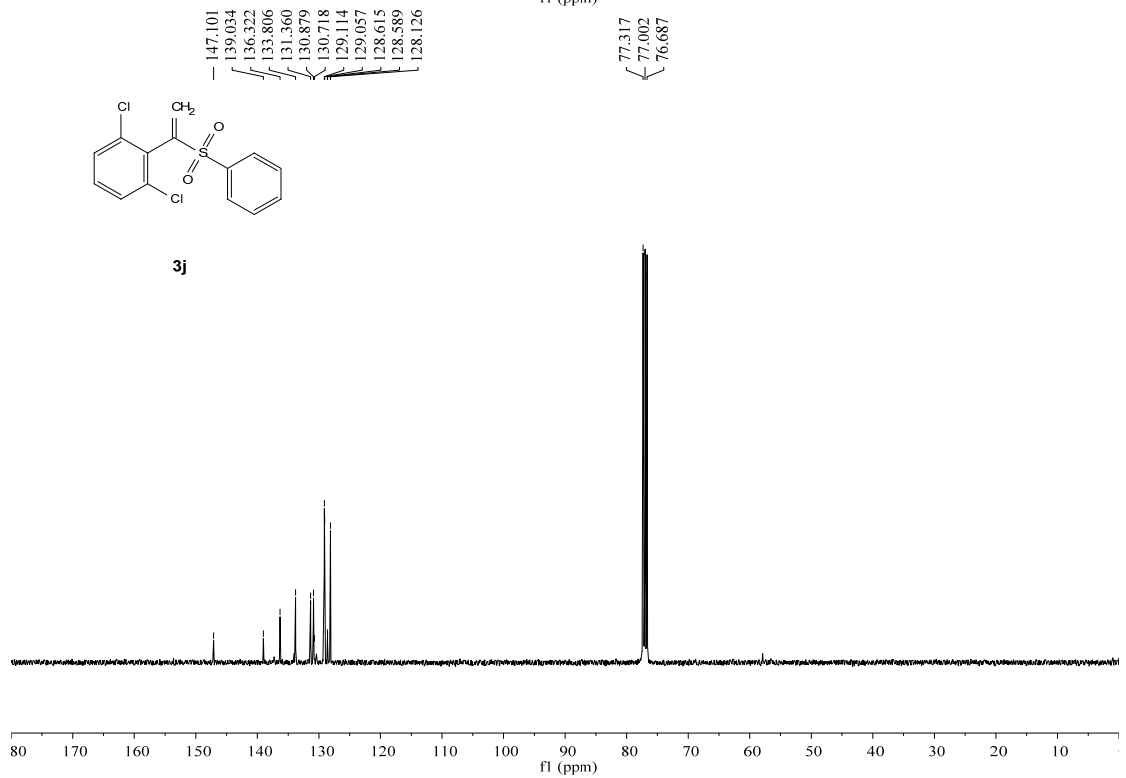
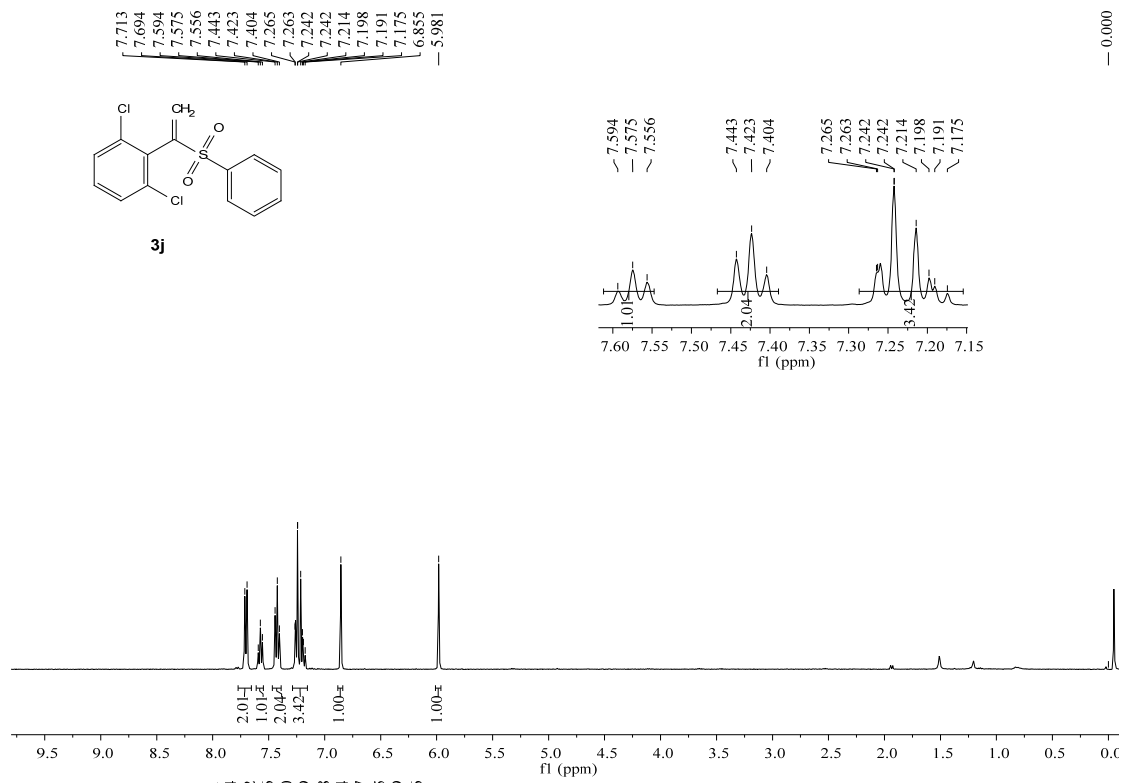


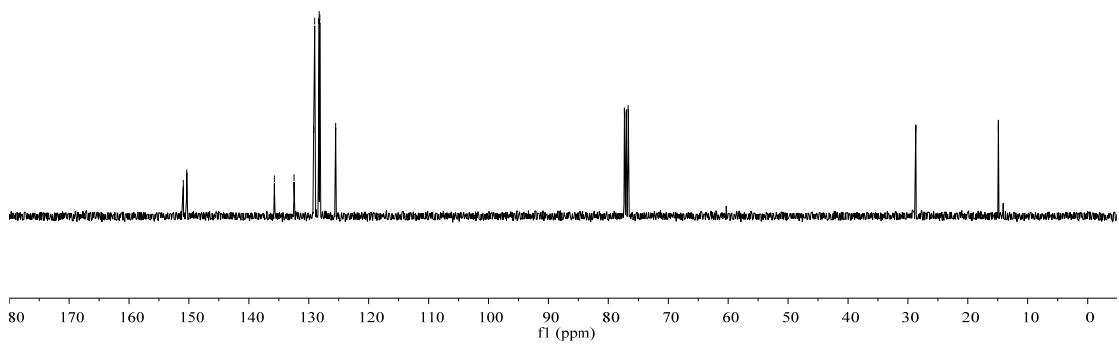
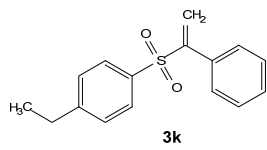
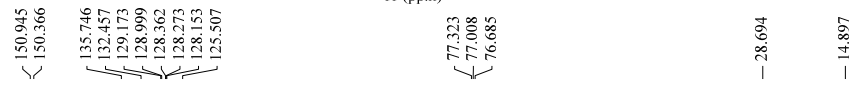
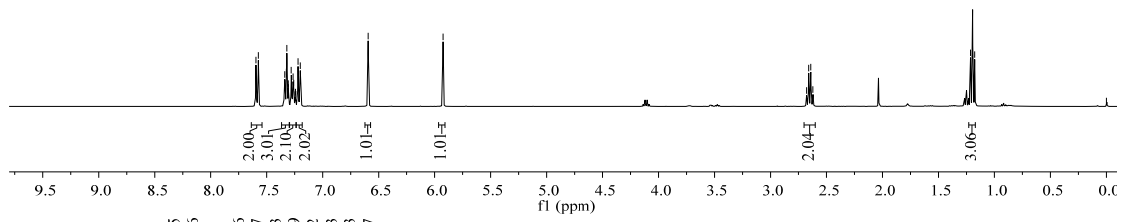
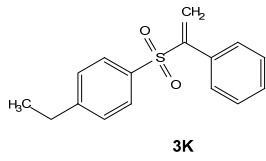


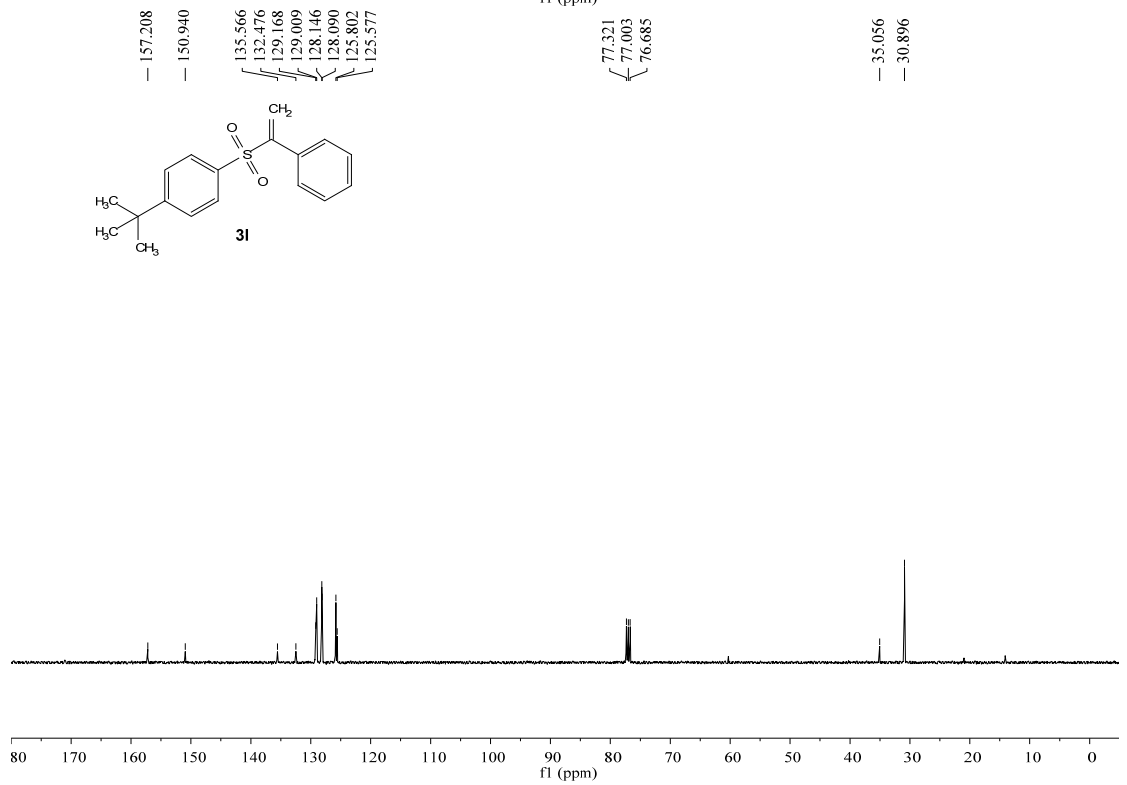
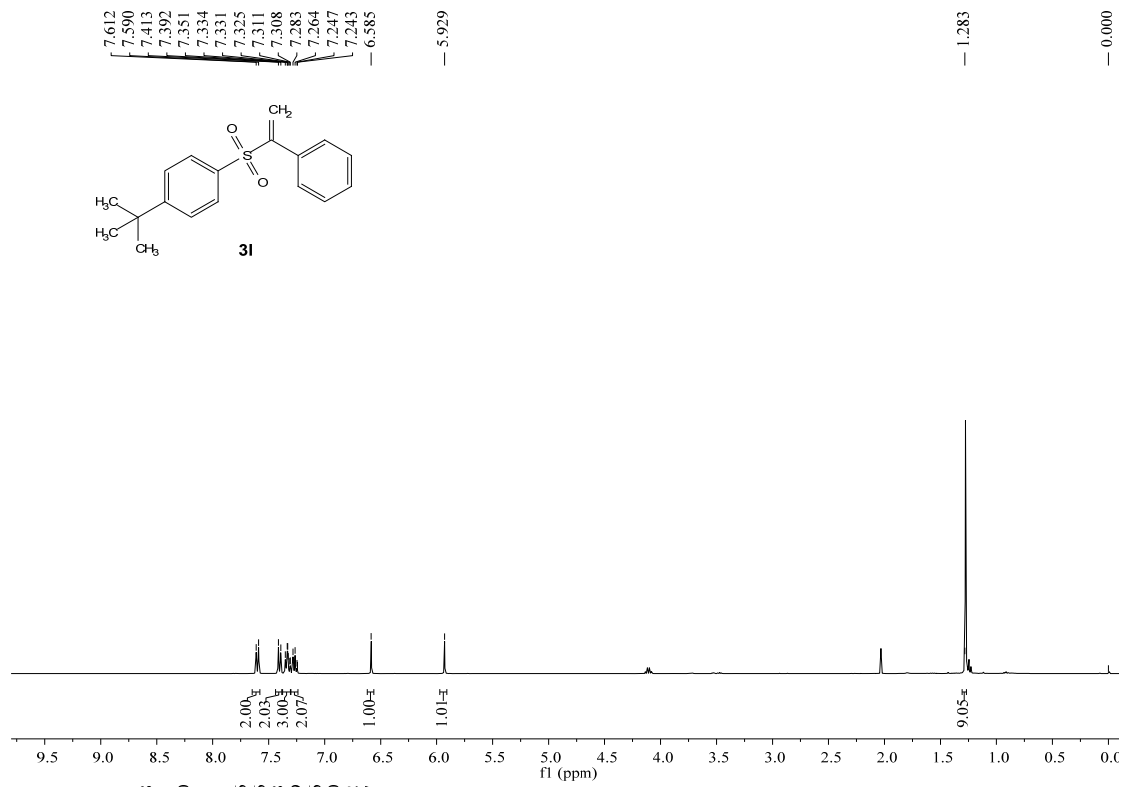


