

Supplementary Information for

Base-catalyzed Stereoselective Thiosulfonylation of Yrones for Facile Synthesis of Thio-functionalized Vinyl Sulfones

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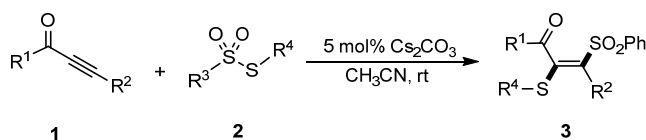
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1. General Information

Unless otherwise indicated, all reactions were conducted under air atmosphere in oven-dried glassware with magnetic stirring bar. All other chemicals were obtained from commercial supplies and used as received without any further purification. Column chromatograph was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F₂₅₄. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz, 100 MHz and 376 MHz, respectively). Melting points of the products were measured on a micro melting point apparatus (SGW X-4) and uncorrected. High-resolution mass spectra (HRMS) were obtained on an LTQ Orbitrap XL mass spectrometry equipped with an ESI source from Thermo Scientific at Keecloud Biotech in Shanghai. X-ray diffraction study for product **3aj** and **5j** were carried out on Bruker D8 VENTURE photon II diffractometer with I μ s 3.0 microfocus X-ray source using APEX III program.

2. General procedure for synthesis of products **3**



To an oven-dried 10 mL Schlenk tube equipped with a stir bar was added ynone **1** (0.6 mmol), thiosulfonate **2** (0.4 mmol), anhydrous Cs₂CO₃ (5 mol%) and 4.0 mL of CH₃CN. Then the reaction mixture was reacted at room temperature until thiosulfonate was consumed completely which was monitored by TLC. The solvent was evaporated, then the crude product was purified by column chromatography on silica gel (200~300 mesh) using ethyl acetate in petroleum ether (v/v = 20:1) as the eluent to afford the corresponding product **3** in moderate to excellent yields.

3. Single-crystal X-ray structure analysis **3aj**

Figure S1. Crystal structure of **3aj**

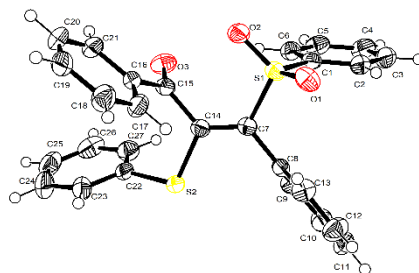


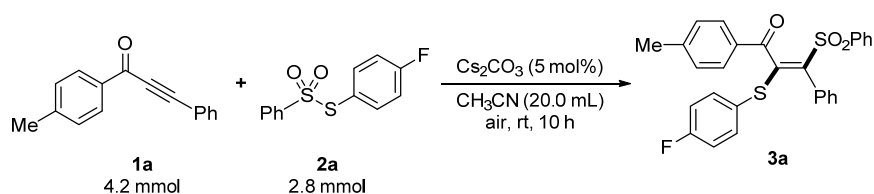
Table S1. Crystal data and structure refinement for **3aj**

Identification code	3aj	
Empirical formula	C ₂₇ H ₂₀ O ₃ S ₂	
Formula weight	456.55	
Temperature	173.0 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 8.5368(2) Å	α = 90°.
	b = 11.7485(3) Å	β = 90°.
	c = 22.2440(4) Å	γ = 90°.
Volume	2230.95(9) Å ³	
Z	4	
Density (calculated)	1.359 Mg/m ³	
Absorption coefficient	2.383 mm ⁻¹	
F (000)	952	
Crystal size	0.14 x 0.12 x 0.09 mm ³	
Theta range for data collection	4.256 to 72.127°.	
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 14, -27 ≤ l ≤ 27	
Reflections collected	49617	
Independent reflections	4400 [R(int) = 0.0638]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.6584	
Refinement method	Full-matrix least-squares on F ²	

Data / restraints / parameters	4400 / 0 / 289
Goodness-of-fit on F^2	1.049
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0286, wR2 = 0.0695
R indices (all data)	R1 = 0.0308, wR2 = 0.0711
Absolute structure parameter	0.041(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.167 and -0.260 e. \AA^{-3}

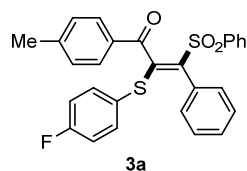
The CCDC number of product **3aj** is 2153291.

4. Gram-scale preparation of **3a**



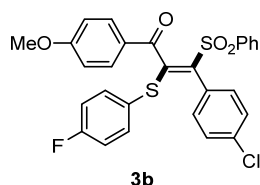
To an oven-dried 100 mL Schlenk tube equipped with a stir bar was added ynone **1a** (1.5 equiv, 4.2 mmol, 0.9244 g), thiosulfonate **2a** (1.0 equiv, 2.8 mmol, 0.7504 g), anhydrous Cs_2CO_3 (5 mol%, 45 mg) and 20.0 mL of CH_3CN . Then the reaction mixture was stirred at room temperature for 10 h. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel (200~300 mesh) using ethyl acetate in petroleum ether (v/v = 20:1) as the eluent to afford the corresponding product **3a** (95% yield, 1.31 g).

5. Characterization of products **3**

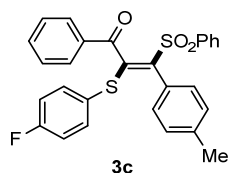


(E)-2-((4-fluorophenyl)thio)-3-phenyl-3-(phenylsulfonyl)-1-(p-tolyl)prop-2-en-1-one (3a): white solid, 191.3 mg, 98% yield; m.p. 118.7-119.5 °C; IR (cm^{-1}): 3062, 2924, 2855, 2359, 2341, 1897, 1673, 1605, 1582, 1489, 1446, 1408, 1320, 1235, 1177, 1150, 1086, 1065, 1015, 943, 838, 806, 736, 697; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.73

– 7.64 (m, 2H), 7.64 – 7.52 (m, 3H), 7.45 – 7.36 (m, 5H), 7.26 – 7.16 (m, 4H), 7.11 – 7.05 (m, 2H), 6.76 – 6.68 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.6, 163.8 (d, $J = 250.5$ Hz), 152.5, 144.8, 139.3 (d, $J = 8.9$ Hz), 139.0, 134.2, 133.5, 133.4, 131.3, 131.1, 129.8, 129.4, 129.3, 128.9, 128.9, 121.9 (d, $J = 3.3$ Hz), 115.9 (d, $J = 22.0$ Hz), 22.0; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.6; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{FO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 511.0808, found 511.0813.

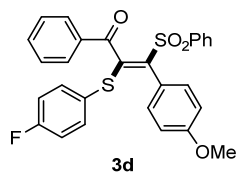


(*E*)-3-(4-chlorophenyl)-2-((4-fluorophenyl)thio)-1-(4-methoxyphenyl)-3-(phenylsulfonyl)prop-2-en-1-one (3b): yellow solid, 210.9 mg, 98% yield; m.p. 125.1-125.9 °C; IR (cm^{-1}): 3064, 2935, 2845, 1901, 1665, 1598, 1510, 1488, 1446, 1422, 1397, 1319, 1257, 1151, 1086, 1065, 1025, 937, 909, 833, 738, 706, 688; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 2H), 7.65 – 7.60 (m, 2H), 7.60 – 7.55 (m, 1H), 7.47 – 7.41 (m, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.23 – 7.13 (m, 2H), 7.12 – 7.05 (m, 2H), 6.88 (d, $J = 9.2$ Hz, 2H), 6.77 – 6.71 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.2, 164.1, 163.9 (d, $J = 250.8$ Hz), 153.3, 139.2 (d, $J = 8.8$ Hz), 138.9, 136.1, 133.7, 132.5, 131.9, 131.5, 129.7, 129.3, 129.0, 128.8, 121.7 (d, $J = 3.4$ Hz), 116.0 (d, $J = 22.0$ Hz), 114.0, 55.7; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.3; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{20}\text{ClFO}_4\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 561.0367; found 561.0368.



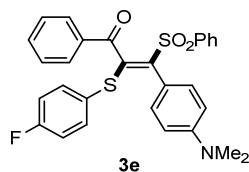
(*E*)-2-((4-fluorophenyl)thio)-1-phenyl-3-(phenylsulfonyl)-3-(p-tolyl)prop-2-en-1-one (3c): yellow solid, 191.3 mg, 98% yield; m.p. 145.0-145.8 °C; IR (cm^{-1}): 3063, 2923, 2863, 2360, 1901, 1680, 1590, 1489, 1448, 1399, 1320, 1236, 1151, 1085, 1063, 1022, 940, 838, 783, 752, 720, 688; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.73 (m, 2H), 7.65 – 7.59 (m, 2H), 7.59 – 7.50 (m, 2H), 7.46 – 7.37 (m, 4H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.17 – 7.02 (m, 4H), 6.74 – 6.67 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.1, 163.8 (d, $J = 250.6$ Hz), 152.2, 140.0, 139.3 (d, $J = 8.8$ Hz), 139.0, 136.5, 133.7, 133.7, 133.5, 130.9, 129.7, 129.2, 128.9, 128.6, 128.2, 121.9 (d, J

= 3.4 Hz), 115.9 (d, $J = 22.0$ Hz), 21.6; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.5; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{FO}_3\text{S}_2\text{Na}^+ [\text{M}+\text{Na}]^+$ 511.0808, found 511.0811.



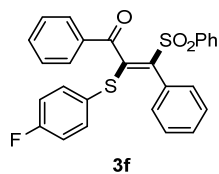
(E)-2-((4-fluorophenyl)thio)-3-(4-methoxyphenyl)-1-phenyl-3-

(phenylsulfonyl)prop-2-en-1-one (3d): yellow solid, 187.5 mg, 93% yield; m.p. 161.0-161.7 °C; IR (cm^{-1}): 3065, 2964, 2839, 1899, 1677, 1590, 1506, 1491, 1448, 1399, 1319, 1252, 1174, 1150, 1085, 1063, 1025, 947, 840, 816, 782, 755, 724, 688; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.73 (m, 2H), 7.62 – 7.58 (m, 2H), 7.58 – 7.49 (m, 2H), 7.46 – 7.37 (m, 4H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.10 – 7.03 (m, 2H), 6.95 – 6.89 (m, 2H), 6.75 – 6.66 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.1, 163.8 (d, $J = 250.6$ Hz), 160.7, 152.5, 139.3 (d, $J = 8.9$ Hz), 139.0, 136.5, 133.7, 133.6, 133.3, 132.5, 129.2, 128.9, 128.8, 128.6, 123.1, 121.9 (d, $J = 3.4$ Hz), 116.0 (d, $J = 22.0$ Hz), 114.4, 55.4; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.5; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{FO}_4\text{S}_2\text{Na}^+ [\text{M}+\text{Na}]^+$ 527.0757, found 527.0759.

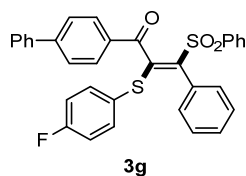


(E)-3-(4-(dimethylamino)phenyl)-2-((4-fluorophenyl)thio)-1-phenyl-3-

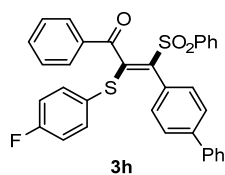
(phenylsulfonyl)prop-2-en-1-one (3e): yellow solid, 186.2 mg, 90% yield; m.p. 93.2-94.1 °C; IR (cm^{-1}): 3064, 2923, 2810, 1898, 1673, 1607, 1518, 1489, 1447, 1361, 1308, 1228, 1190, 1149, 1084, 1062, 1024, 950, 836, 753, 723, 688; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, $J = 7.6$ Hz, 2H), 7.63 – 7.58 (m, 2H), 7.54 – 7.46 (m, 2H), 7.42 – 7.34 (m, 4H), 7.14 – 7.02 (m, 4H), 6.72 – 6.63 (m, 4H), 2.96 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.1, 163.6 (d, $J = 250.3$ Hz), 151.6, 150.9, 139.2, 139.2 (d, $J = 8.7$ Hz), 136.5, 133.9, 133.5, 133.2, 131.8, 129.0, 128.7, 128.7, 128.4, 122.2 (d, $J = 3.4$ Hz), 117.5, 115.7 (d, $J = 22.0$ Hz), 111.7, 40.1; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.9; HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{24}\text{FNO}_3\text{S}_2\text{Na}^+ [\text{M}+\text{Na}]^+$ 540.1073, found 540.1077.



(E)-2-((4-fluorophenyl)thio)-1,3-diphenyl-3-(phenylsulfonyl)prop-2-en-1-one (3f): yellow solid, 183.9 mg, 97% yield; m.p. 110.6-111.5 °C; IR (cm⁻¹): 3065, 2926, 1904, 1809, 1678, 1589, 1489, 1447, 1399, 1318, 1236, 1149, 1085, 1063, 1023, 944, 836, 769, 698; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.75 (m, 2H), 7.62 – 7.58 (m, 2H), 7.58 – 7.50 (m, 2H), 7.46 – 7.38 (m, 7H), 7.24 (d, *J* = 6.0 Hz, 2H), 7.10 – 7.03 (m, 2H), 6.74 – 6.67 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.0, 163.8 (d, *J* = 250.7 Hz), 152.3, 139.3 (d, *J* = 8.9 Hz), 138.9, 136.5, 133.8, 133.7, 133.6, 131.2, 131.1, 129.8, 129.2, 129.0, 128.9, 128.9, 128.7, 121.8 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 22.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.4; HRMS (ESI) *m/z* calcd for C₂₇H₁₉FO₃S₂Na⁺ [M+Na]⁺ 497.0651, found 497.0652.

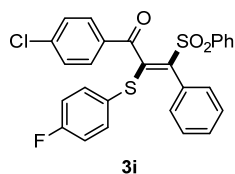


(E)-1-([1,1'-biphenyl]-4-yl)-2-((4-fluorophenyl)thio)-3-phenyl-3-(phenylsulfonyl)prop-2-en-1-one (3g): yellow solid, 206.8 mg, 94% yield; m.p. 150.7-151.5 °C; IR (cm⁻¹): 3329, 3062, 2926, 2855, 1898, 1809, 1672, 1603, 1489, 1447, 1405, 1320, 1235, 1178, 1085, 1067, 1007, 944, 831, 768, 741, 697; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.68 – 7.60 (m, 6H), 7.59 – 7.54 (m, 1H), 7.51 – 7.46 (m, 2H), 7.46 – 7.37 (m, 6H), 7.30 – 7.21 (m, 2H), 7.15 – 7.07 (m, 2H), 6.76 – 6.67 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.6, 163.9 (d, *J* = 250.7 Hz), 152.3, 146.4, 139.9, 139.3 (d, *J* = 8.9 Hz), 138.9, 135.3, 133.7, 133.6, 131.2, 131.1, 129.8, 129.7, 129.1, 129.0, 128.9, 128.9, 128.5, 127.4, 127.3, 121.8 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 22.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.3; HRMS (ESI) *m/z* calcd for C₃₃H₂₃FO₃S₂Na⁺ [M+Na]⁺ 573.0964, found 573.0967.



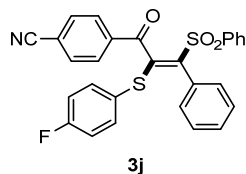
(E)-3-([1,1'-biphenyl]-4-yl)-2-((4-fluorophenyl)thio)-1-phenyl-3-

(phenylsulfonyl)prop-2-en-1-one (3h): white solid, 211.2 mg, 96% yield; m.p. 187.2-188.2 °C; IR (cm⁻¹): 3063, 1899, 1675, 1589, 1488, 1448, 1399, 1319, 1235, 1150, 1085, 1062, 1013, 942, 838, 771, 727, 688, 661; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.76 (m, 2H), 7.69 – 7.61 (m, 6H), 7.61 – 7.52 (m, 2H), 7.49 – 7.36 (m, 7H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.13 – 7.03 (m, 2H), 6.77 – 6.67 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.1, 163.8 (d, *J* = 250.9 Hz), 152.5, 142.5, 140.2, 139.3 (d, *J* = 8.9 Hz), 139.0, 136.5, 133.8, 133.6, 133.4, 131.5, 130.0, 129.2, 129.0, 129.0, 128.9, 128.7, 128.0, 127.6, 127.3, 121.8 (d, *J* = 3.3 Hz), 116.0 (d, *J* = 22.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.4; HRMS (ESI) *m/z* calcd for C₃₃H₂₃FO₃S₂Na⁺ [M+Na]⁺ 573.0964, found 573.0966.



(E)-1-(4-chlorophenyl)-2-((4-fluorophenyl)thio)-3-phenyl-3-

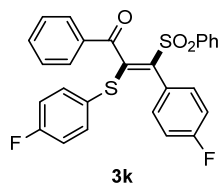
(phenylsulfonyl)prop-2-en-1-one (3i): white solid, 199.2 mg, 98% yield; m.p. 204.9-205.5 °C; IR (cm⁻¹): 3063, 2923, 2887, 1899, 1678, 1588, 1489, 1446, 1400, 1320, 1235, 1150, 1091, 1023, 943, 830, 805, 730, 697; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 2H), 7.62 – 7.55 (m, 3H), 7.47 – 7.37 (m, 7H), 7.26 – 7.17 (m, 2H), 7.12 – 7.05 (m, 2H), 6.80 – 6.72 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.9, 163.9 (d, *J* = 251.1 Hz), 151.6, 139.3 (d, *J* = 8.9 Hz), 138.7, 134.9, 134.1, 133.7, 131.0, 131.0, 130.4, 129.9, 129.1, 129.0, 128.9, 121.6 (d, *J* = 3.4 Hz), 116.2 (d, *J* = 22.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.0; HRMS (ESI) *m/z* calcd for C₂₇H₁₈ClFO₃S₂Na⁺ [M+Na]⁺ 531.0262, found 531.0266.



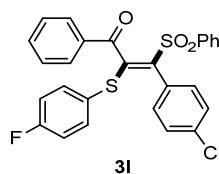
(E)-4-(2-((4-fluorophenyl)thio)-3-phenyl-3-(phenylsulfonyl)acryloyl)benzonitrile

(3j): white solid, 195.6 mg, 98% yield; m.p. 102.5-103.1 °C; IR (cm⁻¹): 3052, 2358, 1681, 1587, 1487, 1404, 1315, 1266, 1233, 1151, 1084, 1061, 1027, 952, 863, 750, 695; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.84 (m, 2H), 7.76 – 7.69 (m, 2H), 7.63 – 7.54 (m, 3H), 7.49 – 7.37 (m, 5H), 7.26 – 7.16 (m, 2H), 7.11 – 7.03 (m, 2H), 6.81 –

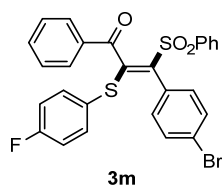
6.72 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.9, 164.0 (d, $J = 251.8$ Hz), 150.7, 139.3 (d, $J = 9.1$ Hz), 138.4, 135.0, 133.9, 132.5, 130.9, 130.6, 130.1, 129.3, 129.1, 129.1, 128.8, 121.3 (d, $J = 3.5$ Hz), 118.0, 116.8, 116.3 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.4; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{18}\text{FNO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 522.0604, found 522.0607.



(*E*)-3-(4-fluorophenyl)-2-((4-fluorophenyl)thio)-1-phenyl-3-(phenylsulfonyl)prop-2-en-1-one (3k): white solid, 181.1 mg, 92% yield; m.p. 146.6-147.5 °C; IR (cm^{-1}): 3066, 1899, 1676, 1589, 1503, 1488, 1448, 1399, 1320, 1226, 1151, 1085, 1063, 1024, 948, 863, 790, 756, 723, 688; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.73 (m, 2H), 7.62 – 7.51 (m, 4H), 7.47 – 7.38 (m, 4H), 7.26 – 7.17 (m, 2H), 7.14 – 7.03 (m, 4H), 6.75 – 6.68 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.9, 163.9 (d, $J = 251.0$ Hz), 163.5 (d, $J = 249.0$ Hz), 153.0, 139.3 (d, $J = 8.9$ Hz), 138.8, 136.4, 133.9, 133.7, 133.2 (d, $J = 8.4$ Hz), 132.6, 129.1, 129.0, 128.8, 128.7, 127.0 (d, $J = 3.2$ Hz), 121.5 (d, $J = 3.4$ Hz), 116.2 (d, $J = 21.6$ Hz), 116.0 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.2, -110.3; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{F}_2\text{O}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 515.0557, found 515.0558.

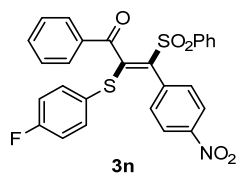


(*E*)-3-(4-chlorophenyl)-2-((4-fluorophenyl)thio)-1-phenyl-3-(phenylsulfonyl)prop-2-en-1-one (3l): yellow solid, 199.2 mg, 98% yield; m.p. 149.6-150.3 °C; IR (cm^{-1}): 3067, 2925, 1904, 1676, 1589, 1488, 1448, 1396, 1320, 1236, 1150, 1086, 1015, 940, 837, 799, 755, 722, 688; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, $J = 8.0$ Hz, 2H), 7.62 – 7.50 (m, 4H), 7.47 – 7.36 (m, 6H), 7.19 (d, $J = 7.2$ Hz, 2H), 7.10 – 7.02 (m, 2H), 6.76 – 6.67 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.8, 163.9 (d, $J = 251.0$ Hz), 153.0, 139.3 (d, $J = 8.9$ Hz), 138.7, 136.3, 136.2, 133.9, 133.8, 132.5, 132.5, 129.6, 129.4, 129.1, 129.1, 128.8, 128.7, 121.4 (d, $J = 3.5$ Hz), 116.0 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.1; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{ClFO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 531.0262, found 531.0265.

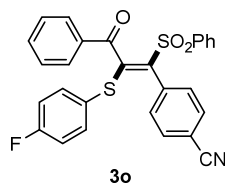


(E)-3-(4-bromophenyl)-2-((4-fluorophenyl)thio)-1-phenyl-3-

(phenylsulfonyl)prop-2-en-1-one (3m): yellow solid, 216.4 mg 98% yield; m.p. 102.4-103.2 °C; IR (cm⁻¹): 3064, 2923, 2851, 1900, 1676, 1589, 1489, 1448, 1391, 1320, 1257, 1236, 1151, 1085, 1064, 1017, 939, 837, 797, 754, 737, 688; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.71 (m, 2H), 7.63 – 7.49 (m, 6H), 7.47 – 7.36 (m, 4H), 7.20 – 7.09 (m, 2H), 7.08 – 7.01 (m, 2H), 6.75 – 6.67 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.9, 163.8 (d, *J* = 251.0 Hz), 153.0, 139.3 (d, *J* = 8.9 Hz), 138.7, 136.3, 133.9, 133.8, 132.7, 132.4, 132.3, 130.0, 129.1, 129.0, 128.8, 128.6, 124.5, 121.3 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 22.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.1; HRMS (ESI) *m/z* calcd for C₂₇H₁₈BrFO₃S₂Na⁺ [M+Na]⁺ 574.9757, found 574.9760.

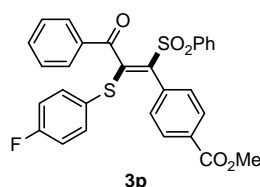


(E)-2-((4-fluorophenyl)thio)-3-(4-nitrophenyl)-1-phenyl-3-(phenylsulfonyl)prop-2-en-1-one (3n): yellow solid, 203.5 mg, 98% yield; m.p. 243.5-244.2 °C; IR (cm⁻¹): 3079, 1663, 1569, 1518, 1488, 1445, 1347, 1322, 1220, 1147, 1083, 942, 831, 759, 686, 580, 567, 448; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.30 – 8.23 (m, 2H), 7.79 – 7.73 (m, 2H), 7.64 – 7.59 (m, 3H), 7.58 – 7.53 (m, 1H), 7.50 – 7.40 (m, 6H), 7.10 – 7.02 (m, 2H), 6.76 – 6.70 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.5, 164.0 (d, *J* = 251.6 Hz), 153.8, 148.6, 139.3 (d, *J* = 8.9 Hz), 138.5, 137.9, 136.2, 134.1, 132.5, 131.7, 129.3, 129.1, 128.8, 128.8, 124.2, 123.0, 120.8 (d, *J* = 3.2 Hz), 116.2 (d, *J* = 22.1 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -108.6; HRMS (ESI) *m/z* calcd for C₂₇H₁₈FNO₅S₂Na⁺ [M+Na]⁺ 542.0502, found 542.0504.

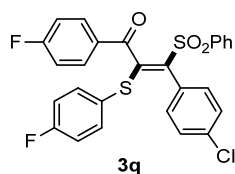


(E)-4-(2-((4-fluorophenyl)thio)-3-oxo-3-phenyl-1-(phenylsulfonyl)prop-1-en-1-yl)benzotrile (3o): white solid, 183.7 mg, 92% yield; m.p. 176.1-177.0 °C; IR (cm⁻¹)

¹): 3064, 2923, 2230, 1903, 1676, 1589, 1490, 1448, 1400, 1322, 1236, 1151, 1084, 1063, 1021, 943, 840, 726, 688; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.72 (m, 2H), 7.70 (m, *J* = 8.8 Hz, 2H), 7.64 – 7.57 (m, 3H), 7.57 – 7.52 (m, 1H), 7.50 – 7.34 (m, 6H), 7.10 – 7.01 (m, 2H), 6.77 – 6.69 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.5, 164.0 (d, *J* = 251.4 Hz), 153.6, 139.3 (d, *J* = 9.0 Hz), 138.5, 136.2, 136.0, 134.1, 134.0, 132.7, 132.1, 132.0, 129.2, 129.1, 128.8, 120.9 (d, *J* = 3.5 Hz), 118.3, 116.2 (d, *J* = 22.1 Hz), 113.6; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -108.7; HRMS (ESI) *m/z* calcd for C₂₈H₁₈FNO₃S₂Na⁺ [M+Na]⁺ 522.0604, found 522.0607.

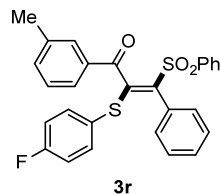


methyl (*E*)-4-(2-((4-fluorophenyl)thio)-3-oxo-3-phenyl-1-(phenylsulfonyl)prop-1-en-1-yl)benzoate (3p**):** white solid, 206.4 mg, 97% yield; m.p. 118.3-118.9 °C; IR (cm⁻¹): 3065, 2953, 2831, 1904, 1724, 1676, 1589, 1490, 1448, 1401, 1321, 1277, 1237, 1151, 1111, 1085, 1062, 1020, 944, 868, 835, 772, 736, 701, 682; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.82 – 7.74 (m, 2H), 7.62 – 7.57 (m, 2H), 7.57 – 7.48 (m, 2H), 7.46 – 7.29 (m, 6H), 7.10 – 7.01 (m, 2H), 6.75 – 6.66 (m, 2H), 3.91 (d, *J* = 1.6 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.7, 166.5, 163.8 (d, *J* = 251.0 Hz), 152.8, 139.3 (d, *J* = 8.9 Hz), 138.6, 136.3, 135.8, 133.9, 133.8, 132.8, 131.3, 131.2, 130.1, 129.1, 129.0, 128.8, 128.7, 121.3 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 22.1 Hz), 52.4; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.1; HRMS (ESI) *m/z* calcd for C₂₉H₂₁FO₅S₂Na⁺ [M+Na]⁺ 555.0706, found 555.0707.

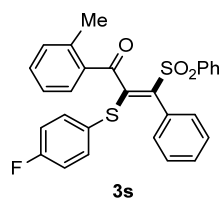


(*E*)-3-(4-chlorophenyl)-1-(4-fluorophenyl)-2-((4-fluorophenyl)thio)-3-(phenylsulfonyl)prop-2-en-1-one (3q**):** yellow solid, 204.1 mg, 97% yield; m.p. 141.4-142.1 °C; IR (cm⁻¹): 3068, 1678, 1598, 1488, 1444, 1413, 1320, 1241, 1152, 1086, 1015, 936, 834, 720, 689, 631, 583, 521, 450; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.74 (m, 2H), 7.64 – 7.56 (m, 3H), 7.49 – 7.42 (m, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.12 (m, 2H), 7.12 – 7.04 (m, 4H), 6.90 – 6.72 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.3, 166.0 (d, *J* = 255.0 Hz), 163.9 (d, *J* = 251.3 Hz), 152.6, 139.3

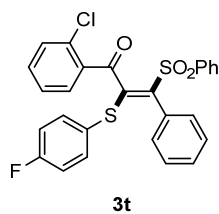
(d, $J = 8.9$ Hz), 138.6, 136.2, 133.8, 133.0, 132.9, 132.7, 132.5, 131.7 (d, $J = 9.6$ Hz), 129.4, 129.1, 128.8, 128.2 (d, $J = 2.0$ Hz), 121.3 (d, $J = 3.5$ Hz), 116.1 (d, $J = 22.3$ Hz), 115.9 (d, $J = 22.5$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.2, -108.8; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{17}\text{ClF}_2\text{O}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 549.0167, found 549.0169.



(*E*)-2-((4-fluorophenyl)thio)-3-phenyl-3-(phenylsulfonyl)-1-(*m*-tolyl)prop-2-en-1-one (3r): white solid, 183.5 mg, 94% yield; m.p. 110.5-111.1 °C; IR (cm^{-1}): 3063, 2924, 2860, 1899, 1673, 1587, 1488, 1446, 1399, 1319, 1264, 1233, 1149, 1085, 1030, 1000, 958, 878, 835, 786, 723, 699; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, $J = 7.2$ Hz, 1H), 7.61 – 7.53 (m, 3H), 7.51 (s, 1H), 7.46 – 7.37 (m, 5H), 7.35 – 7.28 (m, 2H), 7.27 – 7.19 (m, 2H), 7.10 – 7.03 (m, 2H), 6.75 – 6.68 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.1, 163.8 (d, $J = 250.6$ Hz), 152.5, 139.3 (d, $J = 8.9$ Hz), 138.9, 138.4, 136.5, 134.6, 133.6, 133.5, 131.2, 131.1, 129.8, 129.1, 128.9, 128.9, 128.5, 126.8, 121.8 (d, $J = 3.4$ Hz), 115.9 (d, $J = 22.0$ Hz), 21.4; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.6; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{FO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 511.0808, found 511.0811.



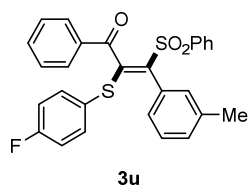
(*E*)-2-((4-fluorophenyl)thio)-3-phenyl-3-(phenylsulfonyl)-1-(*o*-tolyl)prop-2-en-1-one (3s): yellow solid, 191.3 mg, 98% yield; m.p. 164.3-165.1 °C; IR (cm^{-1}): 3063, 2971, 2929, 1674, 1590, 1448, 1402, 1318, 1235, 1151, 1084, 1050, 1030, 942, 837, 766, 736, 711, 691, 636, 578, 519, 485; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, $J = 7.2$ Hz, 1H), 7.63 – 7.58 (m, 2H), 7.58 – 7.53 (m, 1H), 7.44 – 7.32 (m, 7H), 7.25 – 7.18 (m, 2H), 7.10 (d, $J = 7.2$ Hz, 1H), 7.08 – 7.02 (m, 2H), 6.76 – 6.70 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.8, 163.8 (d, $J = 250.7$ Hz), 153.3, 141.2, 139.2 (d, $J = 8.8$ Hz), 139.0, 134.3, 133.5, 133.4, 133.0, 132.8, 132.2, 131.3, 131.1, 129.7, 128.9, 128.9, 125.9, 121.9 (d, $J = 3.4$ Hz), 115.9 (d, $J = 21.9$ Hz), 21.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.5; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{21}\text{FO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 511.0808, found 511.0812.



3t

(E)-1-(2-chlorophenyl)-2-((4-fluorophenyl)thio)-3-phenyl-3-

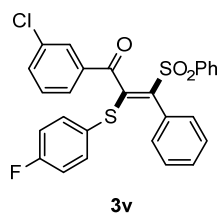
(phenylsulfonyl)prop-2-en-1-one (3t): yellow solid, 199.2 mg, 98% yield; m.p. 181.1-182.0 °C; IR (cm⁻¹): 3067, 2924, 2853, 2359, 2197, 1892, 1683, 1588, 1489, 1446, 1399, 1318, 1269, 1232, 1149, 1085, 1045, 944, 834, 765, 734, 697; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.4 Hz, 1H), 7.71–7.65 (m, 2H), 7.61–7.54 (m, 1H), 7.48–7.33 (m, 7H), 7.33–7.27 (m, 1H), 7.25–7.15 (m, 2H), 7.14–7.07 (m, 2H), 6.79–6.70 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 187.8, 163.9 (d, *J* = 250.7 Hz), 152.9, 138.9 (d, *J* = 8.8 Hz), 134.7, 133.9, 133.6, 133.5, 133.4, 133.3, 131.8, 131.2, 130.8, 129.8, 129.0, 128.9, 128.9, 126.8, 121.6 (d, *J* = 3.3 Hz), 116.2 (d, *J* = 22.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.4; HRMS (ESI) *m/z* calcd for C₂₇H₁₈ClFO₃S₂Na⁺ [M+Na]⁺ 531.0262, found 531.0263.



3u

(E)-2-((4-fluorophenyl)thio)-1-phenyl-3-(phenylsulfonyl)-3-(m-tolyl)prop-2-en-1-

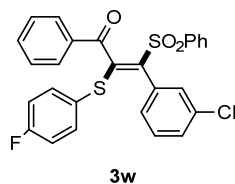
one (3u): yellow solid, 189.4 mg, 97% yield; m.p. 180.7-181.3 °C; IR (cm⁻¹): 3063, 2923, 2855, 1900, 1676, 1589, 1489, 1448, 1399, 1319, 1263, 1234, 1149, 1085, 1063, 1024, 1014, 966, 870, 838, 782, 736, 702, 688; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.63–7.49 (m, 4H), 7.46–7.36 (m, 4H), 7.29–7.21 (m, 2H), 7.13–7.02 (m, 3H), 6.96 (s, 1H), 6.75–6.64 (m, 2H), 2.35 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.1, 163.8 (d, *J* = 250.7 Hz), 152.1, 139.3 (d, *J* = 8.8 Hz), 138.9, 138.7, 136.5, 133.8, 133.7, 133.6, 131.5, 131.0, 130.6, 129.1, 128.9, 128.8, 128.7, 128.6, 128.0, 121.8 (d, *J* = 3.5 Hz), 115.9 (d, *J* = 22.0 Hz), 21.5; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.5; HRMS (ESI) *m/z* calcd for C₂₈H₂₁FO₃S₂Na⁺ [M+Na]⁺ 511.0808, found 511.0810.



3v

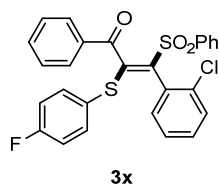
(E)-1-(3-chlorophenyl)-2-((4-fluorophenyl)thio)-3-phenyl-3-

(phenylsulfonyl)prop-2-en-1-one (3v): yellow solid, 197.1 mg, 97% yield; m.p. 118.3-118.9 °C; IR (cm⁻¹): 3066, 2924, 2853, 1899, 1681, 1589, 1490, 1446, 1426, 1321, 1236, 1150, 1085, 1062, 1032, 1014, 998, 957, 836, 790, 736, 699; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.65 (m, 2H), 7.62 – 7.54 (m, 3H), 7.53 – 7.48 (m, 1H), 7.47 – 7.34 (m, 6H), 7.26 – 7.17 (m, 2H), 7.13 – 7.05 (m, 2H), 6.80 – 6.73 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.9, 164.0 (d, *J* = 251.4 Hz), 151.4, 139.3 (d, *J* = 8.9 Hz), 138.7, 138.0, 135.0, 134.4, 133.8, 133.6, 131.0, 130.9, 130.0, 130.0, 129.0, 128.9, 128.8, 127.4, 121.5 (d, *J* = 3.4 Hz), 116.2 (d, *J* = 22.0 Hz), 100.1; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -108.9; HRMS (ESI) *m/z* calcd for C₂₇H₁₈ClFO₃S₂Na⁺ [M+Na]⁺ 531.0262, found 531.0264.



(E)-3-(3-chlorophenyl)-2-((4-fluorophenyl)thio)-1-phenyl-3-

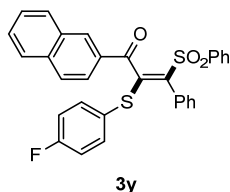
(phenylsulfonyl)prop-2-en-1-one (3w): yellow solid, 180.9 mg, 89% yield; m.p. 179.6-180.5 °C; IR (cm⁻¹): 3066, 1677, 1590, 1490, 1448, 1402, 1319, 1237, 1149, 1083, 1062, 1025, 963, 834, 726, 689, 635, 581, 519, 452; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.42 (m, 4H), 7.39 – 7.29 (m, 5H), 7.27 – 7.21 (m, 1H), 7.17 (s, 1H), 7.06 – 6.93 (m, 3H), 6.66 – 6.59 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.7, 163.8 (d, *J* = 251.1 Hz), 153.1, 139.3 (d, *J* = 8.9 Hz), 138.6, 136.2, 134.7, 133.9, 133.8, 132.8, 132.2, 131.0, 130.2, 130.0, 129.3, 129.0, 129.0, 128.8, 128.6, 121.3 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 22.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.1; HRMS (ESI) *m/z* calcd for C₂₇H₁₈ClFO₃S₂Na⁺ [M+Na]⁺ 531.0262, found 531.0264.



(E)-3-(2-chlorophenyl)-2-((4-fluorophenyl)thio)-1-phenyl-3-

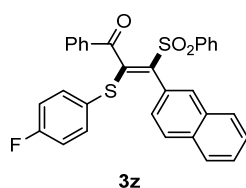
(phenylsulfonyl)prop-2-en-1-one (3x): white solid, 199.2 mg, 98% yield; m.p. 156.6-157.5 °C; IR (cm⁻¹): 3065, 1676, 1589, 1446, 1320, 1238, 1152, 1087, 1022, 944, 836, 771, 723, 689, 632, 576, 519, 455; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.78

(m, 2H), 7.65 – 7.35 (m, 10H), 7.31 – 7.22 (m, 1H), 7.14 – 7.03 (m, 2H), 7.02 – 6.83 (m, 1H), 6.78 – 6.64 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.7, 163.8 (d, $J = 250.8$ Hz), 154.6, 139.3 (d, $J = 8.9$ Hz), 138.7, 136.4, 135.8, 133.8, 132.0, 131.3, 130.2, 130.0, 129.2, 129.1, 129.0, 128.9, 128.5, 127.3, 121.2 (d, $J = 3.3$ Hz), 115.9 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.3; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{18}\text{ClFO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 531.0262, found 531.0263.



(E)-2-((4-fluorophenyl)thio)-1-(naphthalen-2-yl)-3-phenyl-3-

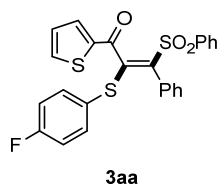
(phenylsulfonyl)prop-2-en-1-one (3y): white solid, 205.4 mg, 98% yield; m.p. 195.5-196.2 °C; IR (cm^{-1}): 3059, 2924, 2854, 2360, 1895, 1671, 1625, 1589, 1489, 1446, 1398, 1353, 1319, 1277, 1225, 1184, 1149, 1085, 1070, 1030, 966, 934, 868, 835, 817, 756, 721, 698; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.96 (d, $J = 7.6$ Hz, 1H), 7.89 – 7.77 (m, 3H), 7.65 – 7.53 (m, 5H), 7.48 – 7.36 (m, 5H), 7.30 (d, $J = 4.8$ Hz, 2H), 7.10 – 7.00 (m, 2H), 6.66 – 6.57 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.8, 163.8 (d, $J = 250.7$ Hz), 152.3, 139.2 (d, $J = 8.8$ Hz), 138.9, 136.0, 134.0, 133.9, 133.6, 132.5, 131.5, 131.3, 131.1, 130.0, 129.9, 129.0, 129.0, 128.9, 128.6, 128.0, 127.0, 124.1, 121.8 (d, $J = 3.4$ Hz), 116.0 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.4; HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{21}\text{FO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 547.0808, found 547.0811.



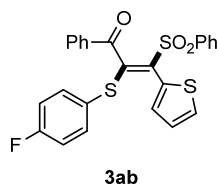
(E)-2-((4-fluorophenyl)thio)-3-(naphthalen-2-yl)-1-phenyl-3-

(phenylsulfonyl)prop-2-en-1-one (3z): yellow solid, 184.5 mg, 88% yield; m.p. 194.2-194.9 °C; IR (cm^{-1}): 3060, 2924, 2852, 1902, 1676, 1589, 1489, 1448, 1399, 1319, 1236, 1176, 1151, 1085, 1062, 1023, 977, 932, 898, 866, 836, 815, 784, 742, 688; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.71 (m, 6H), 7.62 – 7.58 (m, 2H), 7.56 – 7.47 (m, 4H), 7.44 – 7.27 (m, 5H), 7.10 – 7.00 (m, 2H), 6.74 – 6.64 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.0, 163.8 (d, $J = 250.7$ Hz), 152.6, 139.2 (d, $J = 8.9$ Hz), 138.9, 136.4, 133.8, 133.6, 133.5, 133.2, 131.2, 129.1, 128.9, 128.8, 128.7, 128.6,

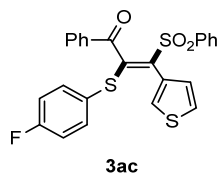
128.5, 128.4, 127.9, 127.7, 127.4, 126.6, 121.7 (d, $J = 3.4$ Hz), 115.9 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform- d) δ -109.4; HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{21}\text{FO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 547.0808, found 547.0811.



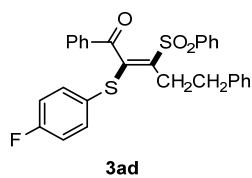
(E)-2-((4-fluorophenyl)thio)-3-phenyl-3-(phenylsulfonyl)-1-(thiophen-2-yl)prop-2-en-1-one (3aa): white solid, 186.3 mg, 97% yield; m.p. 163.3-163.9 °C; IR (cm^{-1}): 3064, 2922, 1898, 1654, 1589, 1514, 1489, 1446, 1410, 1354, 1320, 1265, 1233, 1150, 1085, 1063, 1026, 924, 833, 780, 734, 698; ^1H NMR (400 MHz, Chloroform- d) δ 7.74 (dd, $J = 4.0, 1.2$ Hz, 1H), 7.66 – 7.53 (m, 4H), 7.45 – 7.35 (m, 5H), 7.25 – 7.09 (m, 5H), 6.83 – 6.75 (m, 2H); ^{13}C NMR (100 MHz, Chloroform- d) δ 181.8, 163.9 (d, $J = 250.8$ Hz), 151.6, 144.0, 139.2 (d, $J = 8.9$ Hz), 138.8, 135.2, 134.6, 133.7, 133.6, 131.2, 131.0, 129.8, 128.9, 128.9, 128.2, 122.0 (d, $J = 3.5$ Hz), 116.1 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform- d) δ -109.3; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{17}\text{FO}_3\text{S}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 503.0216, found 503.0218.



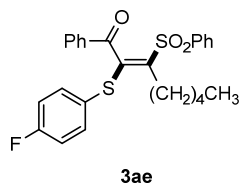
(E)-2-((4-fluorophenyl)thio)-1-phenyl-3-(phenylsulfonyl)-3-(thiophen-2-yl)prop-2-en-1-one (3ab): brown solid, 182.4 mg, 95% yield; m.p. 130.5-131.1 °C; IR (cm^{-1}): 3066, 2922, 1901, 1676, 1589, 1489, 1448, 1421, 1319, 1228, 1149, 1085, 1060, 1023, 911, 834, 786, 752, 719, 687; ^1H NMR (400 MHz, Chloroform- d) δ 7.77 – 7.71 (m, 2H), 7.69 – 7.64 (m, 2H), 7.60 – 7.50 (m, 3H), 7.47 – 7.37 (m, 4H), 7.14 – 7.05 (m, 4H), 6.76 – 6.68 (m, 2H); ^{13}C NMR (100 MHz, Chloroform- d) δ 189.7, 163.9 (d, $J = 250.9$ Hz), 155.8, 139.3 (d, $J = 8.9$ Hz), 138.6, 136.4, 133.8, 133.7, 132.0, 130.3, 129.8, 129.1, 129.0, 128.8, 128.7, 127.4, 127.1, 121.5 (d, $J = 3.4$ Hz), 116.0 (d, $J = 22.1$ Hz); ^{19}F NMR (376 MHz, Chloroform- d) δ -109.2; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{17}\text{FO}_3\text{S}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 503.0216, found 503.0218.



(E)-2-((4-fluorophenyl)thio)-1-phenyl-3-(phenylsulfonyl)-3-(thiophen-3-yl)prop-2-en-1-one (3ac): brown solid, 180.5 mg, 94% yield; m.p. 132.3-133.2 °C; IR (cm⁻¹): 3102, 2985, 2922, 1902, 1676, 1589, 1489, 1448, 1400, 1318, 1236, 1149, 1084, 1062, 1024, 981, 890, 836, 781, 736, 687; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.72 (m, 2H), 7.64 – 7.58 (m, 2H), 7.58 – 7.48 (m, 2H), 7.45 – 7.34 (m, 6H), 7.12 – 7.04 (m, 3H), 6.75 – 6.67 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.9, 163.8 (d, *J* = 250.7 Hz), 152.8, 139.3 (d, *J* = 8.9 Hz), 139.1, 136.4, 133.7, 133.6, 133.6, 130.3, 129.1, 129.0, 128.9, 128.9, 128.6, 126.2, 126.2, 121.6 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 22.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.3; HRMS (ESI) *m/z* calcd for C₂₅H₁₇FO₃S₃Na⁺ [M+Na]⁺ 503.0216, found 503.0217.

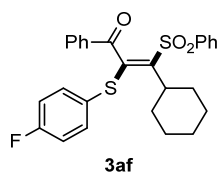


(E)-2-((4-fluorophenyl)thio)-1,5-diphenyl-3-(phenylsulfonyl)pent-2-en-1-one (3ad): white solid, 188.8 mg, 94% yield; m.p. 104.3-105.2 °C; IR (cm⁻¹): 3063, 3028, 2925, 2856, 1900, 1671, 1589, 1489, 1448, 1399, 1309, 1236, 1176, 1146, 1098, 1056, 1024, 986, 869, 833, 738, 688; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.67 – 7.45 (m, 6H), 7.37 – 7.21 (m, 7H), 7.11 – 7.00 (m, 2H), 6.80 – 6.66 (m, 2H), 3.16 – 2.66 (m, 4H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.2, 163.8 (d, *J* = 250.8 Hz), 150.4, 140.6, 139.4, 139.1 (d, *J* = 8.9 Hz), 136.3, 133.7, 133.5, 132.9, 129.3, 129.1, 128.7, 128.6, 128.5, 128.4, 126.5, 121.3 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 22.1 Hz), 33.6, 32.4; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.2; HRMS (ESI) *m/z* calcd for C₂₉H₂₄FO₃S₂⁺ [M+H]⁺ 503.1149, found 503.1139.

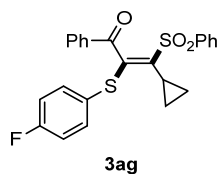


(E)-2-((4-fluorophenyl)thio)-1-phenyl-3-(phenylsulfonyl)oct-2-en-1-one (3ae): yellow solid, 179.8 mg, 96% yield; m.p. 67.7-68.7 °C; IR (cm⁻¹): 3066, 2957, 2931,

2861, 1901, 1673, 1590, 1489, 1448, 1399, 1310, 1235, 1155, 1086, 1046, 1023, 936, 833, 744, 688; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.92 (m, 2H), 7.72 – 7.64 (m, 2H), 7.63 – 7.58 (m, 1H), 7.57 – 7.51 (m, 2H), 7.51 – 7.46 (m, 1H), 7.39 – 7.32 (m, 2H), 7.15 – 7.05 (m, 2H), 6.81 – 6.71 (m, 2H), 2.65 – 2.39 (m, 2H), 1.86 – 1.50 (m, 2H), 1.41 – 1.31 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.3, 163.8 (d, $J = 250.6$ Hz), 149.3, 139.5, 139.1 (d, $J = 8.8$ Hz), 136.5, 134.3, 133.6, 133.5, 129.3, 129.1, 128.5, 128.5, 121.6 (d, $J = 3.4$ Hz), 116.0 (d, $J = 22.1$ Hz), 32.0, 30.2, 27.2, 22.2, 14.1; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.4; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{25}\text{FO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 491.1121, found 491.1122.

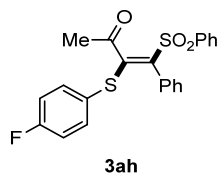


(*E*)-3-cyclohexyl-2-((4-fluorophenyl)thio)-1-phenyl-3-(phenylsulfonyl)prop-2-en-1-one (3af): white solid, 186.3 mg, 97% yield; m.p. 143.7-144.3 °C; IR (cm^{-1}): 3065, 2933, 2856, 1901, 1737, 1674, 1590, 1490, 1449, 1399, 1373, 1308, 1234, 1155, 1085, 1046, 1023, 983, 931, 873, 834, 752, 689; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.96 (m, 2H), 7.68 – 7.62 (m, 2H), 7.61 – 7.51 (m, 3H), 7.50 – 7.44 (m, 1H), 7.33 (t, $J = 7.2$ Hz, 2H), 7.13 – 7.03 (m, 2H), 6.81 – 6.73 (m, 2H), 2.88 – 2.72 (m, 1H), 2.29 – 2.14 (m, 1H), 2.04 – 1.92 (m, 1H), 1.85 – 1.52 (m, 5H), 1.28 – 1.18 (m, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.9, 163.7 (d, $J = 250.6$ Hz), 149.5, 140.6, 139.1 (d, $J = 8.8$ Hz), 137.9, 136.7, 133.3, 133.3, 129.1, 129.0, 128.4, 128.3, 122.1 (d, $J = 3.4$ Hz), 116.0 (d, $J = 22.0$ Hz), 42.0, 29.4, 26.9, 25.6; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.5; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{FO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 503.1121, found 503.1123.

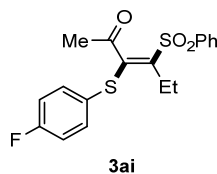


(*E*)-3-cyclopropyl-2-((4-fluorophenyl)thio)-1-phenyl-3-(phenylsulfonyl)prop-2-en-1-one (3ag): white solid, 157.7 mg, 90% yield; m.p. 70.8-71.5 °C; IR (cm^{-1}): 3065, 3012, 2925, 1902, 1673, 1589, 1489, 1448, 1399, 1308, 1236, 1157, 1086, 1023, 913, 880, 836, 753, 688; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, $J = 7.6$ Hz, 2H), 7.66 – 7.42 (m, 6H), 7.39 – 7.28 (m, 2H), 7.18 – 6.97 (m, 2H), 6.84 – 6.61 (m, 2H), 1.48 –

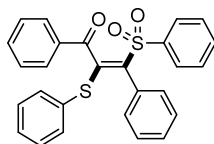
1.34 (m, 1H), 1.26 (s, 1H), 0.94 (s, 2H), 0.79 (s, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.8, 163.7 (d, $J = 250.5$ Hz), 154.2, 140.5, 139.3 (d, $J = 8.8$ Hz), 136.5, 133.4, 131.5, 129.1, 129.0, 128.4, 128.2, 121.9 (d, $J = 3.4$ Hz), 115.8 (d, $J = 22.0$ Hz), 10.5, 8.5, 7.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.6; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{19}\text{FO}_3\text{S}_2\text{Na}^+ [\text{M}+\text{Na}]^+$ 461.0651, found 461.0655.



(*E*)-3-((4-fluorophenyl)thio)-4-phenyl-4-(phenylsulfonyl)but-3-en-2-one (3ah): yellow solid, 150.0 mg, 91% yield; m.p. 174.5-175.5 °C; IR (cm^{-1}): 3064, 1907, 1707, 1588, 1489, 1446, 1352, 1318, 1225, 1187, 1149, 1085, 988, 960, 835, 802, 757, 717, 697; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.54 (m, 3H), 7.47 – 7.30 (m, 7H), 7.15 – 6.95 (m, 4H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.3, 164.0 (d, $J = 251.1$ Hz), 153.8, 138.8, 138.5 (d, $J = 8.8$ Hz), 133.7, 132.5, 130.9, 130.8, 129.7, 129.0, 128.8, 128.7, 122.7 (d, $J = 3.4$ Hz), 116.8 (d, $J = 22.0$ Hz), 32.1; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.9; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{17}\text{FO}_3\text{S}_2\text{Na}^+ [\text{M}+\text{Na}]^+$ 435.0495, found 435.0496.

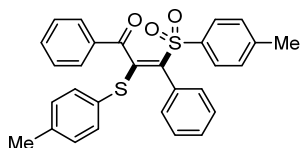


(*E*)-3-((4-fluorophenyl)thio)-4-(phenylsulfonyl)hex-3-en-2-one (3ai): yellow solid, 135.4 mg, 93% yield; m.p. 109.3-110.3 °C; IR (cm^{-1}): 3068, 2975, 2936, 2877, 1904, 1705, 1590, 1490, 1447, 1400, 1352, 1308, 1230, 1195, 1158, 1131, 1082, 1014, 978, 947, 836, 742, 688; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.89 (m, 2H), 7.66 – 7.60 (m, 1H), 7.59 – 7.53 (m, 2H), 7.49 – 7.40 (m, 2H), 7.10 – 7.03 (m, 2H), 2.46 (q, $J = 7.2$ Hz, 2H), 2.19 (s, 3H), 1.10 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.5, 163.9 (d, $J = 250.7$ Hz), 150.7, 139.5, 138.0 (d, $J = 8.8$ Hz), 134.3, 133.7, 129.4, 128.4, 122.6 (d, $J = 3.4$ Hz), 116.8 (d, $J = 22.1$ Hz), 31.7, 23.4, 12.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.1; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{FO}_3\text{S}_2\text{Na}^+ [\text{M}+\text{Na}]^+$ 387.0495, found 387.0499.



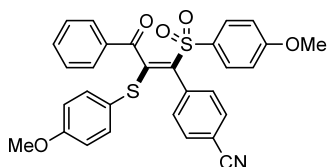
3aj

(E)-1,3-diphenyl-3-(phenylsulfonyl)-2-(phenylthio)prop-2-en-1-one (3aj): yellow solid, 178.8 mg, 98% yield; m.p. 111.7-112.5 °C; IR (cm⁻¹): 3061, 2926, 1901, 1676, 1581, 1474, 1447, 1319, 1252, 1215, 1149, 1086, 1062, 1024, 1001, 945, 848, 815, 750, 721, 698; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.72 (m, 2H), 7.64 – 7.59 (m, 2H), 7.59 – 7.54 (m, 1H), 7.53 – 7.48 (m, 1H), 7.46 – 7.34 (m, 7H), 7.28 – 7.21 (m, 2H), 7.20 – 7.14 (m, 1H), 7.11 – 7.16 (m, 2H), 7.04 – 6.98 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.0, 152.7, 139.0, 137.2, 136.5, 133.6, 133.5, 133.5, 131.4, 131.2, 130.1, 129.8, 129.2, 128.9, 128.9, 128.7, 128.5, 126.5; HRMS (ESI) m/z calcd for C₂₇H₂₀O₃S₂Na⁺ [M+Na]⁺ 479.0746, found 479.0745.



3ak

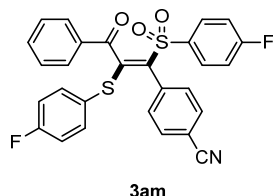
(E)-1,3-diphenyl-2-(p-tolylthio)-3-tosylprop-2-en-1-one (3ak): yellow solid, 189.8 mg, 98% yield; m.p. 158.0-158.9 °C; IR (cm⁻¹): 3061, 2926, 2866, 1896, 1675, 1595, 1492, 1446, 1399, 1318, 1246, 1216, 1148, 1088, 1016, 944, 817, 769, 740, 697, 638, 595, 574, 506, 429; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.66 (m, 2H), 7.42 – 7.36 (m, 3H), 7.33 – 7.24 (m, 5H), 7.16 (d, *J* = 10.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 7.6 Hz, 2H), 2.28 (s, 3H), 2.08 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.0, 152.4, 144.4, 140.3, 136.9, 136.5, 136.0, 133.3, 131.4, 131.0, 129.5, 129.4, 129.4, 129.0, 128.7, 128.3, 122.8, 21.6, 21.2; HRMS (ESI) m/z calcd for C₂₉H₂₄O₃S₂Na⁺ [M+Na]⁺ 507.1059, found 507.1061.



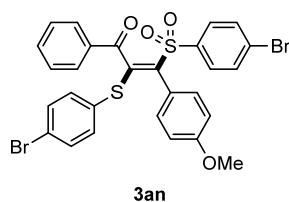
3al

(E)-4-(1-((4-methoxyphenyl)sulfonyl)-2-((4-methoxyphenyl)thio)-3-oxo-3-phenylprop-1-en-1-yl)benzotrile (3al): yellow solid, 199.1 mg, 92% yield; m.p. 175.7-176.2 °C; IR (cm⁻¹): 3060, 2943, 2842, 2230, 1902, 1679, 1592, 1495, 1449, 1408, 1321, 1301, 1254, 1175, 1146, 1087, 1064, 1025, 945, 861, 837, 800, 773, 736, 689;

^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.73 (m, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.54 – 7.47 (m, 3H), 7.45 – 7.34 (m, 4H), 6.99 – 6.92 (m, 2H), 6.692 – 6.85 (m, 2H), 6.56 – 6.48 (m, 2H), 3.82 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.9, 163.8, 161.2, 153.4, 138.6, 136.4, 136.3, 133.6, 132.5, 132.0, 131.7, 130.9, 130.1, 129.0, 128.5, 118.3, 115.8, 114.4, 114.3, 113.3, 55.7, 55.3; HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{NO}_5\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 564.0909, found 564.0911.

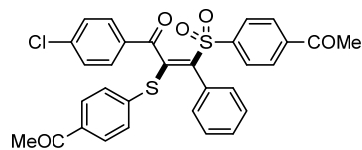


(*E*)-4-(1-((4-fluorophenyl)sulfonyl)-2-((4-fluorophenyl)thio)-3-oxo-3-phenylprop-1-en-1-yl)benzotrile (3am): yellow solid, 200.6 mg, 97% yield; m.p. 216.2-216.9 °C; IR (cm^{-1}): 3095, 3066, 2234, 1900, 1658, 1587, 1487, 1449, 1399, 1328, 1232, 1145, 1082, 1007, 944, 836, 723, 685, 643, 577, 522, 489; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.69 (m, 4H), 7.65 – 7.59 (m, 2H), 7.58 – 7.53 (m, 1H), 7.47 – 7.35 (m, 4H), 7.18 – 7.11 (m, 2H), 7.08 – 7.01 (m, 2H), 6.77 – 6.69 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.7, 165.9 (d, $J = 255.8$ Hz), 164.0 (d, $J = 251.6$ Hz), 154.1, 139.3 (d, $J = 8.9$ Hz), 136.1, 135.8, 134.6 (d, $J = 3.0$ Hz), 134.1, 132.8, 132.1, 131.6 (d, $J = 9.4$ Hz), 129.1, 128.8, 120.8 (d, $J = 3.4$ Hz), 118.2, 116.5 (d, $J = 22.5$ Hz), 116.2 (d, $J = 22.2$ Hz), 113.9; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.6, -108.5; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{17}\text{F}_2\text{NO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 540.0510, found 540.0512.



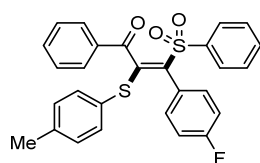
(*E*)-3-((4-bromophenyl)sulfonyl)-2-((4-bromophenyl)thio)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (3an): yellow solid, 241.4 mg, 94% yield; m.p. 165.8-166.4 °C; IR (cm^{-1}): 3062, 2928, 2835, 1675, 1604, 1575, 1504, 1470, 1386, 1320, 1252, 1148, 1068, 1010, 947, 821, 783, 737, 687, 599, 578, 486, 411; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.71 (m, 2H), 7.59 – 7.55 (m, 2H), 7.55 – 7.51 (m, 1H), 7.47 – 7.42 (m, 2H), 7.42 – 7.37 (m, 2H), 7.22 – 7.16 (m, 2H), 7.16 – 7.12 (m, 2H), 6.97 – 6.90 (m, 4H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.0, 160.9, 152.7, 138.5, 138.2, 136.3, 133.9, 133.2, 132.5, 132.3, 132.0, 130.4, 129.2, 128.9, 128.7, 125.6,

125.3, 122.7, 114.6, 55.4; HRMS (ESI) m/z calcd for $C_{28}H_{20}Br_2O_4S_2Na^+$ $[M+Na]^+$ 666.9042, found 666.9041.



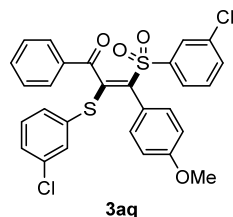
3ao

(E)-3-((4-acetylphenyl)sulfonyl)-2-((4-acetylphenyl)thio)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (3ao): white solid, 222.7 mg, 97% yield; m.p. 182.3-182.9 °C; IR (cm^{-1}): 3062, 2922, 2360, 2342, 1734, 1685, 1587, 1487, 1423, 1397, 1358, 1323, 1259, 1152, 1088, 1064, 1013, 958, 826, 697; 1H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.97 (m, 2H), 7.74 – 7.68 (m, 4H), 7.67 – 7.62 (m, 2H), 7.48 – 7.36 (m, 5H), 7.26 – 7.18 (m, 4H), 2.65 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 197.0, 188.4, 151.9, 142.5, 140.8, 140.5, 137.9, 136.8, 134.7, 134.5, 132.3, 131.0, 130.6, 130.5, 130.2, 129.2, 129.2, 129.1, 128.7, 128.5, 27.1, 26.8; HRMS (ESI) m/z calcd for $C_{31}H_{23}ClO_5S_2Na^+$ $[M+Na]^+$ 597.0567, found 597.0568.

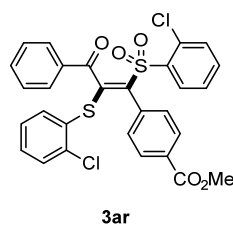


3ap

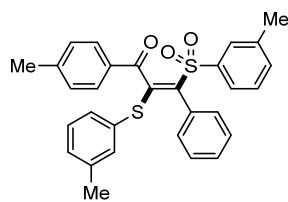
(E)-3-(4-fluorophenyl)-1-phenyl-3-(phenylsulfonyl)-2-(p-tolylthio)prop-2-en-1-one (3ap): yellow solid, 191.3 mg, 98% yield; m.p. 137.9-168.5 °C; IR (cm^{-1}): 3067, 2925, 1904, 1676, 1589, 1488, 1448, 1396, 1320, 1236, 1150, 1086, 1015, 940, 837, 799, 755, 722, 688; 1H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.72 (m, 2H), 7.62 – 7.57 (m, 2H), 7.57 – 7.52 (m, 1H), 7.52 – 7.46 (t(m), 1H), 7.44 – 7.33 (m, 4H), 7.28 – 7.18 (m, 2H), 7.12 – 7.05 (m, 2H), 6.94 (d, $J = 8.0$ Hz, 2H), 6.80 (d, $J = 7.6$ Hz, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.9, 163.4 (d, $J = 248.7$ Hz), 153.9, 140.6, 138.8, 137.0, 136.4, 133.6, 133.5, 133.2 (d, $J = 8.5$ Hz), 131.9, 129.5, 129.1, 128.9, 128.7, 128.4, 127.2 (d, $J = 3.3$ Hz), 122.5, 116.0 (d, $J = 21.6$ Hz), 21.2; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.6; HRMS (ESI) m/z calcd for $C_{28}H_{21}FO_3S_2Na^+$ $[M+Na]^+$ 511.0808, found 511.0811.



(E)-3-((3-chlorophenyl)sulfonyl)-2-((3-chlorophenyl)thio)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (3aq): yellow solid, 206.1 mg, 93% yield; m.p. 143.1-143.8 °C; IR (cm⁻¹): 3064, 2932, 2839, 1902, 1676, 1605, 1571, 1506, 1461, 1402, 1323, 1294, 1252, 1219, 1174, 1152, 1110, 1082, 1062, 1026, 947, 885, 855, 778, 736, 680; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.72 (m, 2H), 7.57 – 7.47 (m, 4H), 7.43 – 7.34 (m, 3H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.16 – 7.12 (m, 1H), 7.05 – 7.01 (m, 2H), 7.01 – 6.97 (m, 1H), 6.97 – 6.94 (m, 2H), 3.84 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.6, 160.9, 152.9, 140.7, 136.8, 136.2, 135.3, 135.1, 134.2, 133.9, 133.7, 133.1, 132.5, 130.4, 130.2, 129.8, 129.1, 128.7, 128.2, 127.0, 122.5, 114.5, 55.4; HRMS (ESI) *m/z* calcd for C₂₈H₂₀Cl₂O₄S₂Na⁺ [M+Na]⁺ 577.0072, found 577.0076.

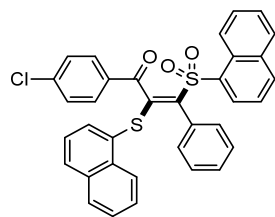


methyl (E)-4-(1-((2-chlorophenyl)sulfonyl)-2-((2-chlorophenyl)thio)-3-oxo-3-phenylprop-1-en-1-yl)benzoate (3ar): yellow solid, 221.2 mg, 95% yield; m.p. 105.3-106.0 °C; IR (cm⁻¹): 3062, 2921, 1723, 1676, 1576, 1489, 1448, 1398, 1321, 1276, 1151, 1108, 1061, 1039, 992, 939, 866, 758, 701; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.88 – 7.84 (m, 2H), 7.71 – 7.67 (m, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.42 – 7.34 (m, 4H), 7.20 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.18 – 7.10 (m, 3H), 6.99 – 6.93 (m, 1H), 3.87 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 187.9, 166.3, 150.7, 140.5, 139.0, 135.7, 135.5, 135.4, 134.9, 133.7, 133.5, 133.3, 132.0, 131.9, 131.5, 131.2, 130.4, 130.0, 129.9, 129.0, 128.4, 127.0, 127.0, 125.7, 52.3; HRMS (ESI) *m/z* calcd for C₂₉H₂₀Cl₂O₅S₂Na⁺ [M+Na]⁺ 605.0021, found 605.0026.



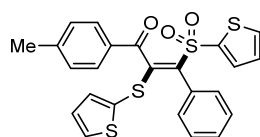
3as

(E)-3-phenyl-1-(p-tolyl)-3-(m-tolylsulfonyl)-2-(m-tolylthio)prop-2-en-1-one (3as): white solid, 185.3 mg, 93% yield; m.p. 157.8-158.7 °C; IR (cm⁻¹): 3055, 2921, 2856, 1895, 1674, 1604, 1571, 1475, 1443, 1408, 1320, 1255, 1215, 1176, 1145, 1084, 1063, 998, 942, 868, 784, 735, 699; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.33 (m, 6H), 7.32 – 7.28 (m, 1H), 7.28 – 7.26 (m, 1H), 7.24 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.92 (m, 3H), 6.84 (s, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 2.05 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.6, 152.8, 144.3, 139.0, 139.0, 138.5, 138.0, 134.5, 134.2, 134.2, 133.1, 131.6, 131.2, 130.8, 129.6, 129.4, 129.2, 129.2, 128.8, 128.7, 128.6, 126.3, 126.1, 21.9, 21.4, 20.9; HRMS (ESI) *m/z* calcd for C₃₀H₂₆O₃S₂Na⁺ [M+Na]⁺ 521.1215, found 521.1217.



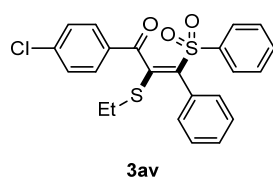
3at

(E)-3-(naphthalen-1-ylsulfonyl)-2-(naphthalen-1-ylthio)-1,3-diphenylprop-2-en-1-one (3at): white solid, 218.0 mg, 98% yield; m.p. 257.0-257.8 °C; IR (cm⁻¹): 3052, 1671, 1584, 1502, 1485, 1442, 1399, 1300, 1252, 1213, 1153, 1118, 1062, 1010, 946, 803, 769, 699, 631, 583, 505, 427; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 8.4 Hz, 1H), 8.03 – 7.98 (m, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.77 (m, 2H), 7.69 – 7.47 (m, 6H), 7.42 – 7.34 (m, 3H), 7.33 – 7.00 (m, 10H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.9, 150.7, 139.6, 138.1, 135.4, 135.4, 135.3, 134.4, 133.8, 133.8, 133.3, 131.8, 131.7, 131.3, 130.5, 130.2, 129.7, 129.4, 128.9, 128.8, 128.6, 128.5, 127.3, 127.0, 126.6, 125.9, 125.2, 124.7, 124.2, 123.9; HRMS (ESI) *m/z* calcd for C₃₅H₂₃O₃ClS₂Na⁺ [M+Na]⁺ 613.0669, found 613.0670.

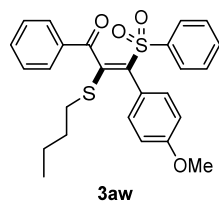


3au

(E)-3-phenyl-3-(thiophen-2-ylsulfonyl)-2-(thiophen-2-ylthio)-1-(p-tolyl)prop-2-en-1-one (3au): yellow solid, 183.2 mg, 95% yield; m.p. 197.9-198.5 °C; IR (cm⁻¹): 3097, 2929, 2849, 1903, 1677, 1606, 1506, 1449, 1400, 1322, 1252, 1222, 1174, 1147, 1085, 1062, 1015, 946, 849, 781, 703, 688; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.80 (m, 2H), 7.61 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.33 (m, 1H), 7.29 – 7.22 (m, 3H), 7.02 (dd, *J* = 4.8, 4.0 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.80 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.74 – 6.69 (m, 1H), 3.85 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.6, 160.9, 152.2, 140.1, 140.1, 136.4, 135.1, 134.6, 133.9, 133.7, 133.7, 132.5, 129.2, 128.6, 127.8, 127.5, 123.2, 122.6, 114.5, 55.4; HRMS (ESI) *m/z* calcd for C₂₄H₁₈O₄S₄Na⁺ [M+Na]⁺ 520.9980, found 520.9983.

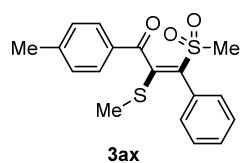


(E)-1-(4-chlorophenyl)-2-(ethylthio)-3-phenyl-3-(phenylsulfonyl)prop-2-en-1-one (3av): yellow solid, 171.5 mg, 97% yield; mp: 139.0-139.7 °C; IR (cm⁻¹): 3062, 2972, 2937, 2877, 1677, 1583, 1488, 1445, 1402, 1307, 1247, 1148, 1088, 1010, 942, 808, 731, 688, 602, 581, 538, 478; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.07 (m, 2H), 7.57 – 7.50 (m, 5H), 7.40 – 7.31 (m, 5H), 7.10 (d, *J* = 6.8 Hz, 2H), 2.62 – 2.51 (m, 1H), 2.39 – 2.28 (m, 1H), 1.02 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.3, 150.8, 140.5, 138.7, 134.6, 134.5, 133.5, 131.2, 130.9, 130.5, 129.6, 129.5, 128.8, 128.7, 128.6, 26.4, 13.7; HRMS (ESI) *m/z* calcd for C₂₃H₁₉ClO₃S₂Na⁺ [M+Na]⁺ 465.0356, found 465.0358.



(E)-2-(butylthio)-3-(4-methoxyphenyl)-1-phenyl-3-(phenylsulfonyl)prop-2-en-1-one (3aw): yellow solid, 177.1 mg, 95% yield; m.p. 146.2-147.0 °C; IR (cm⁻¹): 2957, 2929, 2870, 1675, 1606, 1505, 1447, 1308, 1250, 1174, 1148, 1086, 1025, 953, 862, 755, 723, 688; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.12 (m, 2H), 7.67 – 7.61 (m, 1H), 7.58 – 7.47 (m, 5H), 7.39 – 7.32 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 9.2 Hz, 2H), 3.78 (s, 3H), 2.60 – 2.51 (m, 1H), 2.36 – 2.26 (m, 1H), 1.39 – 1.25 (m, 2H), 1.20 – 1.09 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-

d) δ 190.6, 160.4, 151.7, 139.0, 136.2, 134.1, 133.6, 133.3, 132.4, 129.1, 129.0, 128.7, 128.6, 123.4, 114.2, 55.2, 31.6, 30.6, 21.6, 13.4; HRMS (ESI) m/z calcd for $C_{26}H_{26}O_4S_2Na^+$ $[M+Na]^+$ 489.1164, found 489.1167.

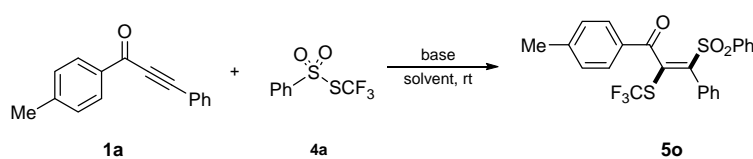


(E)-3-(methylsulfonyl)-2-(methylthio)-3-phenyl-1-(p-tolyl)prop-2-en-1-one (3ax): white solid, 123.2 mg, 89% yield; m.p. 166.2-166.9 °C; IR (cm^{-1}): 3062, 2925, 2851, 1672, 1603, 1573, 1490, 1432, 1308, 1253, 1218, 1177, 1138, 1077, 1030, 964, 811, 780, 739, 699; 1H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, $J = 8.4$ Hz, 2H), 7.58 – 7.46 (m, 5H), 7.34 (d, $J = 8.0$ Hz, 2H), 2.81 (s, 3H), 2.44 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.1, 153.1, 145.5, 133.8, 133.2, 131.8, 130.7, 130.0, 129.4, 129.2, 42.1, 22.0, 14.9; HRMS (ESI) m/z calcd for $C_{18}H_{18}O_3S_2Na^+$ $[M+Na]^+$ 369.0589, found 369.0593.

6. Optimization of reaction conditions for the synthesis of product 5a

The study commenced with the reaction of ynone **1a** and thiosulfonate **4a**. However, with 10 mol% Cs_2CO_3 as catalyst, no desired product was obtained (Table S2, entry 1). Increasing the amount of Cs_2CO_3 cannot promote the reaction (Table S2, entry 2). When DBU was used for the reaction, the desired product was isolated in 14% yield (Table S2, entry 3). Other common bases, such as triethylamine, DIPEA, DABCO, DBN and $tBuOK$, cannot catalyze the reaction (Table S2, entries 4-8). Interestingly, K_3PO_4 catalyzed the reaction to give **5o** in 18% yield (Table S2, entry 9). The subsequent evaluation of reaction media revealed that dimethyl carbonate give the desired product in 30% yield (Table S2, entries 10-18). Increasing the amount of K_3PO_4 to 0.8 equiv. can improve the reaction yield to 77% (Table S2, entries 19 and 20). However, further increasing K_3PO_4 did not give a better yield (Table S2, entry 21).

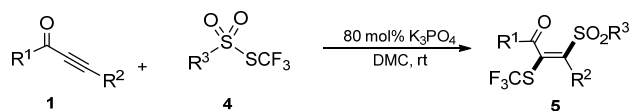
Table S2. Optimization of reaction conditions ^a



entry	base	solvent	E/Z ^c	yield (%) ^b
1	10 mol% Cs ₂ CO ₃	CH ₃ CN	/	trace
2	50 mol% Cs ₂ CO ₃	CH ₃ CN	/	trace
3	10 mol% DBU	CH ₃ CN	>25:1	14
4	10 mol% Et ₃ N	CH ₃ CN	/	trace
5	10 mol% DIPEA	CH ₃ CN	/	trace
6	10 mol% DABCO	CH ₃ CN	/	trace
7	10 mol% DBN	CH ₃ CN	/	trace
8	10 mol% ^t BuOK	CH ₃ CN	/	trace
9	10 mol% K ₃ PO ₄	CH ₃ CN	>25:1	18
10	10 mol% K ₃ PO ₄	toluene	/	trace
11	10 mol% K ₃ PO ₄	MeOH	>25:1	27
12	10 mol% K ₃ PO ₄	DCM	/	trace
13	10 mol% K ₃ PO ₄	THF	/	trace
14	10 mol% K ₃ PO ₄	DMF	/	trace
15	10 mol% K ₃ PO ₄	DMSO	/	trace
16	10 mol% K ₃ PO ₄	1,4-dioxane	>25:1	21
17	10 mol% K ₃ PO ₄	DMC	>25:1	30
18	10 mol% K ₃ PO ₄	EtOAc	>25:1	22
19	50 mol% K ₃ PO ₄	DMC	>25:1	67
20	80 mol% K ₃ PO ₄	DMC	>25:1	77
21	100 mol% K ₃ PO ₄	DMC	>25:1	75

^a Reaction conditions: **1a** (0.15 mmol), **4a** (0.1 mmol), solvent (1.0 mL), 24 h, rt; ^b Isolated yield; ^c Ratio of *E/Z* isomers was determined by ¹H NMR analysis of the crude products.

7. General procedure for synthesis of products **5**



To an oven-dried 10 mL Schlenk tube equipped with a stir bar was added ynone **1** (0.15 mmol), thiosulfonate **4** (0.1 mmol), anhydrous K₃PO₄ (80 mol%) and 0.5 mL of

dimethyl carbonate. Then the reaction mixture was stirred at room temperature until **4** was consumed completely which was monitored by TLC. The solvent was evaporated, then the crude product was purified by column chromatography on silica gel (200~300 mesh) using ethyl acetate in petroleum ether (v/v = 20:1) as the eluent to afford the corresponding product **5**.

8. Single-crystal X-ray structure analysis **5j**

Figure S2. Crystal structure of **5j**

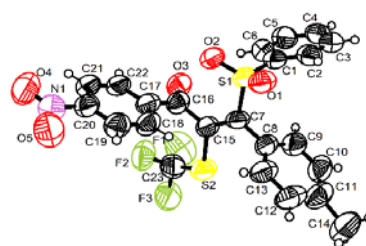


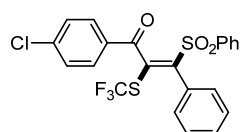
Table S3. Crystal data and structure refinement for **5j**

Identification code	5j	
Empirical formula	C ₂₃ H ₁₆ F ₃ NO ₅ S ₂	
Formula weight	507.49	
Temperature	296.15 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3165(7) Å	α = 82.618(5)°.
	b = 11.1602(9) Å	β = 70.573(4)°.
	c = 11.5520(7) Å	γ = 63.536(5)°.
Volume	1122.57(15) Å ³	
Z	2	
Density (calculated)	1.501 Mg/m ³	
Absorption coefficient	2.709 mm ⁻¹	
F (000)	520	

Crystal size	0.14 x 0.12 x 0.11 mm ³
Theta range for data collection	4.059 to 67.495°.
Index ranges	-11 ≤ h ≤ 12, -11 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected	11762
Independent reflections	3993 [R(int) = 0.0747]
Completeness to theta = 67.495°	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7536 and 0.5013
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3993 / 0 / 295
Goodness-of-fit on F ²	1.111
Final R indices [I > 2σ(I)]	R1 = 0.0896, wR2 = 0.2649
R indices (all data)	R1 = 0.1432, wR2 = 0.3307
Extinction coefficient	n/a
Largest diff. peak and hole	0.717 and -0.422 e.Å ⁻³

The CCDC number of product **5j** is 2195981.

9. Characterization of products 5

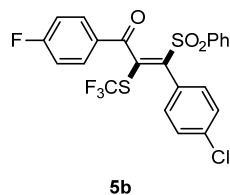


5a

(E)-1-(4-chlorophenyl)-3-phenyl-3-(phenylsulfonyl)-2-

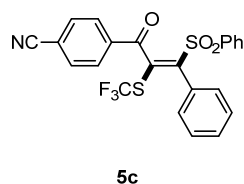
((trifluoromethyl)thio)prop-2-en-1-one (5a): white solid, 42.0 mg, 87% yield; m.p. 128.4-129.1 °C; IR (cm⁻¹): 3060, 2927, 2854, 1683, 1587, 1487, 1444, 1402, 1323, 1248, 1153, 1105, 1084, 1010, 936, 803, 756, 692, 581, 533, 443; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.63 – 7.53 (m, 5H), 7.47 – 7.31 (m, 5H), 7.24 – 6.82 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.0, 146.8, 140.8, 137.7, 137.2, 134.5, 133.7, 130.9, 130.5, 130.3, 129.5, 129.3, 129.2, 128.9, 127.4 (q, *J* = 311.0

Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.6; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{14}\text{ClF}_3\text{O}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 504.9917, found 504.9912.



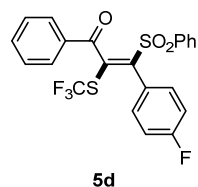
(E)-3-(4-chlorophenyl)-1-(4-fluorophenyl)-3-(phenylsulfonyl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5b): yellow solid, 47.6 mg, 95% yield; m.p. 94.3-95.1 °C; IR (cm^{-1}): 3066, 2926, 2854, 1909, 1682, 1599, 1485, 1449, 1413, 1325, 1243, 1155, 1103, 1015, 933, 835, 758, 721, 685, 582, 520, 442; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.03 (m, 2H), 7.66 – 7.54 (m, 3H), 7.50 – 7.42 (m, 2H), 7.34 (d, $J = 7.6$ Hz, 2H), 7.29 – 7.22 (m, 2H), 7.17 – 6.82 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.4, 166.5 (d, $J = 255.0$ Hz), 145.8, 138.4, 137.0 (d, $J = 7.0$ Hz), 134.7, 132.3, 132.2, 131.7, 131.6 (d, $J = 3.0$ Hz), 129.3, 129.3, 128.7, 127.3 (q, $J = 310.0$ Hz), 116.4 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.6, -102.6. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{13}\text{ClF}_4\text{O}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 522.9823, found 522.9818.



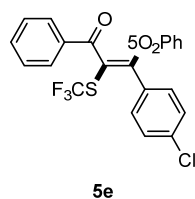
(E)-4-(3-phenyl-3-(phenylsulfonyl)-2-((trifluoromethyl)thio)acryloyl)benzonitrile

(5c): white solid, 44.9 mg, 93% yield; m.p. 175.9-176.6 °C; IR (cm^{-1}): 3065, 2929, 2855, 2232, 1687, 1580, 1444, 1405, 1323, 1244, 1152, 1108, 1084, 1015, 938, 806, 758, 699, 578, 519, 446; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, $J = 8.0$ Hz, 2H), 7.90 (d, $J = 8.4$ Hz, 2H), 7.65 – 7.60 (m, 1H), 7.58 – 7.51 (m, 2H), 7.50 – 7.42 (m, 3H), 7.41 – 7.32 (m, 2H), 7.24 – 6.88 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.9, 147.9, 138.2, 136.8, 136.7, 134.7, 132.9, 130.6, 130.2, 130.0, 129.8, 129.30, 129.29, 129.0, 127.5 (q, $J = 310.0$ Hz), 118.0, 117.4; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.5; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{14}\text{F}_3\text{NO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 496.0259, found 496.0253.



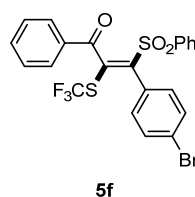
(E)-3-(4-fluorophenyl)-1-phenyl-3-(phenylsulfonyl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5d): white solid, 43.4 mg, 93% yield; m.p. 94.9-95.7 °C; IR (cm⁻¹): 3067, 2924, 2850, 1685, 1601, 1506, 1448, 1327, 1232, 1158, 1106, 1084, 1021, 936, 847, 794, 752, 721, 684, 584, 541, 520, 436; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.2 Hz, 1H), 7.71 – 7.53 (m, 3H), 7.49 – 7.40 (m, 1H), 7.22 – 6.90 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.9, 163.8 (d, *J* = 250.0 Hz), 145.6, 138.9, 137.2, 135.1, 134.5, 134.4, 132.6 (d, *J* = 8.0 Hz), 129.6, 129.3, 129.2, 129.0, 127.4 (q, *J* = 311.0 Hz), 126.4 (d, *J* = 4.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.6, -109.0; HRMS (ESI) *m/z* calcd for C₂₂H₁₄F₄O₃S₂Na⁺ [M+Na]⁺ 489.0212, found 489.0205.



(E)-3-(4-chlorophenyl)-1-phenyl-3-(phenylsulfonyl)-2-

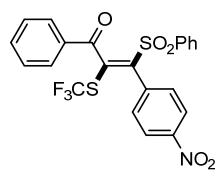
((trifluoromethyl)thio)prop-2-en-1-one (5e): yellow solid, 45.9 mg, 95% yield; m.p. 97.2-98.1 °C; IR (cm⁻¹): 3070, 2924, 2851, 1683, 1595, 1488, 1449, 1395, 1327, 1240, 1152, 1108, 1084, 1060, 1015, 938, 850, 753, 714, 684, 582, 524, 441; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.71 – 7.54 (m, 6H), 7.49 – 7.41 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.23 – 6.85 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.8, 145.6, 138.8, 137.1, 136.9, 135.0, 134.6, 134.4, 131.8, 129.6, 129.3, 129.3, 129.0, 128.9, 127.4 (q, *J* = 311.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.6; HRMS (ESI) *m/z* calcd for C₂₂H₁₄ClF₃O₃S₂Na⁺ [M+Na]⁺ 504.9917, found 504.9912.