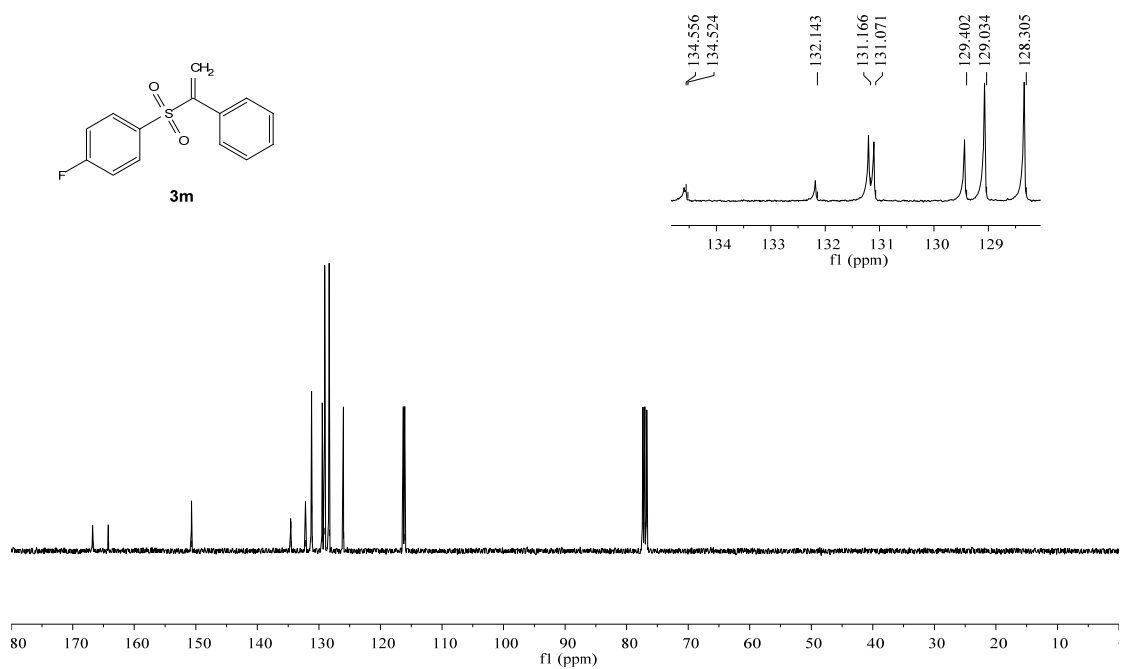
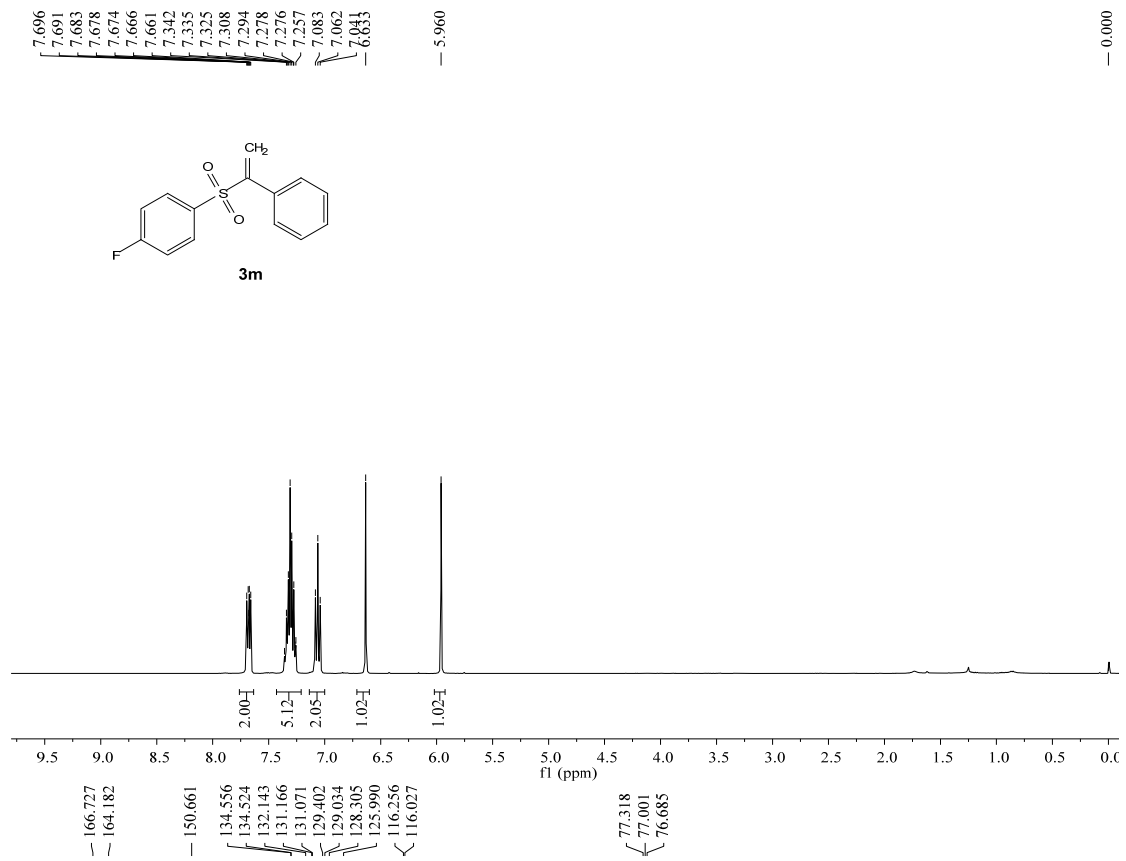
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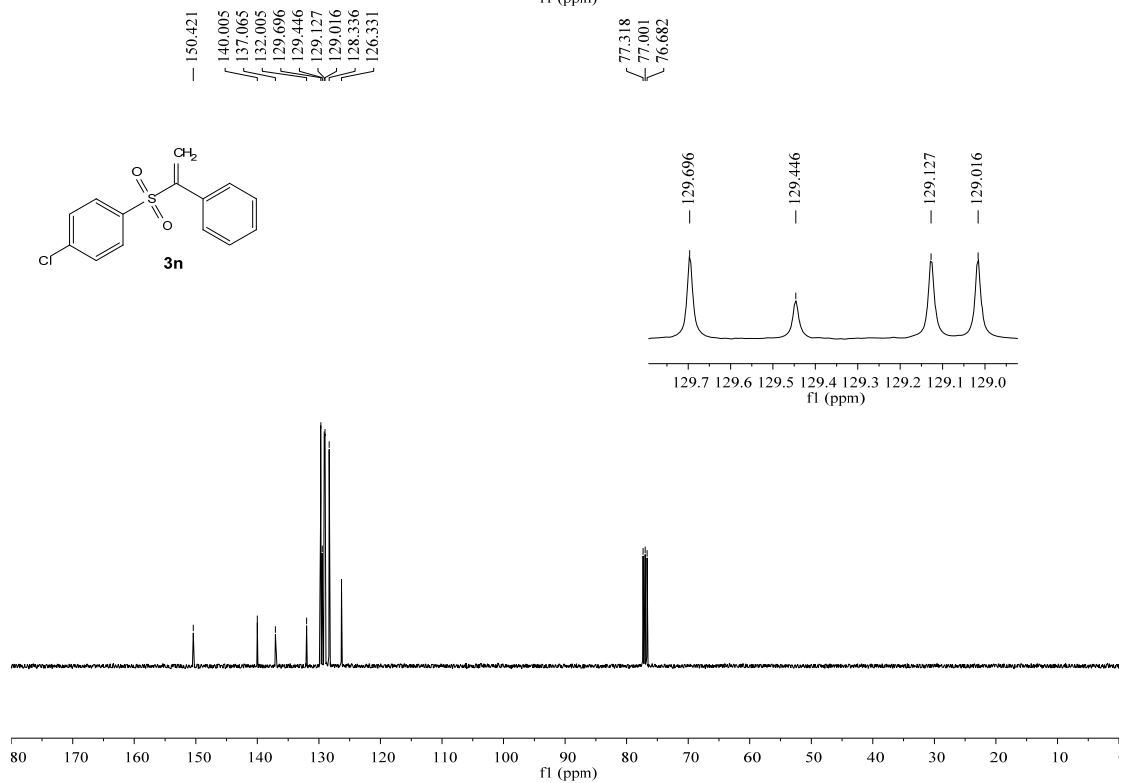
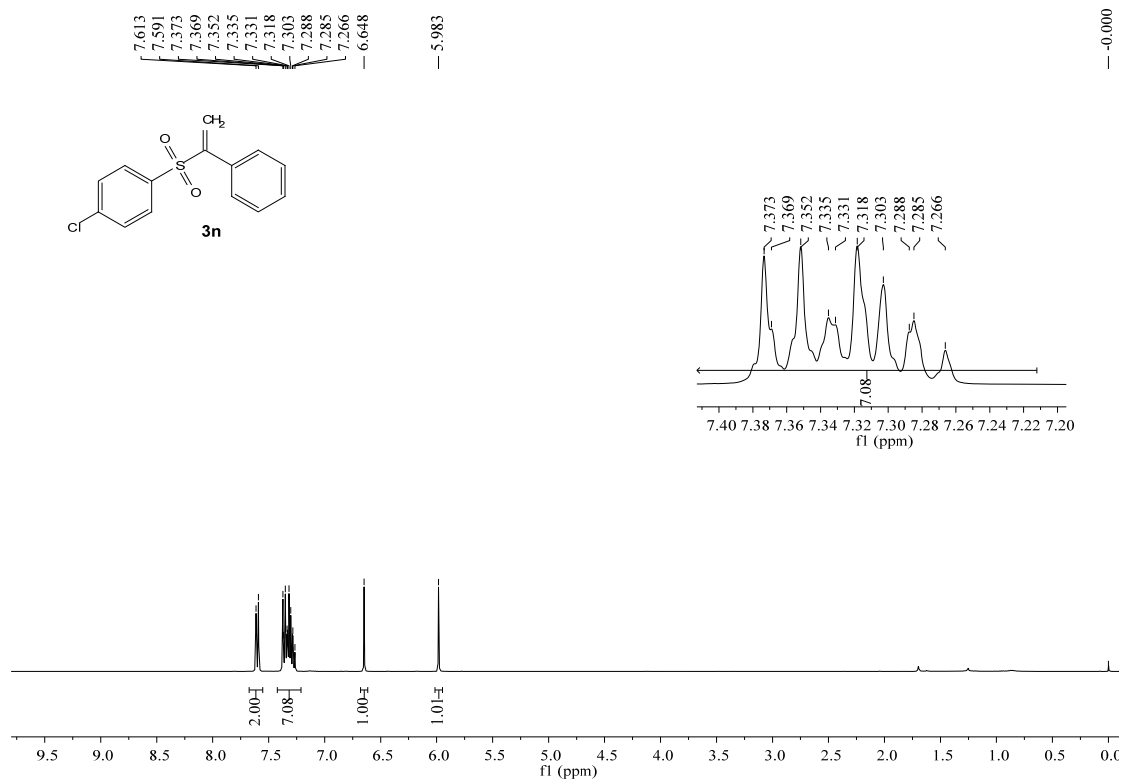