(E)-3-(4-bromophenyl)-1-phenyl-3-(phenylsulfonyl)-2-

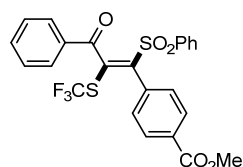
((trifluoromethyl)thio)prop-2-en-1-one (5f): yellow solid, 50.1 mg, 95% yield; m.p. 99.4-100.1 °C; IR (cm⁻¹): 3391, 3066, 2926, 2852, 1682, 1597, 1482, 1447, 1392, 1327, 1238, 1157, 1103, 1083, 1013, 938, 848, 753, 688, 583, 523; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.71 – 7.65 (m, 1H), 7.65 – 7.56 (m, 5H), 7.54 – 7.42 (m, 4H), 7.16 – 6.72 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.8, 145.7, 138.8, 137.1, 135.0, 134.6, 134.4, 132.3, 132.0, 129.6, 129.4, 129.32, 129.30, 129.1, 127.4 (q, *J* = 311.0 Hz), 125.2; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.6;

HRMS (ESI) m/z calcd for $C_{22}H_{14}BrF_3O_3S_2Na^+$ $[M+Na]^+$ 548.9412, found 548.9405.



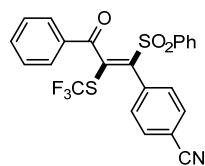
5g

(E)-3-(4-nitrophenyl)-1-phenyl-3-(phenylsulfonyl)-2-((trifluoromethyl)thio)prop-2-en-1-one (5g): yellow solid, 46.9 mg, 95% yield; m.p. 144.3-145.1 °C; IR (cm^{-1}): 3438, 3071, 2921, 2854, 1685, 1597, 1525, 1447, 1351, 1240, 1153, 1104, 1081, 1018, 940, 863, 757, 694, 583, 535; 1H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, $J = 6.4$ Hz, 2H), 8.01 (d, $J = 7.2$ Hz, 2H), 7.69 – 7.48 (m, 7H), 7.45 – 7.39 (m, 2H), 7.19 (s, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.6, 148.9, 145.5, 139.2, 137.0, 136.8, 135.0, 134.7, 134.6, 131.8, 129.6, 129.5, 129.3, 129.1, 127.2 (q, $J = 311.0$ Hz), 124.0; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.5; HRMS (ESI) m/z calcd for $C_{22}H_{14}F_3NO_5S_2Na^+$ $[M+Na]^+$ 516.0157, found 516.0155.



5h

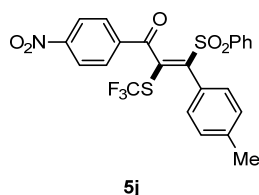
methyl (E)-4-(3-oxo-3-phenyl-1-(phenylsulfonyl)-2-((trifluoromethyl)thio)prop-1-en-1-yl)benzoate (5h): white solid, 48.1 mg, 95% yield; m.p. 119.1-120.0 °C; IR (cm^{-1}): 3064, 2952, 2850, 1724, 1681, 1585, 1451, 1403, 1328, 1279, 1156, 1108, 1081, 1022, 942, 867, 824, 776, 749, 700, 582, 529; 1H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, $J = 8.0$ Hz, 2H), 7.95 (d, $J = 6.4$ Hz, 2H), 7.64 – 7.57 (m, 1H), 7.57 – 7.45 (m, 5H), 7.40 – 7.32 (m, 2H), 7.29 – 6.79 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.8, 166.2, 146.2, 138.5, 137.1, 134.98, 134.96, 134.6, 134.4, 131.8, 130.6, 130.0, 129.6, 129.32, 129.29, 129.1, 127.3 (q, $J = 311.0$ Hz), 52.6; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.6; HRMS (ESI) m/z calcd for $C_{24}H_{17}F_3O_5S_2Na^+$ $[M+Na]^+$ 529.0361, found 529.0365.



5i

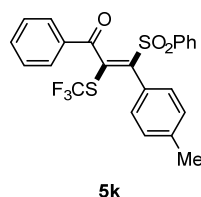
(E)-4-(3-oxo-3-phenyl-1-(phenylsulfonyl)-2-((trifluoromethyl)thio)prop-1-en-1-

yl)benzonitrile (5i): white solid, 45.0 mg, 95% yield; m.p. 146.3-147.1 °C; IR (cm⁻¹): 3069, 2922, 2857, 2233, 1680, 1582, 1501, 1447, 1403, 1327, 1240, 1154, 1105, 1083, 1023, 942, 855, 758, 725, 687, 589, 546, 524; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.55 (m, 4H), 7.51 – 7.43 (m, 1H), 7.37 – 7.04 (m, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.6, 145.6, 139.0, 135.1, 134.9, 134.7, 134.6, 132.5, 131.3, 129.6, 129.4, 129.2, 129.1, 127.2 (q, *J* = 311.0 Hz), 117.9, 114.4; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.5; HRMS (ESI) *m/z* calcd for C₂₃H₁₄F₃NO₃S₂Na⁺ [M+Na]⁺ 496.0259, found 496.0252.



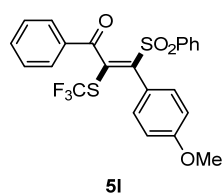
(E)-1-(4-nitrophenyl)-3-(phenylsulfonyl)-3-(p-tolyl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5j): white solid, 48.2 mg, 95% yield; m.p. 188.3-189.1 °C; IR (cm⁻¹): 3065, 2924, 2861, 1687, 1605, 1532, 1449, 1323, 1244, 1152, 1103, 1084, 1011, 938, 831, 748, 723, 684, 592, 514, 441; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.4 Hz, 2H), 8.19 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.19 (s, 1H), 7.11 (d, *J* = 4.8 Hz, 1H), 7.02 – 6.76 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.1, 146.3, 140.7, 138.3, 137.5, 135.3, 134.3, 134.2, 130.2, 129.6, 129.3, 129.1, 129.0, 127.5, 127.4 (q, *J* = 311.0 Hz), 21.6; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.5; HRMS (ESI) *m/z* calcd for C₂₃H₁₆F₃NO₅S₂Na⁺ [M+Na]⁺ 530.0314, found 530.0307.



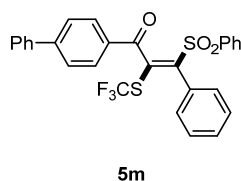
(E)-1-phenyl-3-(phenylsulfonyl)-3-(p-tolyl)-2-((trifluoromethyl)thio)prop-2-en-1-one (5k): white solid, 29.6 mg, 64% yield; m.p. 107.4-108.1 °C; IR (cm⁻¹): 3065, 2923, 2854, 1682, 1582, 1503, 1450, 1328, 1239, 1154, 1107, 1080, 1022, 938, 848, 753, 721, 685, 648, 515; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.70 – 7.64 (m, 1H), 7.62 – 7.53 (m, 5H), 7.46 – 7.39 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.09 – 6.84 (m, 2H), 2.38 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.1, 146.3, 140.7, 138.3, 137.5, 135.3, 134.3, 134.2, 130.2, 129.6, 129.3, 129.1, 129.0, 127.5, 127.4 (q, *J* = 311.0 Hz), 21.6; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.7; HRMS (ESI) *m/z* calcd

for $C_{23}H_{17}F_3O_3S_2Na^+$ $[M+Na]^+$ 485.0463, found 485.0454.



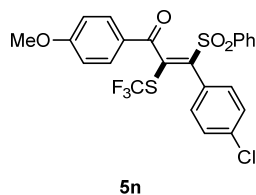
(E)-3-(4-methoxyphenyl)-1-phenyl-3-(phenylsulfonyl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5l): yellow solid, 27.3 mg, 57% yield; m.p. 143.7-144.1 °C; IR (cm^{-1}): 3063, 2934, 2842, 1683, 1608, 1506, 1447, 1324, 1254, 1152, 1104, 1082, 1028, 943, 846, 755, 723, 685, 583, 524; 1H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, $J = 8.4$ Hz, 2H), 7.71 – 7.64 (m, 1H), 7.62 – 7.52 (m, 5H), 7.46 – 7.39 (m, 2H), 7.12 – 6.95 (m, 2H), 6.87 (d, $J = 8.4$ Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.1, 161.1, 145.9, 138.5, 137.5, 135.3, 134.2, 132.0, 129.6, 129.3, 129.1, 129.0, 127.6 (q, $J = 311.0$ Hz), 122.4, 114.4, 55.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.7; HRMS (ESI) m/z calcd for $C_{23}H_{17}F_3O_4S_2Na^+$ $[M+Na]^+$ 501.0412, found 501.0403.



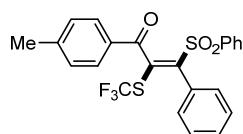
(E)-1-([1,1'-biphenyl]-4-yl)-3-phenyl-3-(phenylsulfonyl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5m): yellow solid, 33.1 mg, 63% yield; m.p. 102.1-102.8 °C; IR (cm^{-1}): 3061, 2925, 2852, 1679, 1600, 1485, 1443, 1406, 1323, 1250, 1161, 1103, 1082, 1009, 941, 836, 810, 768, 695, 585, 522, 443; 1H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, $J = 8.0$ Hz, 2H), 7.80 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H), 7.63 – 7.56 (m, 3H), 7.53 – 7.34 (m, 8H), 7.23 – 6.91 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.6, 147.0, 146.4, 139.9, 138.3, 137.4, 134.4, 134.0, 130.5, 130.4, 130.2, 129.4, 129.1, 128.9, 128.6, 127.7, 127.6, 127.5 (q, $J = 310.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.6; HRMS (ESI) m/z calcd for $C_{28}H_{19}F_3O_3S_2Na^+$ $[M+Na]^+$ 547.0619, found 547.0610.



(E)-3-(4-chlorophenyl)-1-(4-methoxyphenyl)-3-(phenylsulfonyl)-2-

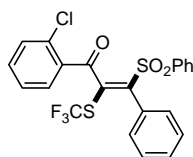
((trifluoromethyl)thio)prop-2-en-1-one (5n): white solid, 35.4 mg, 69% yield; m.p. 175.9-180.7 °C; IR (cm⁻¹): 3070, 2923, 2854, 1677, 1597, 1450, 1397, 1328, 1260, 1159, 1107, 1085, 1017, 832, 758, 737, 685, 642, 573, 479; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.8 Hz, 2H), 7.64 – 7.56 (m, 3H), 7.49 – 7.41 (m, 2H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 4H), 3.92 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 187.3, 164.6, 144.7, 139.3, 137.3, 136.8, 134.5, 132.0, 131.8, 129.28, 129.27, 129.2, 129.1, 128.3, 127.4 (q, *J* = 311.0 Hz), 55.8; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.7; HRMS (ESI) *m/z* calcd for C₂₃H₁₇ClF₃O₄S₂⁺ [M+H]⁺ 513.0203, found 513.0200.



5o

(E)-1-(4-chlorophenyl)-3-phenyl-3-(phenylsulfonyl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5o): yellow solid, 35.7 mg, 77% yield; m.p. 106.3-107.1 °C; IR (cm⁻¹): 3065, 3032, 2926, 1679, 1607, 1445, 1328, 1256, 1156, 1106, 1083, 1000, 938, 799, 760, 694, 582, 521, 476; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.37 – 7.19 (m, 7H), 7.17 – 6.75 (m, 2H), 2.35 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.5, 146.0, 145.4, 138.3, 137.3, 134.3, 132.8, 130.5, 130.2, 129.7, 129.6, 129.2, 129.0, 128.8, 127.4 (q, *J* = 310.0 Hz), 21.9; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.7; HRMS (ESI) *m/z* calcd for C₂₃H₁₈F₃O₃S₂⁺ [M+H]⁺ 463.0644, found 463.0640.

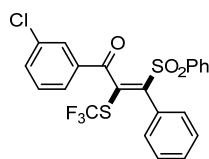


5p

(E)-1-(2-chlorophenyl)-3-phenyl-3-(phenylsulfonyl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5p): yellow oil liquid, 45.9 mg, 95% yield; IR (cm⁻¹): 3066, 2927, 2852, 1669, 1588, 1438, 1326, 1273, 1230, 1149, 1107, 1085, 1042, 941, 839, 769, 732, 695, 646, 582, 523, 421; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 7.6 Hz, 1H), 7.68 – 7.54 (m, 5H), 7.51 – 7.40 (m, 4H), 7.38 – 7.31 (m, 2H), 7.14 – 6.99 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 186.9, 138.9, 137.2, 134.8, 134.6, 134.4, 133.4, 132.6, 131.9, 130.7, 130.2, 130.0, 129.5, 129.1, 128.7, 127.7 (q, *J* = 311.0 Hz), 127.3; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -37.0; HRMS (ESI) *m/z*

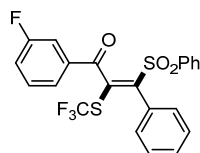
calcd for $C_{22}H_{14}ClF_3O_3S_2Na^+$ $[M+Na]^+$ 504.9917, found 504.9911.



5q

(E)-1-(3-chlorophenyl)-3-phenyl-3-(phenylsulfonyl)-2-

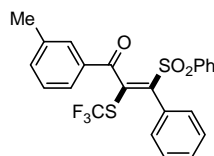
((trifluoromethyl)thio)prop-2-en-1-one (5q): yellow solid, 45.9 mg, 95% yield; m.p. 109.3-110.1 °C; IR (cm^{-1}): 3067, 2931, 2856, 1684, 1573, 1477, 1447, 1427, 1327, 1236, 1156, 1105, 1085, 1000, 954, 788, 758, 698, 582, 521; 1H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.97 (d, $J = 7.6$ Hz, 1H), 7.66 – 7.51 (m, 5H), 7.47 – 7.32 (m, 5H), 7.22 – 6.89 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.8, 147.2, 137.4, 137.1, 136.7, 135.4, 134.5, 134.2, 130.5, 130.4, 130.3, 130.2, 129.3, 129.2, 129.1, 129.0, 128.9, 127.9, 127.4 (q, $J = 310.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.6; HRMS (ESI) m/z calcd for $C_{22}H_{14}ClF_3O_3S_2Na^+$ $[M+Na]^+$ 504.9917, found 504.9912.



5r

(E)-1-(3-fluorophenyl)-3-phenyl-3-(phenylsulfonyl)-2-

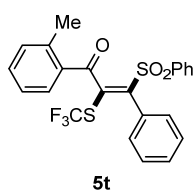
((trifluoromethyl)thio)prop-2-en-1-one (5r): yellow solid, 44.3 mg, 95% yield; m.p. 84.6-85.1 °C; IR (cm^{-1}): 3071, 2924, 2854, 1686, 1590, 1484, 1444, 1328, 1262, 1157, 1106, 1086, 970, 885, 829, 784, 759, 723, 699, 583, 517; 1H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, $J = 7.6$ Hz, 1H), 7.79 (d, $J = 8.8$ Hz, 1H), 7.64 – 7.52 (m, 4H), 7.48 – 7.32 (m, 6H), 7.22 – 6.89 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.8, 163.0 (d, $J = 247.0$ Hz), 147.1, 137.5, 137.3, 137.2, 137.1, 134.5, 130.8 (d, $J = 7.0$ Hz), 130.5, 130.3, 129.3, 129.2, 128.9, 127.4 (q, $J = 311.0$ Hz), 125.6 (d, $J = 3.0$ Hz), 121.4 (d, $J = 21.0$ Hz), 115.9 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.6, -111.2; HRMS (ESI) m/z calcd for $C_{22}H_{14}F_4O_3S_2Na^+$ $[M+Na]^+$ 489.0212, found 489.0204.



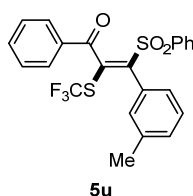
5s

(E)-3-phenyl-3-(phenylsulfonyl)-1-(m-tolyl)-2-((trifluoromethyl)thio)prop-2-en-1-

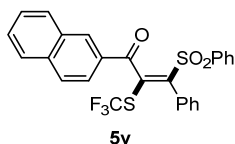
one (5s): white solid, 35.6 mg, 77% yield; m.p. 116.1-117.1 °C; IR (cm⁻¹): 3064, 2925, 2861, 1681, 1584, 1483, 1446, 1328, 1264, 1152, 1109, 1082, 997, 954, 832, 784, 757, 725, 698, 580, 527; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.87 (d, *J* = 6.4 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.49 – 7.39 (m, 5H), 7.39 – 7.32 (m, 2H), 7.21 – 6.96 (m, 2H), 2.48 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.1, 146.2, 138.9, 138.4, 137.4, 135.23, 135.18, 134.3, 130.6, 130.4, 130.3, 129.7, 129.3; 129.1, 128.9, 127.5 (q, *J* = 310.0 Hz), 127.2, 21.6; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.7; HRMS (ESI) *m/z* calcd for C₂₃H₁₇F₃O₃S₂Na⁺ [M+Na]⁺ 485.0463, found 485.0455.



(*E*)-3-phenyl-3-(phenylsulfonyl)-1-(*o*-tolyl)-2-((trifluoromethyl)thio)prop-2-en-1-one (5t): colorless oil liquid, 19.9 mg, 43% yield; IR (cm⁻¹): 3064, 2966, 2929, 1678, 1570, 1487, 1446, 1327, 1234, 1156, 1104, 1084, 1048, 934, 841, 758, 696, 583, 515; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.55 – 7.49 (m, 3H), 7.46 – 7.32 (m, 7H), 7.20 – 6.90 (m, 2H), 2.78 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.7, 145.4, 142.0, 139.7, 137.5, 134.3, 133.4, 133.3, 132.9, 132.8, 130.7, 130.5, 130.3, 129.3, 129.1, 128.8, 127.7 (q, *J* = 311.0 Hz), 126.0, 22.2; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.8; HRMS (ESI) *m/z* calcd for C₂₃H₁₇F₃O₃S₂Na⁺ [M+Na]⁺ 485.0463, found 485.0458.

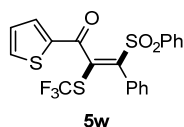


(*E*)-1-phenyl-3-(phenylsulfonyl)-3-(*m*-tolyl)-2-((trifluoromethyl)thio)prop-2-en-1-one (5u): yellow solid, 29.6 mg, 64% yield; m.p. 94.2-95.1 °C; IR (cm⁻¹): 3064, 2926, 2857, 1679, 1584, 1446, 1324, 1234, 1155, 1106, 1080, 1000, 783, 746, 698, 587, 524, 438; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.04 (m, 2H), 7.70 – 7.54 (m, 6H), 7.48 – 7.39 (m, 2H), 7.29 – 7.15 (m, 2H), 7.05 – 6.55 (m, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.0, 146.3, 138.8, 138.2, 137.4, 135.3, 134.3, 134.3, 131.1, 130.8, 130.4, 129.6, 129.4, 129.0, 129.0, 128.7, 127.5 (q, *J* = 310.0 Hz), 127.4, 21.4; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.7; HRMS (ESI) *m/z* calcd for C₂₃H₁₇F₃O₃S₂Na⁺ [M+Na]⁺ 485.0463, found 485.0456.



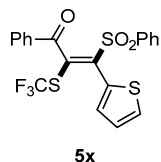
(E)-1-(naphthalen-2-yl)-3-phenyl-3-(phenylsulfonyl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5v): white solid, 46.4 mg, 93% yield; m.p. 112.3-113.1 °C; IR (cm⁻¹): 3060, 2923, 2851, 1675, 1625, 1581, 1444, 1323, 1279, 1158, 1103, 971, 927, 867, 812, 757, 724, 702, 581, 520, 471; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 8.21 – 8.13 (m, 1H), 8.08 – 7.98 (m, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.52 (m, 5H), 7.48 – 7.33 (m, 5H), 7.29 – 6.99 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.9, 146.3, 138.4, 137.3, 136.3, 134.4, 132.7, 132.6, 132.0, 130.6, 130.4, 130.1, 129.3, 129.3, 129.1, 128.9, 128.1, 127.5 (q, *J* = 310.0 Hz), 127.2, 124.5; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.6; HRMS (ESI) *m/z* calcd for C₂₆H₁₇F₃O₃S₂Na⁺ [M+Na]⁺ 521.0463, found 521.0457.



(E)-3-phenyl-3-(phenylsulfonyl)-1-(thiophen-2-yl)-2-((trifluoromethyl)thio)prop-

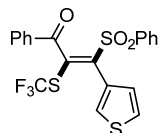
2-en-1-one (5w): white solid, 42.3 mg, 94% yield; m.p. 98.5-96.3 °C; IR (cm⁻¹): 3409, 3062, 2927, 2850, 1654, 1582, 1515, 1447, 1411, 1328, 1261, 1152, 1106, 1085, 1028, 909, 863, 821, 759, 723, 697, 578, 516, 448; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.68 (m, 2H), 7.54 – 7.44 (m, 3H), 7.39 – 7.21 (m, 5H), 7.19 – 7.15 (m, 1H), 7.12 – 6.56 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 181.1, 146.8, 142.5, 137.3, 135.8, 135.0, 134.4, 130.5, 130.3, 130.2, 129.3, 129.1, 128.8, 128.6, 127.5 (q, *J* = 310.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -37.0; HRMS (ESI) *m/z* calcd for C₂₀H₁₃F₃O₃S₃Na⁺ [M+Na]⁺ 476.9871, found 476.9865.



(E)-1-phenyl-3-(phenylsulfonyl)-3-(thiophen-2-yl)-2-((trifluoromethyl)thio)prop-

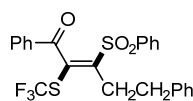
2-en-1-one (5x): brown solid, 40.0 mg, 88% yield; m.p. 81.9-82.8 °C; IR (cm⁻¹): 3067, 2924, 2850, 1681, 1581, 1448, 1421, 1326, 1230, 1150, 1108, 1060, 1023, 906, 853, 789, 752, 715, 689, 588, 513, 434; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.56 – 7.47 (m, 5H), 7.46 – 7.41 (m, 1H), 7.39 – 7.32

(m, 2H), 7.00 – 6.90 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.5, 141.4, 139.5, 137.3, 135.2, 134.41, 134.38, 132.7, 130.8, 129.6, 129.3, 129.2, 129.0, 127.5, 127.4 (q, $J = 311.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.6; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{13}\text{F}_3\text{O}_3\text{S}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 476.9871, found 476.9865.



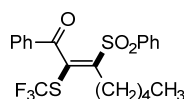
5y

(*E*)-1-phenyl-3-(phenylsulfonyl)-3-(thiophen-3-yl)-2-((trifluoromethyl)thio)prop-2-en-1-one (5y): brown solid, 35.9 mg, 79% yield; m.p. 107.8-108.5 °C; IR (cm^{-1}): 3105, 3066, 2928, 2850, 1682, 1582, 1449, 1327, 1239, 1155, 1106, 1084, 1023, 978, 890, 840, 785, 757, 685, 630, 585, 563, 514; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, $J = 7.2$ Hz, 2H), 7.62 – 7.56 (m, 1H), 7.54 – 7.45 (m, 5H), 7.38 – 7.32 (m, 2H), 7.30 – 7.21 (m, 2H), 6.88 – 6.78 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.9, 142.0, 138.5, 137.6, 135.1, 134.32, 134.31, 129.7, 129.6, 129.4, 129.1, 129.05, 129.01, 128.7, 127.5 (q, $J = 310.0$ Hz), 126.7; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.7; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{13}\text{F}_3\text{O}_3\text{S}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 476.9871, found 476.9863.



5z

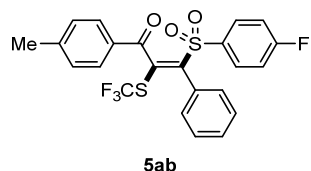
(*E*)-1,5-diphenyl-3-(phenylsulfonyl)-2-((trifluoromethyl)thio)pent-2-en-1-one (5z): yellow solid, 33.8 mg, 71% yield; m.p. 90.6-91.5 °C; IR (cm^{-1}): 3063, 3028, 2923, 2853, 1676, 1581, 1451, 1325, 1245, 1150, 1110, 1085, 990, 840, 735, 689, 639, 564; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, $J = 8.0$ Hz, 2H), 7.83 (d, $J = 8.0$ Hz, 2H), 7.72 – 7.58 (m, 4H), 7.54 – 7.47 (m, 2H), 7.39 – 7.33 (m, 2H), 7.31 – 7.24 (m, 3H), 3.14 – 2.65 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.8, 149.3, 139.5, 137.9, 137.0, 134.7, 134.6, 134.0, 129.7, 129.7, 129.2, 129.1, 128.93, 128.86, 127.6 (q, $J = 311.0$ Hz), 127.0, 34.9, 33.4; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -37.3; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{19}\text{F}_3\text{O}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 499.0619, found 499.0613.



5aa

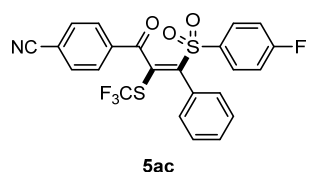
(*E*)-1-phenyl-3-(phenylsulfonyl)-2-((trifluoromethyl)thio)oct-2-en-1-one (5aa): white solid, 28.8 mg, 65% yield; m.p. 78.3-79.0 °C; IR (cm^{-1}): 3065, 2956, 2930, 2864,

1679, 1581, 1450, 1325, 1238, 1157, 1102, 1080, 857, 743, 689, 640, 569; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, $J = 8.0$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.71 – 7.57 (m, 4H), 7.56 – 7.49 (m, 2H), 2.55 (s, 2H), 1.84 – 1.25 (m, 7H), 0.89 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.9, 151.0, 138.1, 135.1, 134.9, 134.5, 134.0, 129.6, 129.0, 128.9, 127.6 (q, $J = 310.0$ Hz), 32.0, 31.4, 29.3, 22.2, 14.0; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -37.2; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{21}\text{F}_3\text{O}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 465.0776, found 465.0768.



(E)-3-((4-fluorophenyl)sulfonyl)-3-phenyl-1-(p-tolyl)-2-

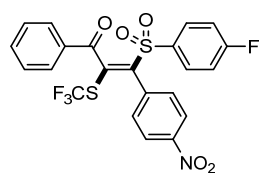
((trifluoromethyl)thio)prop-2-en-1-one (5ab): white solid, 31.7 mg, 66% yield; m.p. 107.1-108.1 °C; IR (cm^{-1}): 3066, 2926, 2859, 1679, 1592, 1491, 1405, 1328, 1241, 1150, 1106, 1082, 937, 837, 798, 759, 697, 577, 505; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, $J = 8.0$ Hz, 2H), 7.61 – 7.54 (m, 2H), 7.48 – 7.34 (m, 5H), 7.24 – 6.82 (m, 4H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.7, 166.2 (d, $J = 256.0$ Hz), 145.7, 145.6, 138.9, 133.5 (d, $J = 3.0$ Hz), 132.8, 132.3 (d, $J = 10.0$ Hz), 130.5, 130.4, 129.8, 129.7, 129.0, 127.5 (q, $J = 311.0$ Hz), 116.5 (d, $J = 23.0$ Hz), 22.1; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.7, -102.1; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{16}\text{F}_4\text{O}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 503.0369, found 503.0363.



(E)-4-(3-((4-fluorophenyl)sulfonyl)-3-phenyl-2-

((trifluoromethyl)thio)acryloyl)benzotrile (5ac): white solid, 46.7 mg, 95% yield; m.p. 149.4-150.0 °C; IR (cm^{-1}): 3102, 3073, 2922, 2854, 2233, 1688, 1591, 1494, 1407, 1324, 1295, 1242, 1149, 1106, 1081, 1057, 1018, 941, 839, 804, 761, 697, 576, 508, 445; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, $J = 8.4$ Hz, 2H), 7.90 (d, $J = 8.4$ Hz, 2H), 7.62 – 7.53 (m, 2H), 7.52 – 7.35 (m, 3H), 7.26 – 6.91 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.9, 167.4 (d, $J = 257.0$ Hz), 147.6, 138.1, 137.0, 132.9, 132.9, 132.3 (d, $J = 10.0$ Hz), 130.8, 130.2, 129.84, 129.80, 129.1, 127.3 (q, $J = 311.0$ Hz), 117.9, 117.4, 116.7 (d, $J = 23.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.5, -101.1; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{13}\text{F}_4\text{NO}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 514.0165, found

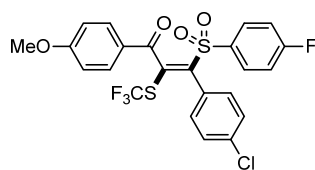
514.0167.



5ad

(E)-3-((4-fluorophenyl)sulfonyl)-3-(4-nitrophenyl)-1-phenyl-2-

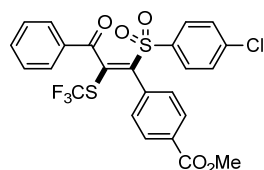
((trifluoromethyl)thio)prop-2-en-1-one (5ad): white solid, 48.6 mg, 95% yield; m.p. 175.2-176.0 °C; IR (cm⁻¹): 3070, 2962, 2868, 1682, 1593, 1528, 1490, 1453, 1349, 1241, 1152, 1106, 1082, 1058, 1016, 942, 838, 763, 693, 576, 505; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 6.4 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.78 – 7.51 (m, 6H), 7.26 – 7.06 (m, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.7, 166.5 (d, *J* = 258.0 Hz), 149.0, 145.2, 139.7, 136.8, 134.7, 134.6, 132.9 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 10.0 Hz), 131.8, 129.6, 129.2, 127.1 (q, *J* = 311.0 Hz), 124.1, 117.0 (d, *J* = 23.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.4, -100.5; HRMS (ESI) *m/z* calcd for C₂₂H₁₃F₄NO₅S₂Na⁺ [M+Na]⁺ 534.0063, found 534.0065.



5ae

(E)-3-(4-chlorophenyl)-3-((4-fluorophenyl)sulfonyl)-1-(4-methoxyphenyl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5ae): white solid, 42.5 mg, 80% yield; m.p. 178.2-179.0 °C; IR (cm⁻¹): 3074, 2936, 2847, 1669, 1597, 1492, 1420, 1332, 1254, 1154, 1104, 1083, 1060, 1016, 933, 833, 756, 718, 684, 579, 513, 435; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.62 (dd, *J* = 8.4, 4.8 Hz, 2H), 7.37 (d, *J* = 6.4 Hz, 2H), 7.24 – 6.68 (m, 6H), 3.92 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 187.4, 166.3 (d, *J* = 257.0 Hz), 164.7, 144.4, 139.7, 136.9, 133.4 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 9.0 Hz), 132.0, 131.8, 129.4, 128.9, 128.2, 127.4 (q, *J* = 310.0 Hz), 116.7 (d, *J* = 22.0 Hz), 114.4, 55.8; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.6, -101.6; HRMS (ESI) *m/z* calcd for C₂₃H₁₅ClF₄O₄S₂Na⁺ [M+Na]⁺ 552.9928, found 552.9923.

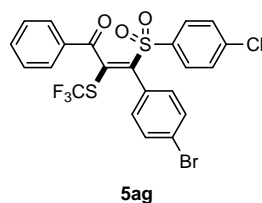


5af

methyl

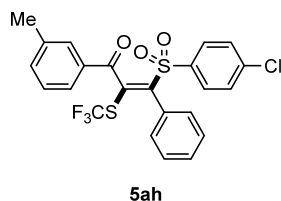
(E)-4-(1-((4-chlorophenyl)sulfonyl)-3-oxo-3-phenyl-2-

((trifluoromethyl)thio)prop-1-en-1-yl)benzoate (5af): white solid, 45.4 mg, 84% yield; m.p. 60.3-61.1 °C; IR (cm⁻¹): 3092, 3069, 2955, 2846, 1727, 1682, 1585, 1476, 1447, 1396, 1333, 1276, 1162, 1105, 1082, 1059, 1020, 940, 865, 831, 774, 705, 574, 471; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.2 Hz, 4H), 7.72 – 7.65 (m, 1H), 7.63 – 7.55 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.36 – 6.82 (m, 2H), 3.95 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.8, 166.2, 145.5, 141.6, 139.3, 135.6, 134.9, 134.7, 134.5, 132.0, 130.7, 130.1, 129.7, 129.6, 129.1, 127.3 (q, *J* = 311.0 Hz), 52.6; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.5; HRMS (ESI) *m/z* calcd for C₂₄H₁₆ClF₃O₅S₂Na⁺ [M+Na]⁺ 562.9972, found 562.9967.



(E)-3-(4-bromophenyl)-3-((4-chlorophenyl)sulfonyl)-1-phenyl-2-

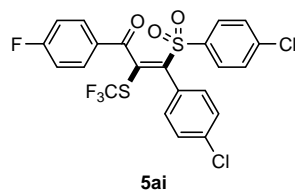
((trifluoromethyl)thio)prop-2-en-1-one (5ag): yellow solid, 53,4 mg, 95% yield; m.p. 132,7-133,4 °C; IR (cm⁻¹): 3086, 2927, 2856, 1681, 1583, 1479, 1452, 1392, 1332, 1244, 1162, 1102, 1080, 1058, 1014, 938, 829, 763, 714, 687, 577, 473; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.71 – 7.65 (m, 1H), 7.61 – 7.48 (m, 6H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.20 – 6.84 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.8, 145.0, 141.6, 139.6, 135.7, 134.9, 134.5, 132.4, 130.7, 129.7, 129.6, 129.13, 129.09, 127.3 (q, *J* = 311.0 Hz), 125.4; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.5; HRMS (ESI) *m/z* calcd for C₂₂H₁₃BrClF₃O₃S₂Na⁺ [M+Na]⁺ 582.9022, found 582.9017.



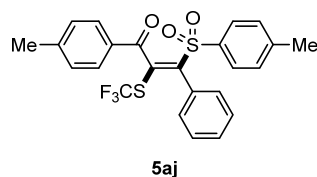
(E)-3-((4-chlorophenyl)sulfonyl)-3-phenyl-1-(m-tolyl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5ah): white solid, 30.3 mg, 61% yield; m.p. 94.7-95.3 °C; IR (cm⁻¹): 3030, 2923, 2856, 1689, 1607, 1530, 1473, 1391, 1329, 1242, 1155, 1103, 1083, 1057, 1011, 939, 826, 759, 713, 605, 574, 502, 471, 451; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.85 (d, *J* = 6.8 Hz, 1H), 7.50 – 7.44 (m, 5H), 7.40 (d, *J* = 8.8 Hz, 4H), 7.24 – 6.90 (m, 2H), 2.48 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.1, 145.6, 141.3, 139.2, 139.0, 136.0, 135.3, 135.1, 130.8, 130.5, 130.5, 130.3, 129.7, 129.5, 129.0, 128.9, 127.4 (q, *J* = 311.0 Hz), 127.2, 21.6; ¹⁹F NMR

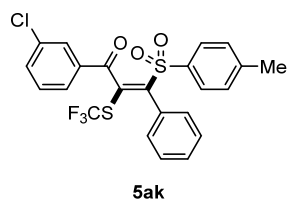
(376 MHz, Chloroform-*d*) δ -36.6; HRMS (ESI) m/z calcd for $C_{23}H_{16}ClF_3O_3S_2Na^+$ $[M+Na]^+$ 519.0073, found 519.0068.



(*E*)-3-(4-chlorophenyl)-3-((4-chlorophenyl)sulfonyl)-1-(4-fluorophenyl)-2-((trifluoromethyl)thio)prop-2-en-1-one (5ai): white solid, 41.8 mg, 78% yield; m.p. 151.5-152.2 °C; IR (cm^{-1}): 3091, 2926, 2858, 1681, 1596, 1488, 1396, 1334, 1243, 1158, 1106, 1084, 1055, 1016, 931, 834, 754, 714, 572, 475; 1H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.02 (m, 2H), 7.55 – 7.36 (m, 6H), 7.30 – 7.23 (m, 2H), 7.20 – 6.81 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.5, 166.5 (d, $J = 256.0$ Hz), 145.1, 141.7, 139.3, 137.2, 135.6, 132.3 (d, $J = 10.0$ Hz), 131.8, 131.5, 130.7, 129.7, 129.5, 128.5, 127.3 (q, $J = 311.0$ Hz), 116.5 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.5, -102.3; HRMS (ESI) m/z calcd for $C_{22}H_{12}Cl_2F_4O_3S_2Na^+$ $[M+Na]^+$ 556.9433, found 556.9429.

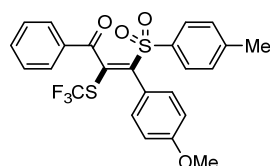


(*E*)-3-phenyl-1-(p-tolyl)-3-tosyl-2-((trifluoromethyl)thio)prop-2-en-1-one (5aj): white solid, 34.8 mg, 73% yield; m.p. 117.5-118.1 °C; IR (cm^{-1}): 3062, 2920, 2852, 1680, 1584, 1485, 1442, 1399, 1326, 1244, 1153, 1108, 1082, 1060, 853, 749, 702, 681, 638, 595, 507; 1H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, $J = 8.0$ Hz, 2H), 7.48 – 7.31 (m, 7H), 7.24 – 6.86 (m, 4H), 2.47 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.7, 146.5, 145.5, 145.4, 137.9, 134.5, 132.9, 130.8, 130.4, 130.2, 129.7, 129.4, 128.8, 127.5 (q, $J = 310.0$ Hz), 22.0, 21.9; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.8; HRMS (ESI) m/z calcd for $C_{24}H_{19}F_3O_3S_2Na^+$ $[M+Na]^+$ 499.0619, found 499.0608.



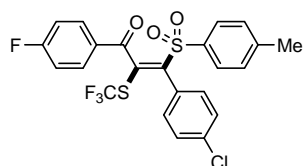
(*E*)-1-(3-chlorophenyl)-3-phenyl-3-tosyl-2-((trifluoromethyl)thio)prop-2-en-1-one

(5ak): white solid, 47.2 mg, 95% yield; m.p. 103.6-104.2 °C; IR (cm⁻¹): 3195, 3067, 2918, 2855, 1676, 1591, 1485, 1453, 1421, 1331, 1241, 1156, 1103, 1082, 1012, 853, 757, 742, 689, 598, 577, 508; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.56 – 7.50 (m, 1H), 7.48 – 7.34 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.18 – 6.92 (m, 2H), 2.41 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 187.9, 147.8, 145.8, 136.8, 136.7, 135.4, 134.1, 134.1, 130.4, 130.3, 129.9, 129.4, 129.2, 128.9, 127.9, 127.5 (q, *J* = 311.0 Hz), 21.9; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.7; HRMS (ESI) *m/z* calcd for C₂₃H₁₆ClF₃O₃S₂Na⁺ [M+Na]⁺ 519.0073, found 519.0066.



5al

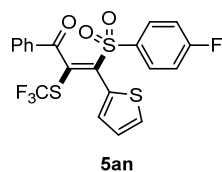
(*E*)-3-(4-methoxyphenyl)-1-phenyl-3-tosyl-2-((trifluoromethyl)thio)prop-2-en-1-one (5al): yellow solid, 31.0 mg, 63% yield; m.p. 59.2-60.1 °C; IR (cm⁻¹): 3074, 2958, 2842, 1678, 1602, 1506, 1450, 1324, 1293, 1253, 1152, 1106, 1086, 1025, 939, 843, 752, 722, 686, 641, 585, 514; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.69 – 7.63 (m, 1H), 7.61 – 7.53 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13 – 6.96 (m, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H), 2.41 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 189.2, 161.1, 146.4, 145.5, 137.8, 135.3, 134.6, 134.2, 132.0, 129.8, 129.6, 129.4, 129.0, 127.6 (q, *J* = 310.0 Hz), 122.5, 55.5, 21.9; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.8; HRMS (ESI) *m/z* calcd for C₂₄H₁₉F₃O₄S₂Na⁺ [M+Na]⁺ 515.0569, found 515.0569.



5am

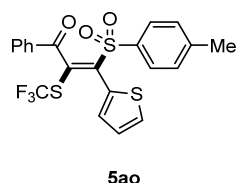
(*E*)-3-(4-chlorophenyl)-1-(4-fluorophenyl)-3-tosyl-2-((trifluoromethyl)thio)prop-2-en-1-one (5am): white solid, 48.9 mg, 95% yield; m.p. 130.5-131.3 °C; IR (cm⁻¹): 3455, 3065, 2924, 2854, 1681, 1595, 1484, 1413, 1327, 1241, 1150, 1105, 1085, 1060, 1014, 933, 837, 741, 711, 680, 640, 605, 579, 514; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.03 (m, 2H), 7.48 – 7.42 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.20 (m, 4H), 7.17 – 6.74 (m, 2H), 2.42 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 187.5, 166.4 (d, *J* = 255.0 Hz), 146.3, 146.0, 137.8, 136.8, 134.0, 132.3 (d, *J* = 10.0 Hz), 131.8,

131.6 (d, $J = 3.0$ Hz), 130.0, 129.3, 129.3, 128.9, 127.4 (q, $J = 311.0$ Hz), 116.4 (d, $J = 22.0$ Hz), 21.9; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.7, -102.7; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{15}\text{ClF}_4\text{O}_3\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 536.9979, found 536.9972.



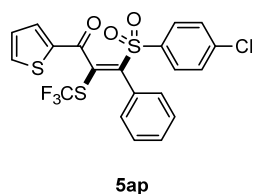
(*E*)-3-((4-fluorophenyl)sulfonyl)-1-phenyl-3-(thiophen-2-yl)-2-

((trifluoromethyl)thio)prop-2-en-1-one (5an): white solid, 40.2 mg, 85% yield; m.p. 104.1-105.0 °C; IR (cm^{-1}): 3108, 2931, 2859, 1680, 1589, 1492, 1447, 1406, 1330, 1238, 1152, 1106, 1086, 1060, 979, 837, 786, 735, 690, 649, 573, 496; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, $J = 8.0$ Hz, 2H), 7.71 – 7.64 (m, 1H), 7.63 – 7.51 (m, 4H), 7.43 – 7.31 (m, 2H), 7.15 – 7.05 (m, 2H), 6.92 (d, $J = 4.8$ Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.0, 166.2 (d, $J = 257.0$ Hz), 141.8, 138.8, 135.1, 134.4, 133.6 (d, $J = 2.0$ Hz), 132.0 (d, $J = 9.0$ Hz), 129.6, 129.6, 129.5, 129.0, 128.7, 127.5 (q, $J = 311.0$ Hz), 126.9, 116.6 (d, $J = 22.0$ Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.7, -101.9; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{12}\text{F}_4\text{O}_3\text{S}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 494.9776, found 494.9773.