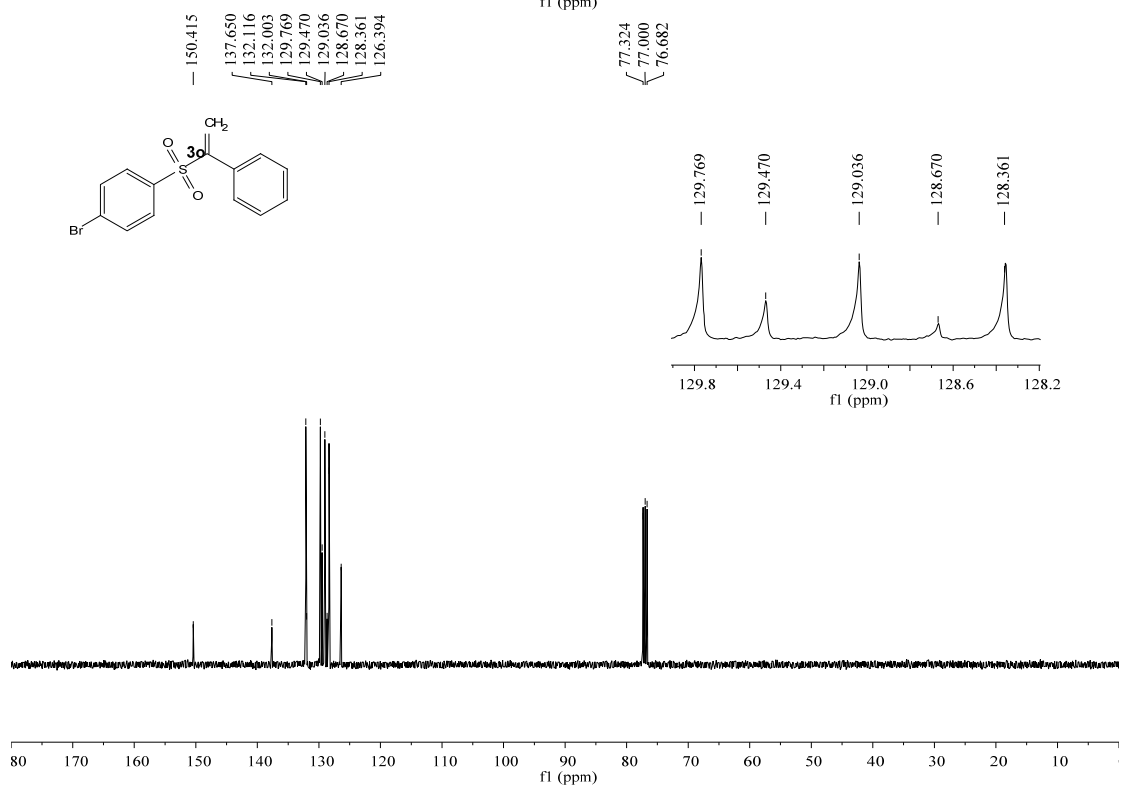
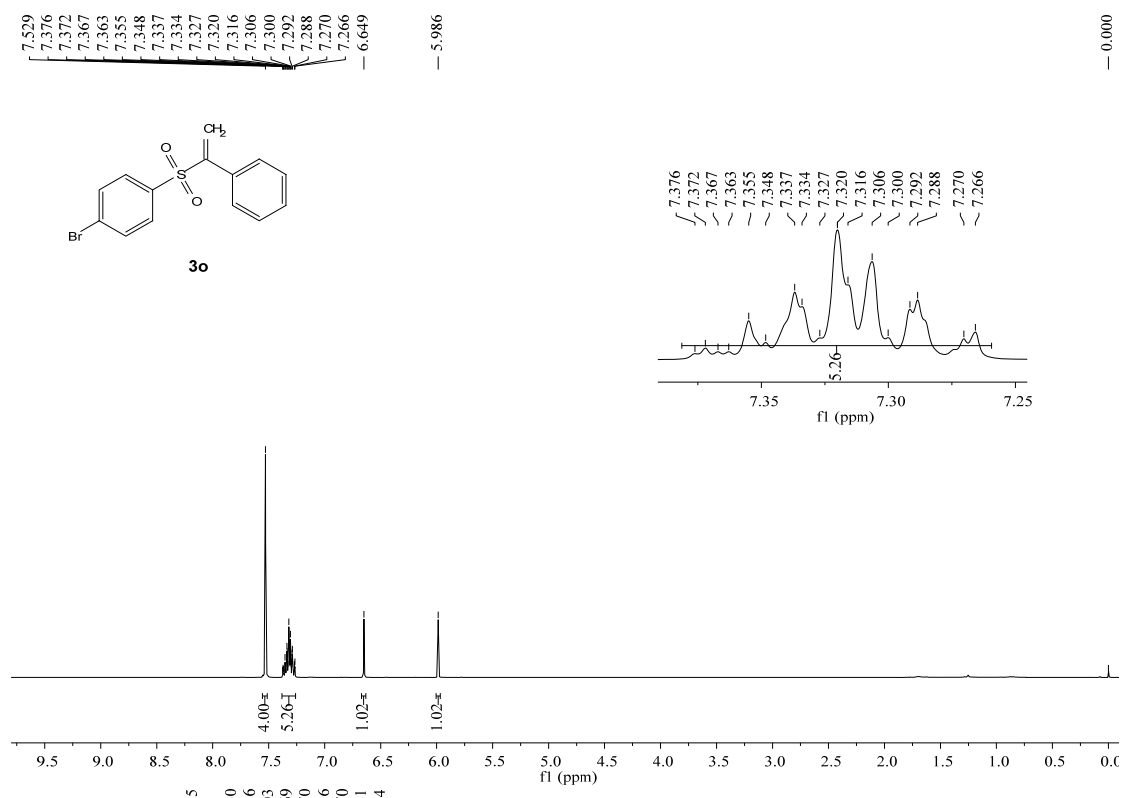


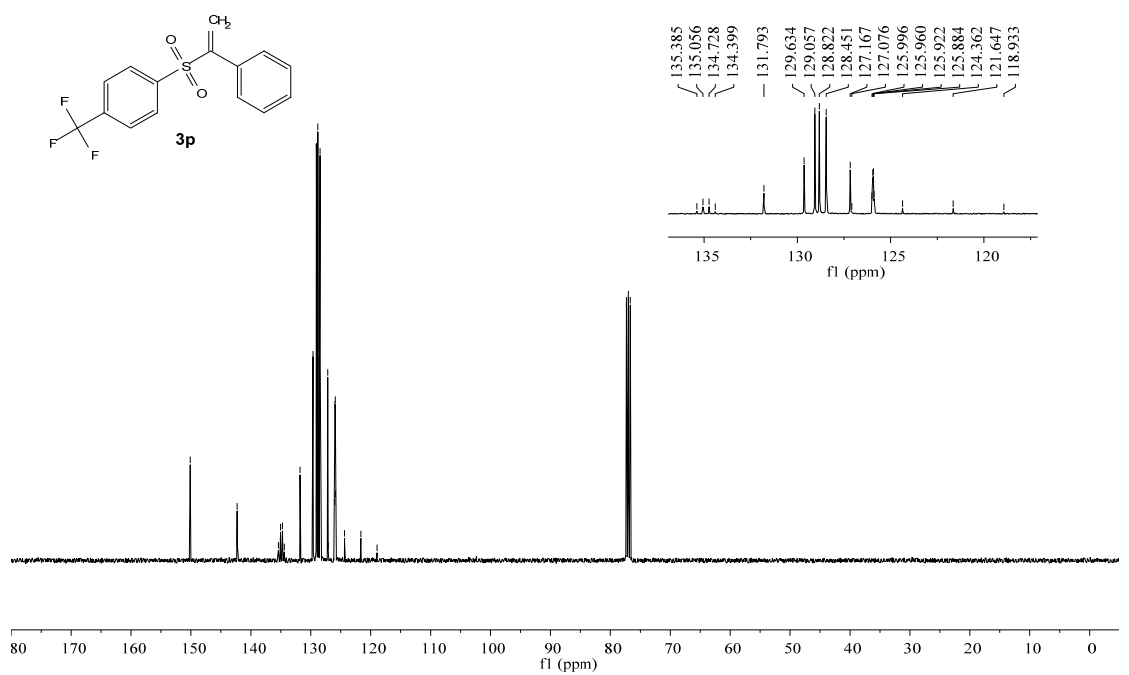
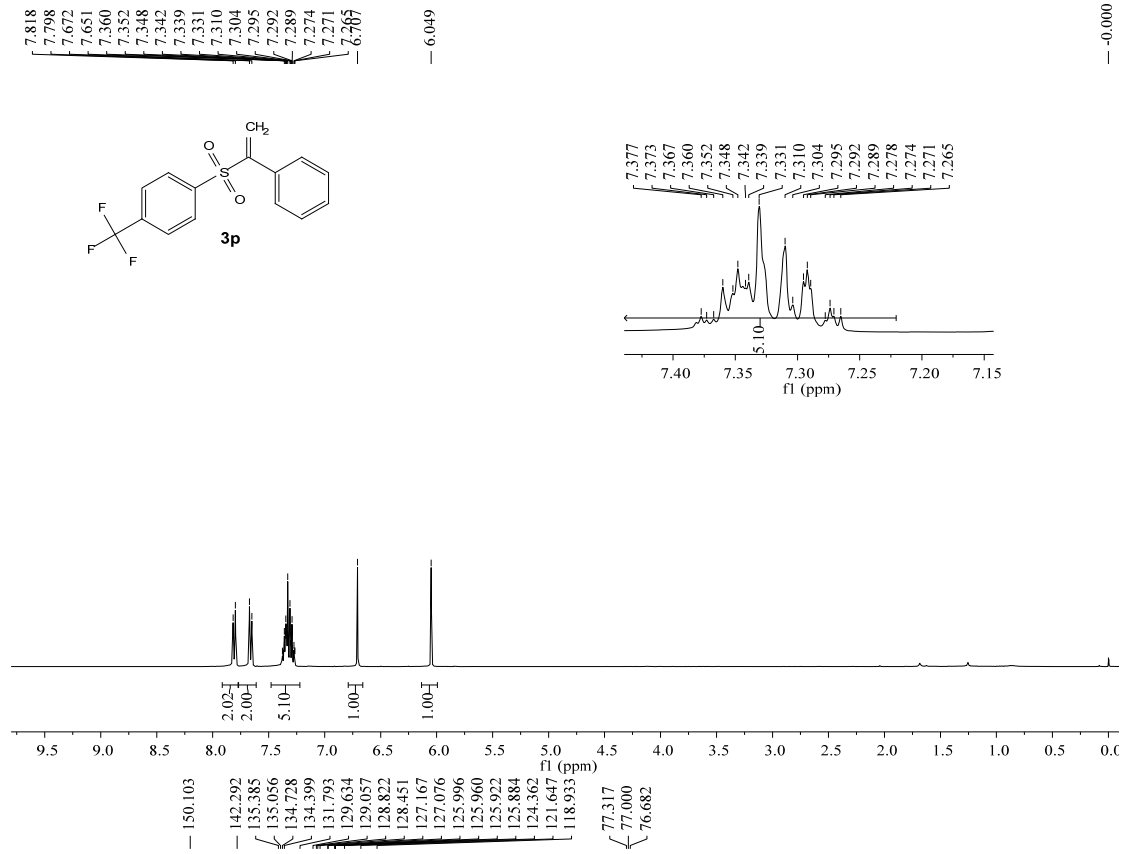


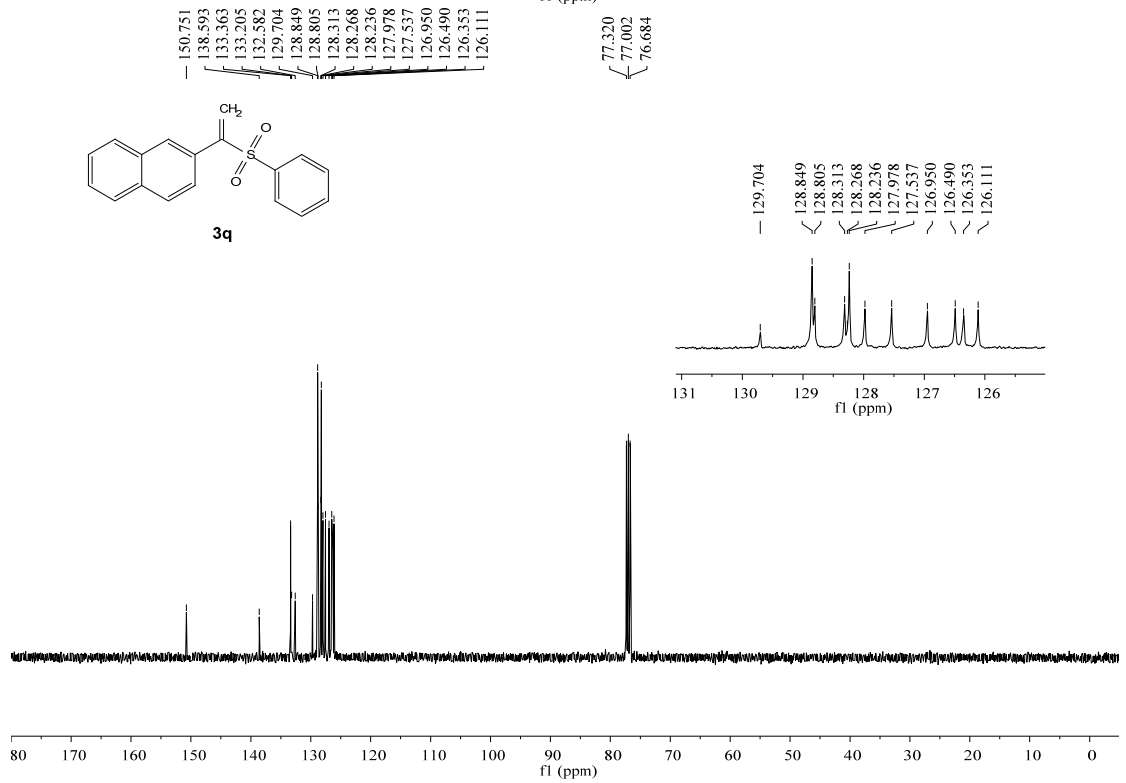
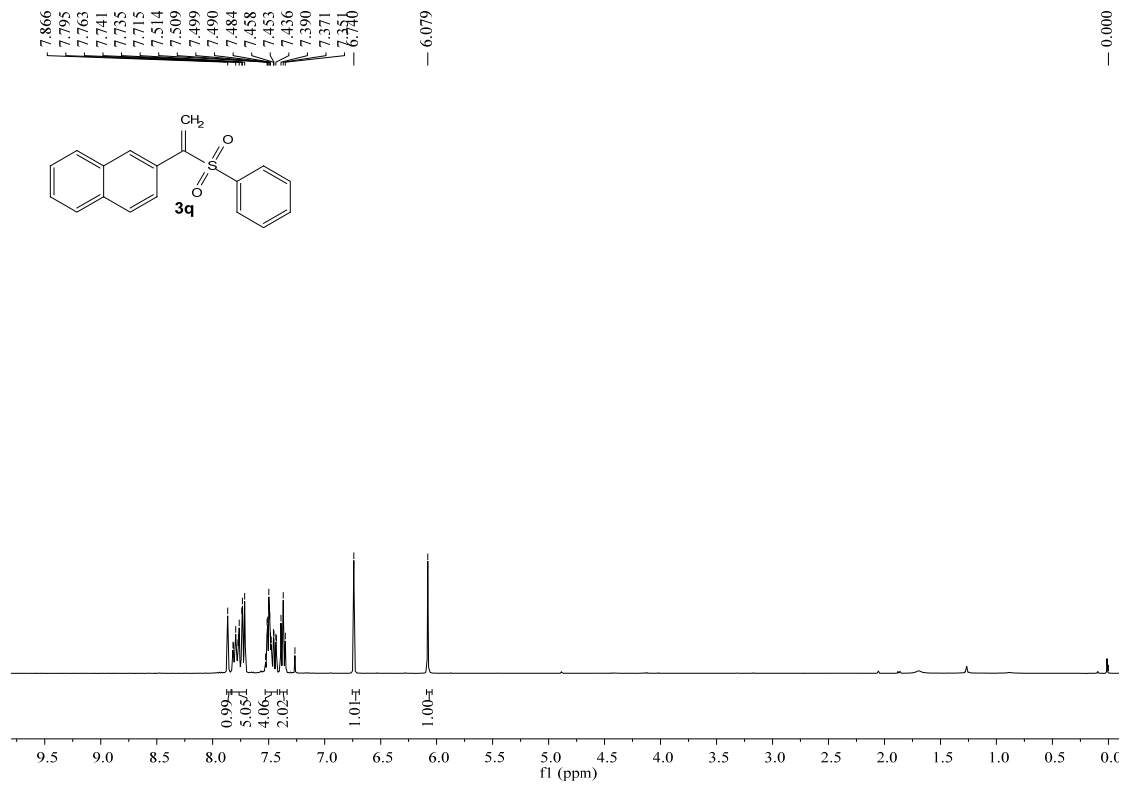


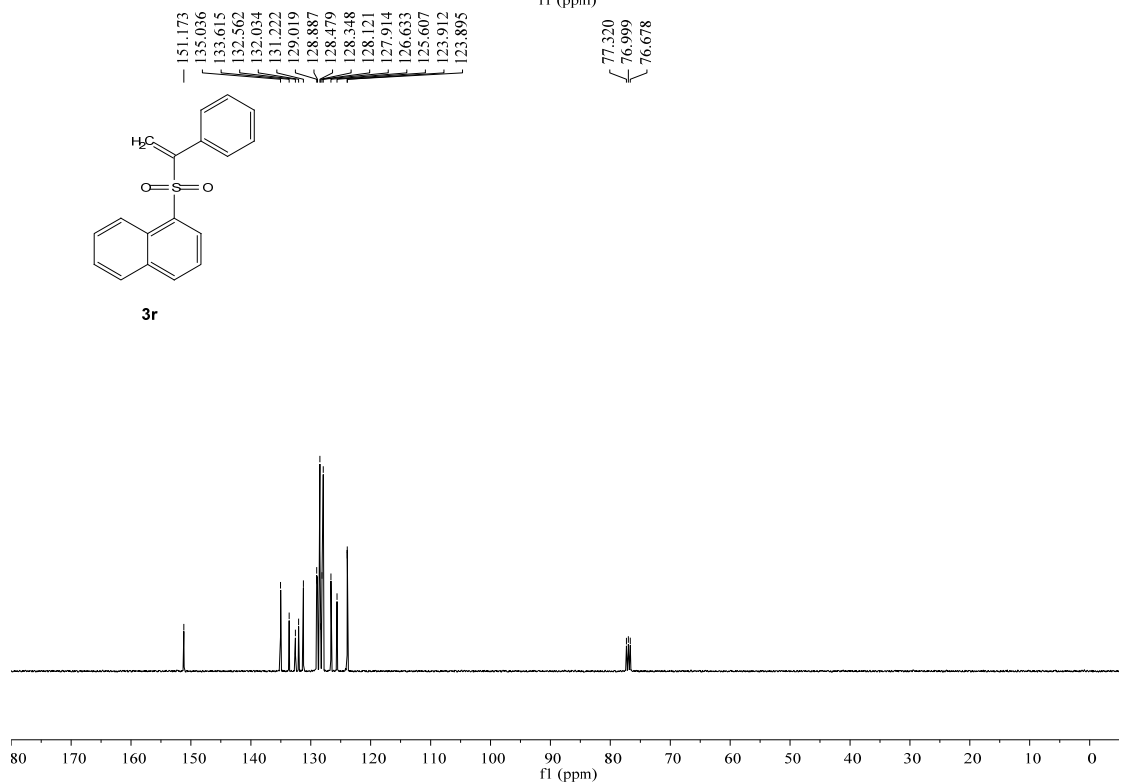
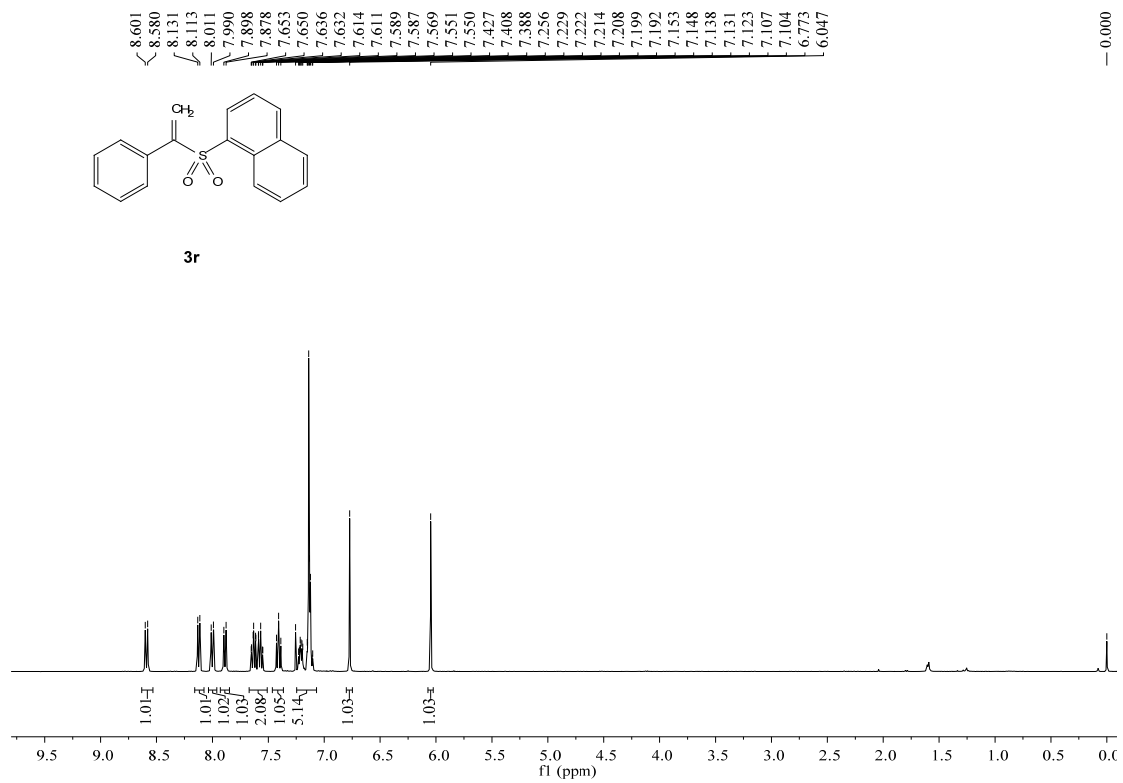


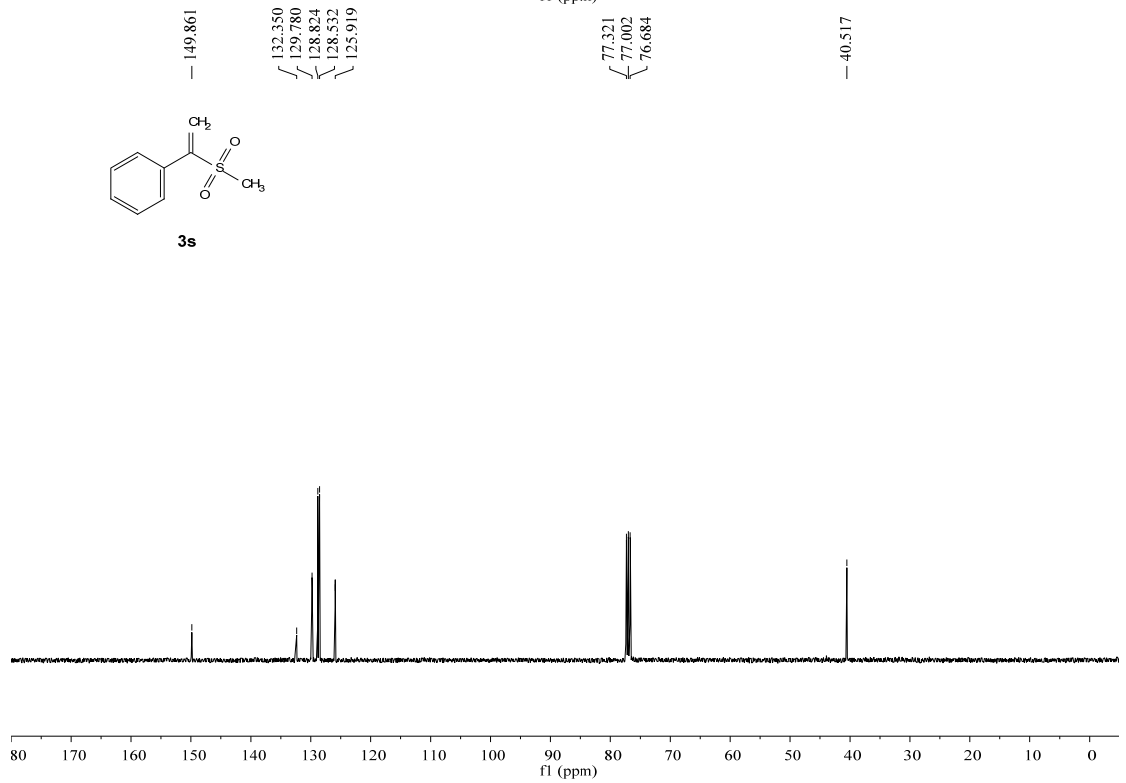
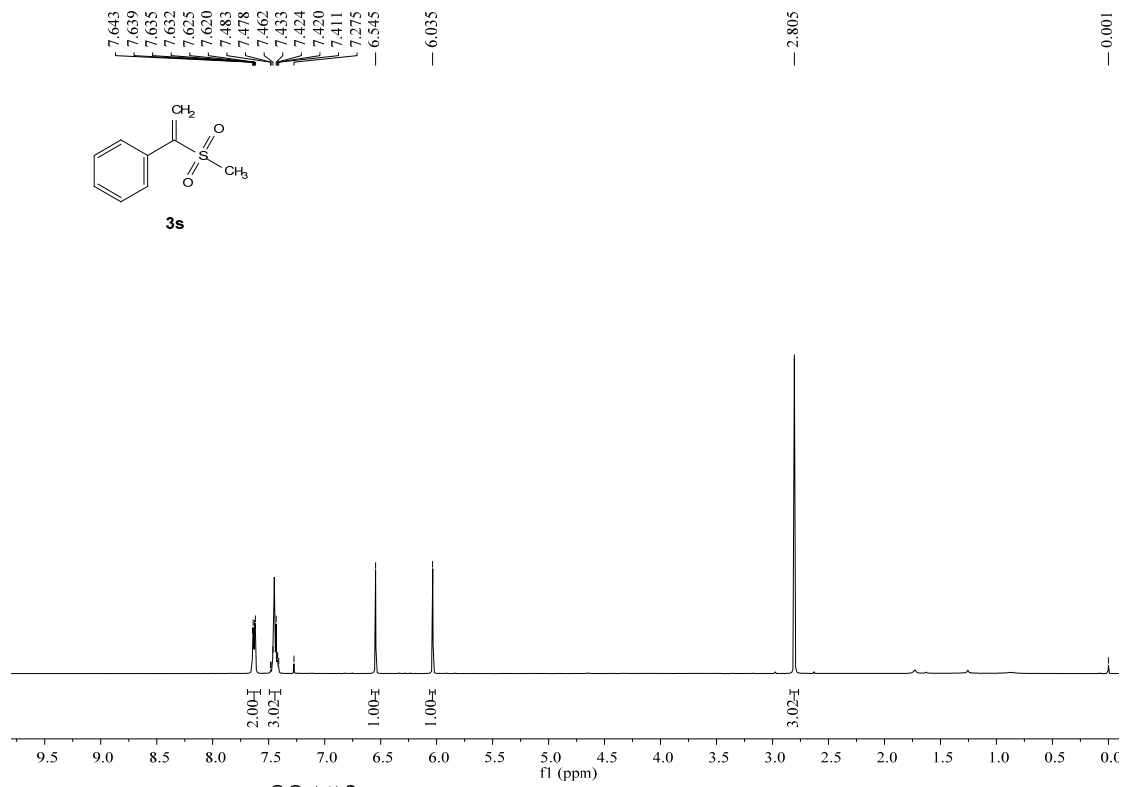