(*E*)-1-phenyl-3-(thiophen-2-yl)-3-tosyl-2-((trifluoromethyl)thio)prop-2-en-1-one

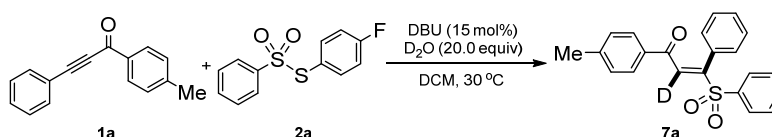
(5ao): brown oil liquid, 44.0 mg, 94% yield; IR (cm^{-1}): 3105, 3060, 2925, 1681, 1597, 1450, 1326, 1231, 1152, 1107, 1084, 1056, 904, 848, 814, 747, 690, 583, 504; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, $J = 8.4$ Hz, 2H), 7.69 – 7.64 (m, 1H), 7.60 – 7.54 (m, 2H), 7.53 – 7.44 (m, 3H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.08 – 6.99 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.6, 145.7, 140.7, 140.0, 135.2, 134.30, 134.28, 132.6, 130.7, 129.8, 129.6, 129.5, 129.2, 129.0, 127.5, 127.4 (q, $J = 311.0$ Hz), 21.9; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -36.6; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{15}\text{F}_3\text{O}_3\text{S}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 491.0027, found 491.0020.



(E)-3-((4-chlorophenyl)sulfonyl)-3-phenyl-1-(thiophen-2-yl)-2-

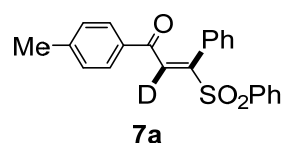
((trifluoromethyl)thio)prop-2-en-1-one (5ap): white solid, 40.6 mg, 83% yield; m.p. 121.0-121.9 °C; IR (cm⁻¹): 3393, 3066, 2922, 2858, 1679, 1583, 1476, 1444, 1396, 1331, 1262, 1155, 1101, 1085, 1016, 957, 828, 786, 759, 700, 609, 577, 470; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.77 (m, 2H), 7.54 – 7.33 (m, 7H), 7.27 – 7.23 (m, 1H), 7.21 – 6.76 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 181.0, 146.2, 142.4, 141.3, 138.1, 136.0, 135.9, 135.1, 130.8, 130.5, 130.3, 129.5, 129.0, 128.6, 127.5 (q, *J* = 307.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -36.9; HRMS (ESI) *m/z* calcd for C₂₀H₁₂ClF₃O₃S₃Na⁺ [M+Na]⁺ 510.9481, found 510.9475.

10. General procedure for synthesis of products 7a



To an oven-dried 10 mL Schlenk tube equipped with a stir bar was added ynone **1a** (0.2 mmol), thiosulfonate **2a** (0.3 mmol), 2.0 mL of DCM, D₂O (20.0 equiv) and DBU (15 mol%). Then the reaction mixture was stirred at room temperature until the substrate was consumed completely which was monitored by TLC. The solvent was evaporated, then the crude product was purified by column chromatography on silica gel (200~300 mesh) using ethyl acetate in petroleum ether (v/v = 40:1~10:1) as the eluent to afford the corresponding product **7a** in 92% yield.

11. Characterization of products 7a

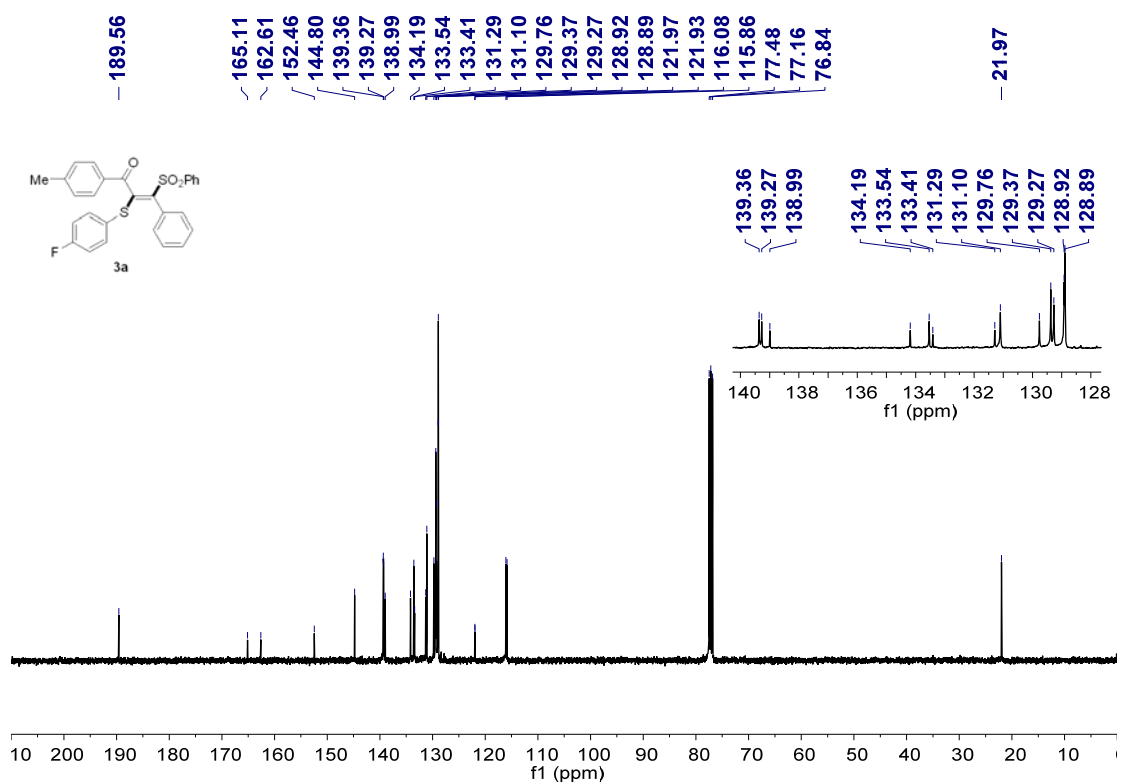
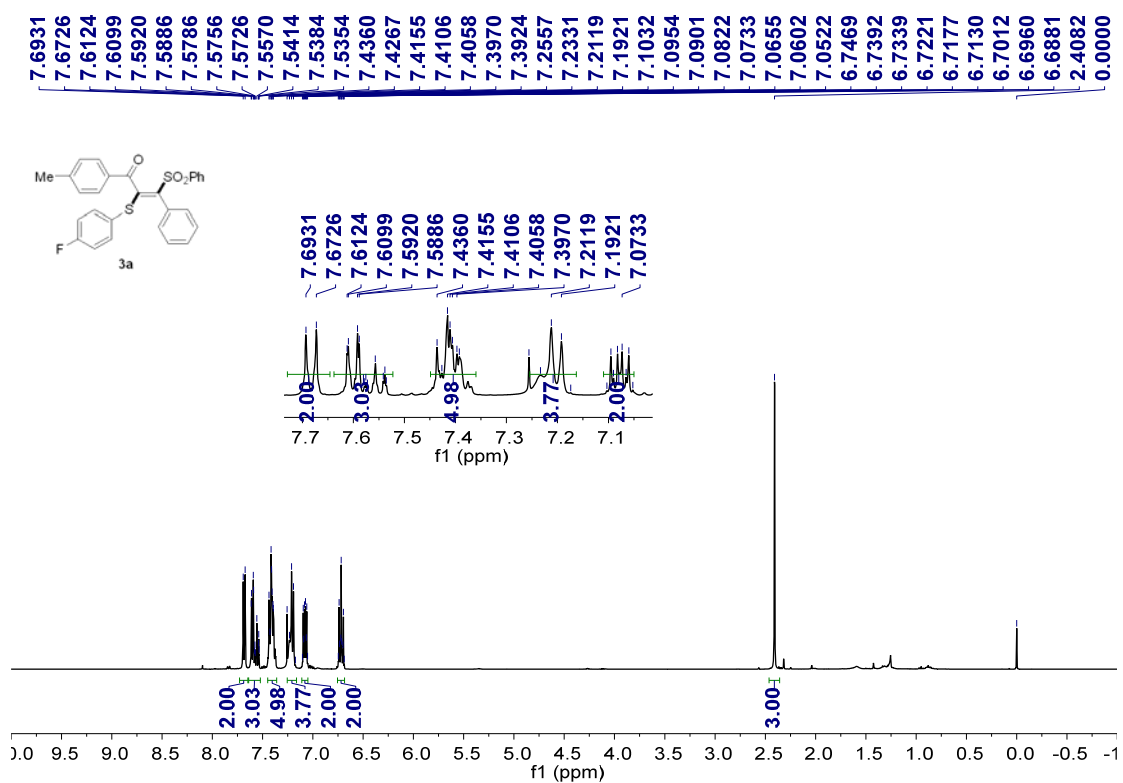


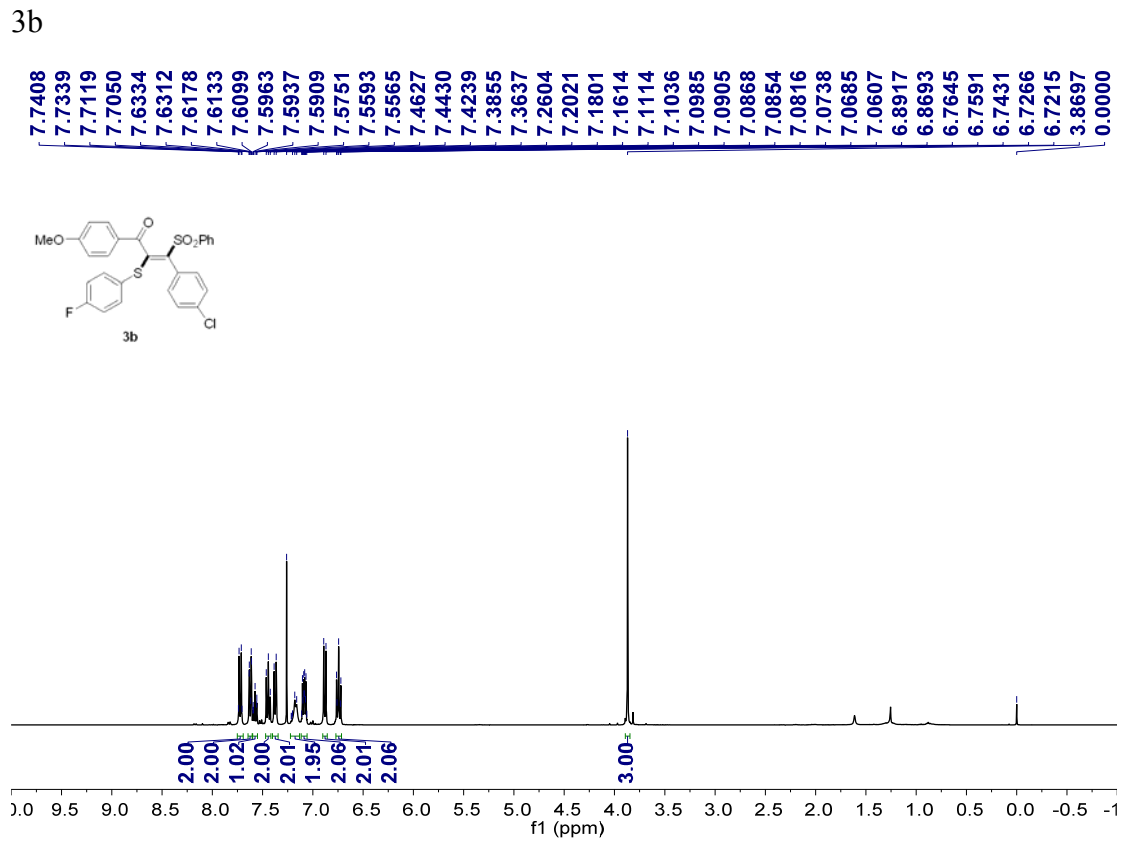
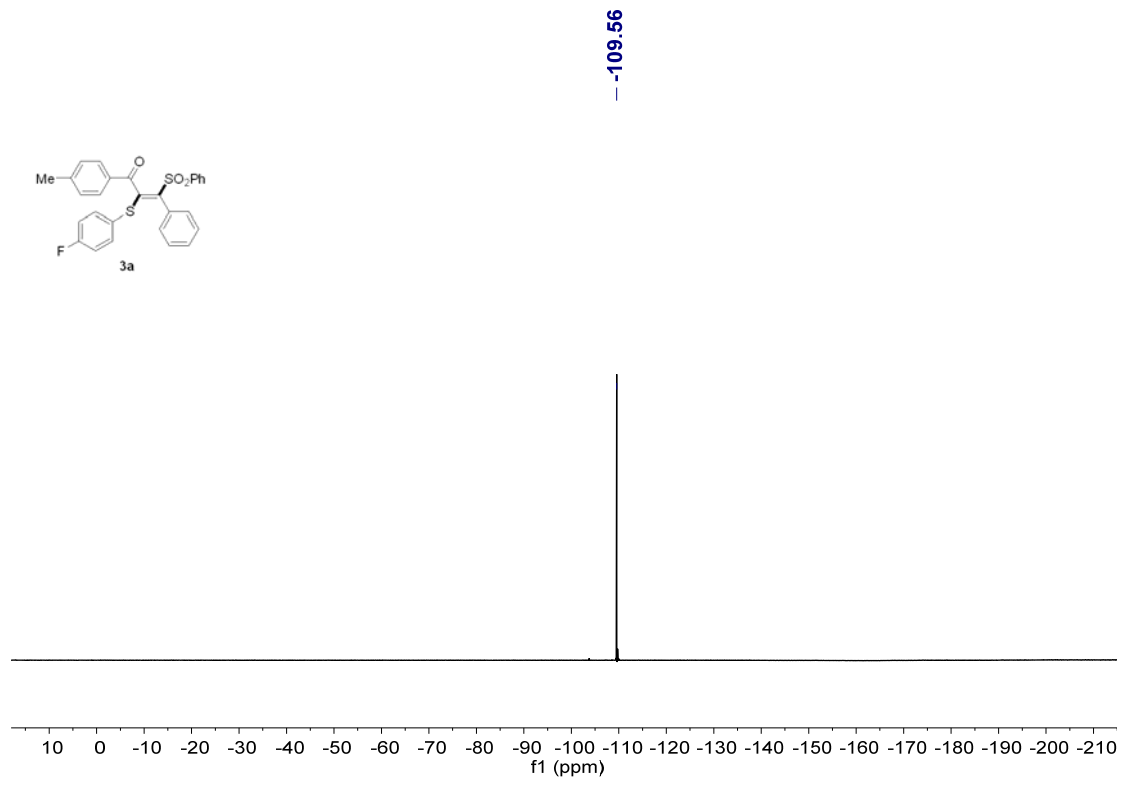
(E)-3-phenyl-3-(phenylsulfonyl)-1-(p-tolyl)prop-2-en-1-one-2-d (7a): yellow solid, 66.9 mg, 92% yield; m.p. 93.2-93.8 °C; IR (cm⁻¹): 3063, 2921, 2251, 1669, 1602, 1490, 1444, 1406, 1315, 1278, 1228, 1177, 1153, 1086, 1065, 1028, 966, 895, 828, 762, 732, 695, 645, 604, 570, 520, 474; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.45 – 7.39 (m, 2H), 7.25 – 7.17 (m, 3H), 7.17 – 7.11 (m, 2H), 7.11 – 7.04 (m, 2H), 2.37 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.7, 150.2, 145.4, 137.3, 133.9, 133.5, 130.3, 129.6, 129.6, 129.5,

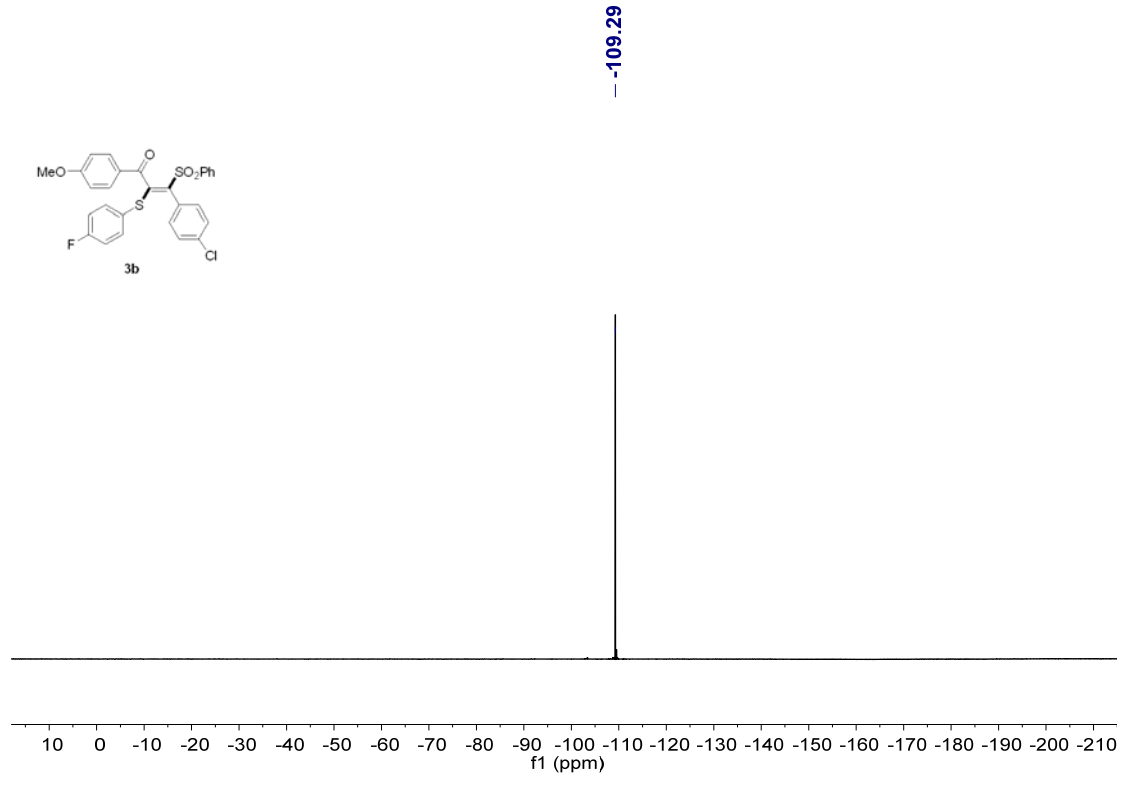
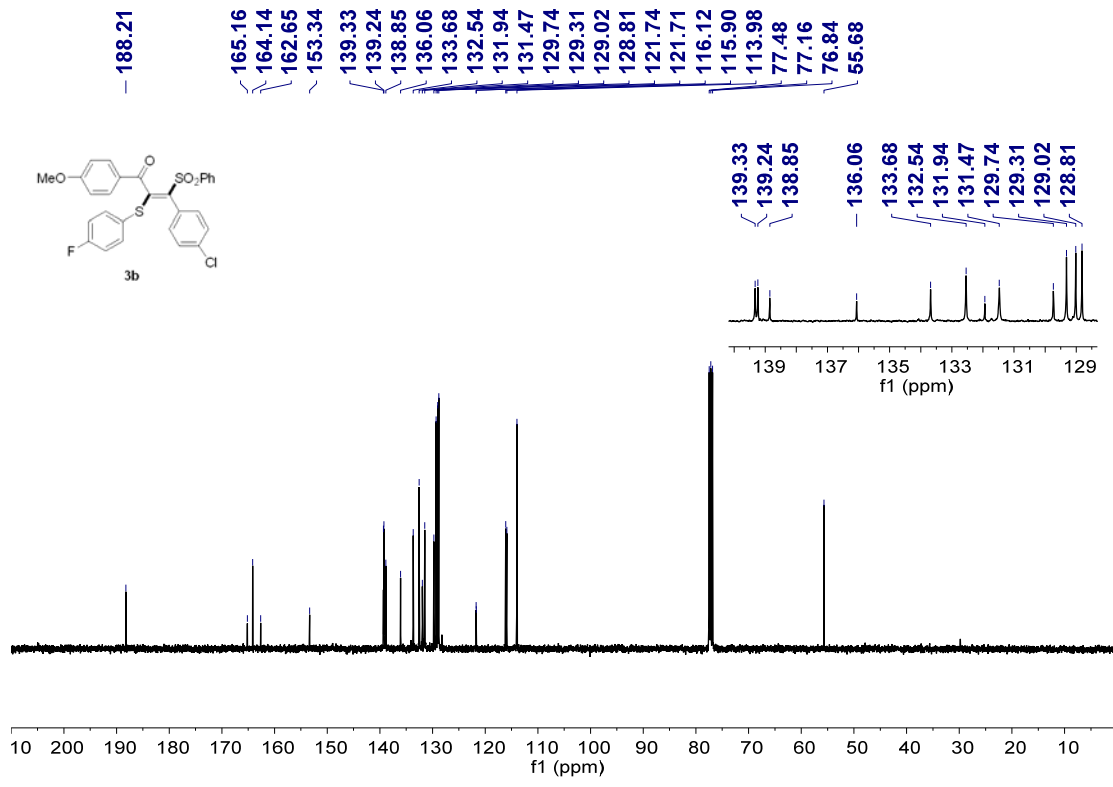
129.3, 129.1, 128.9, 128.1, 21.9; HRMS (ESI) m/z calcd for $C_{22}H_{18}DO_3S^+$ $[M+H]^+$ 364.1111, found, 364.1114.

12. Copies of NMR spectra of products

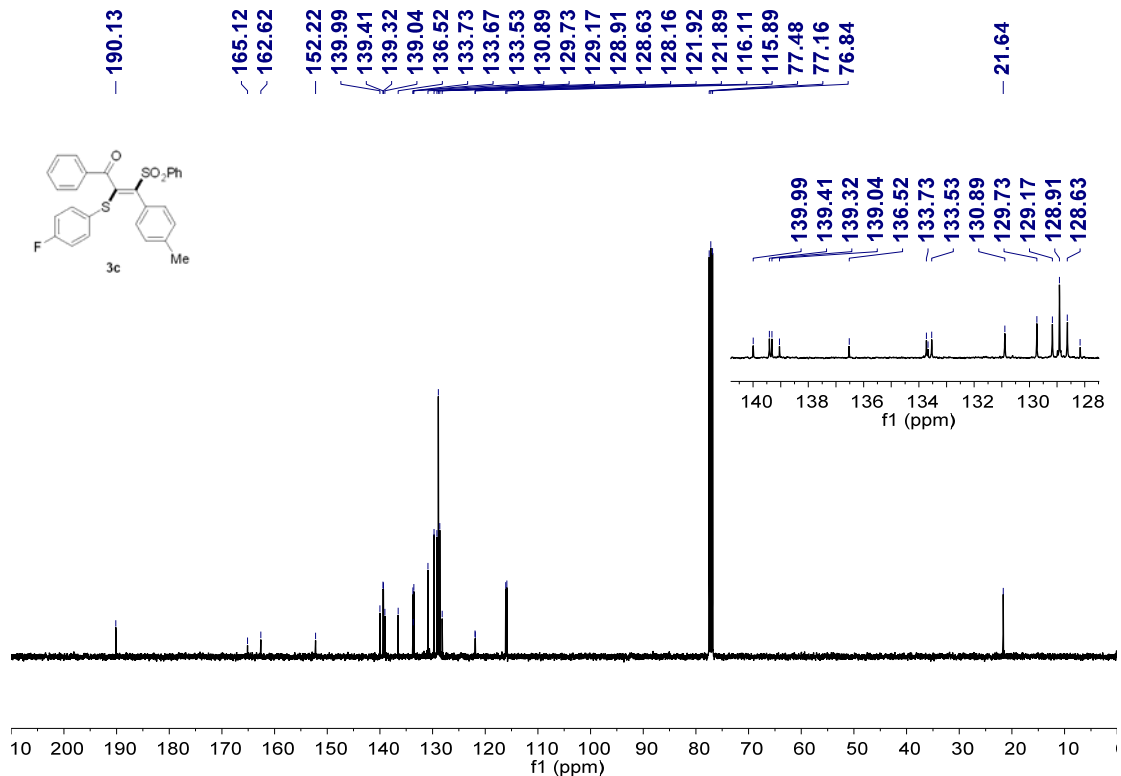
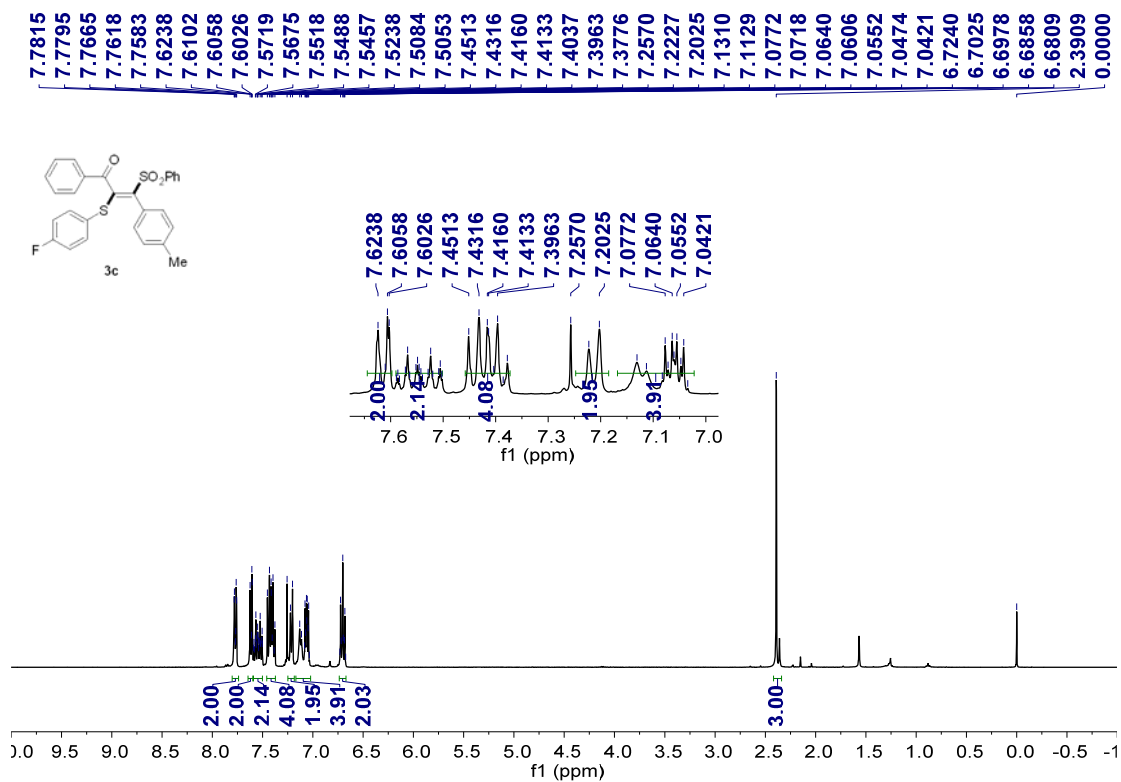
3a

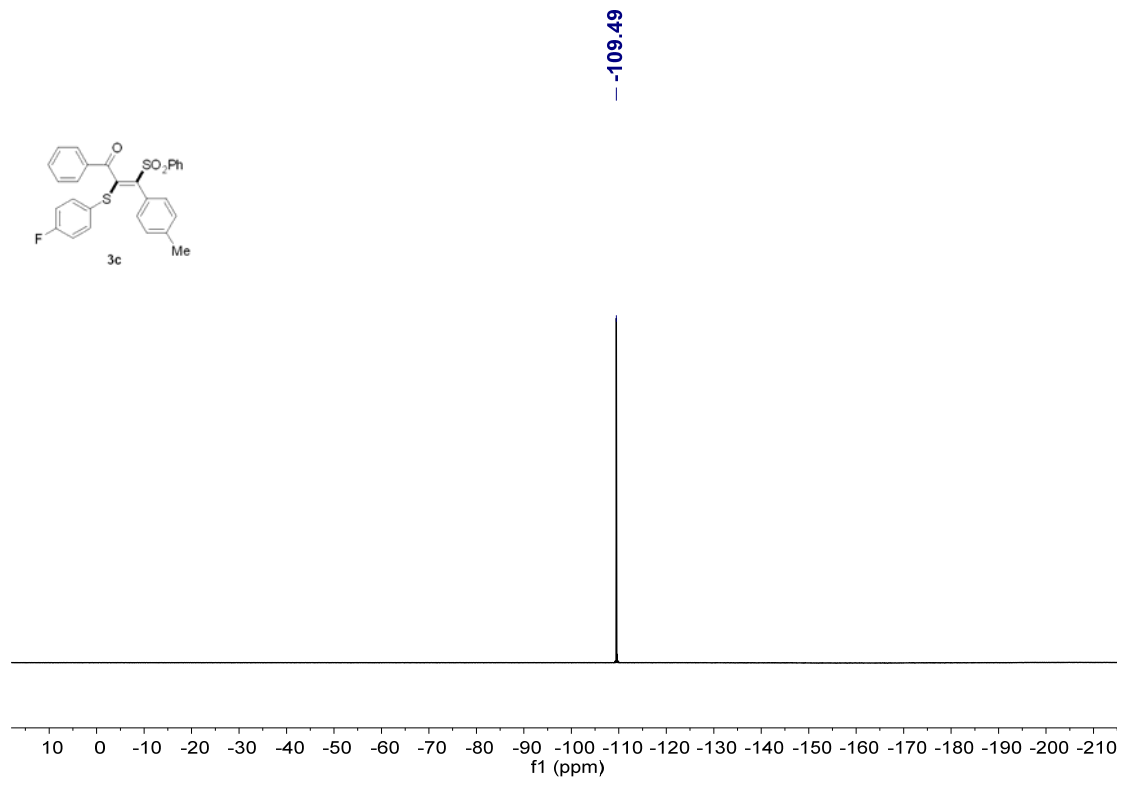




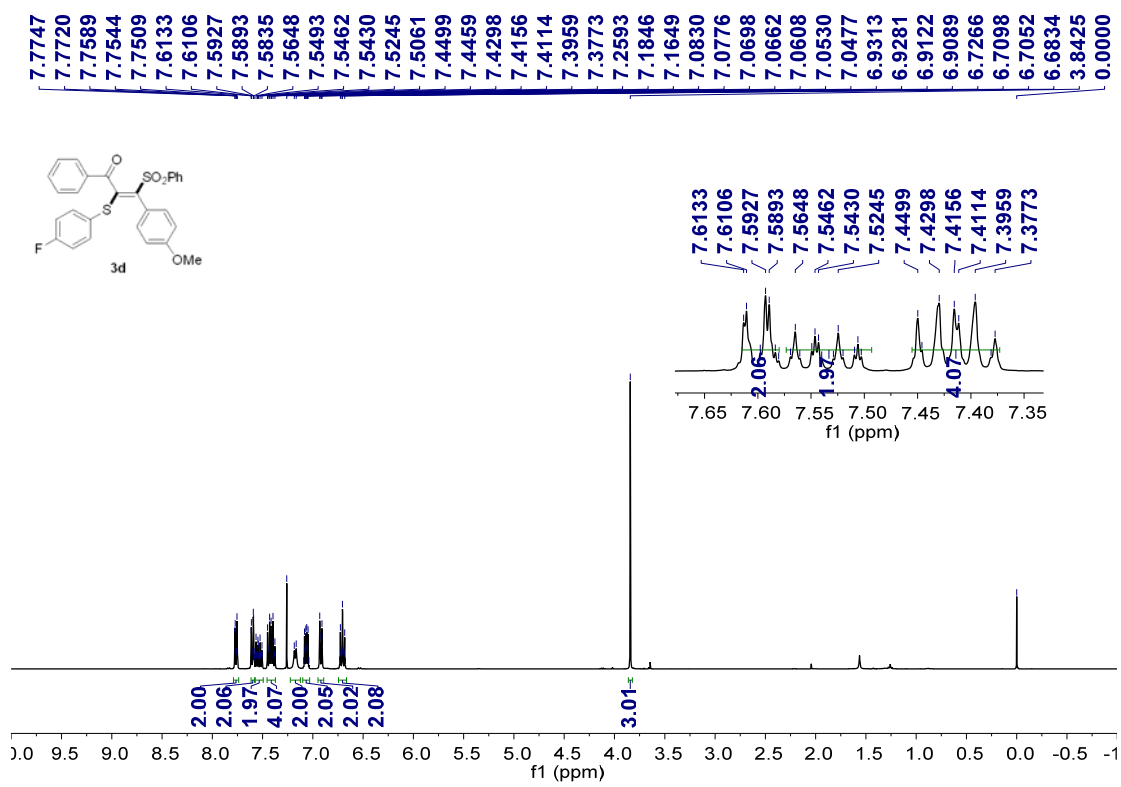


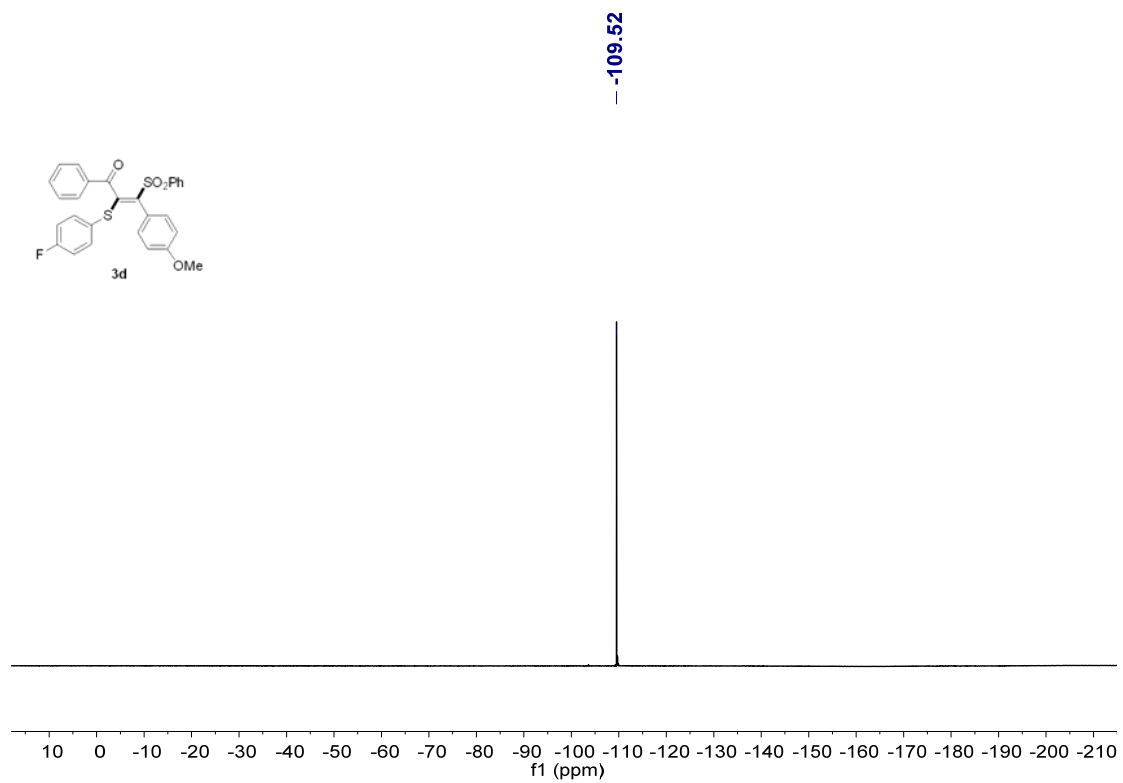
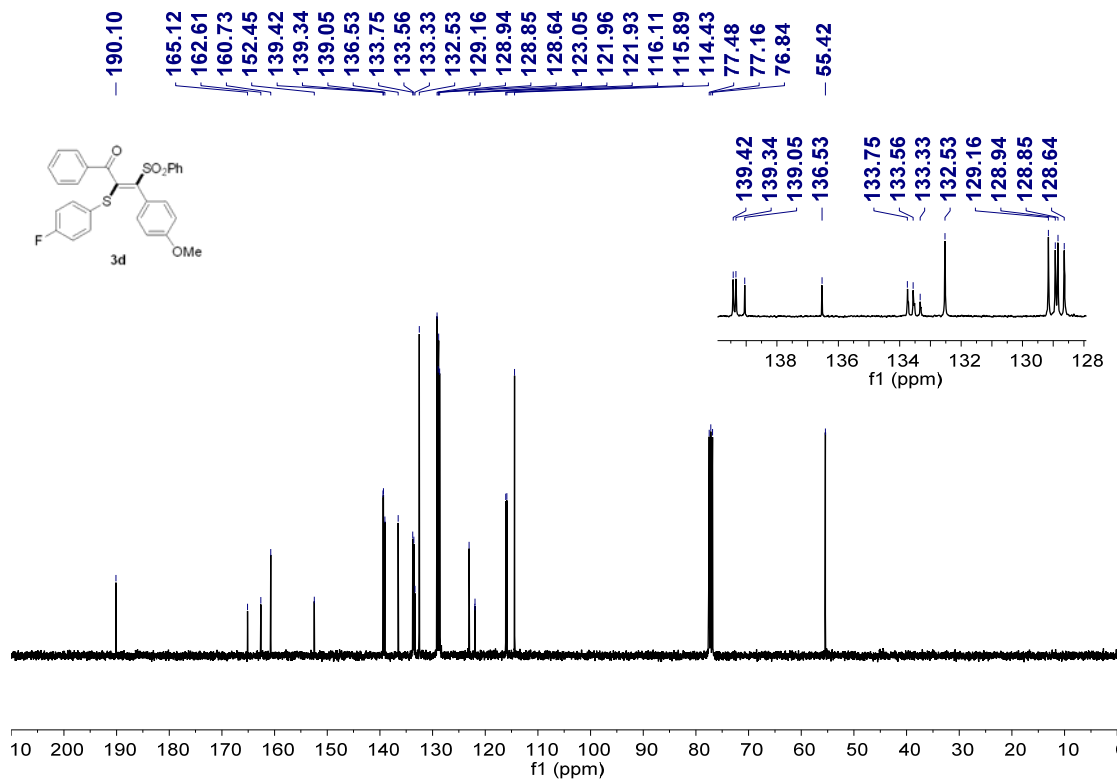
3c



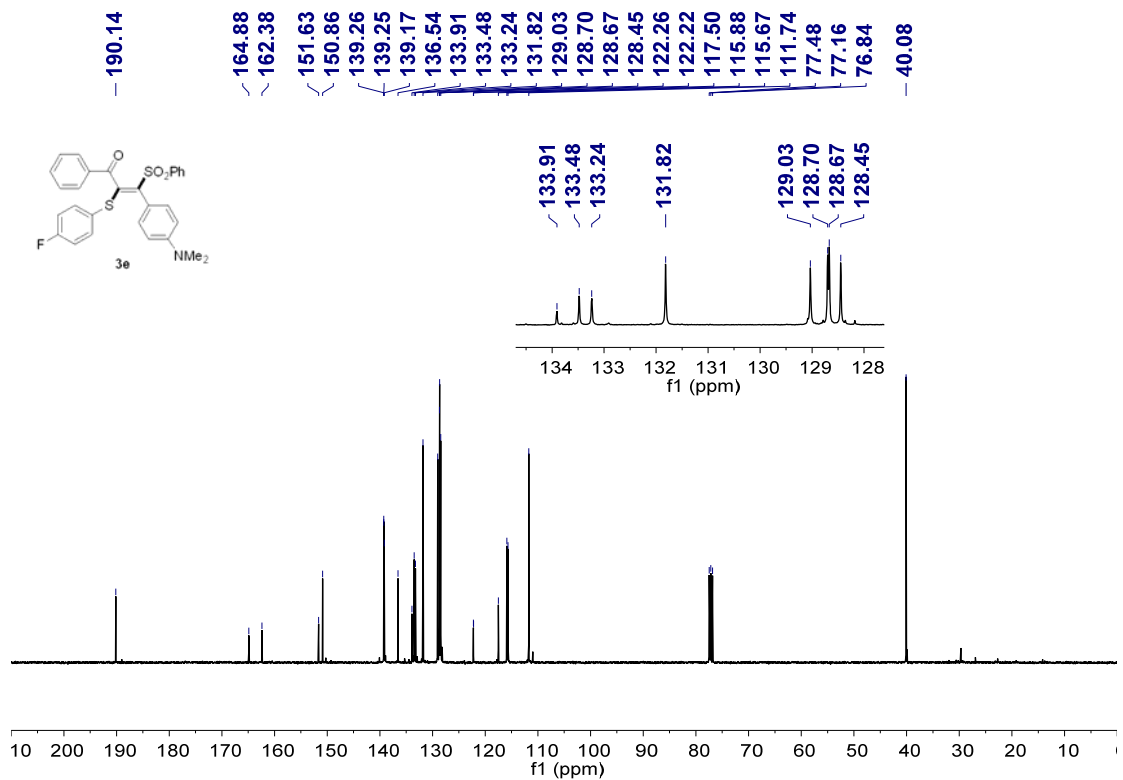
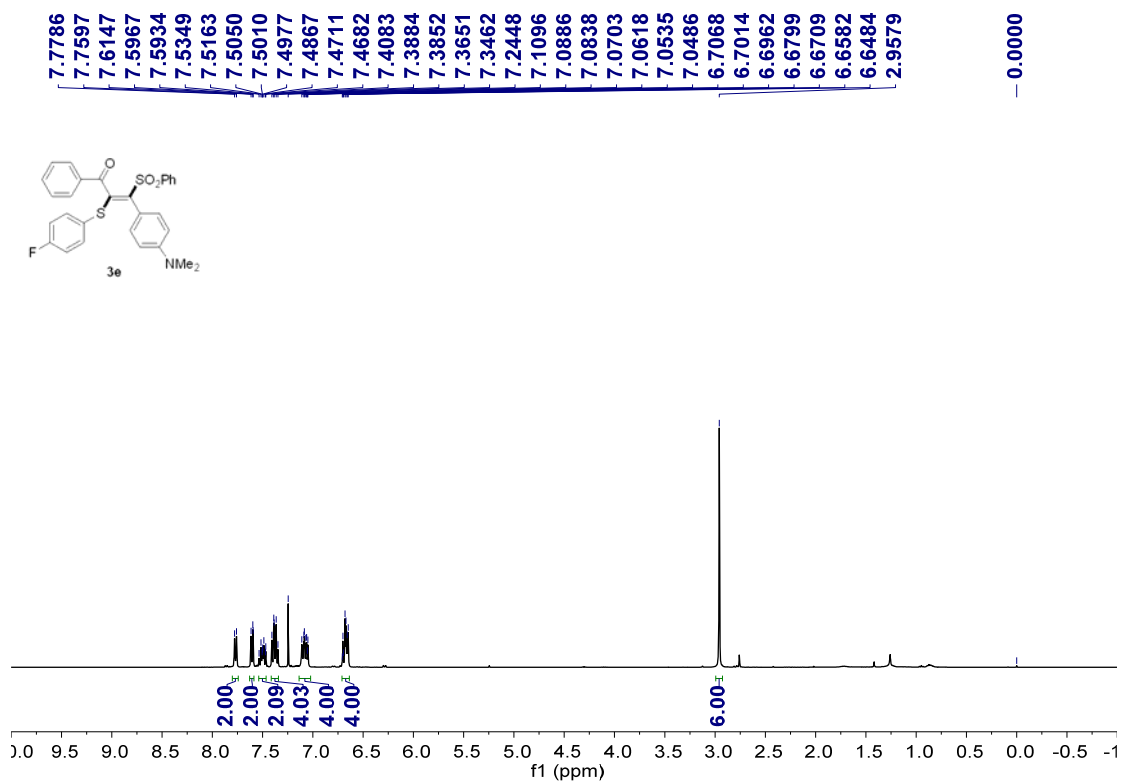


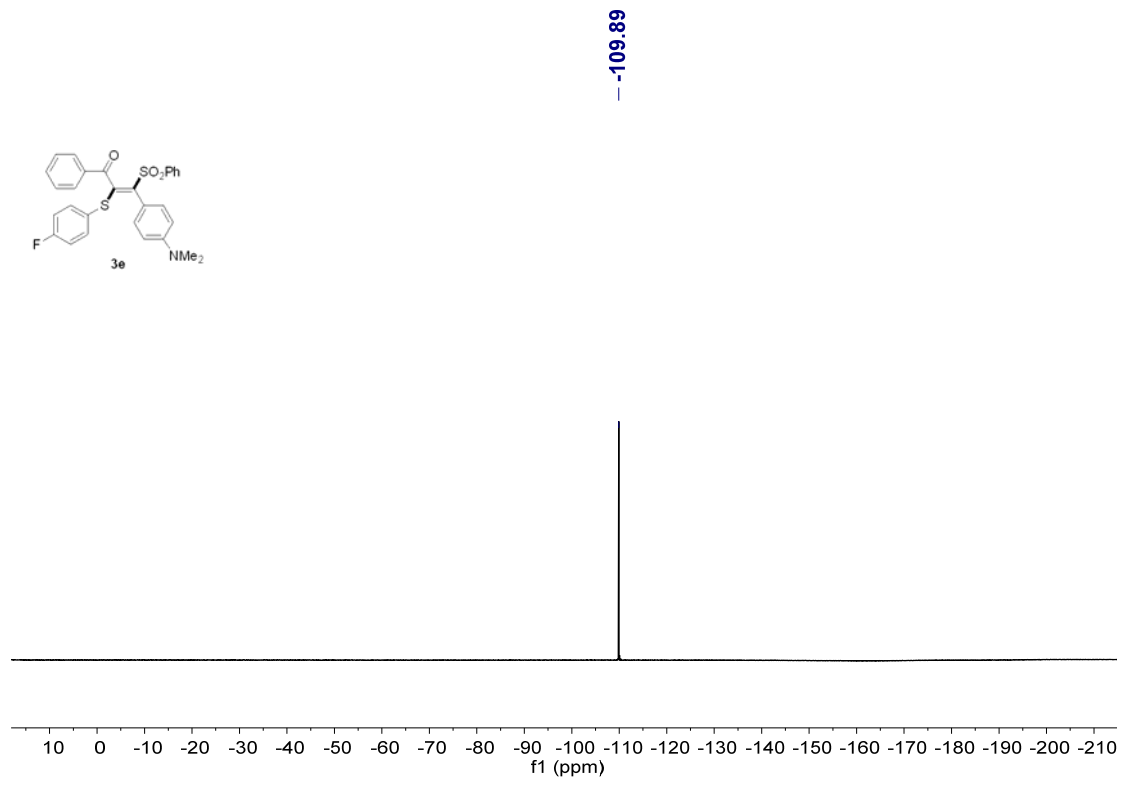
3d



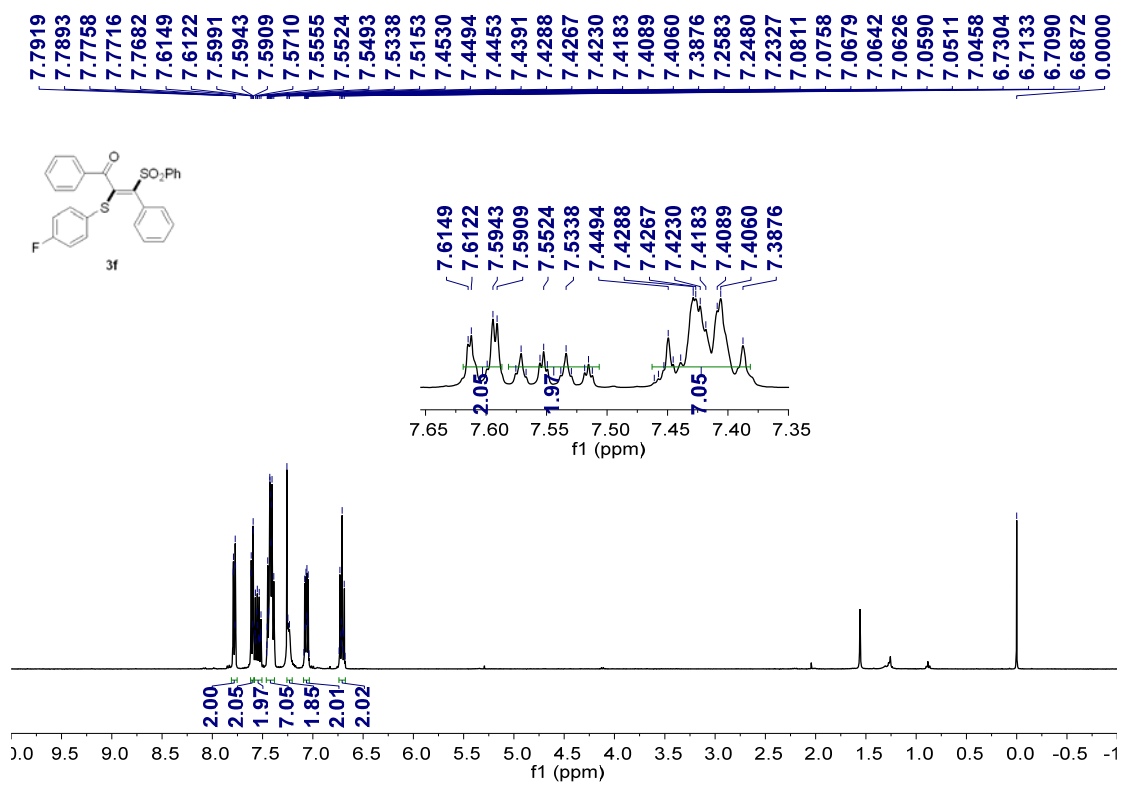


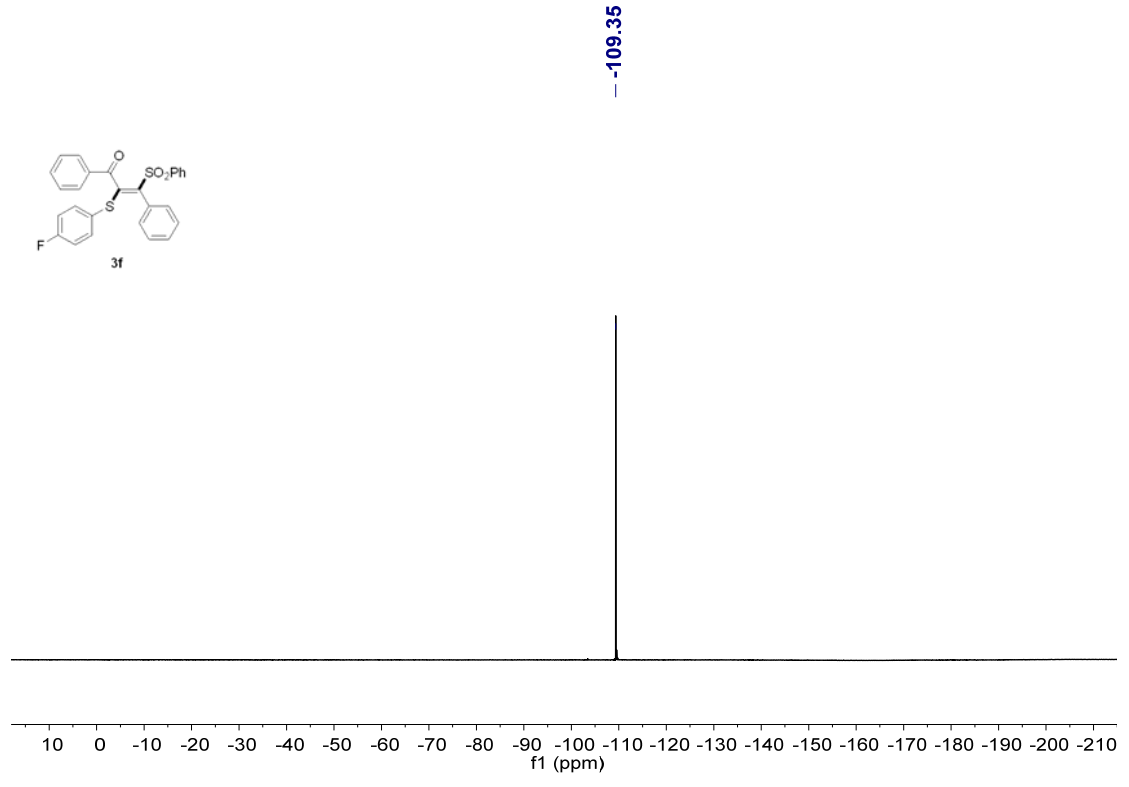
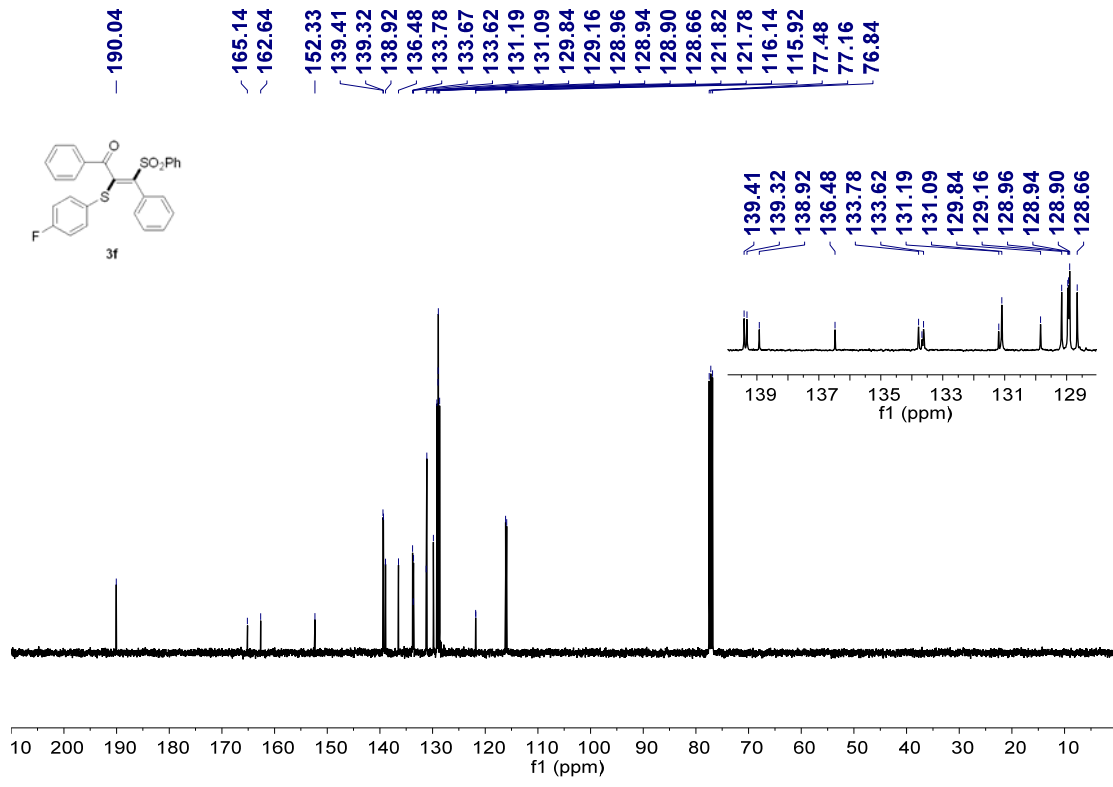
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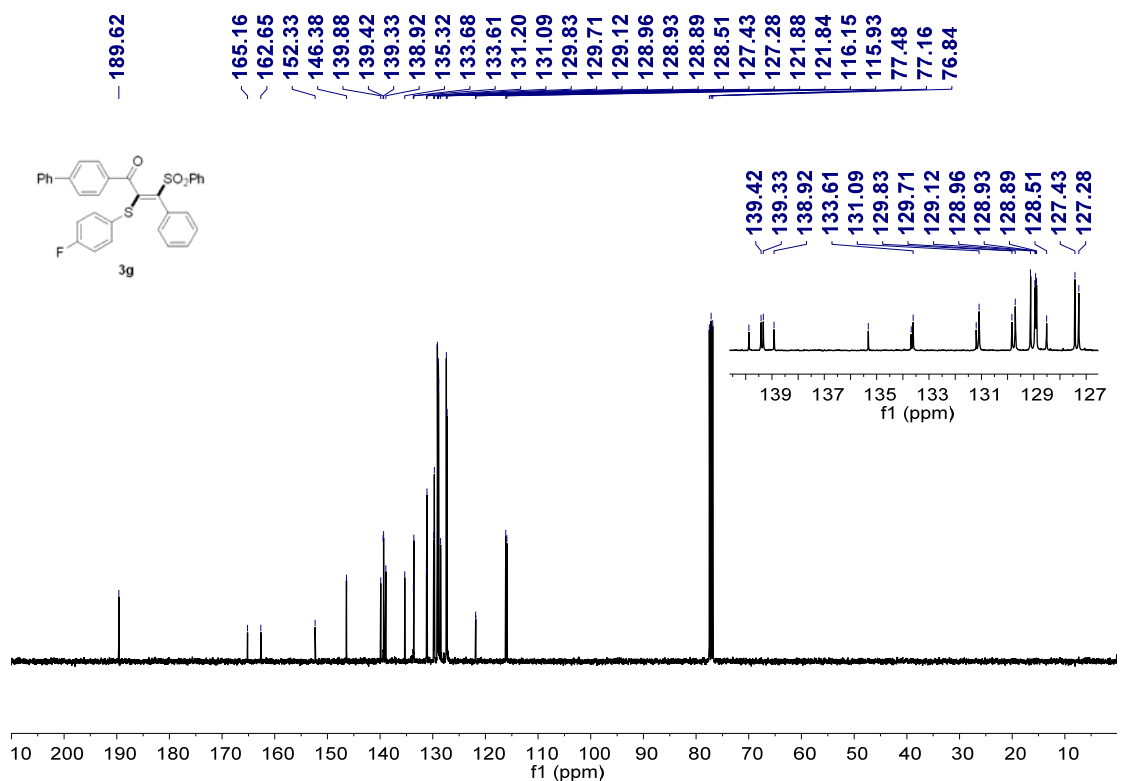
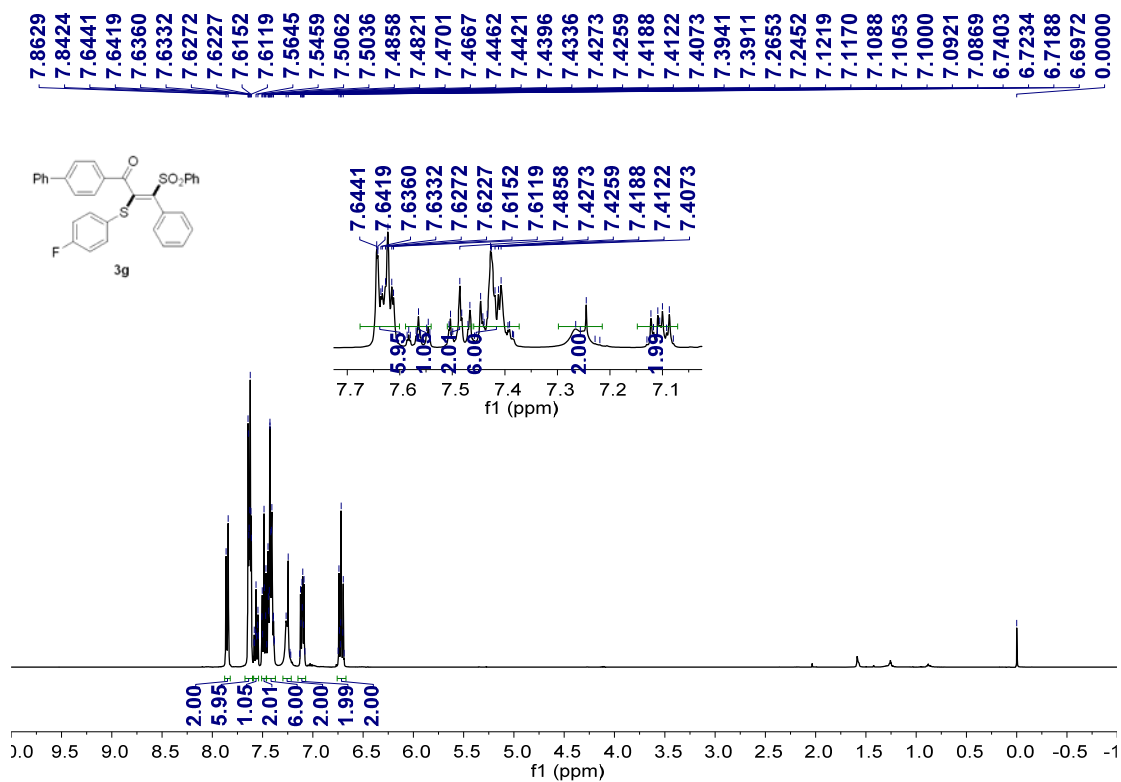


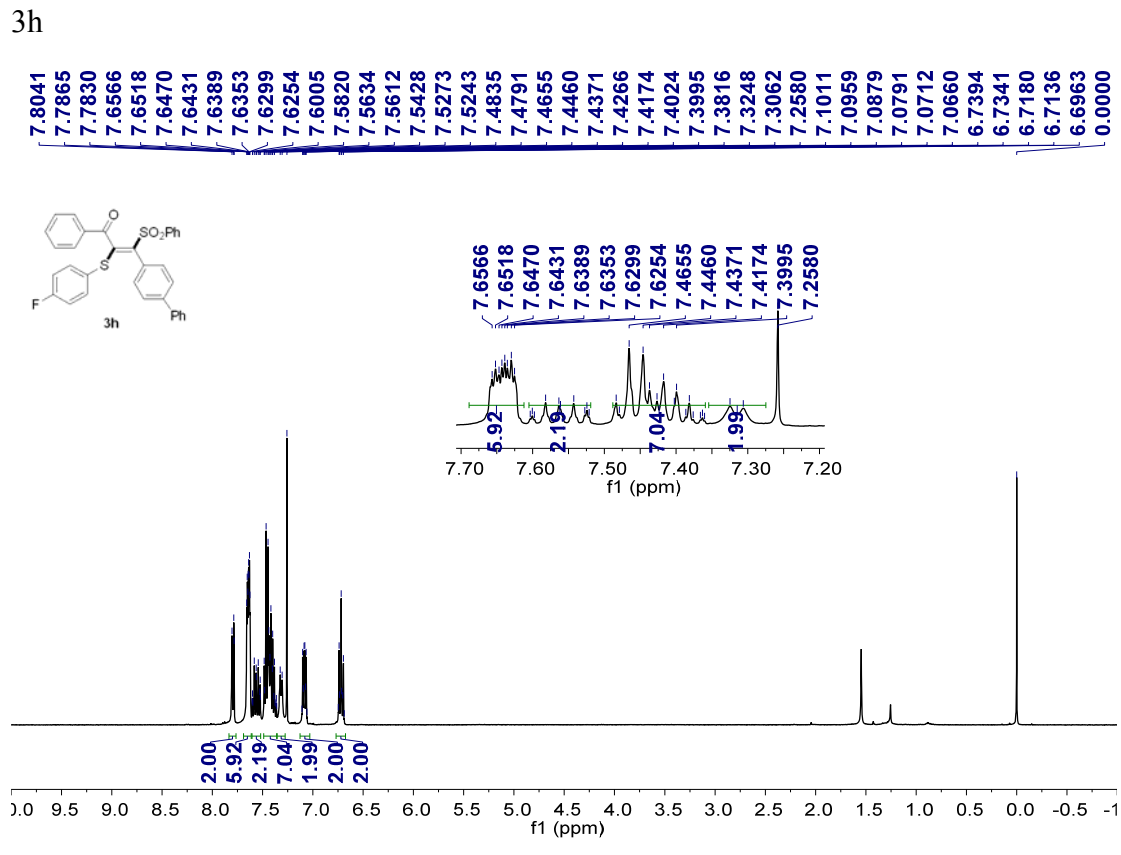
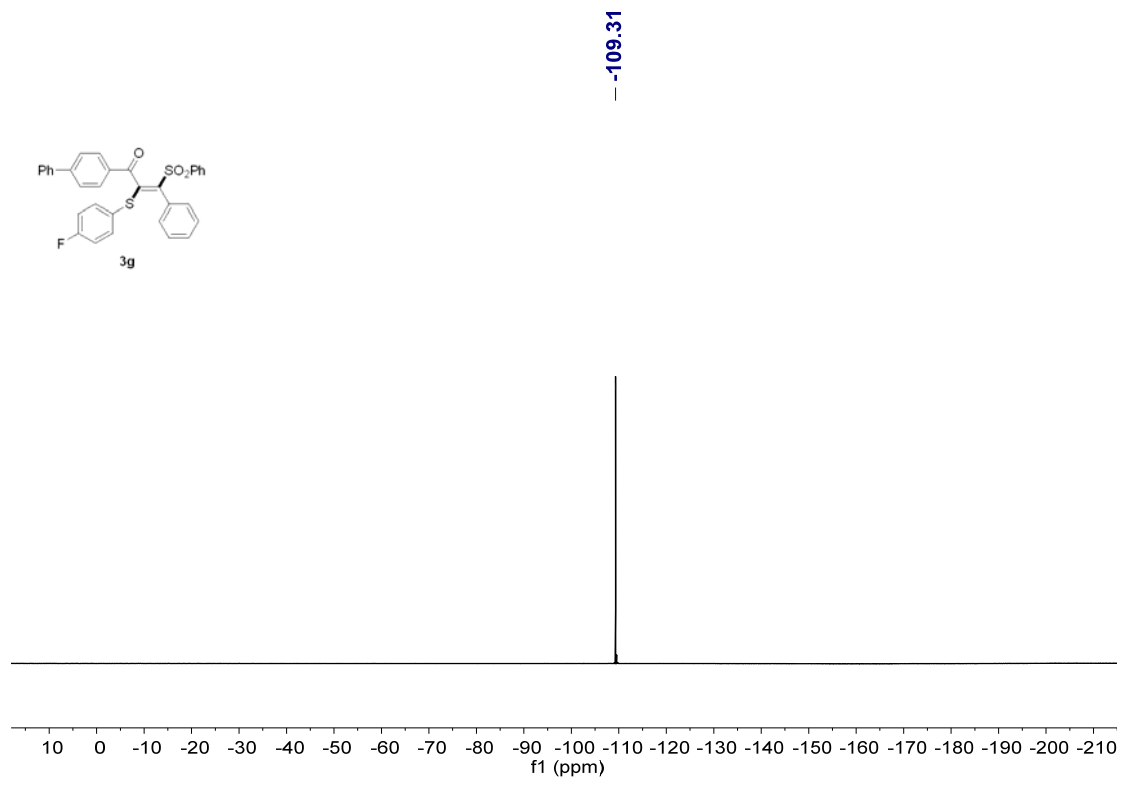
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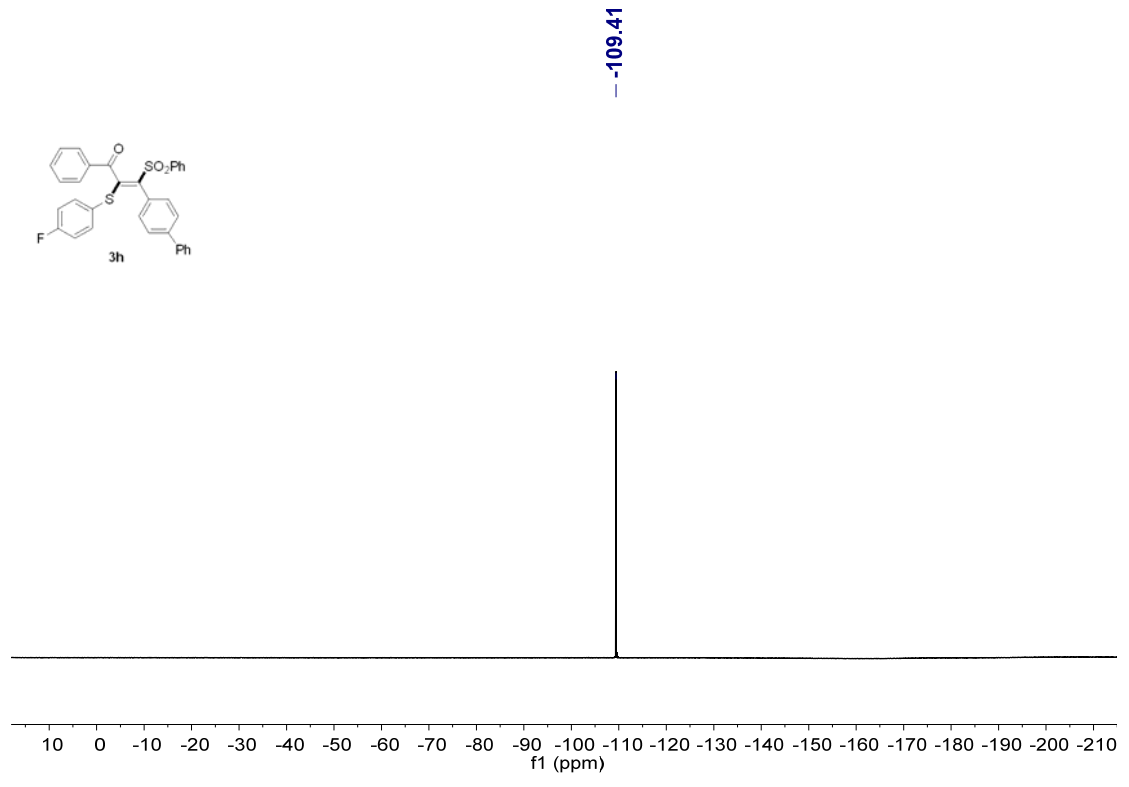
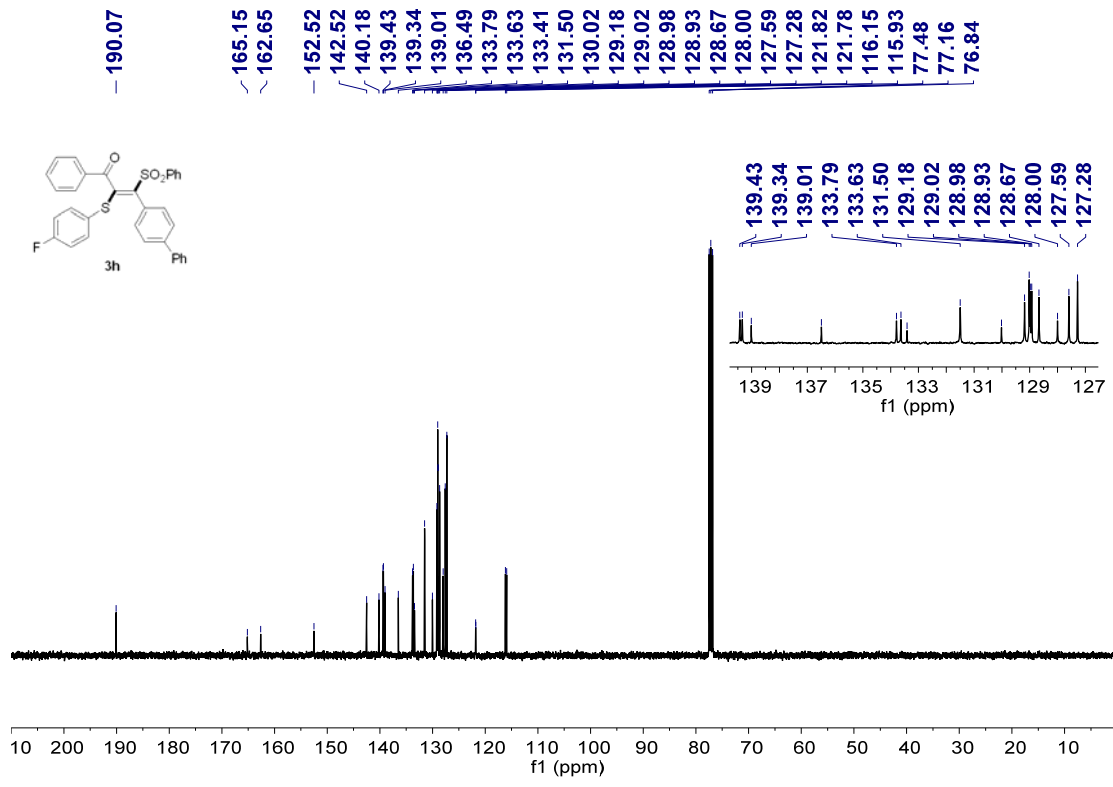




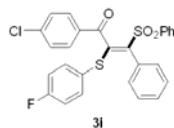
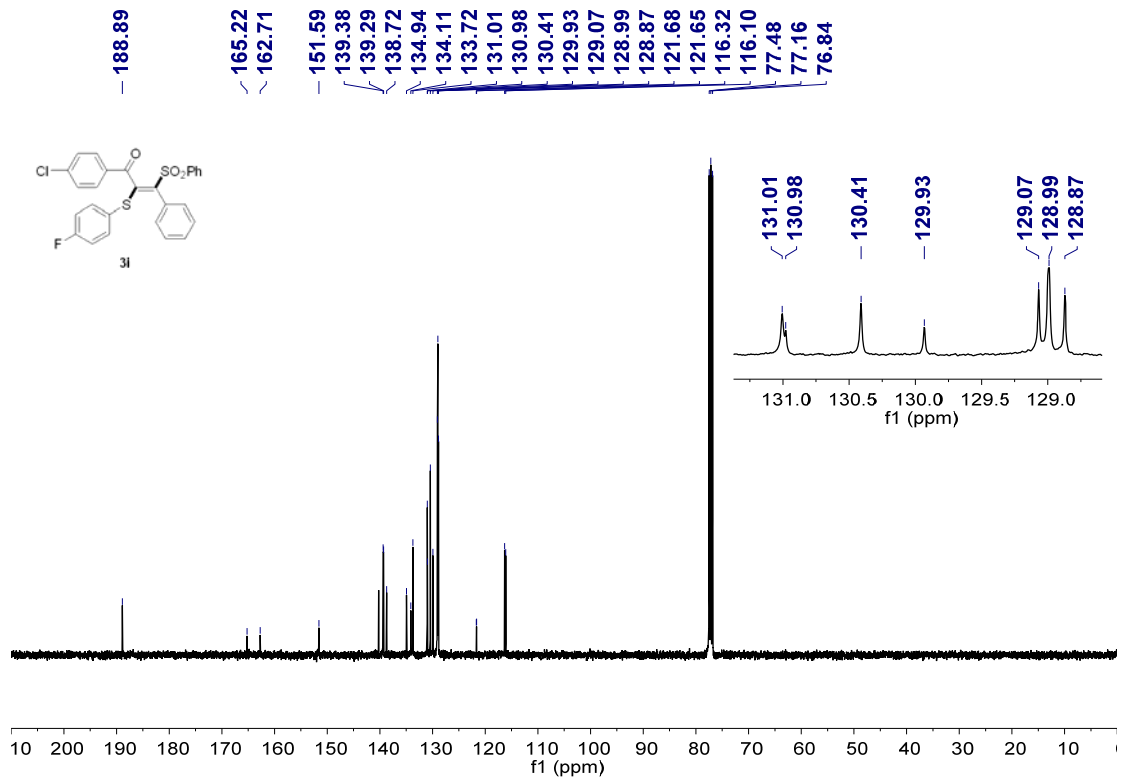
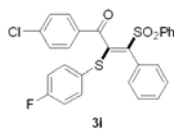
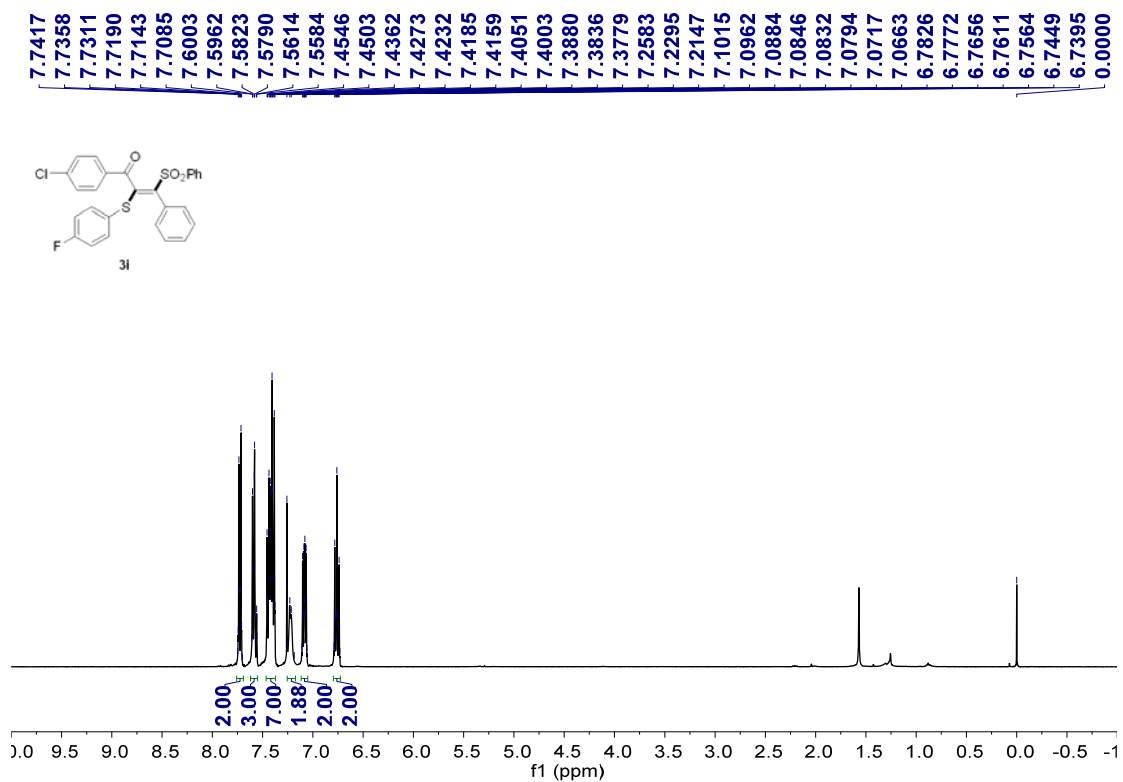
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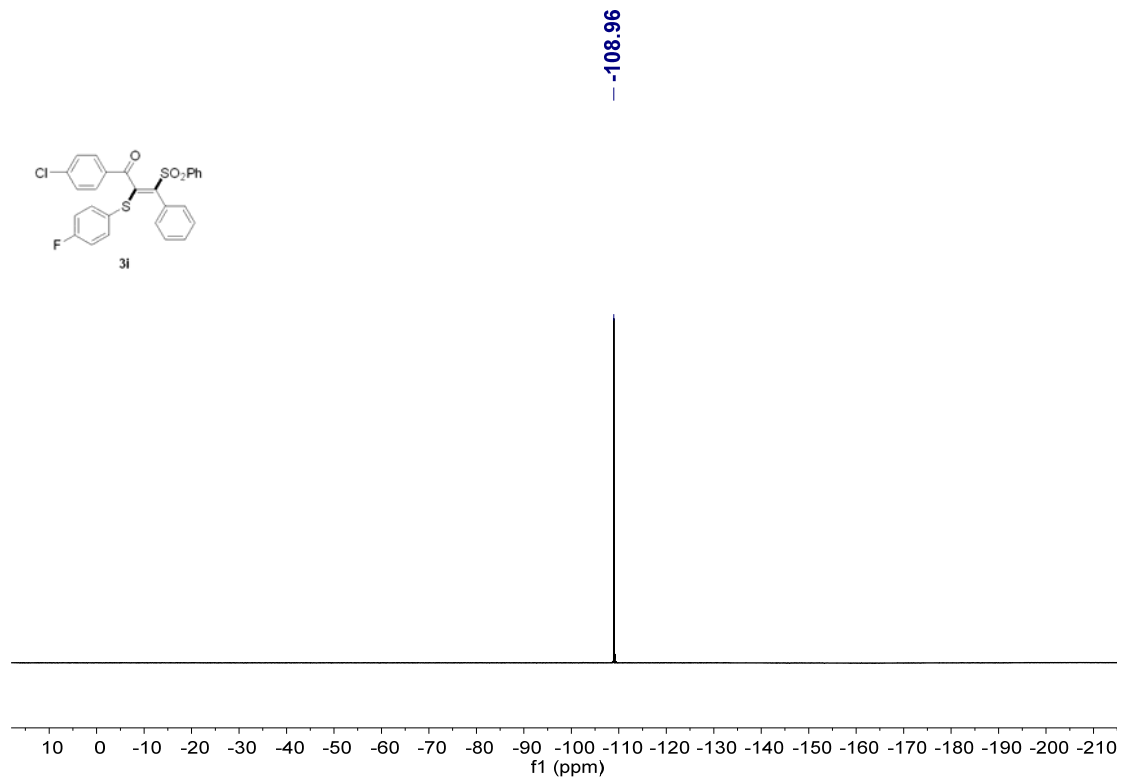