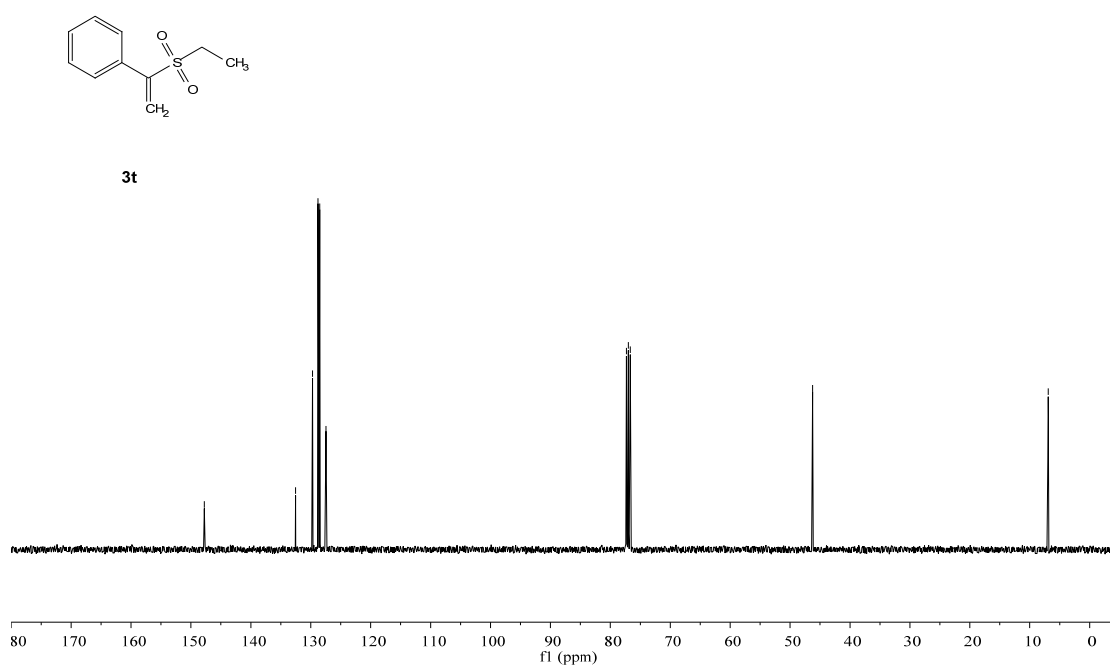
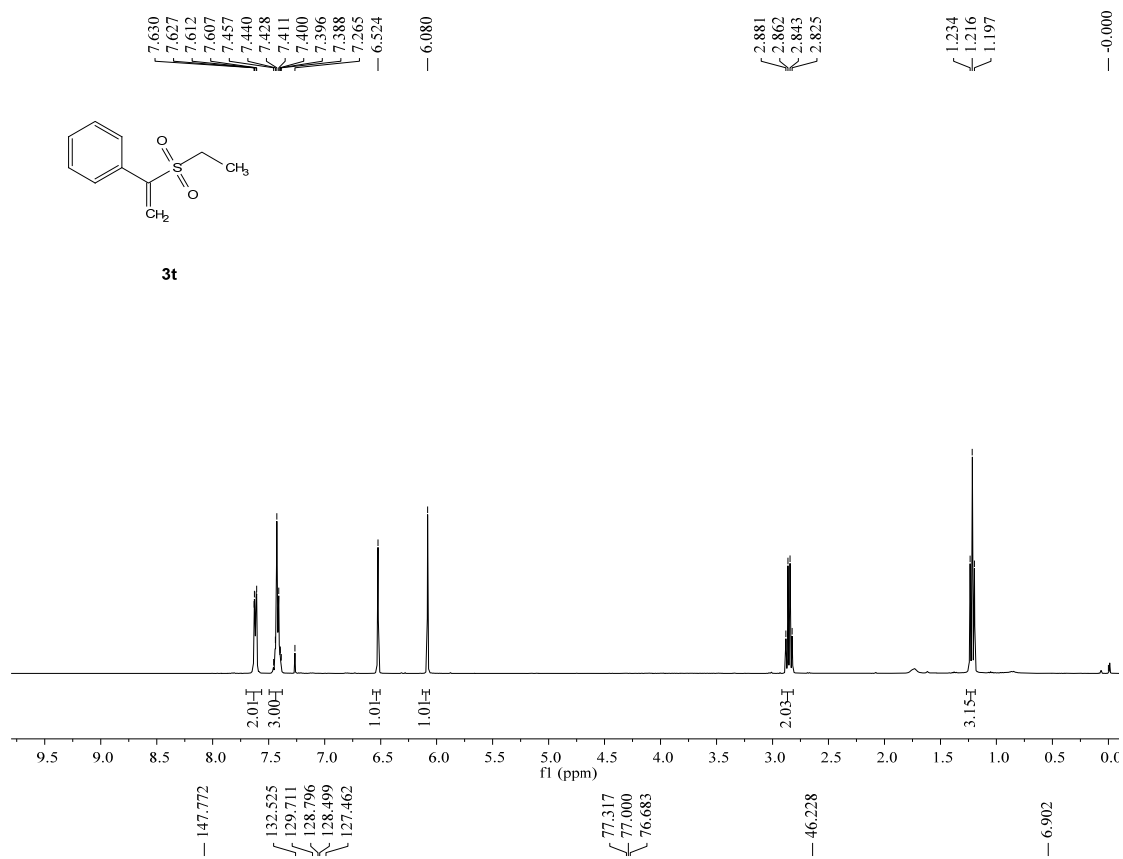


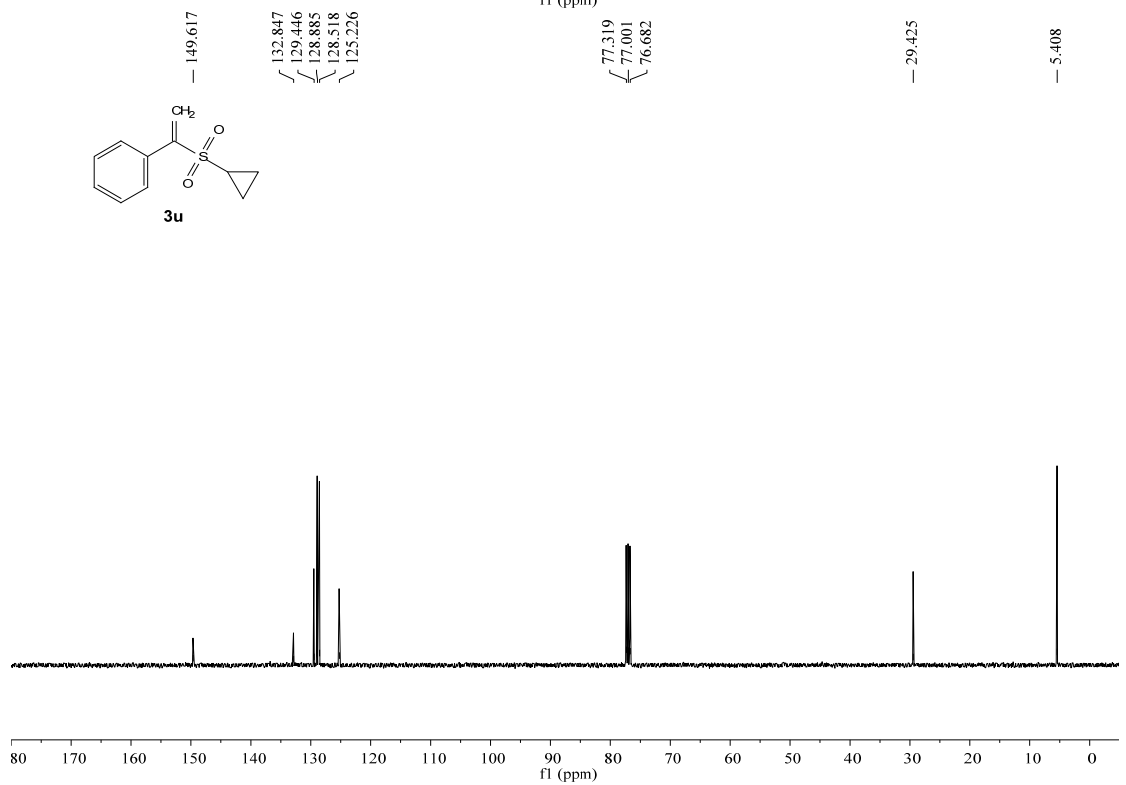
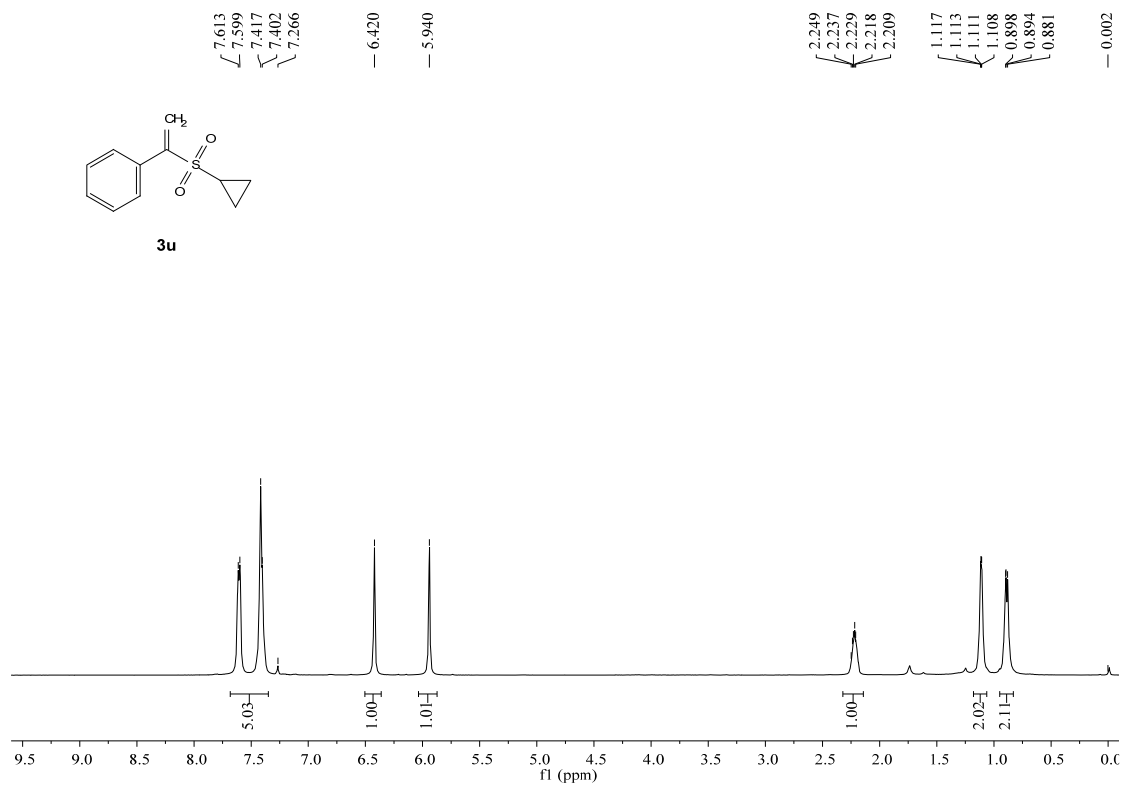