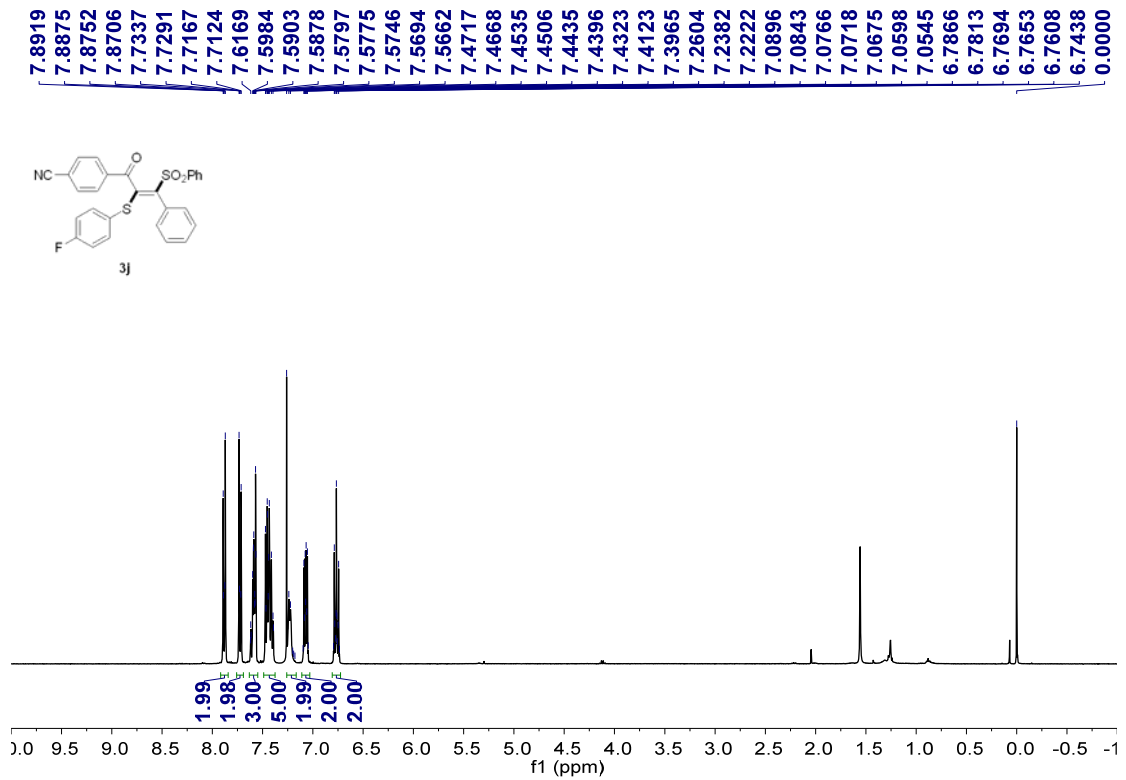


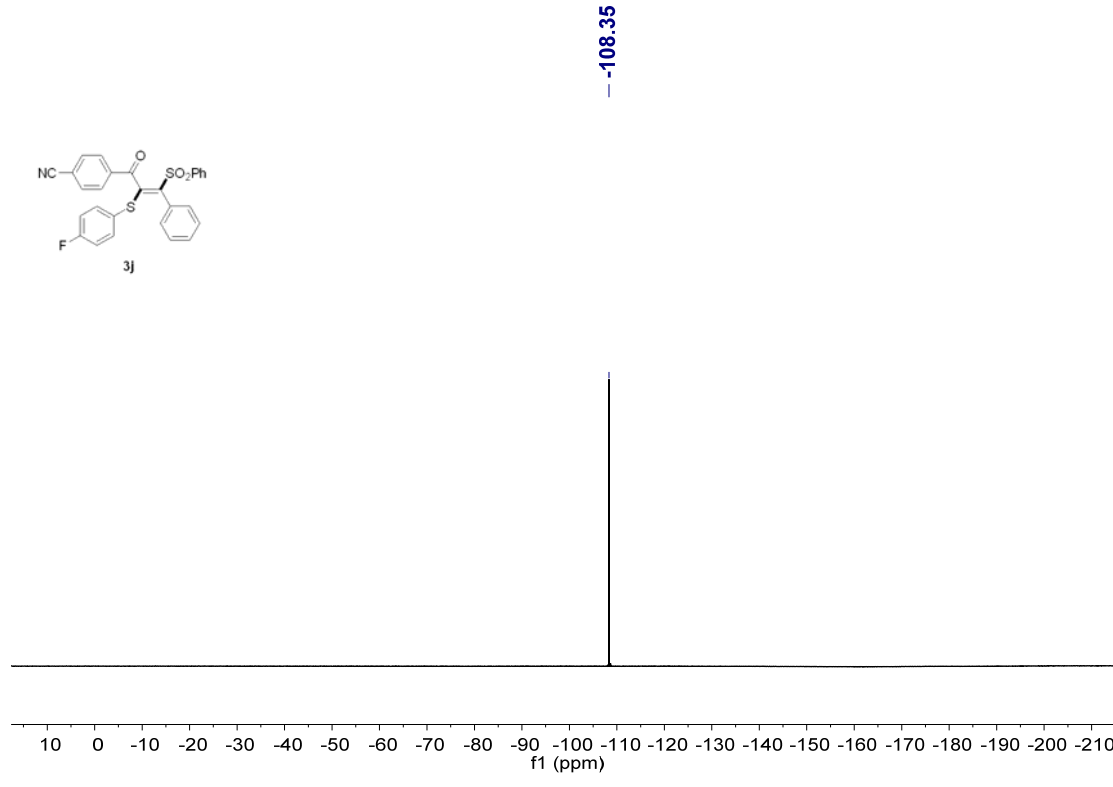
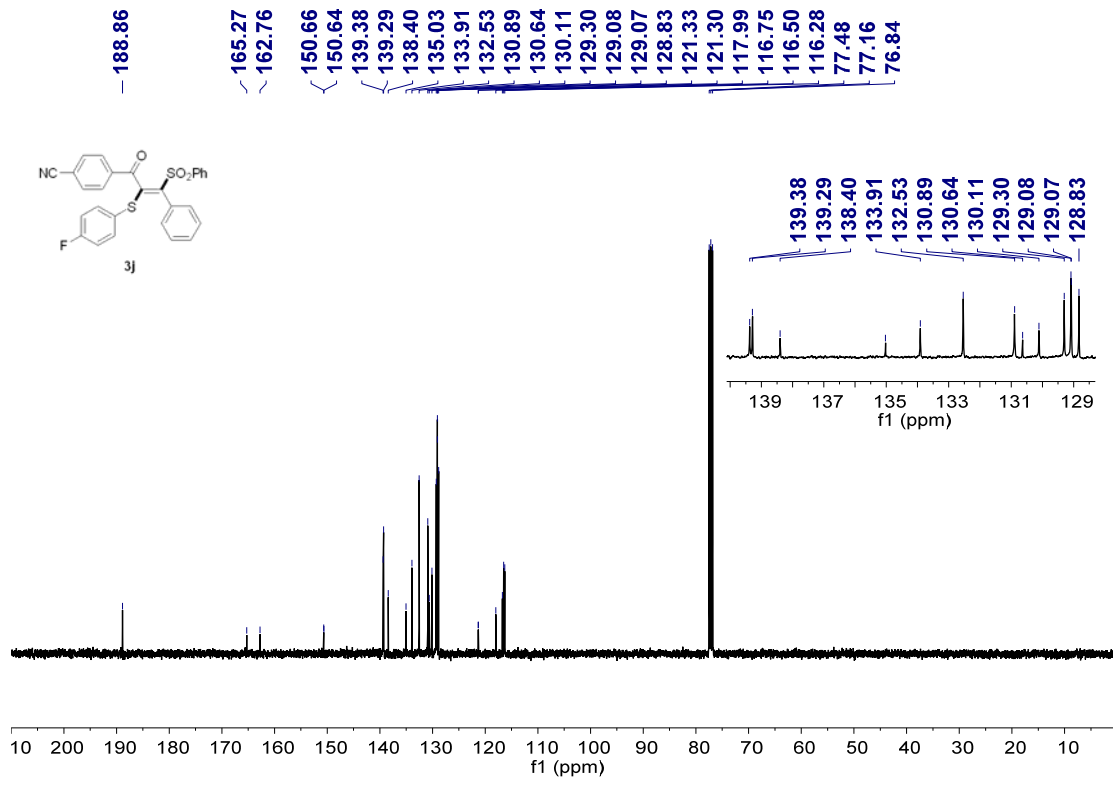
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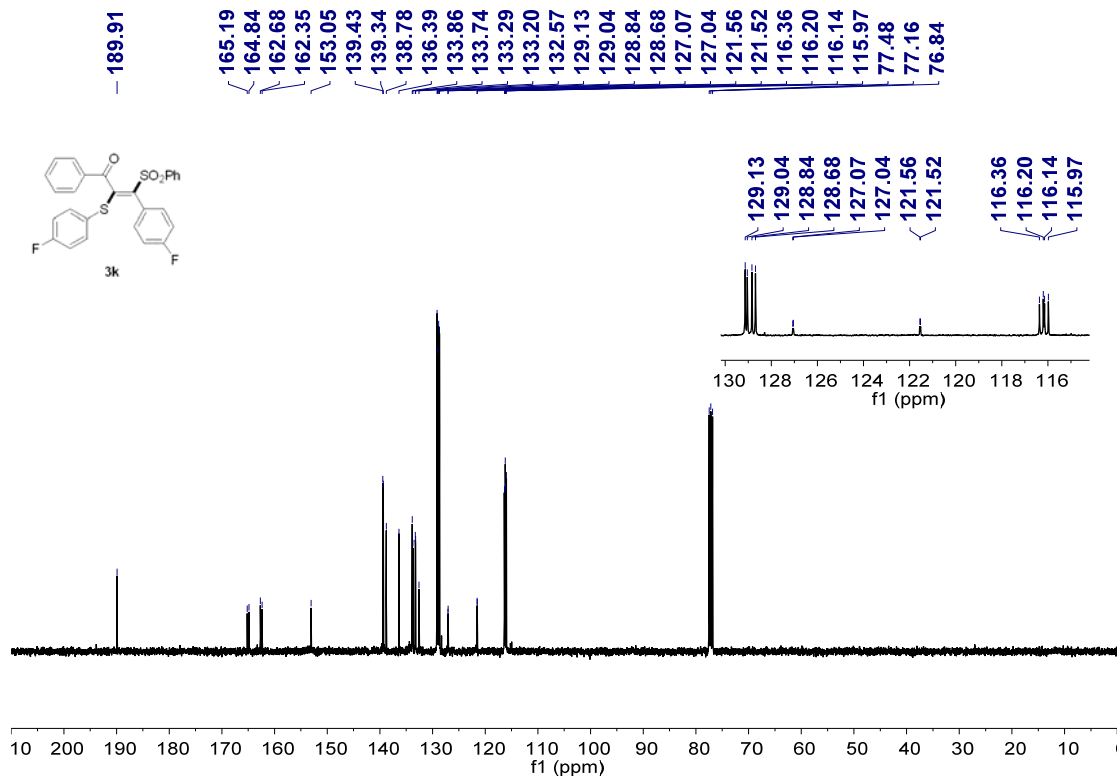
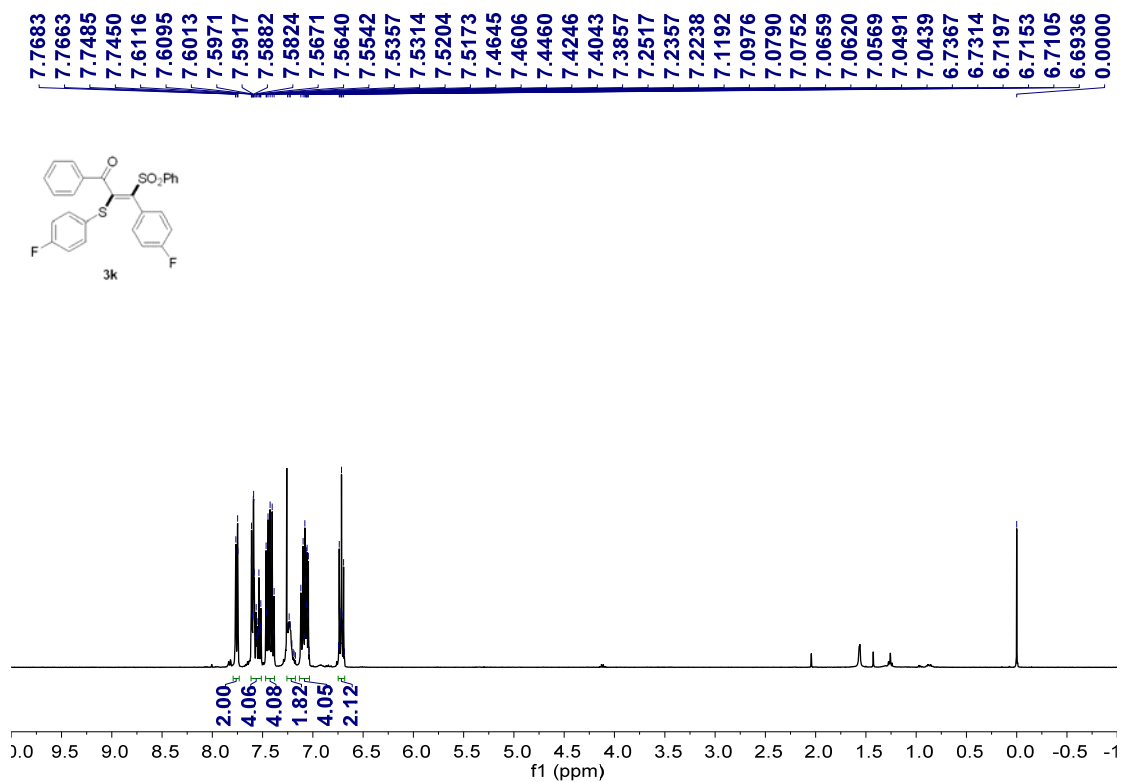


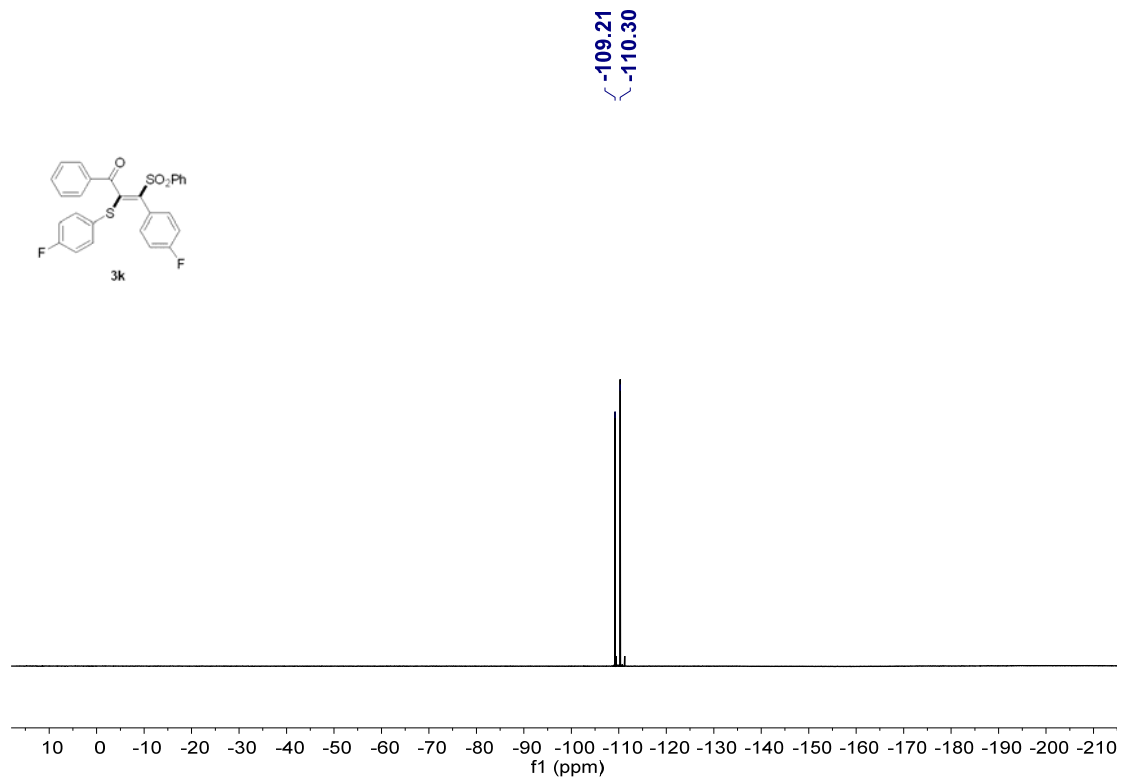
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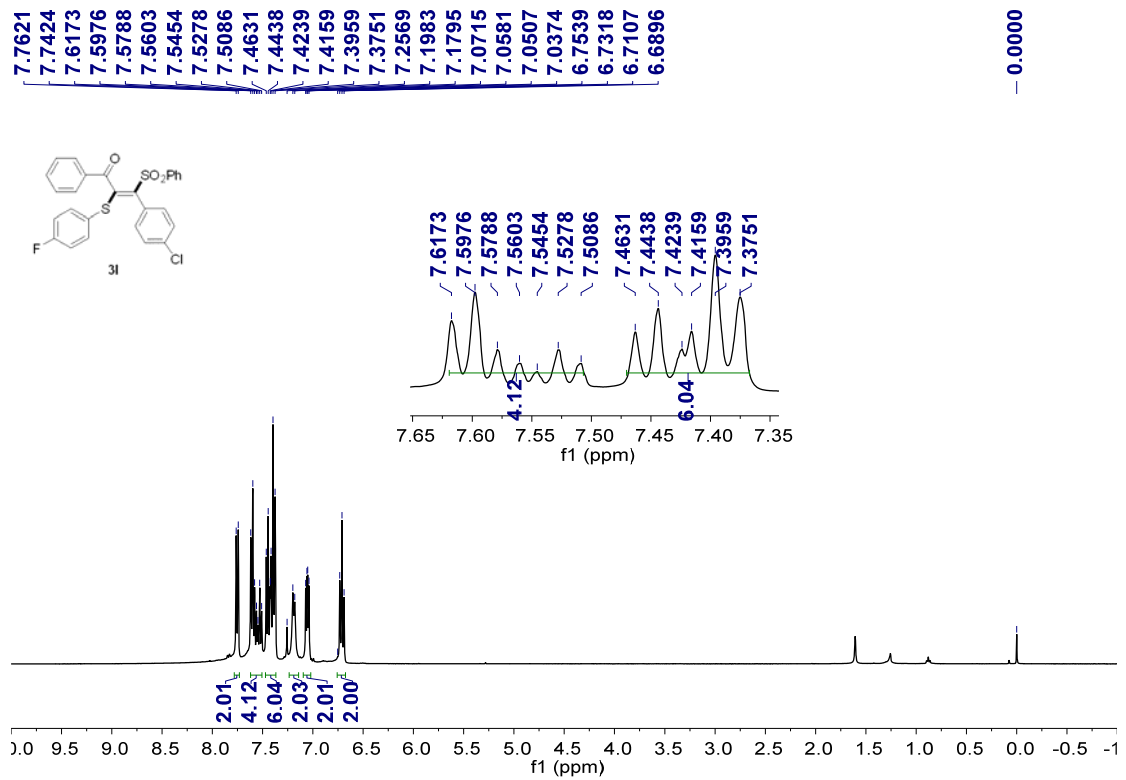


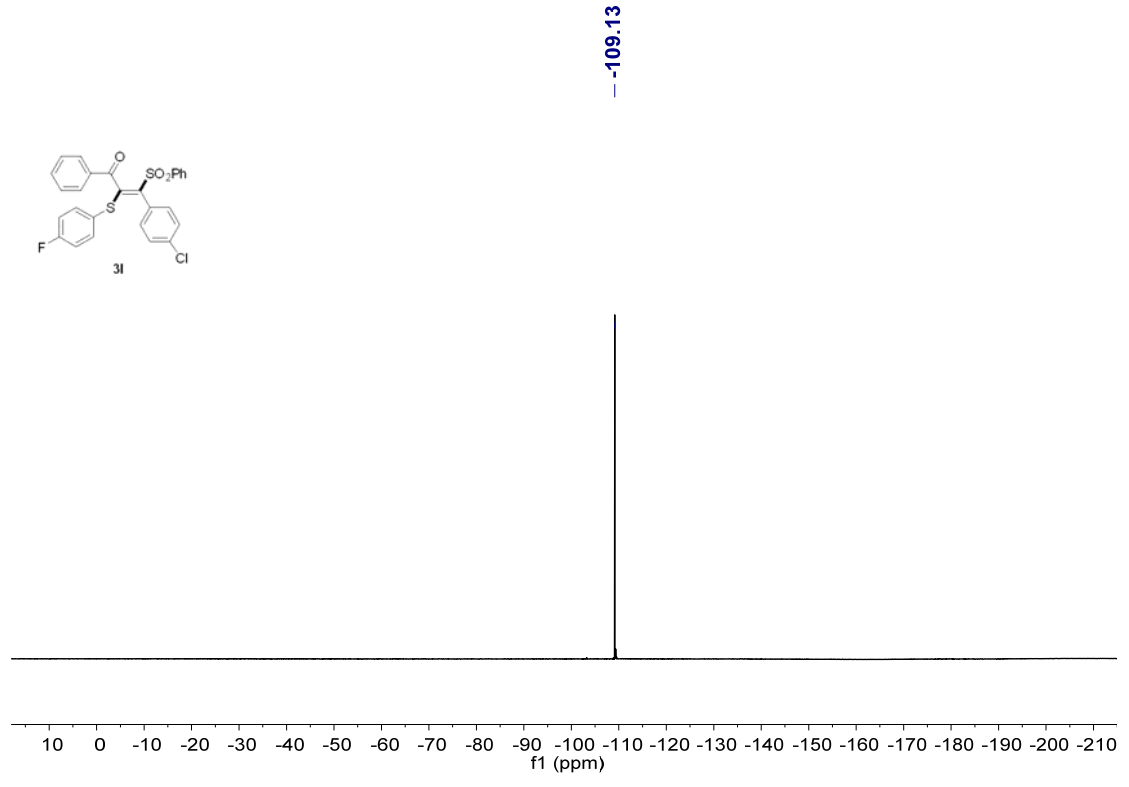
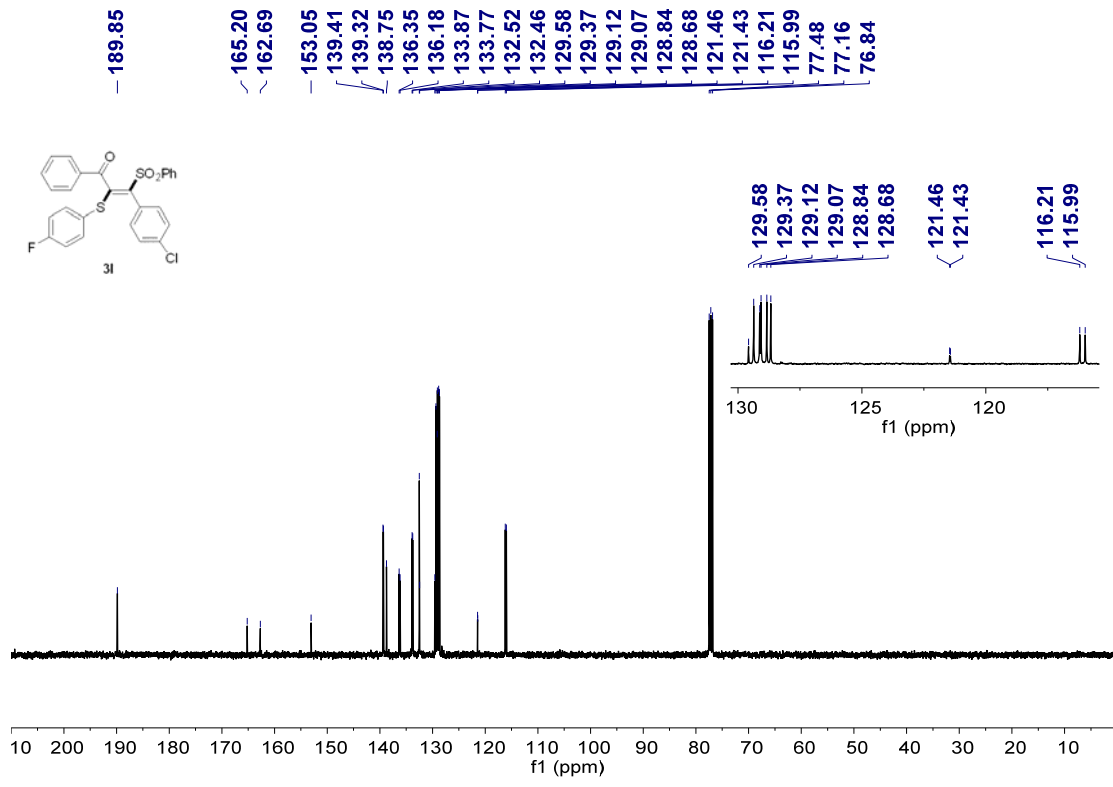
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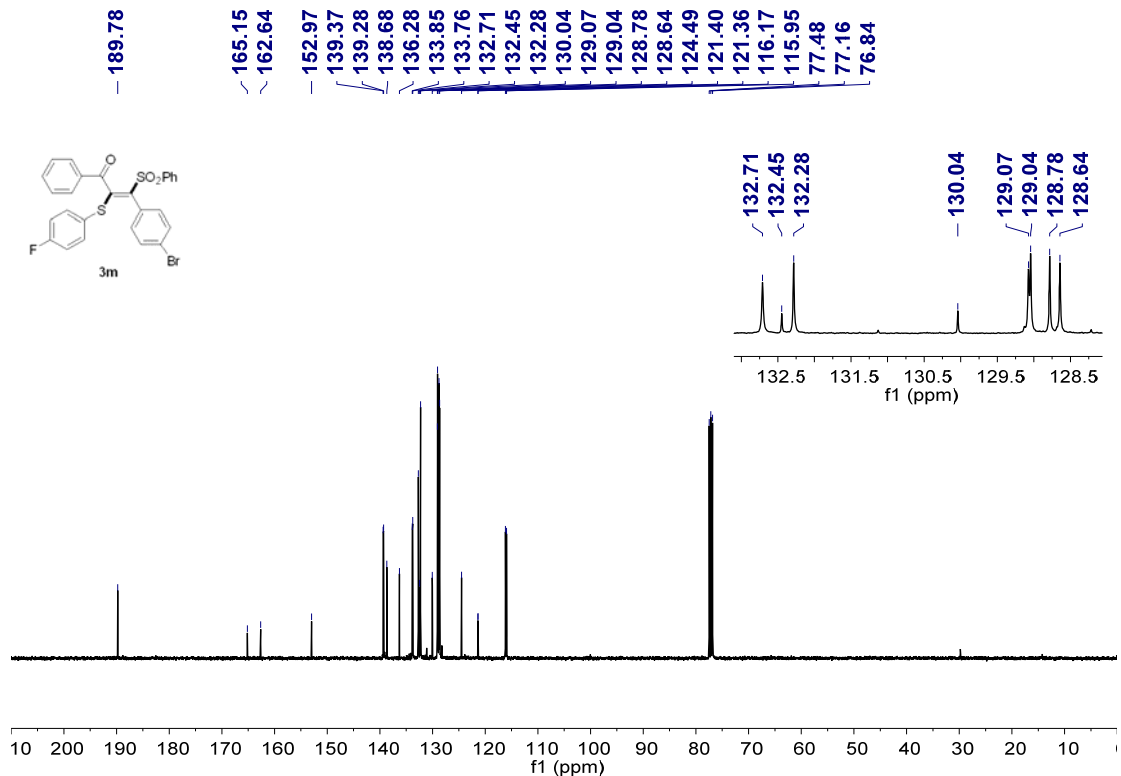
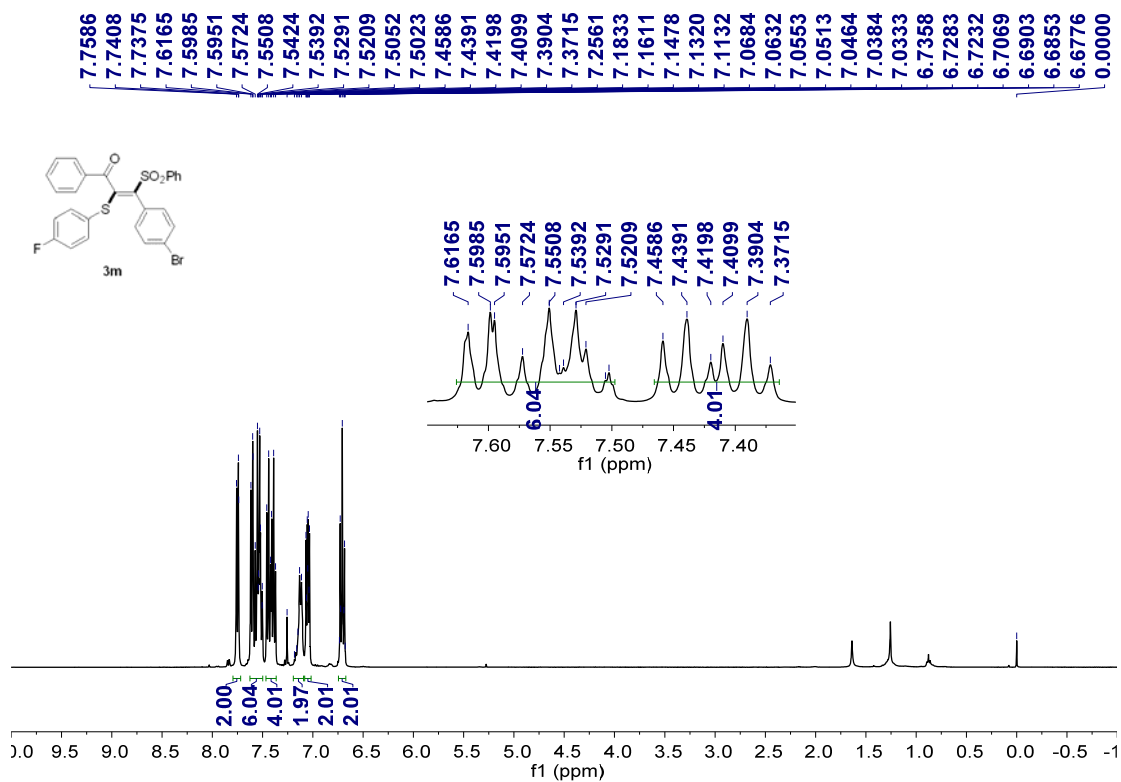


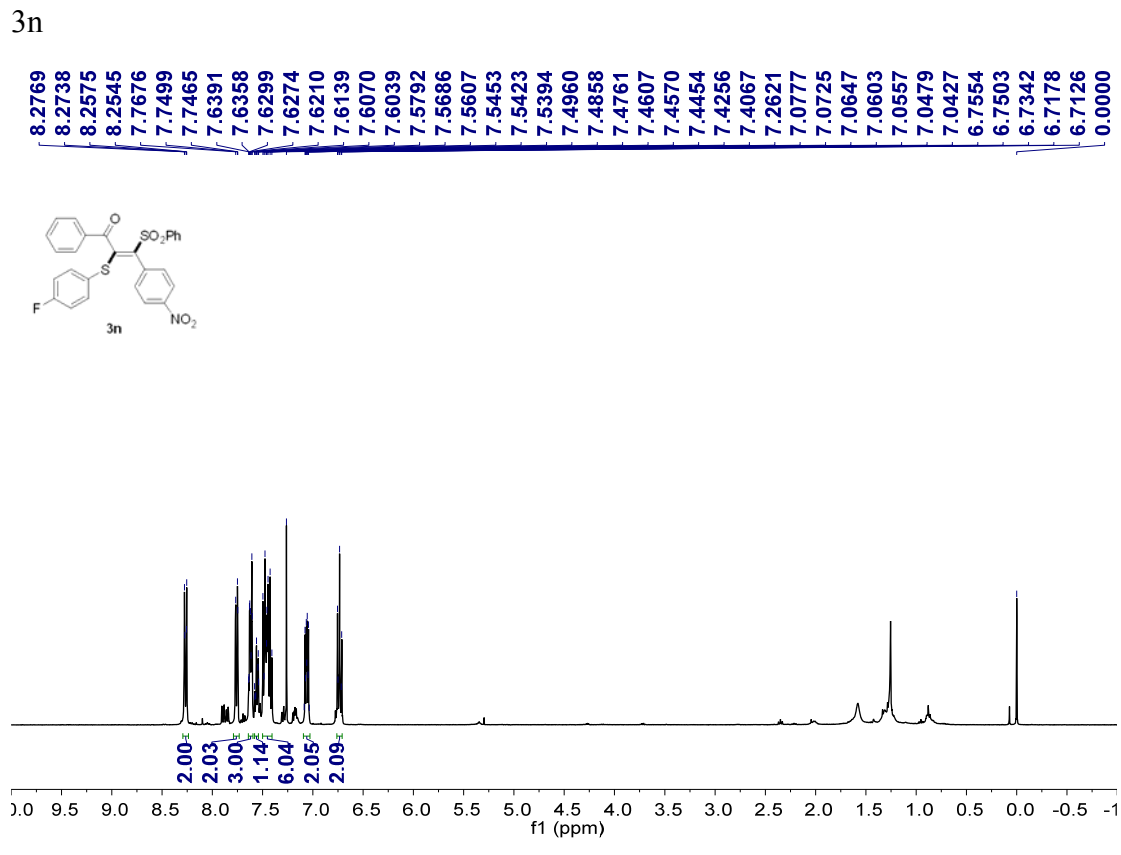
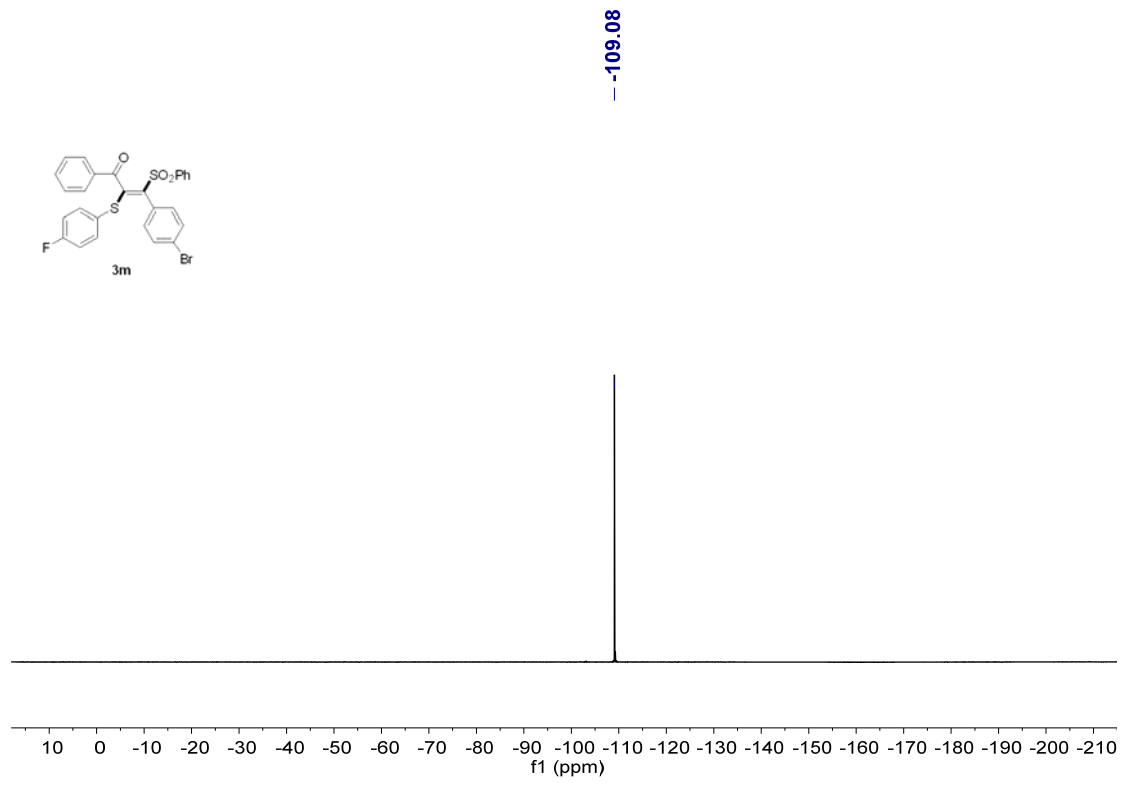
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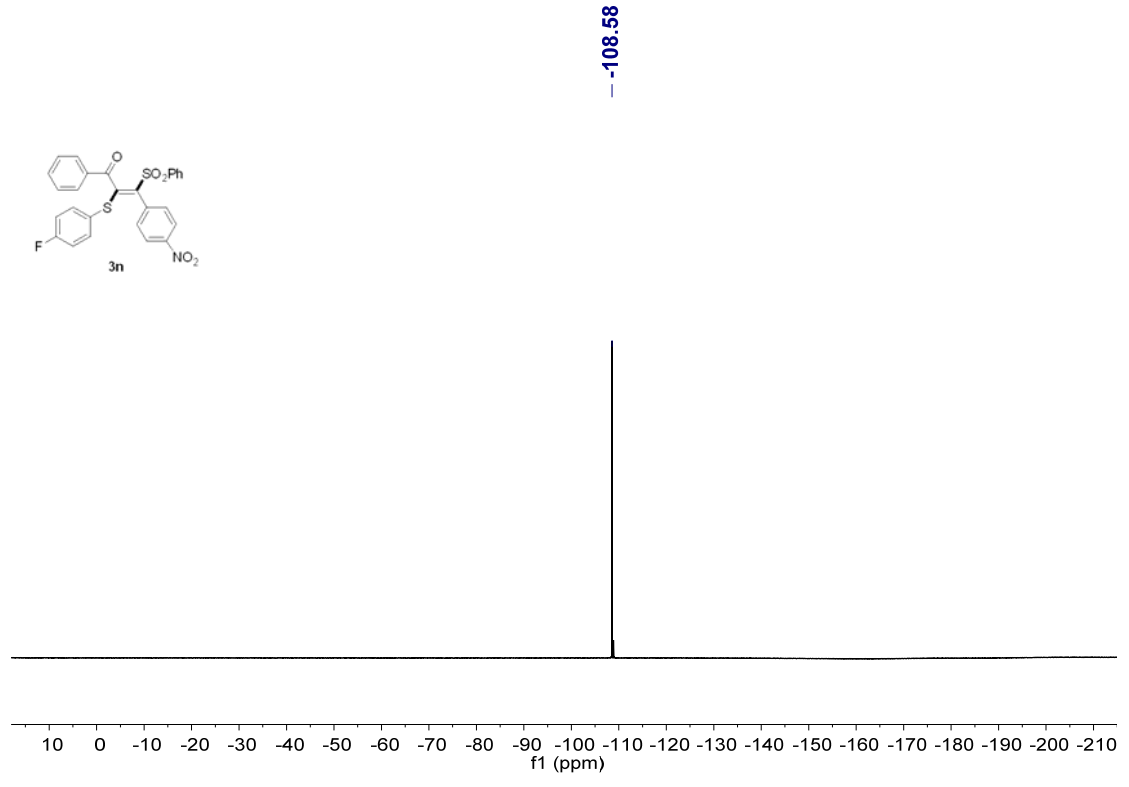
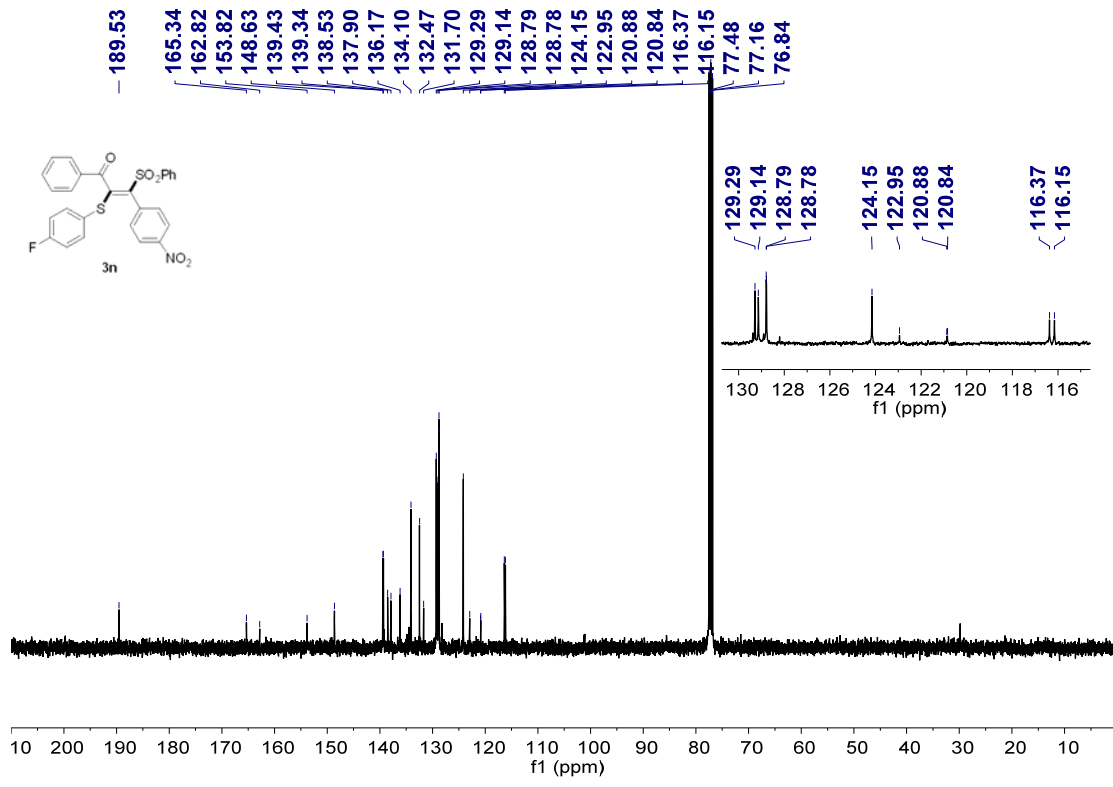




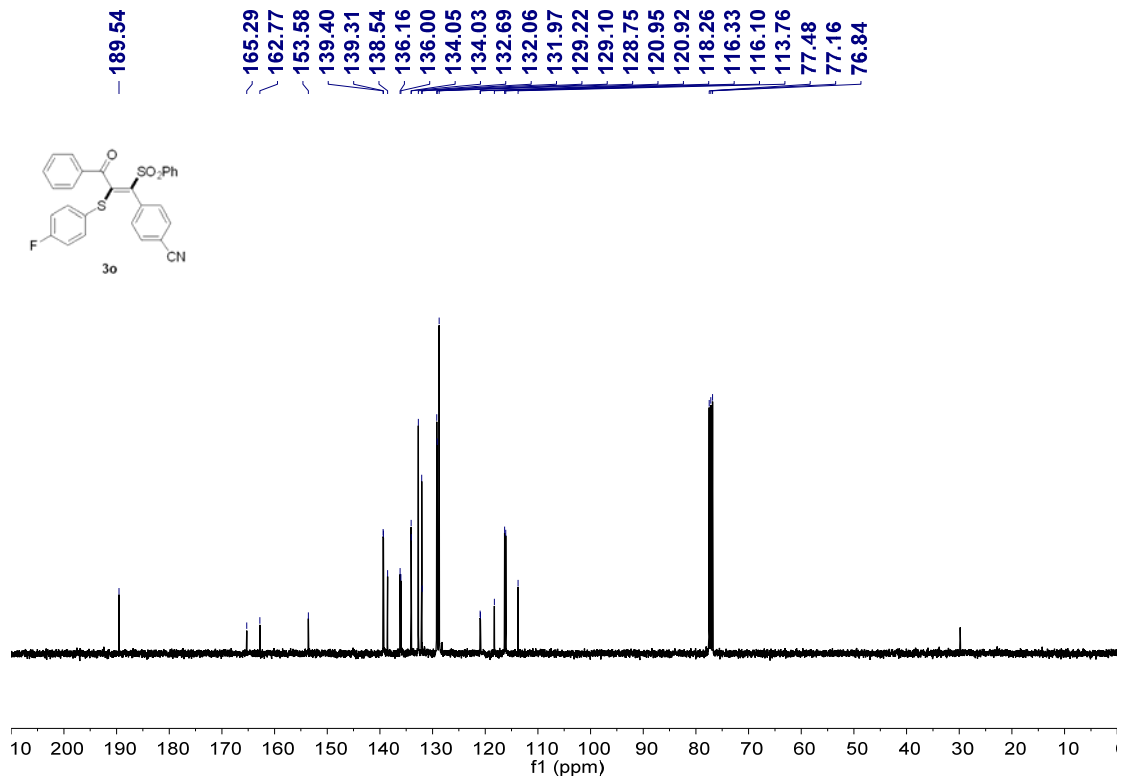
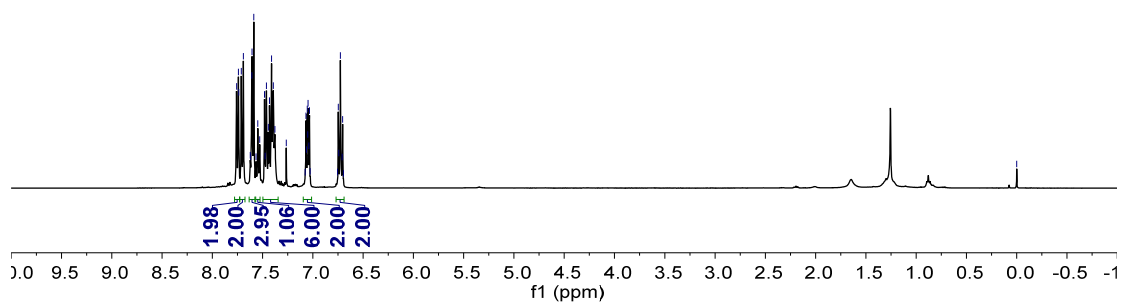
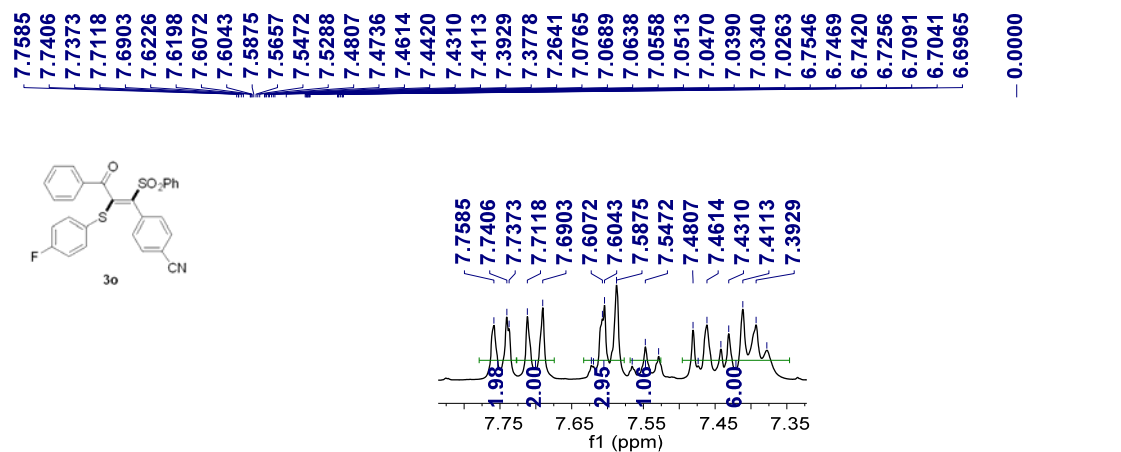
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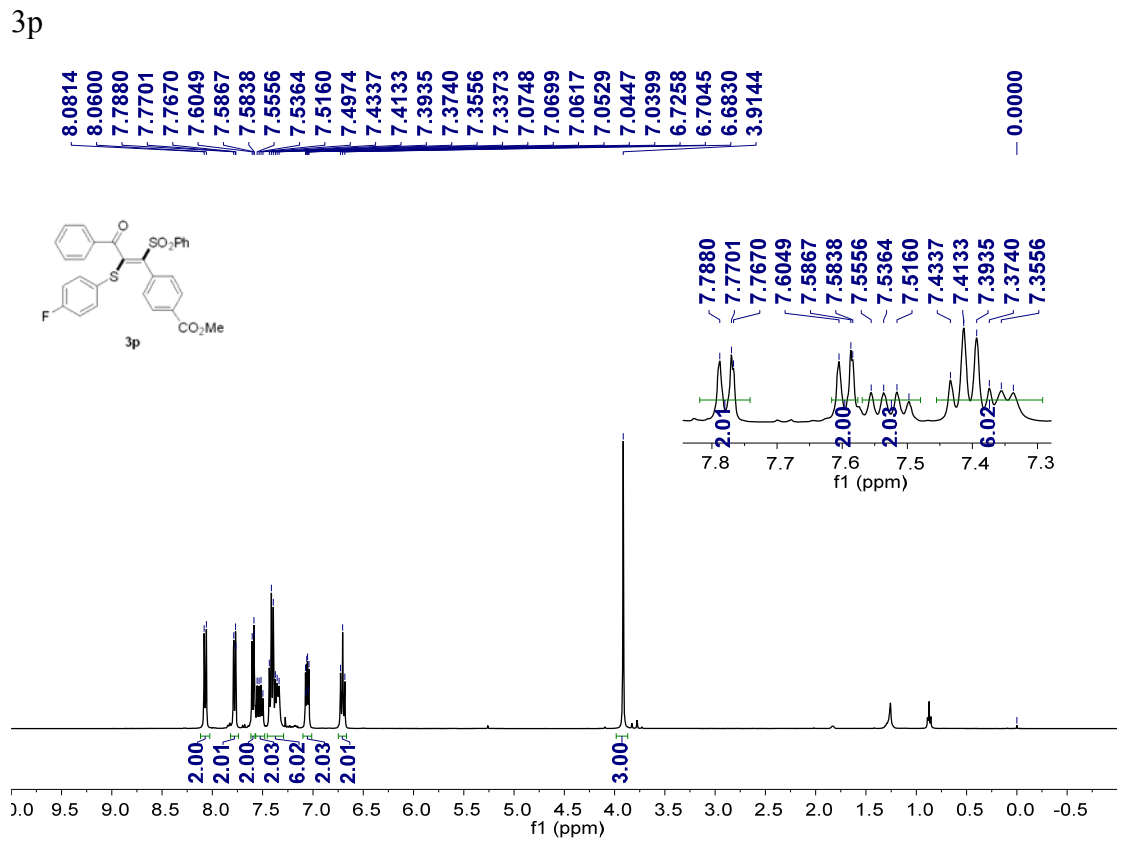
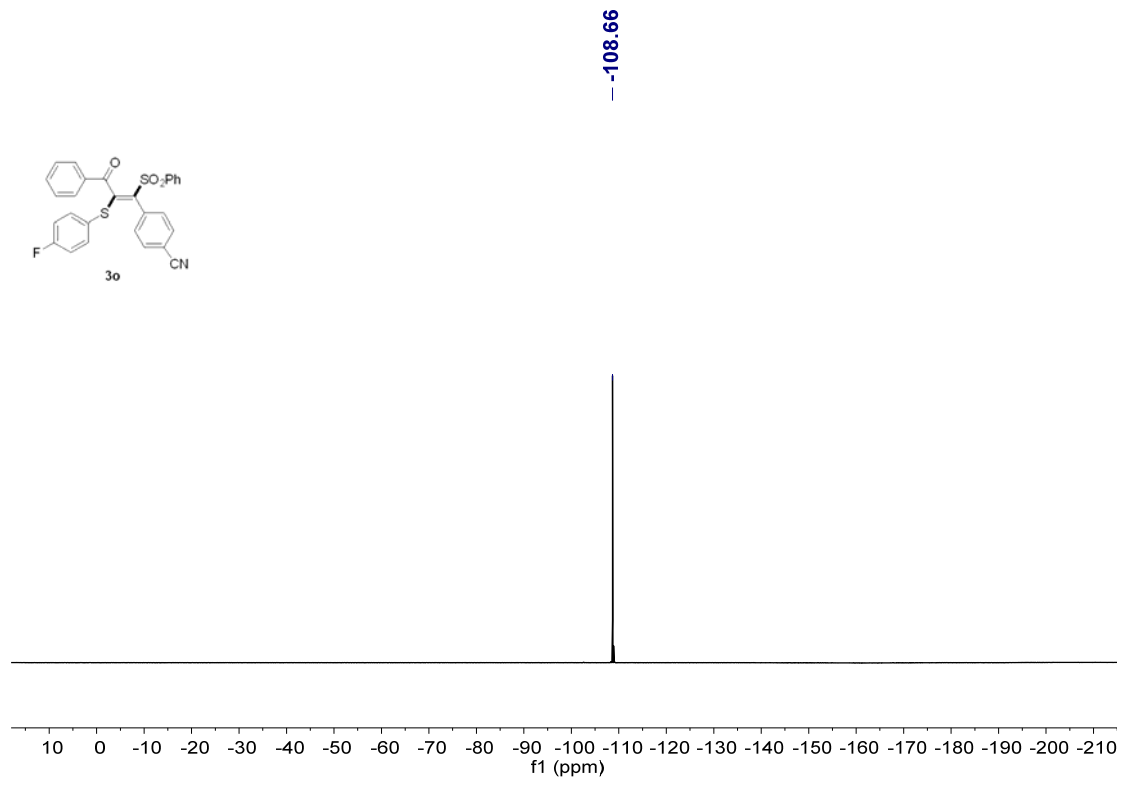


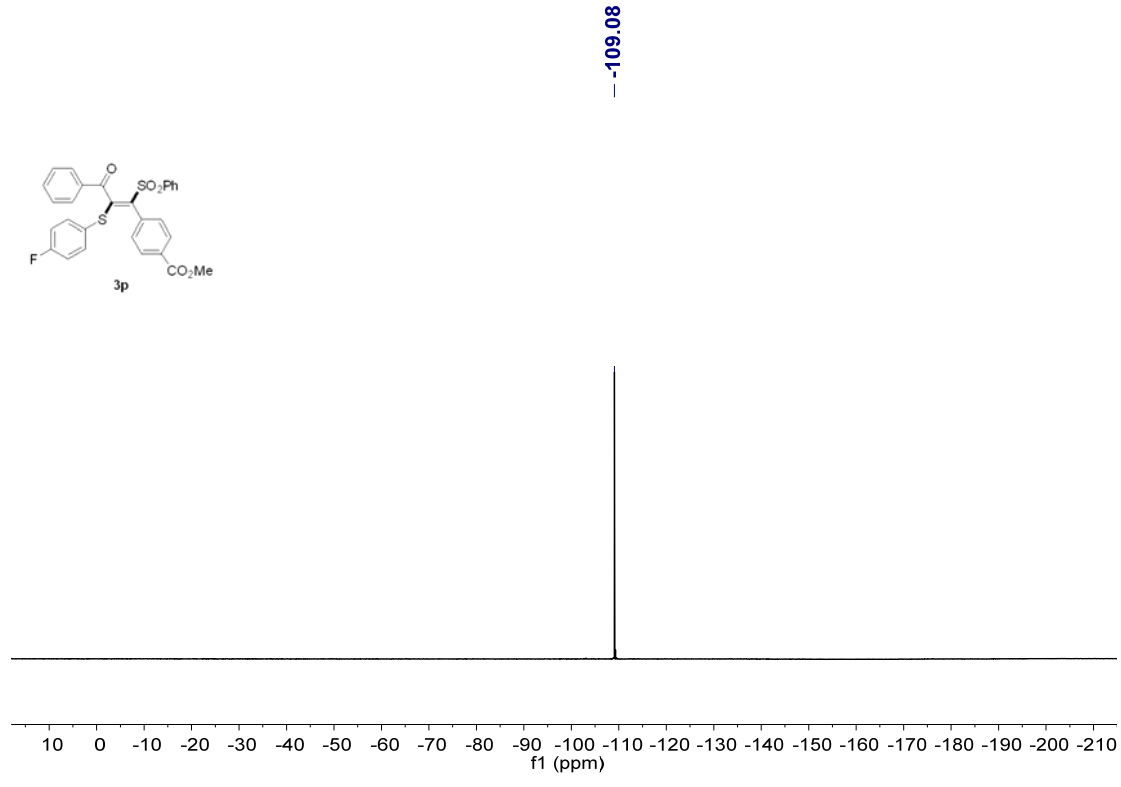
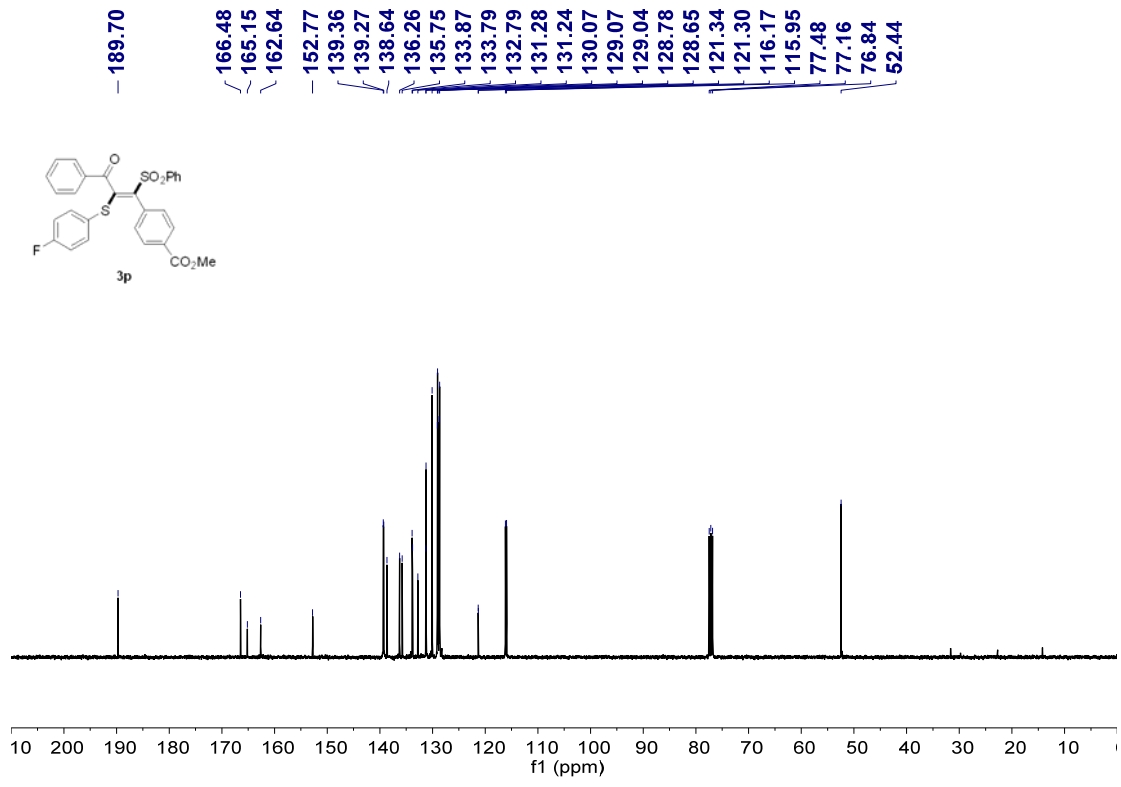




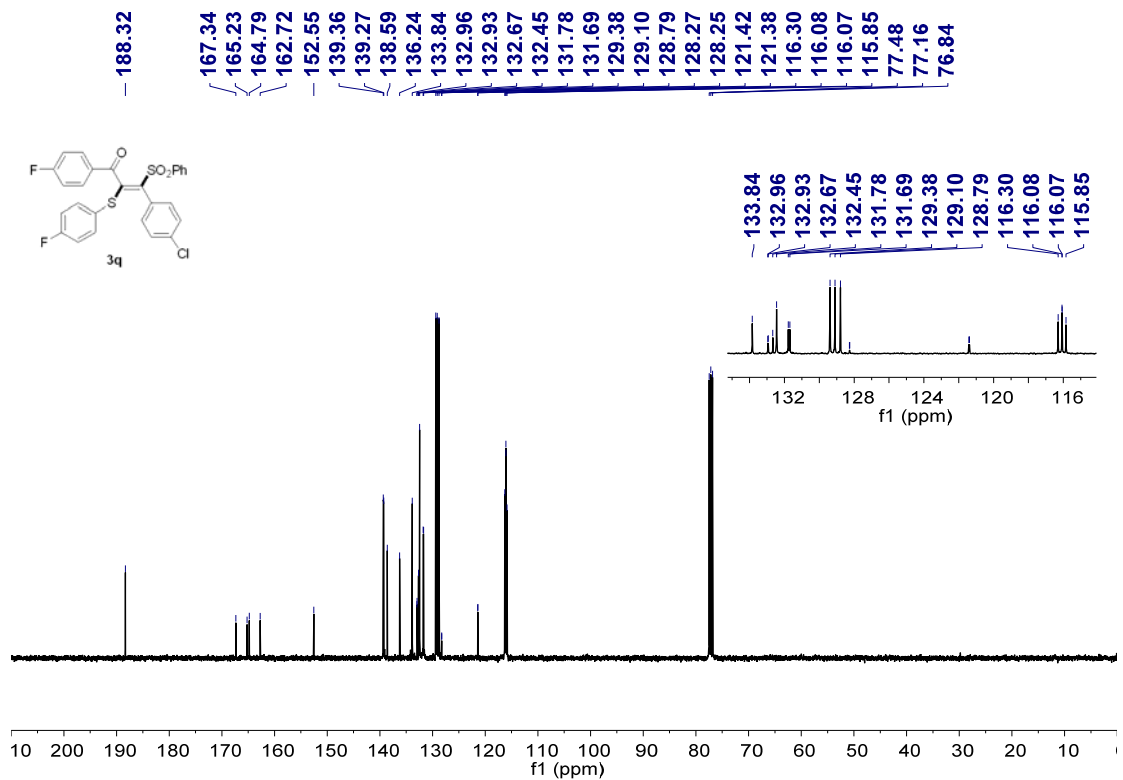
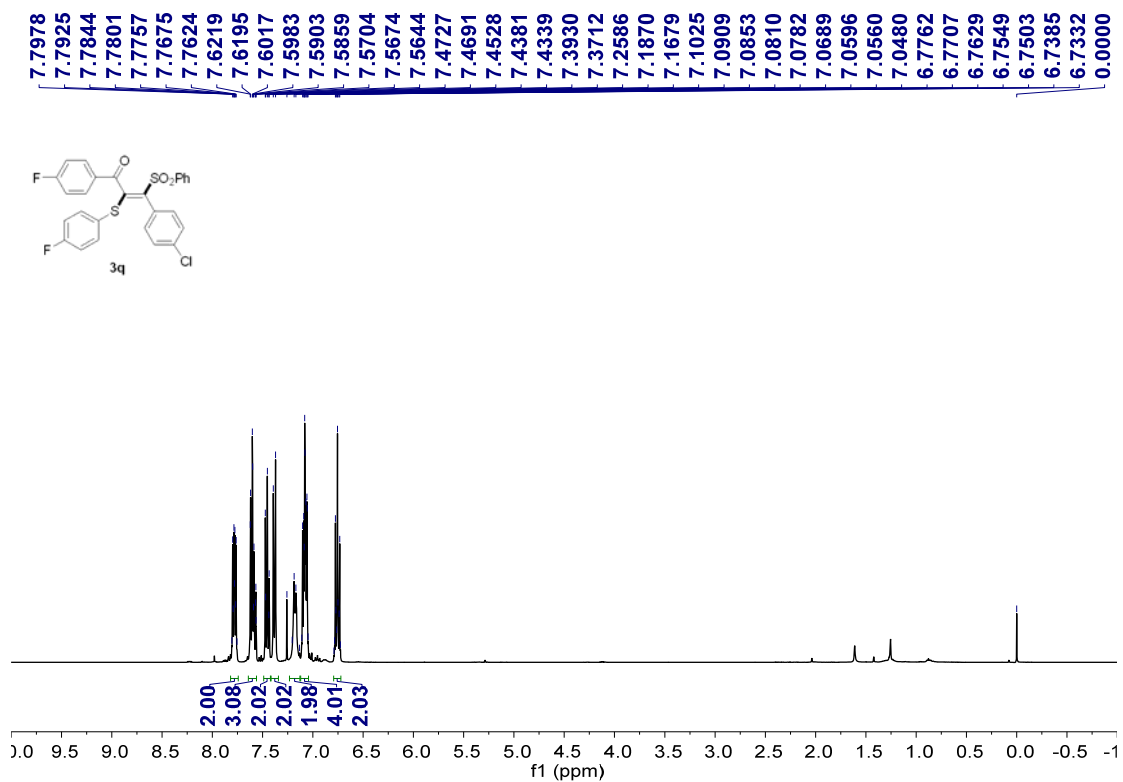
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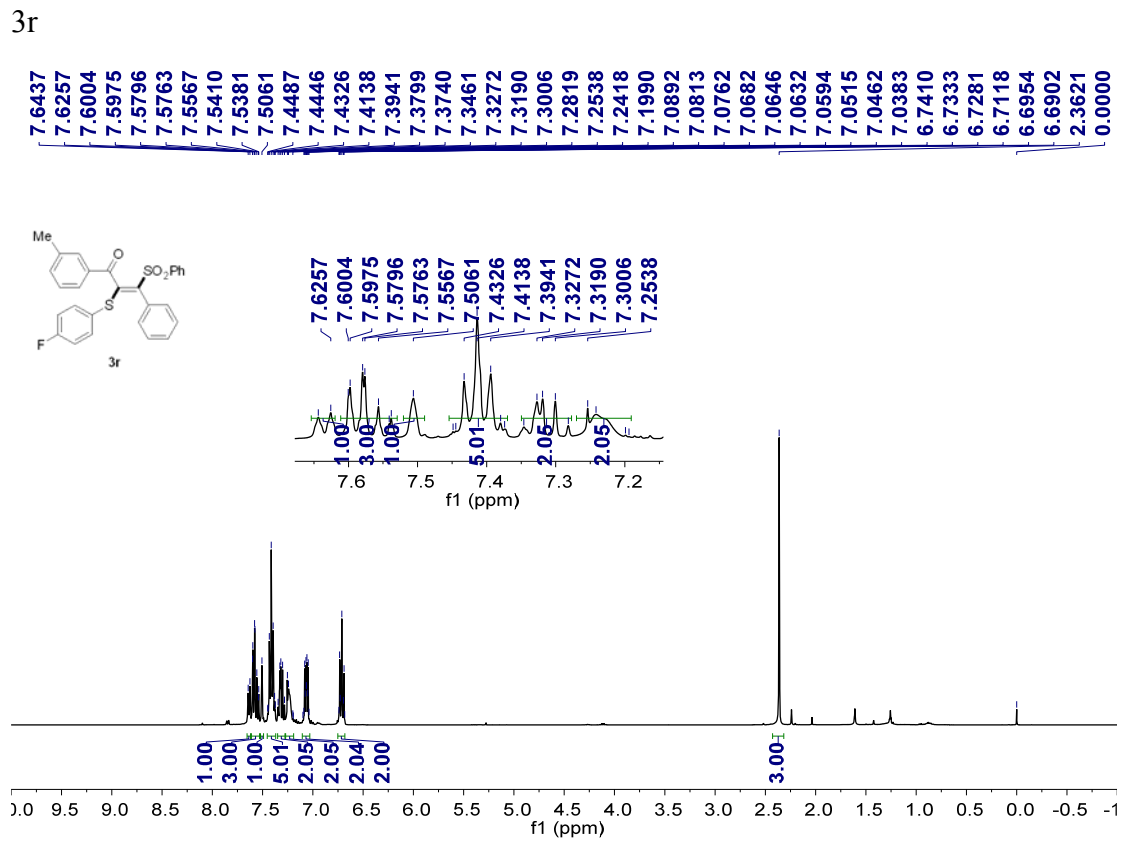
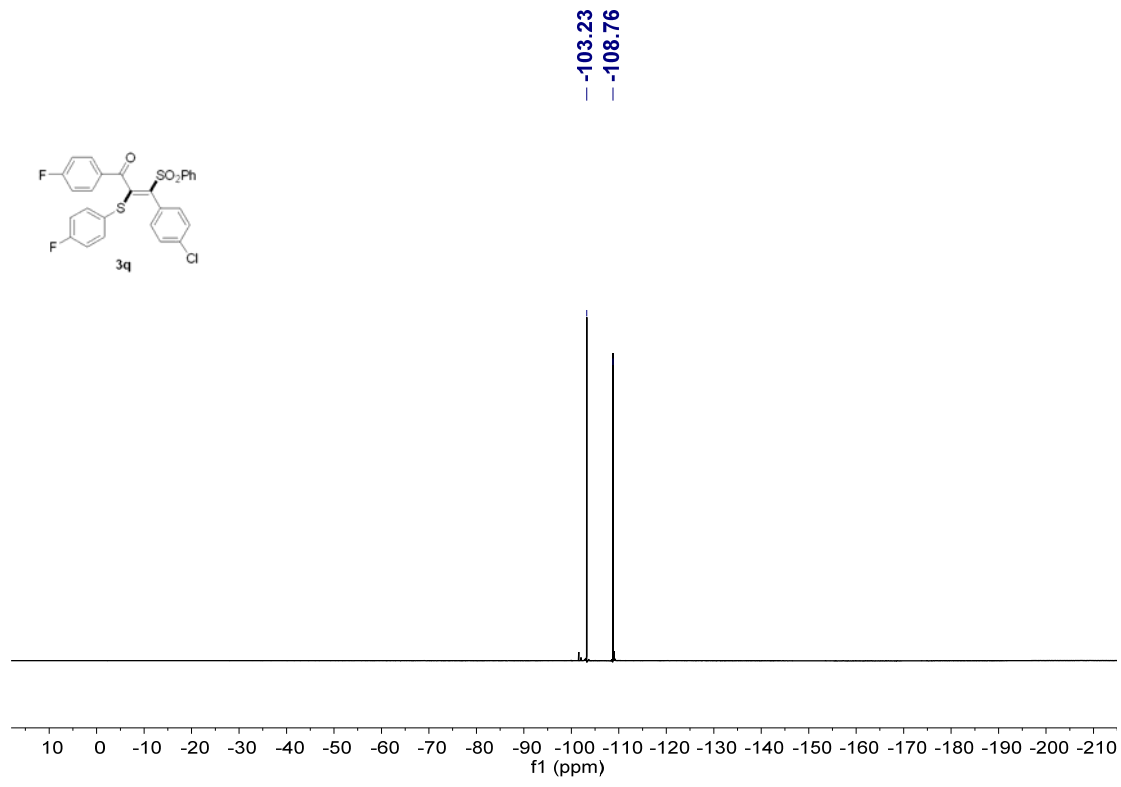


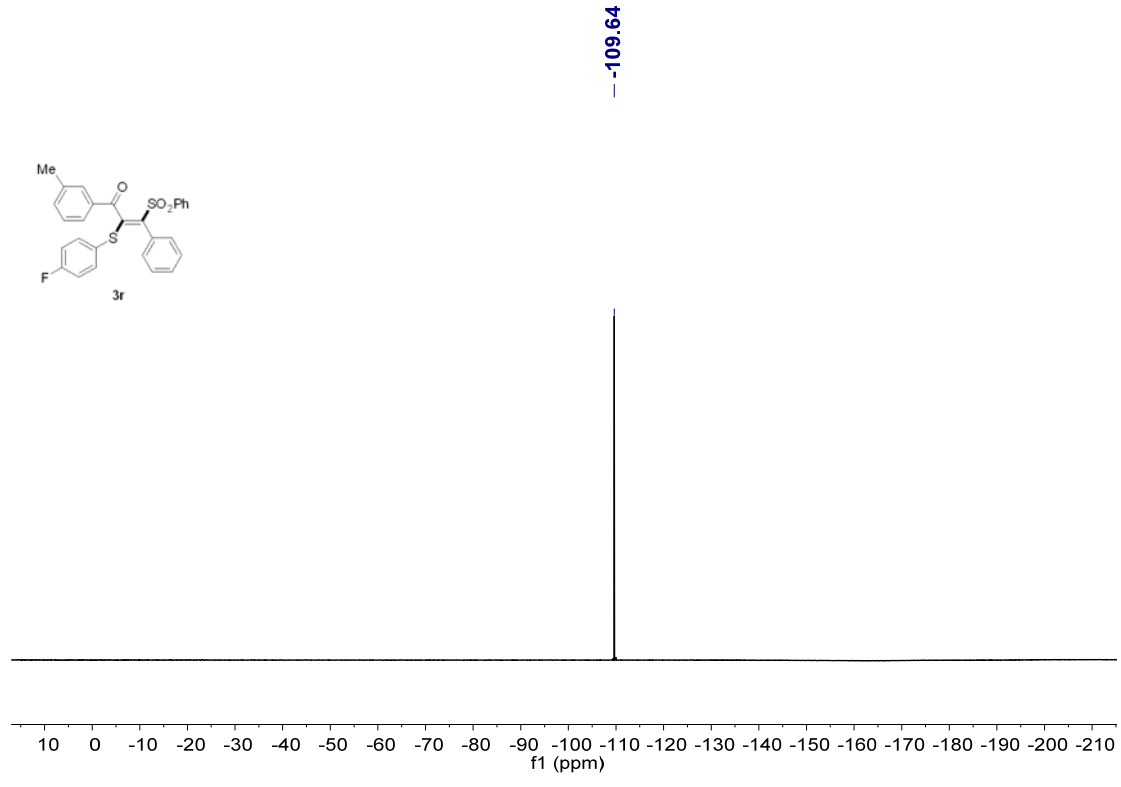
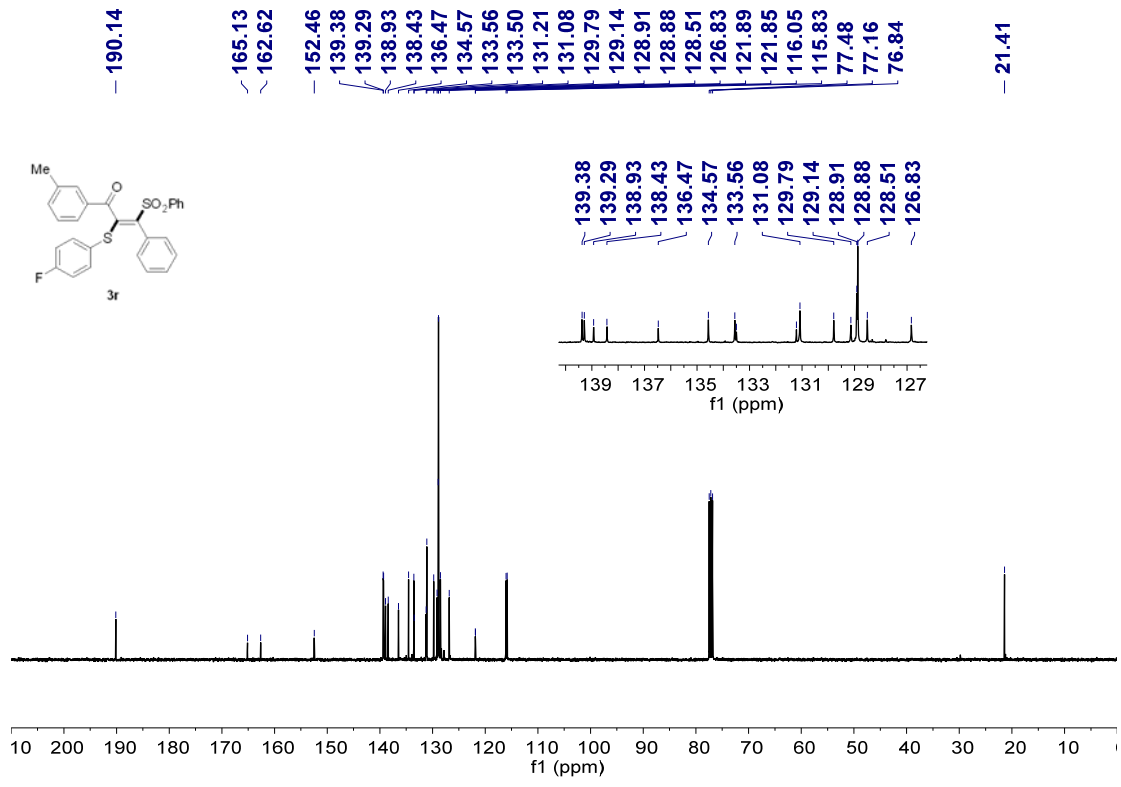




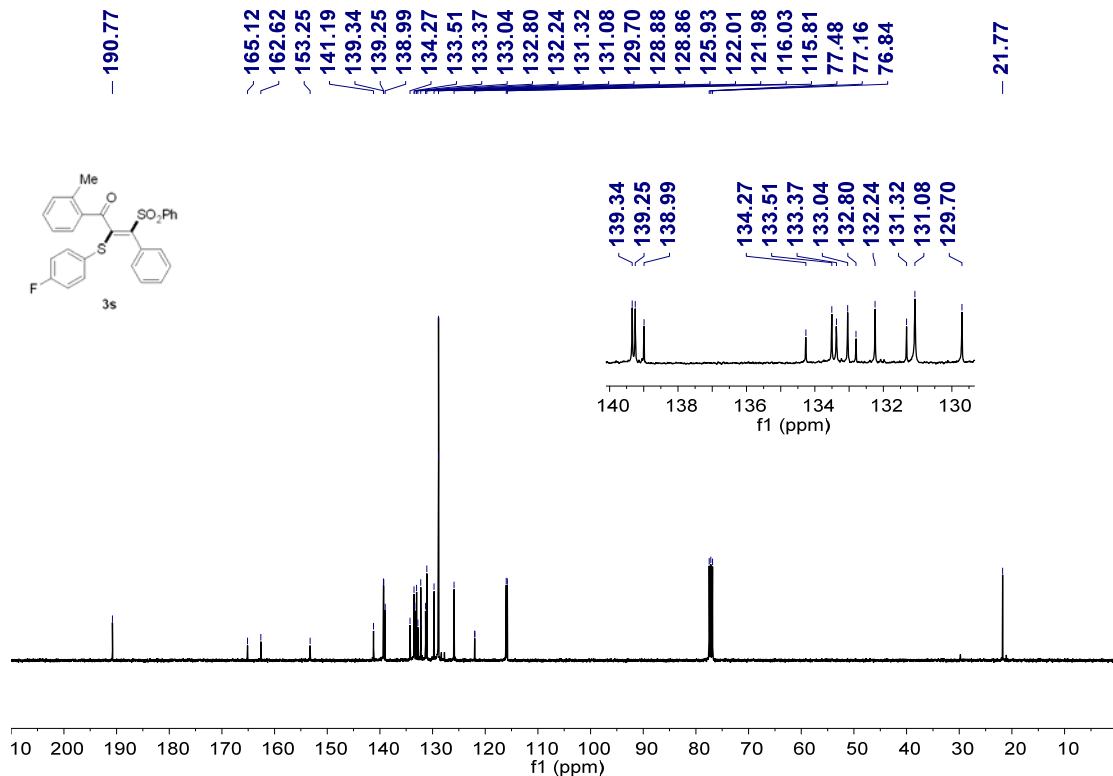
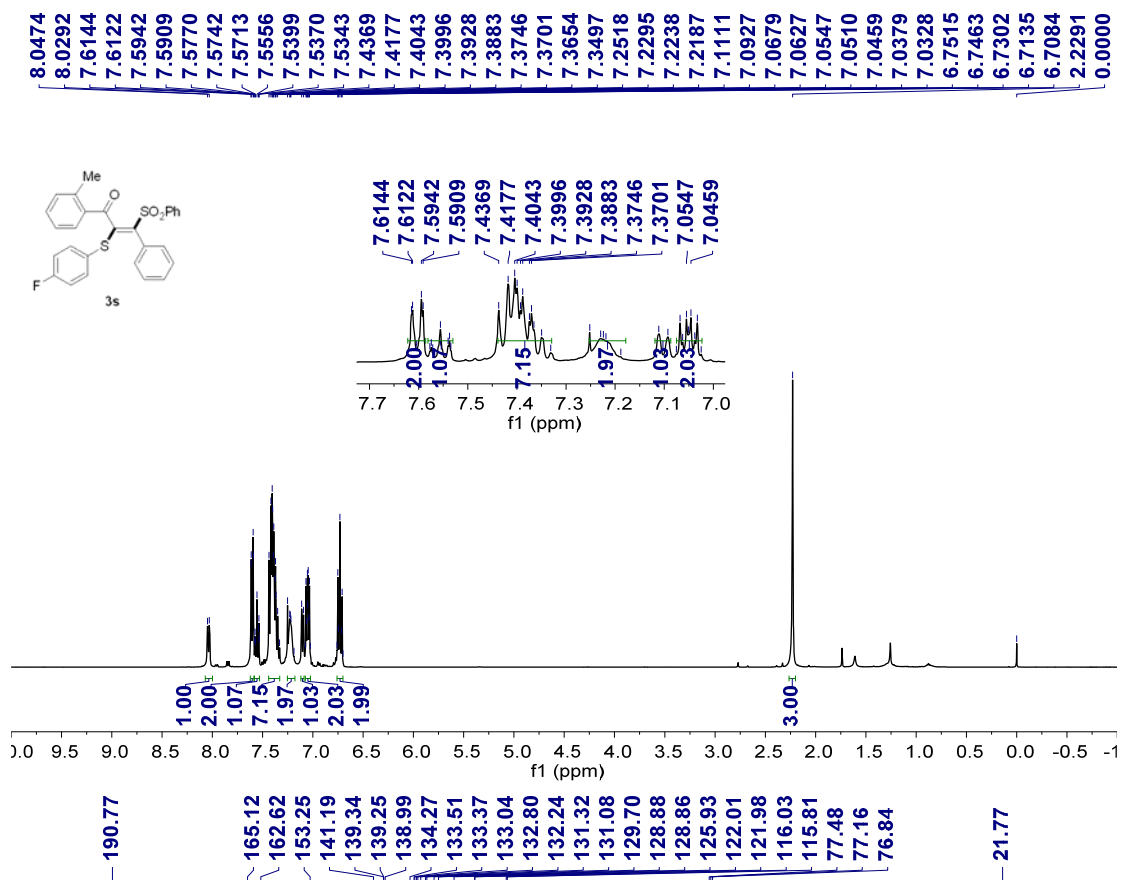
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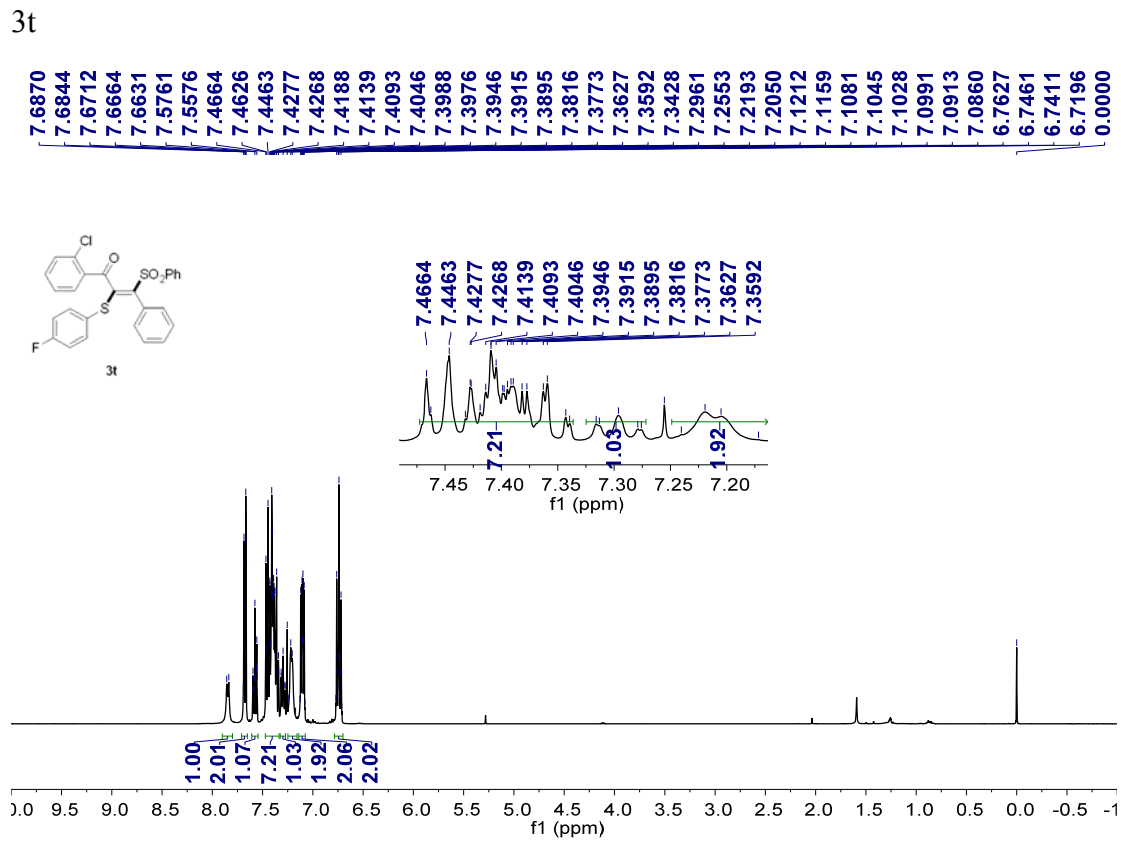
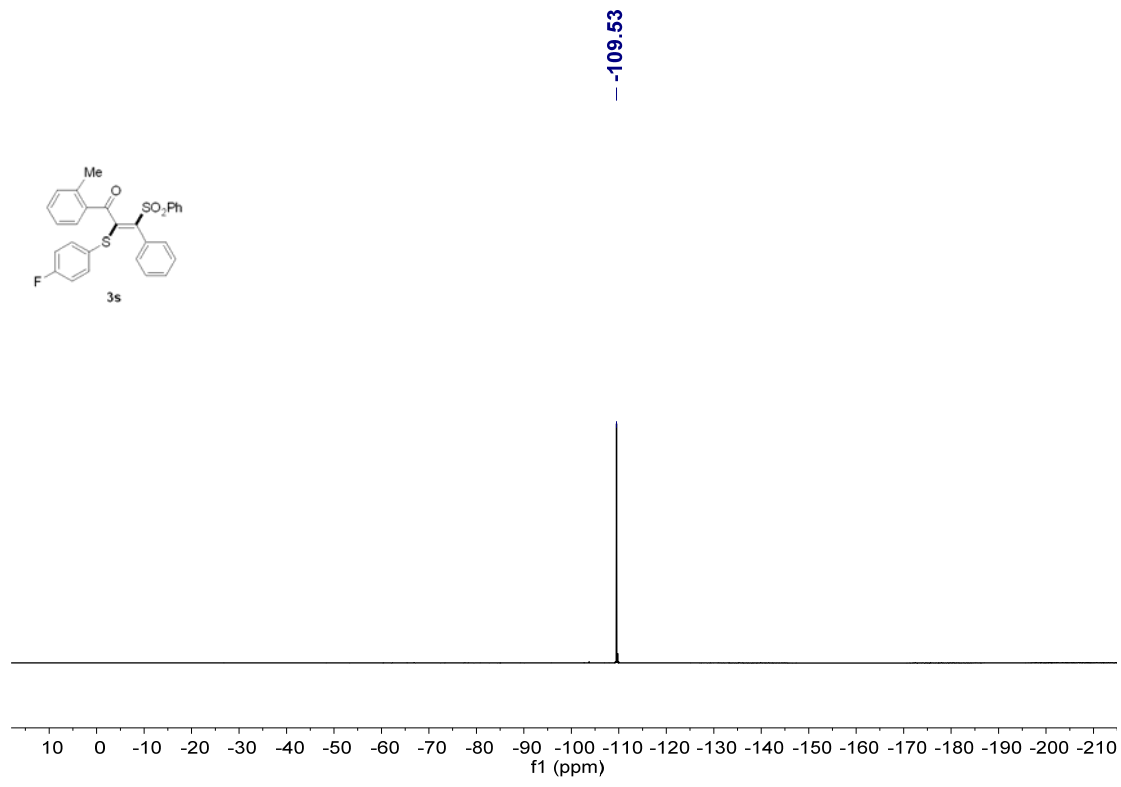