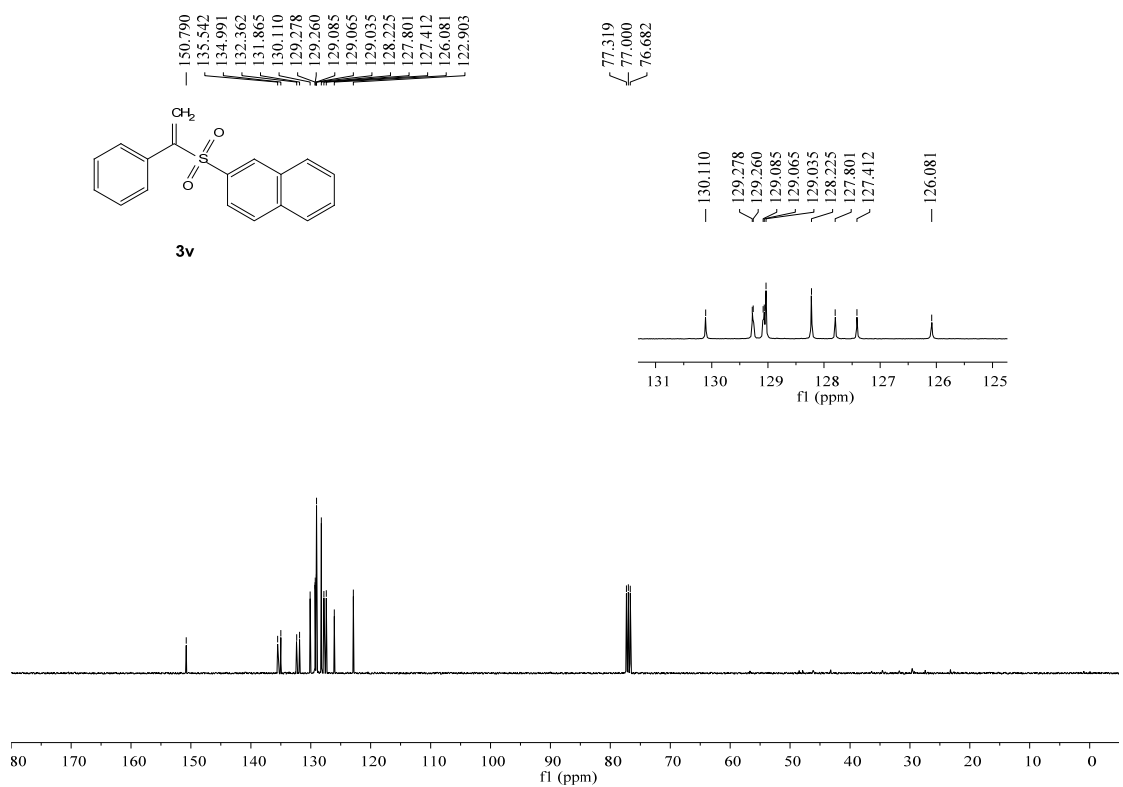
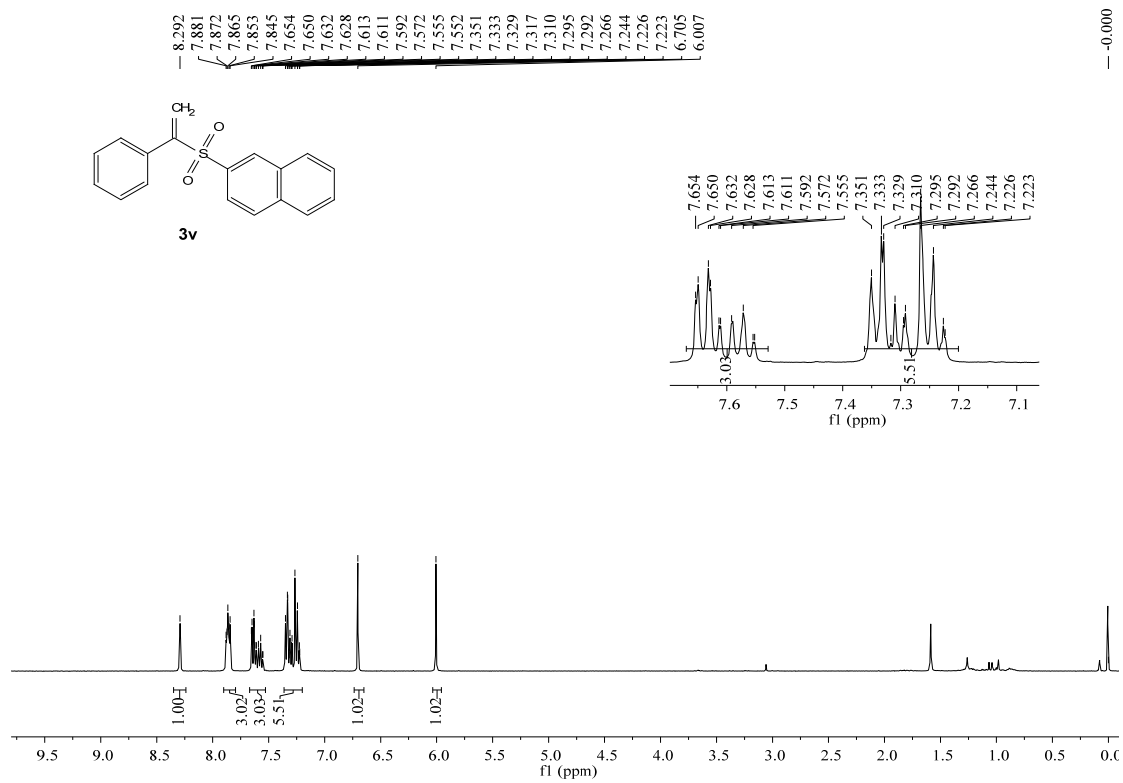


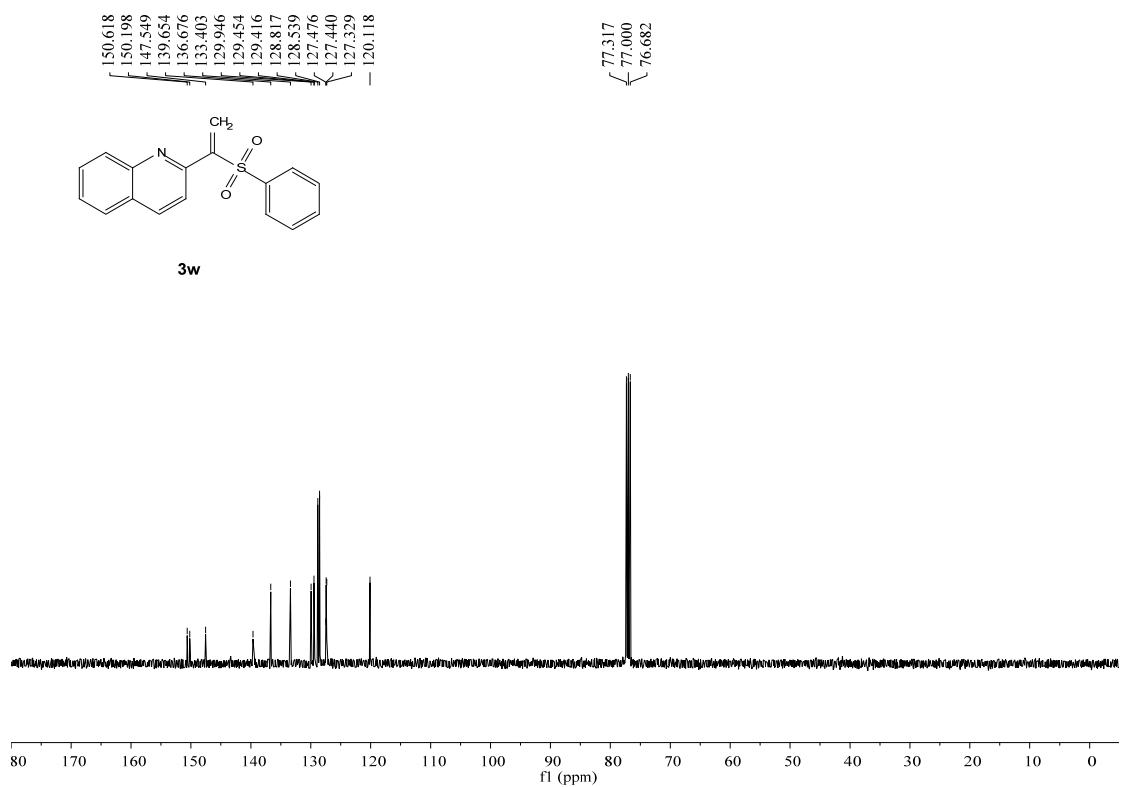
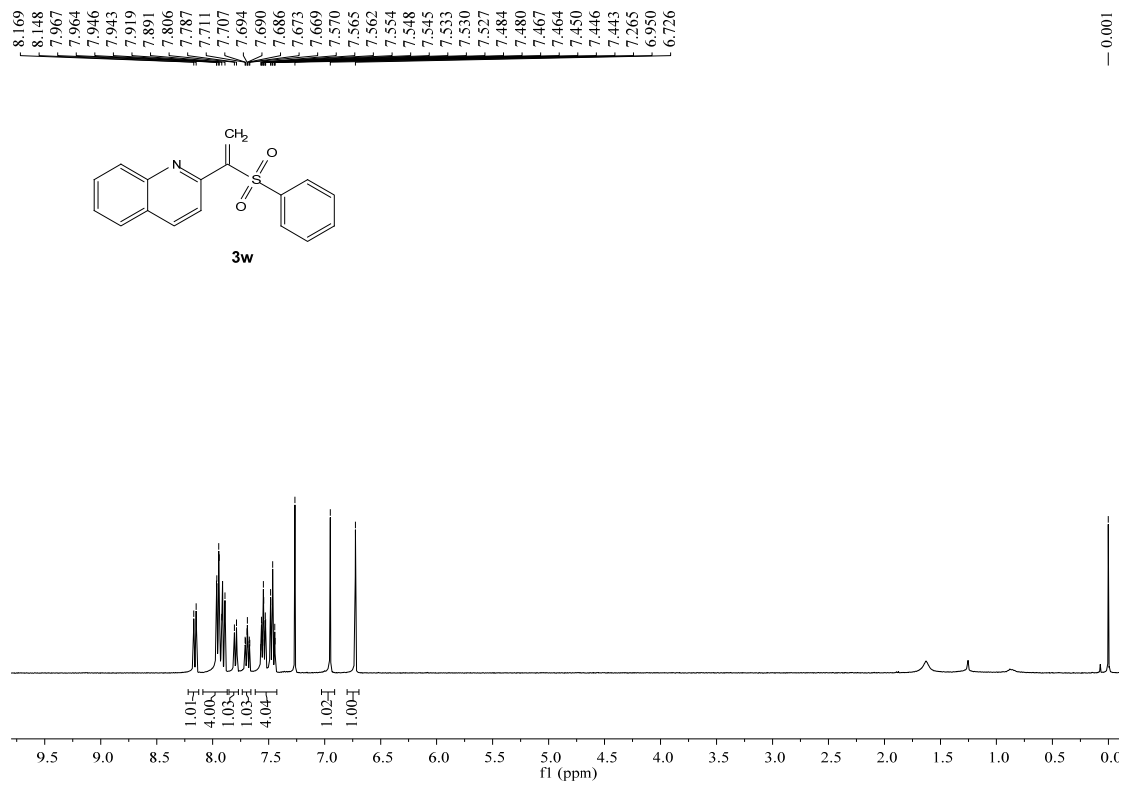


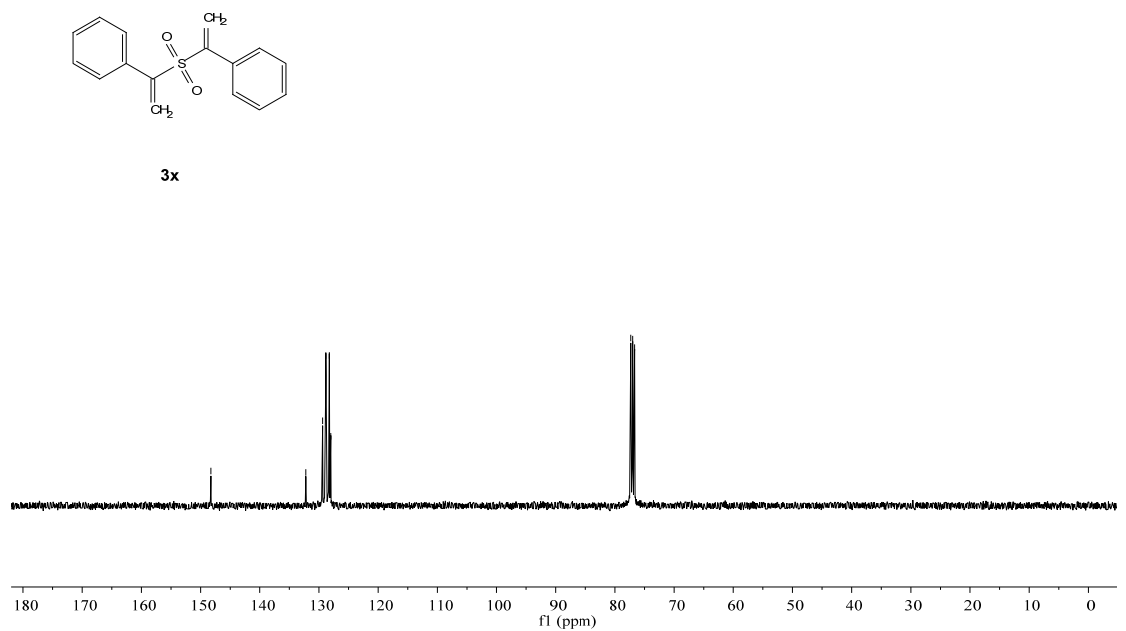
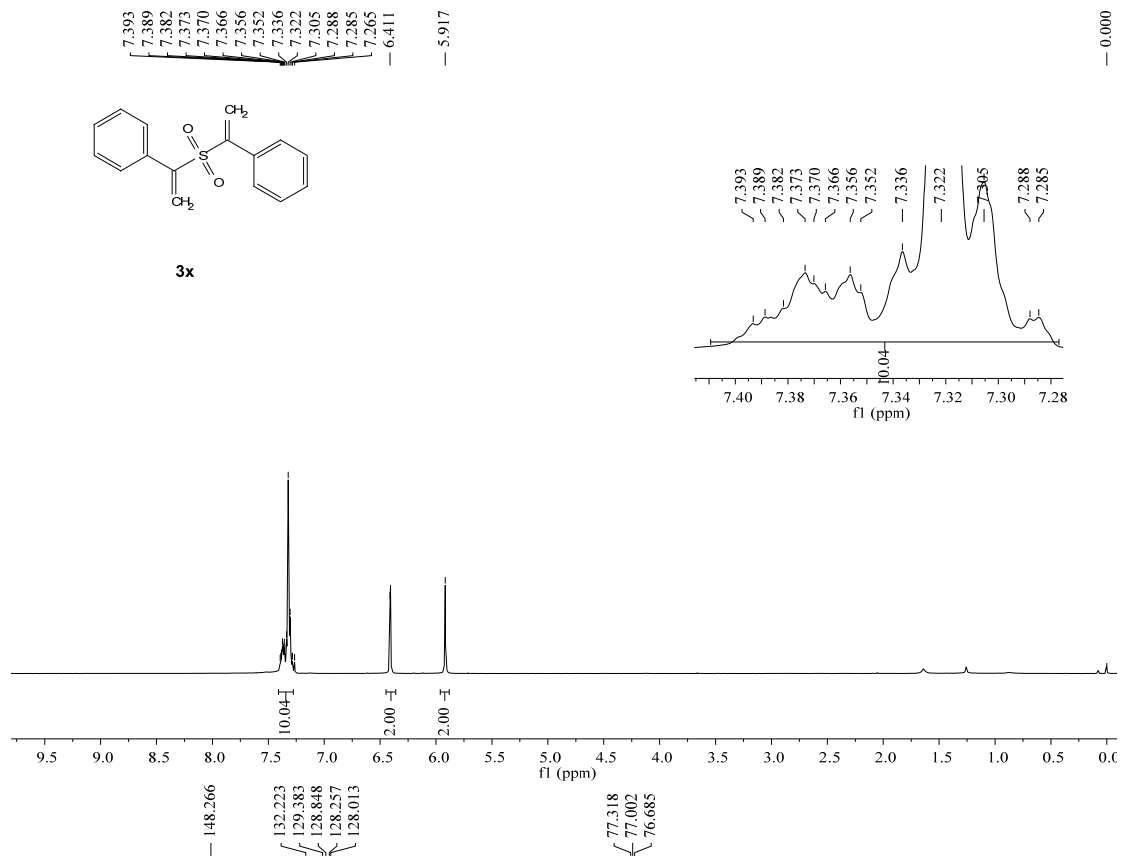


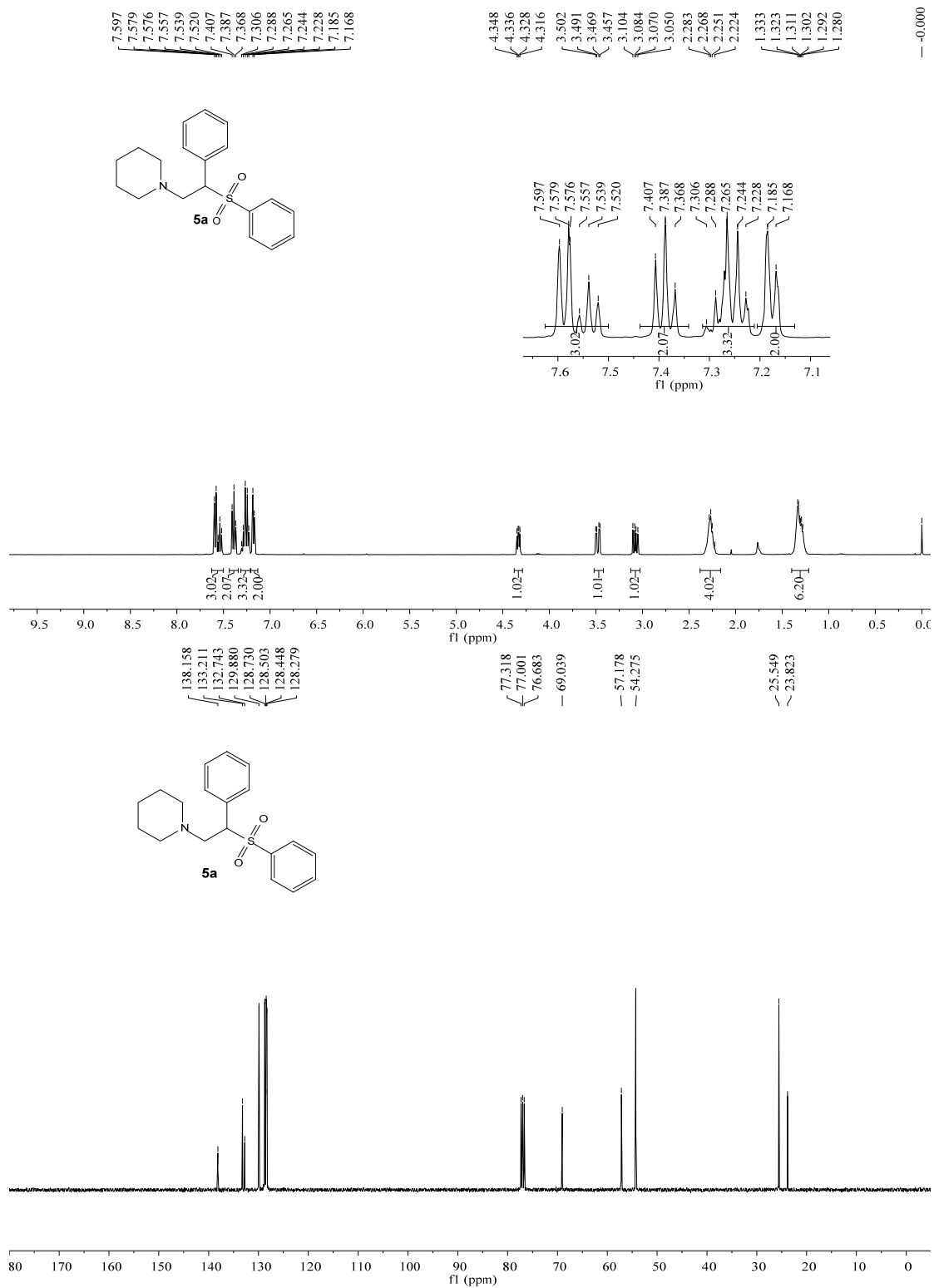


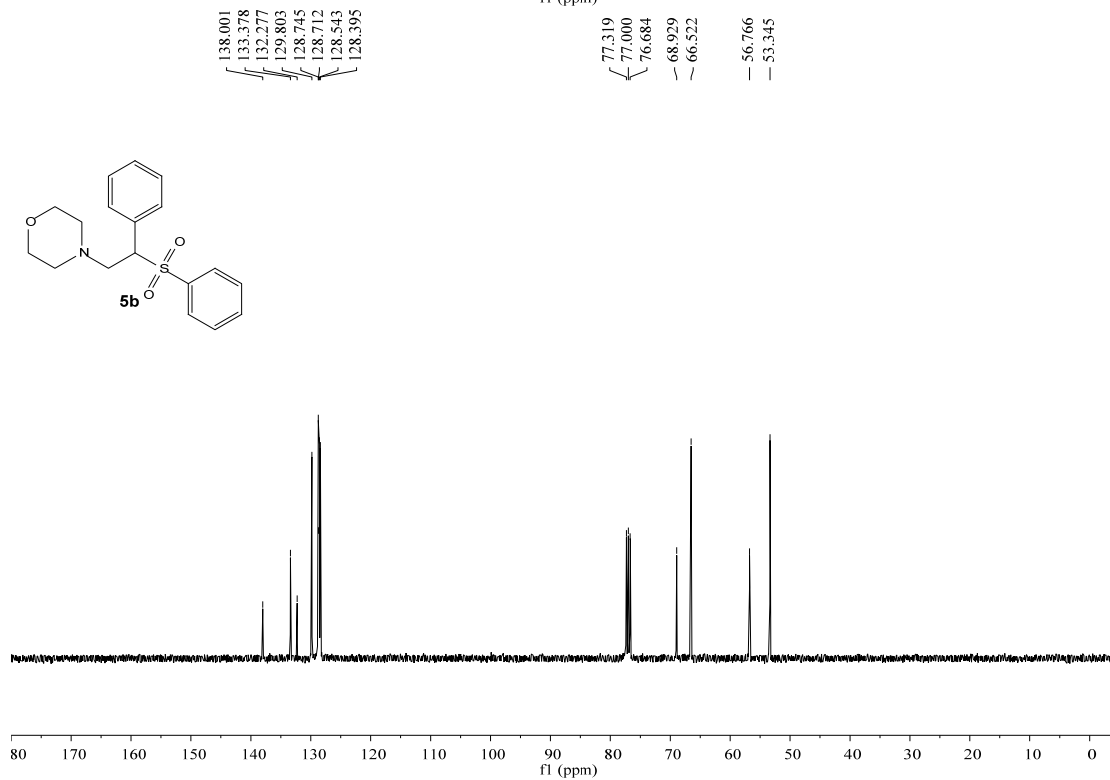
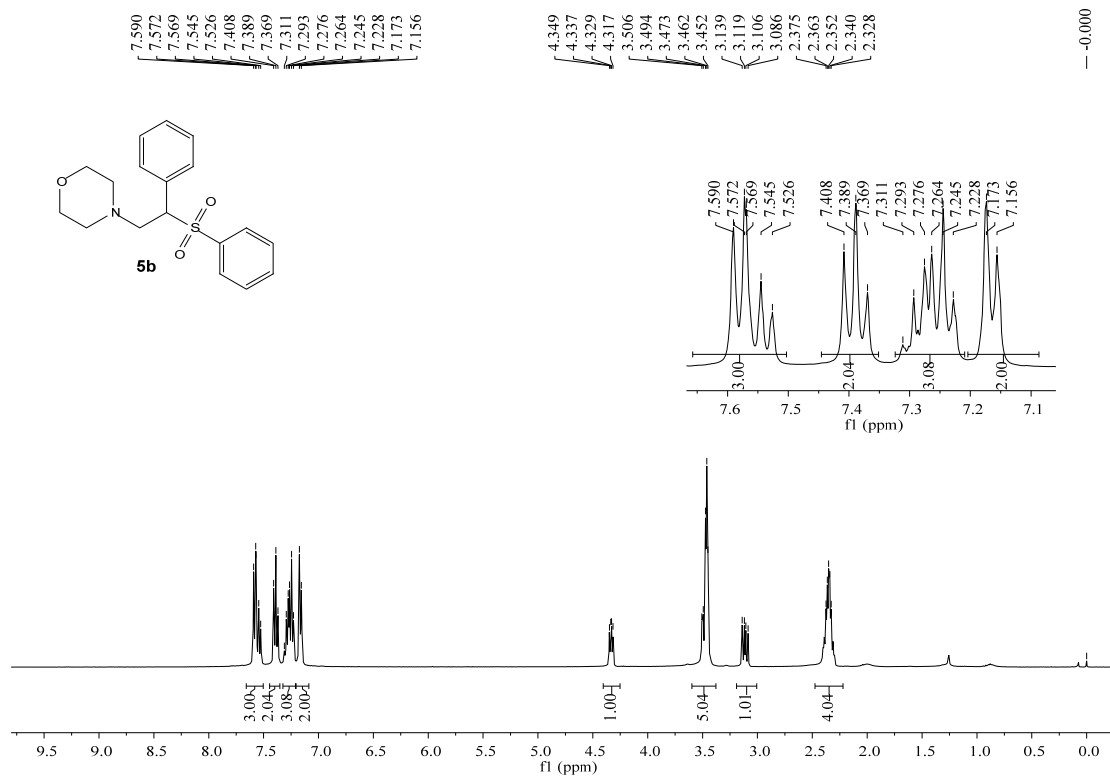


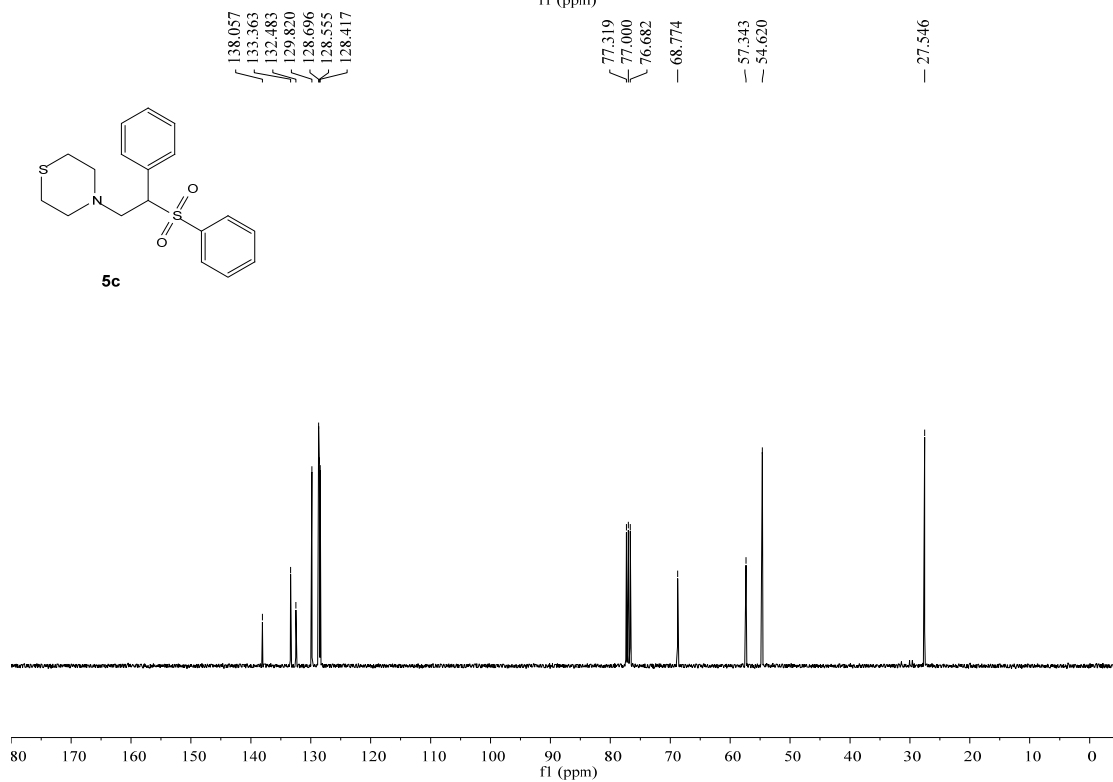
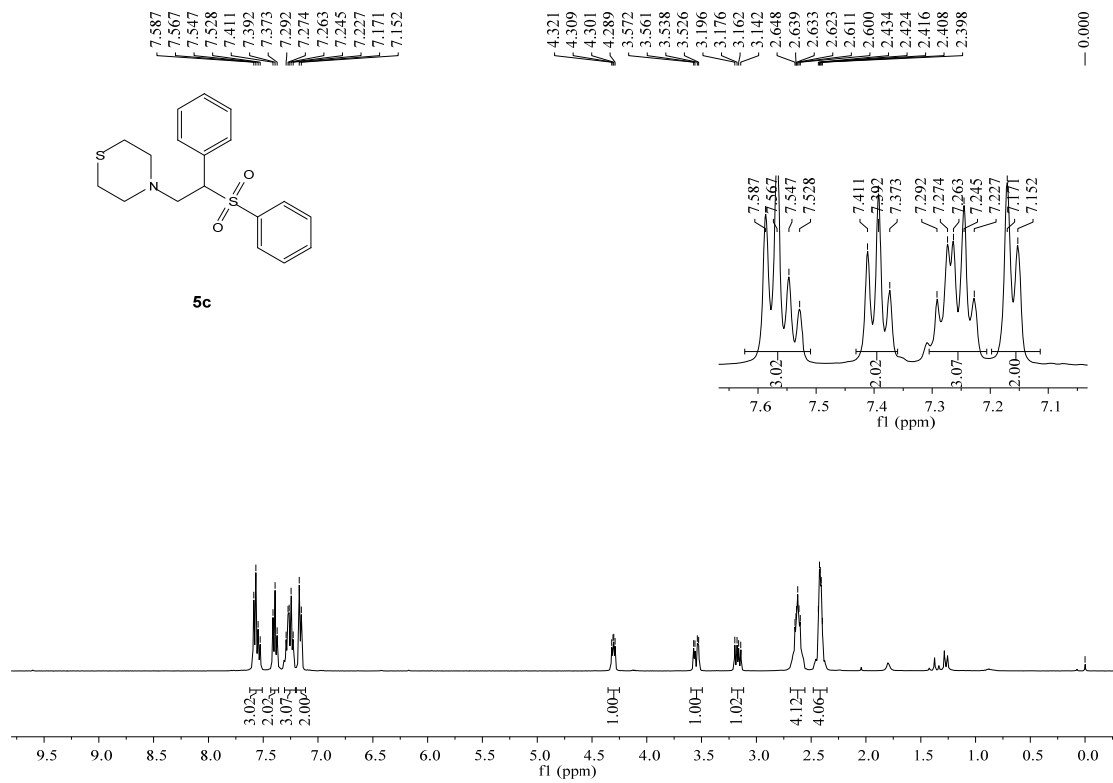


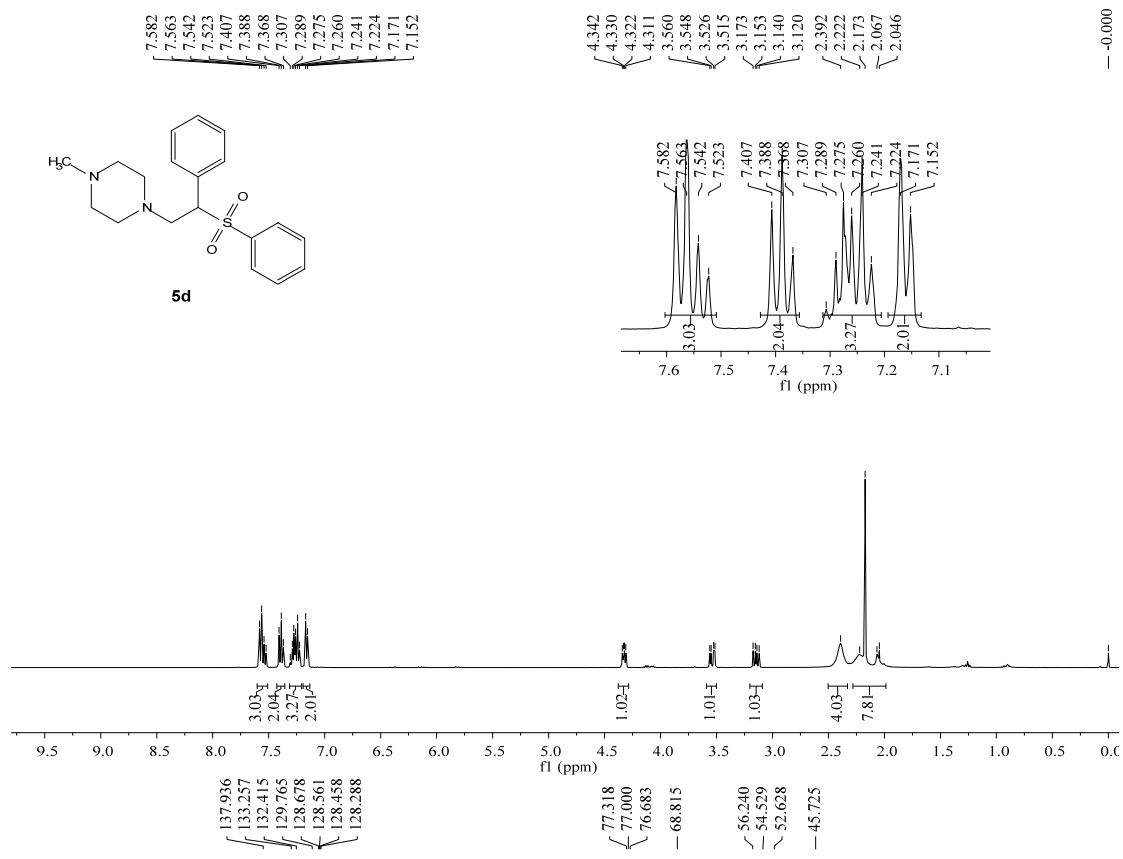




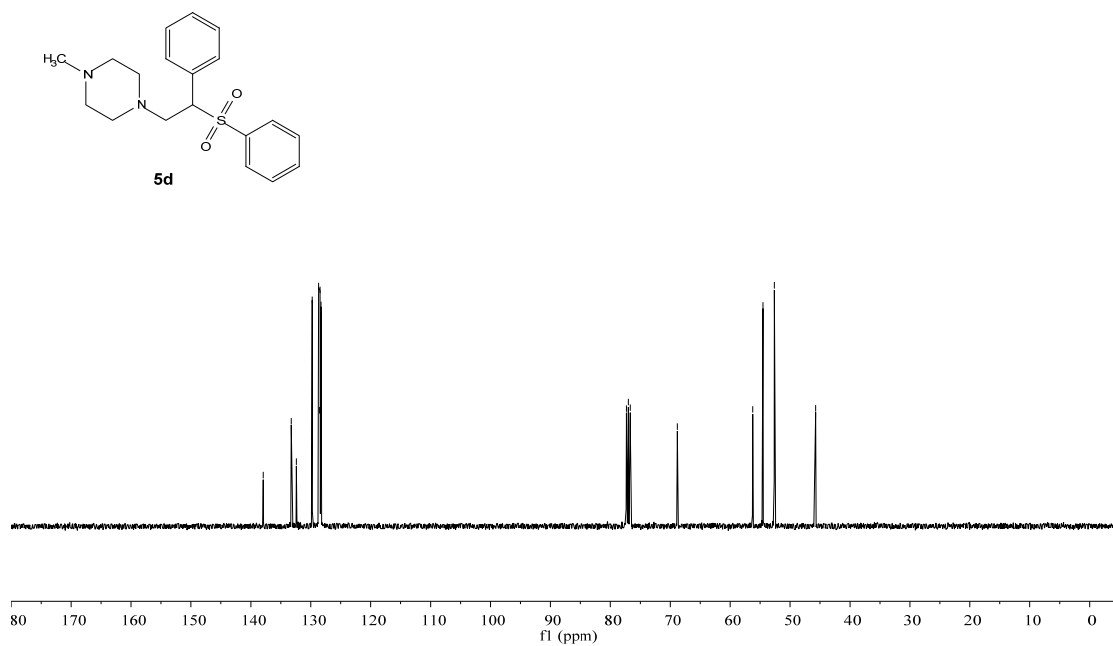








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