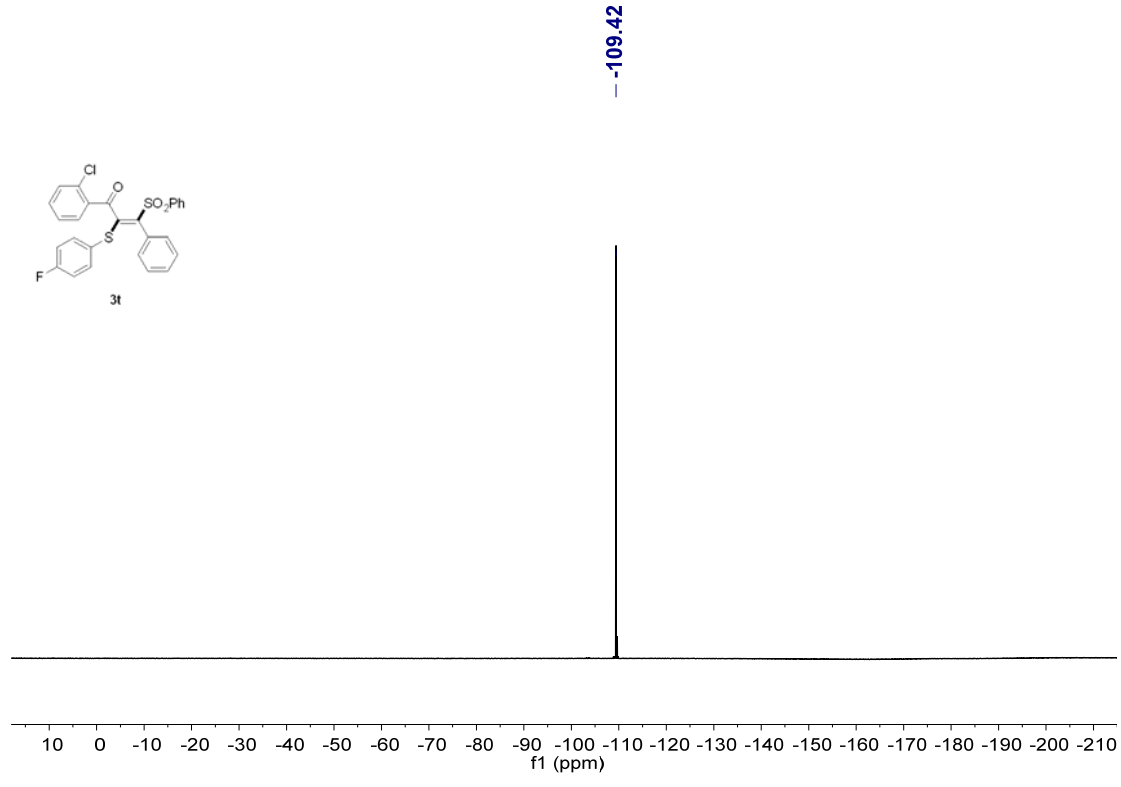
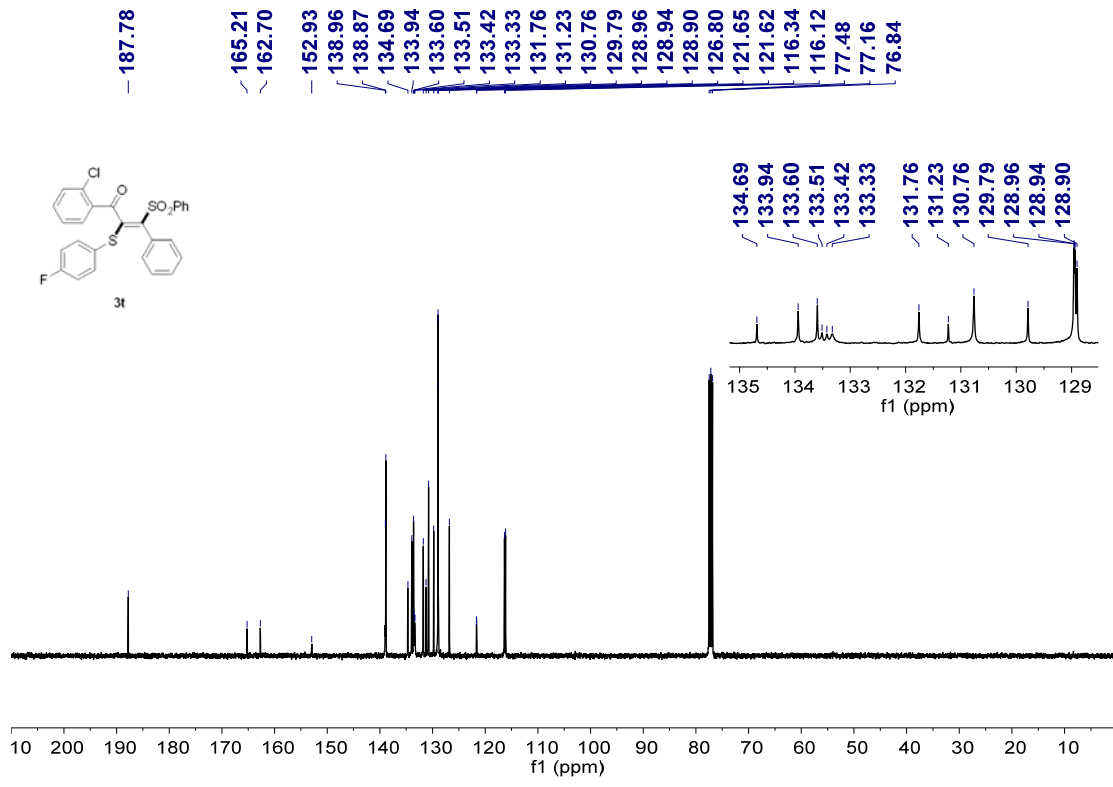




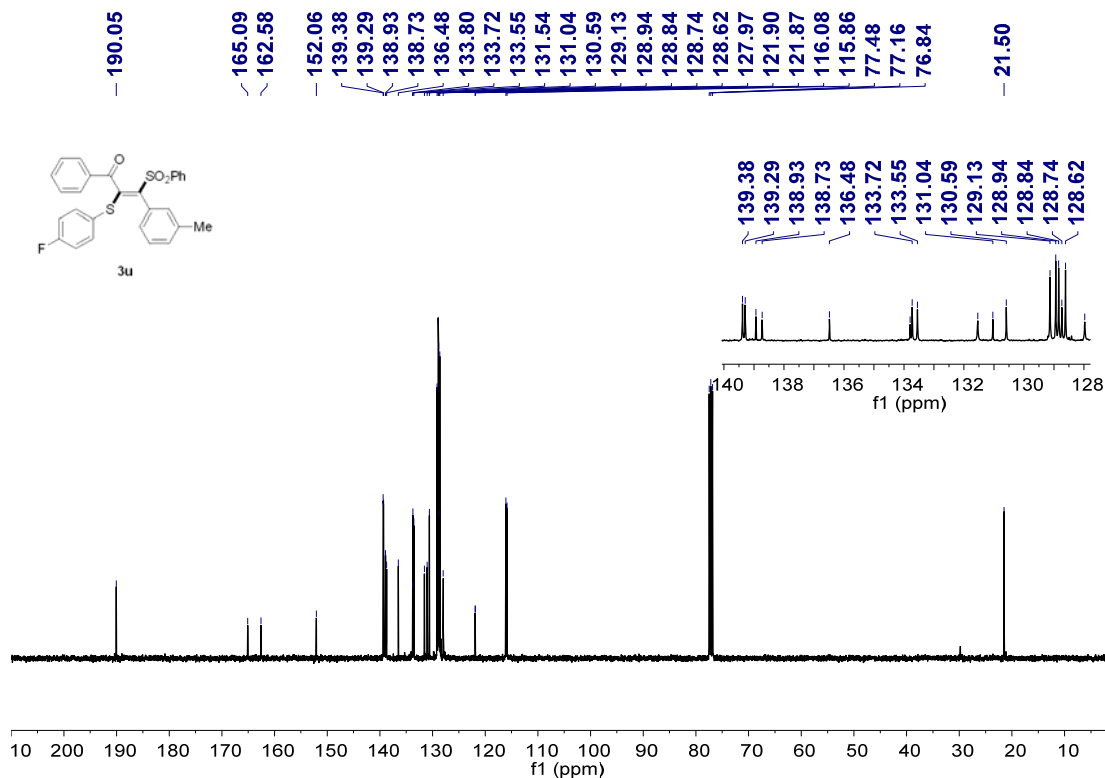
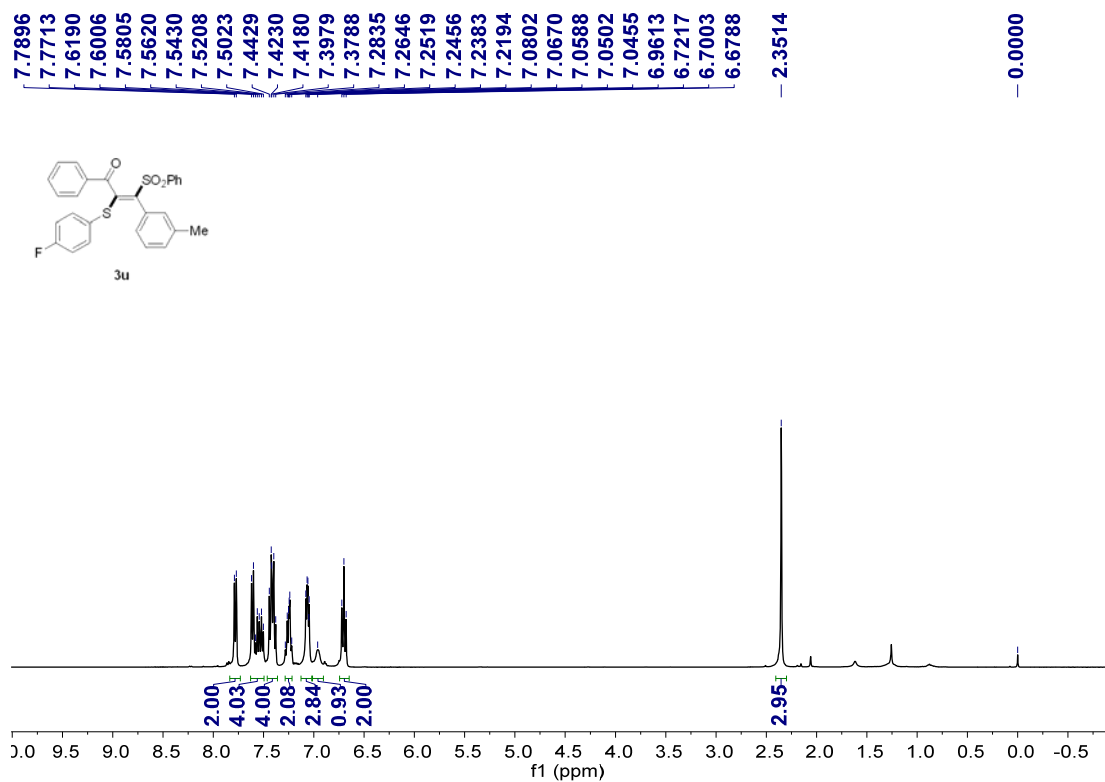
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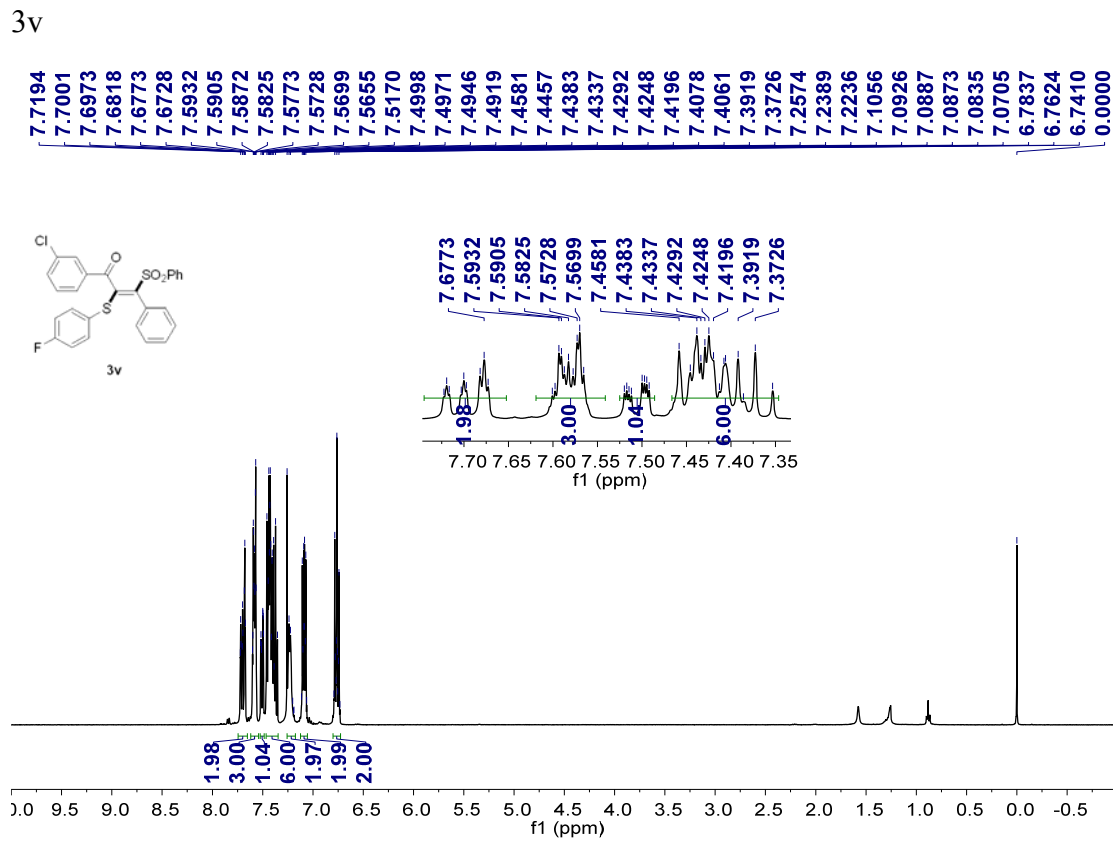
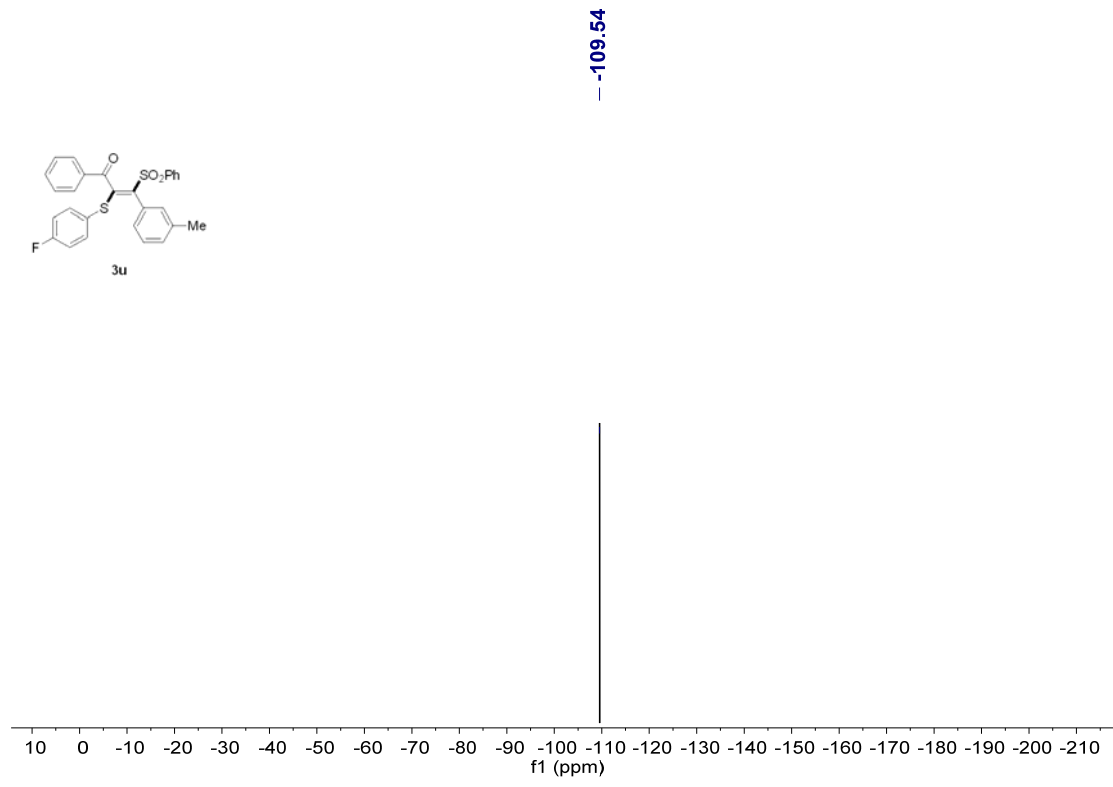


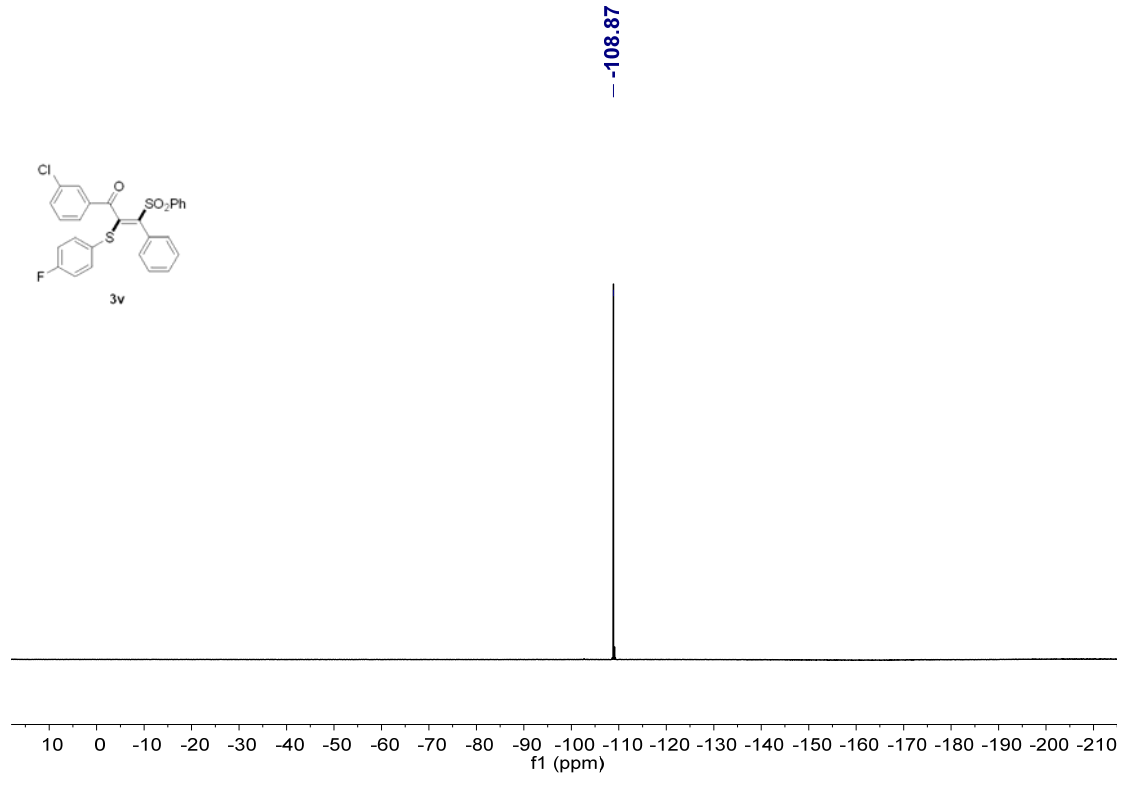
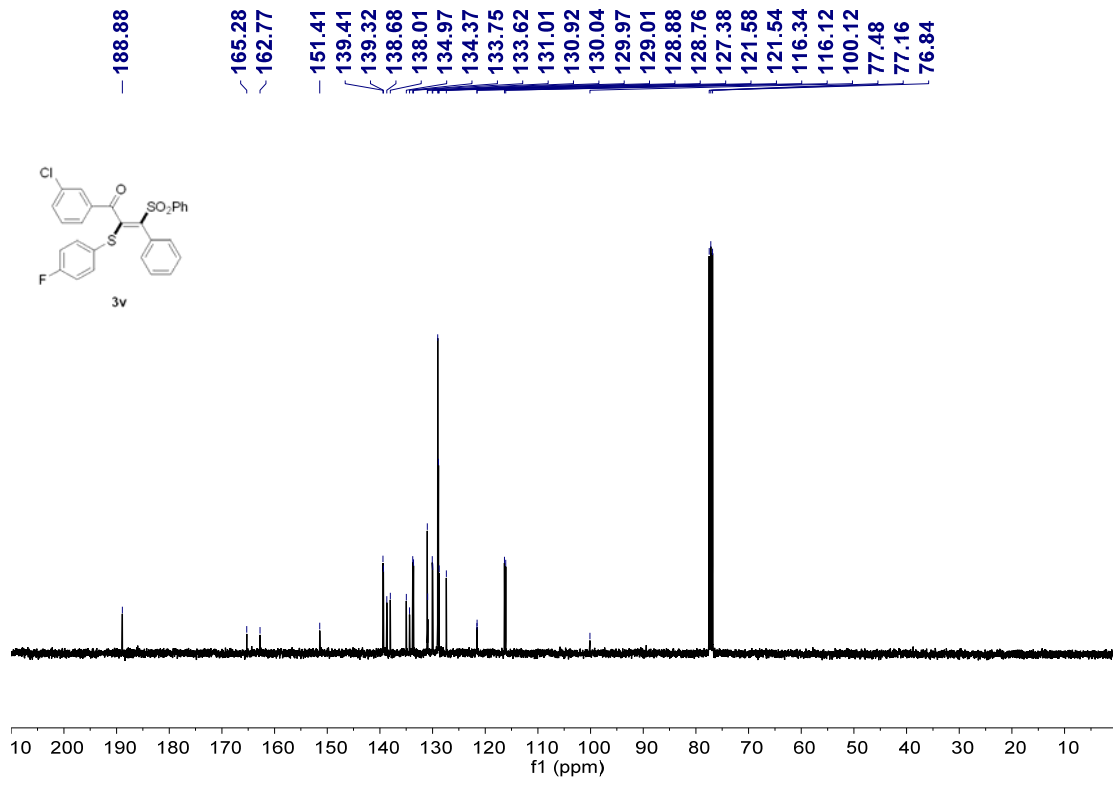




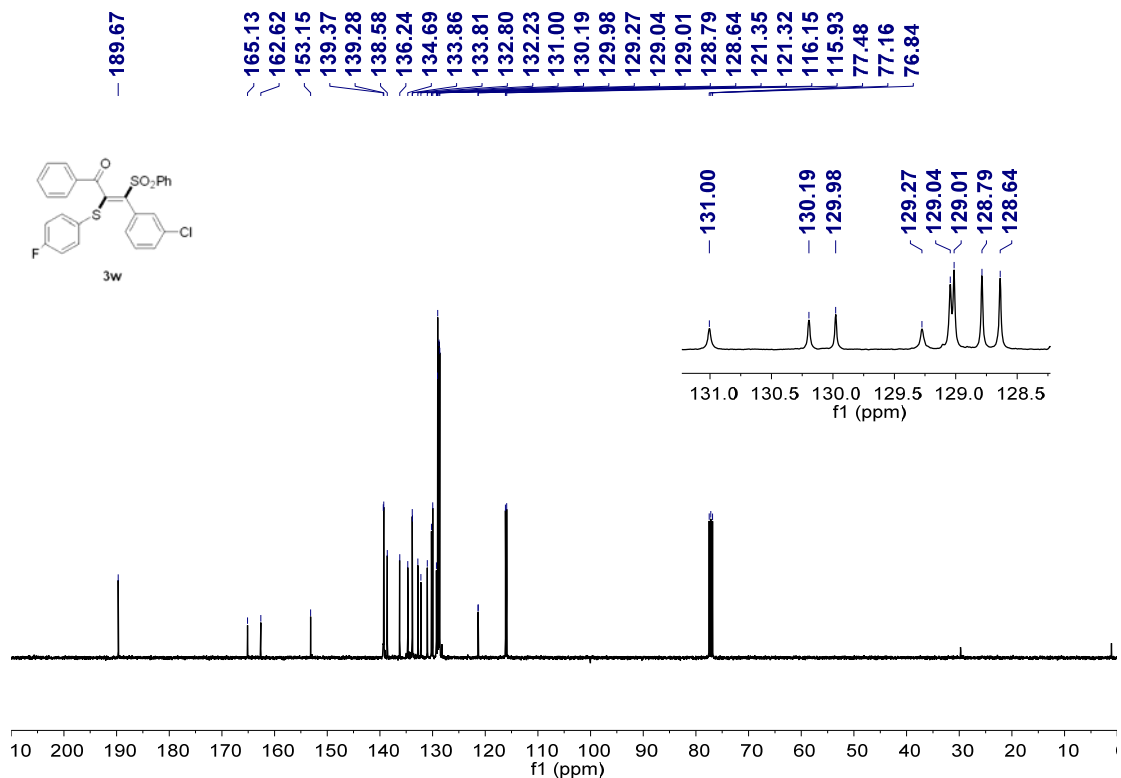
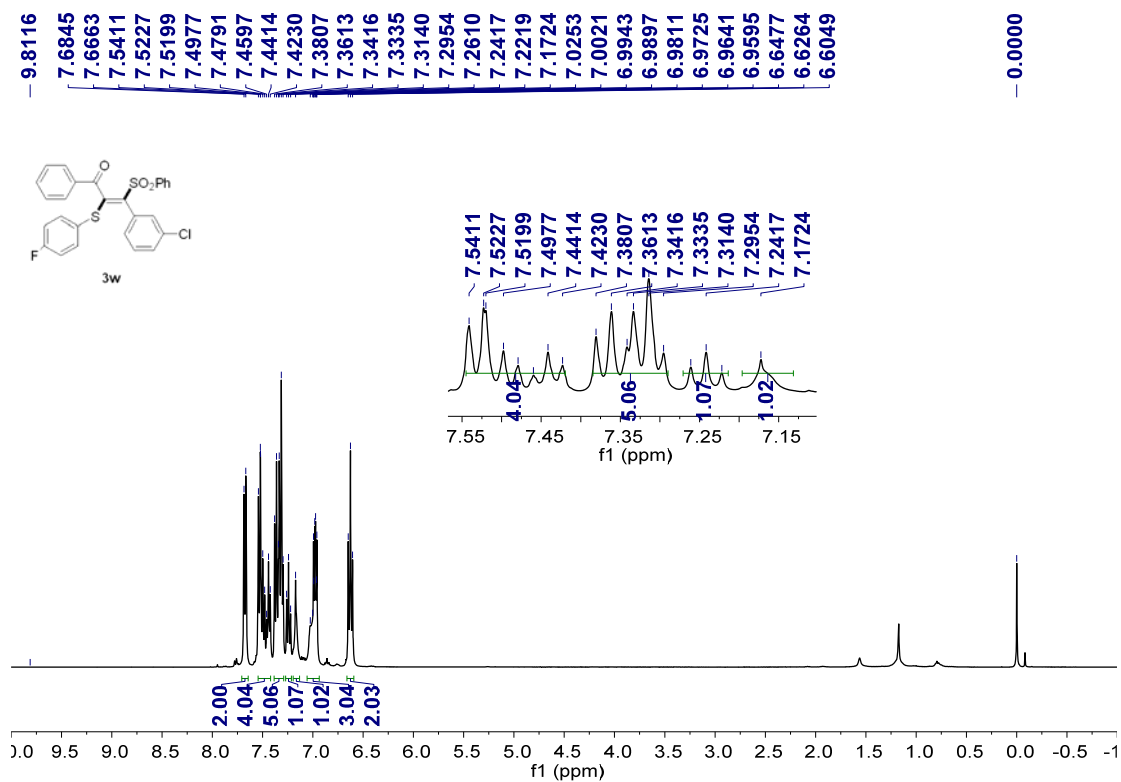
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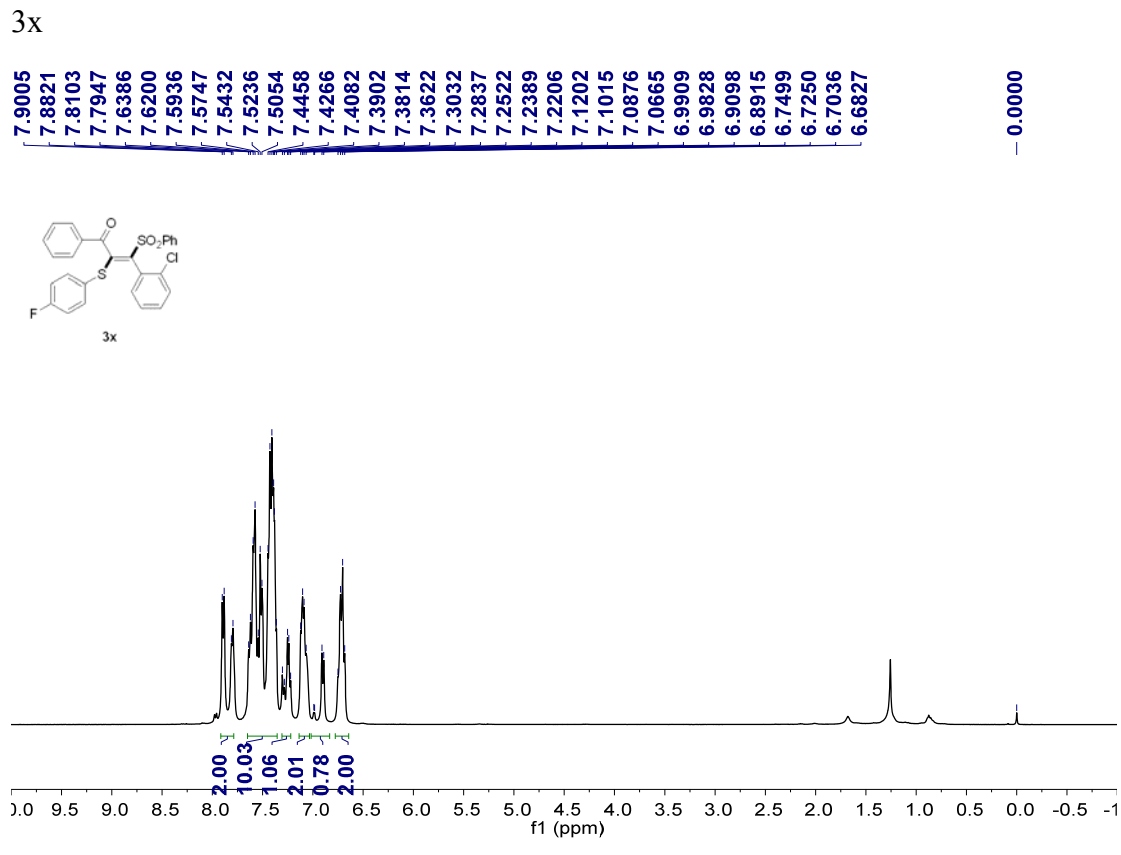
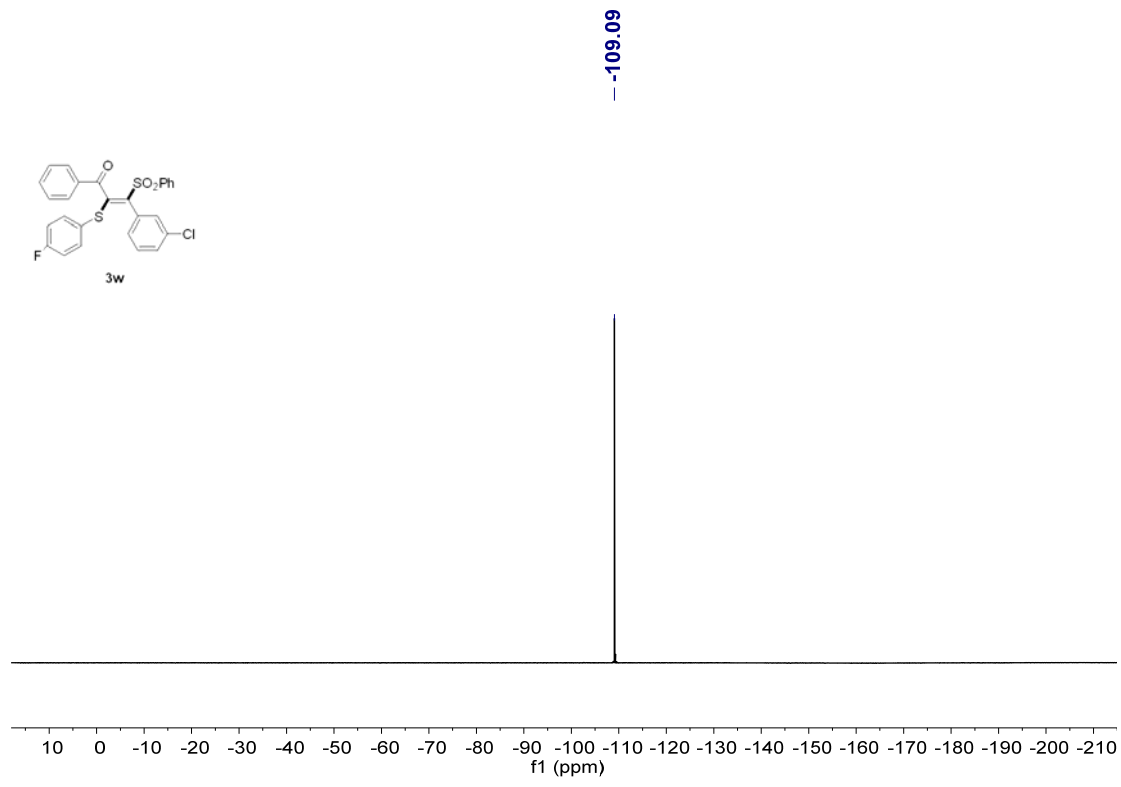


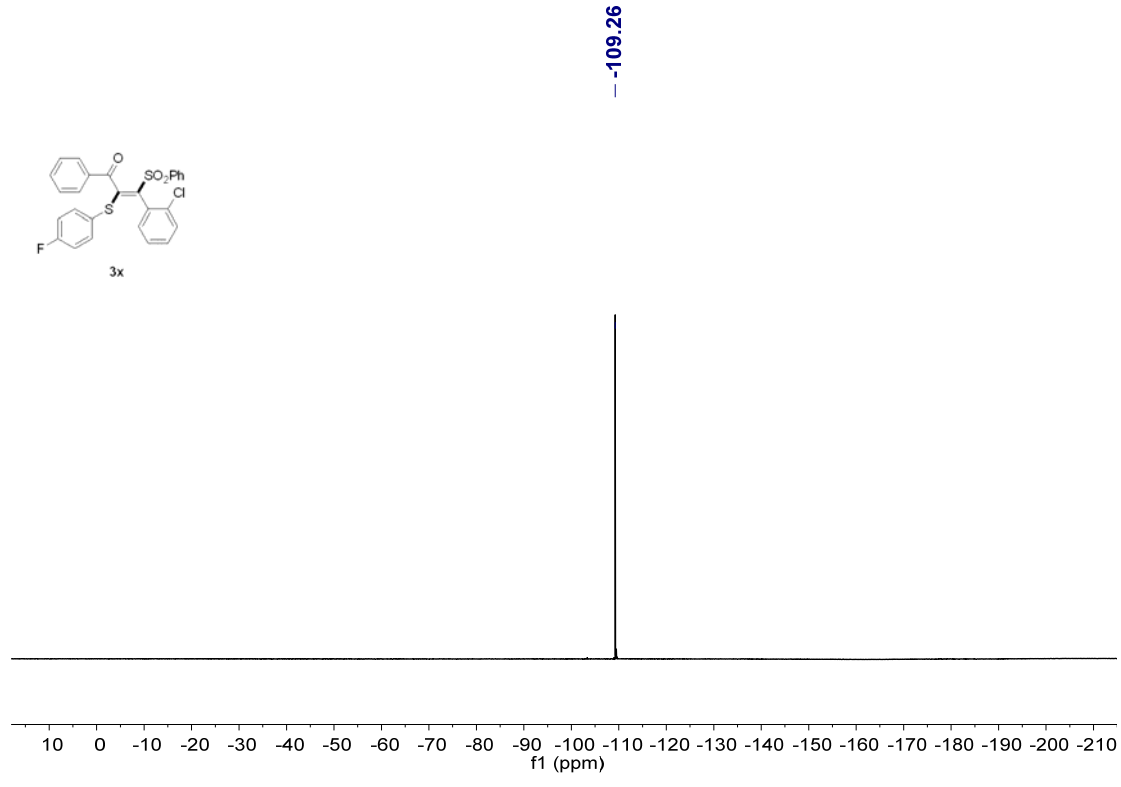
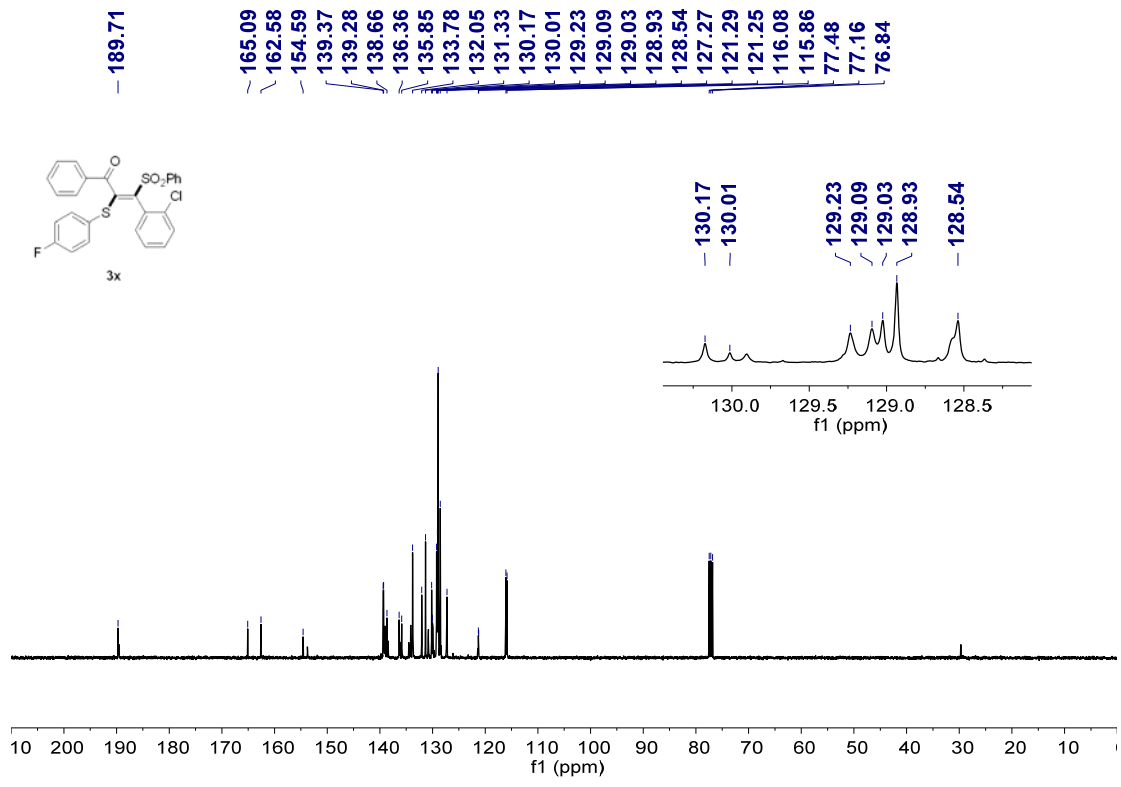




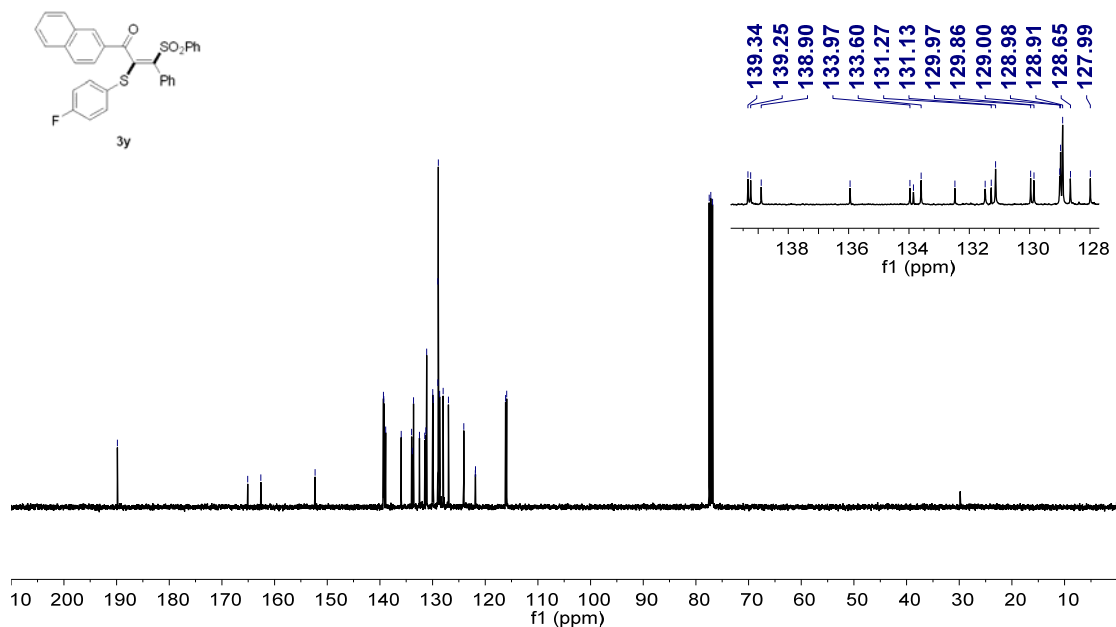
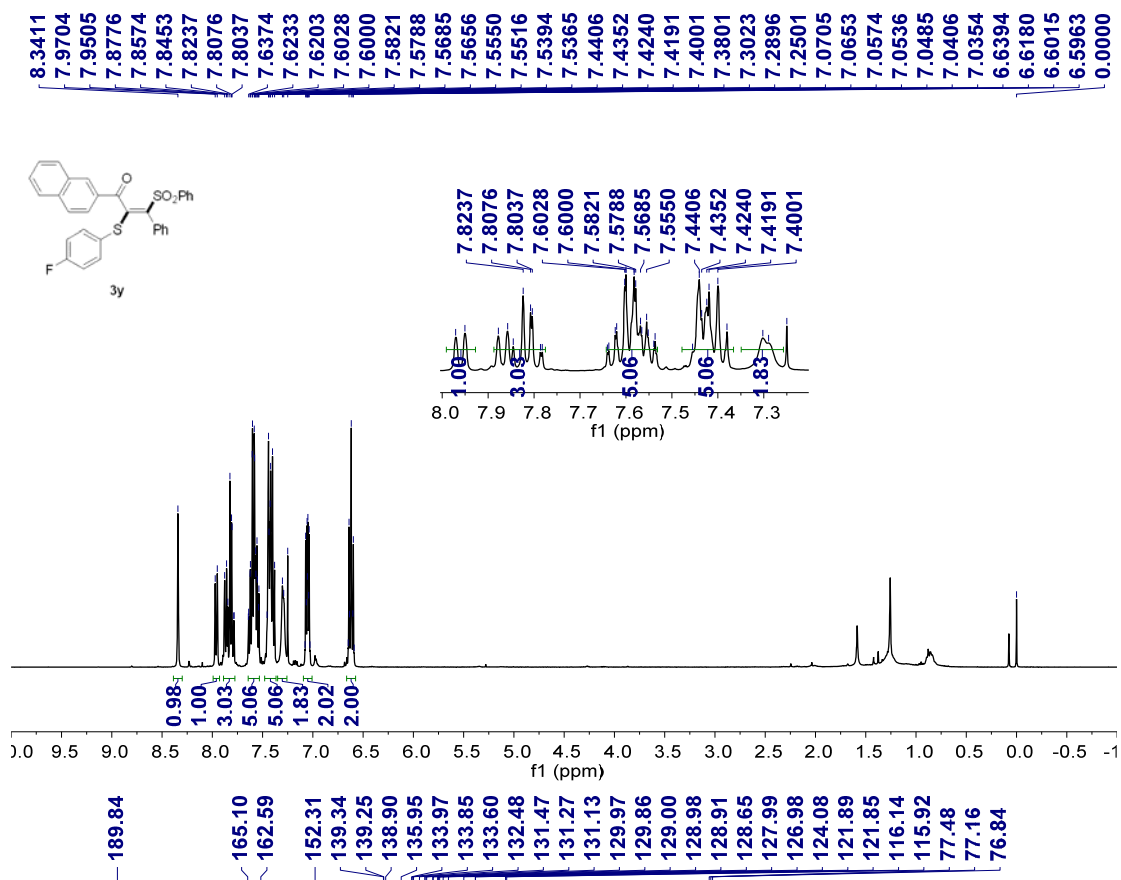
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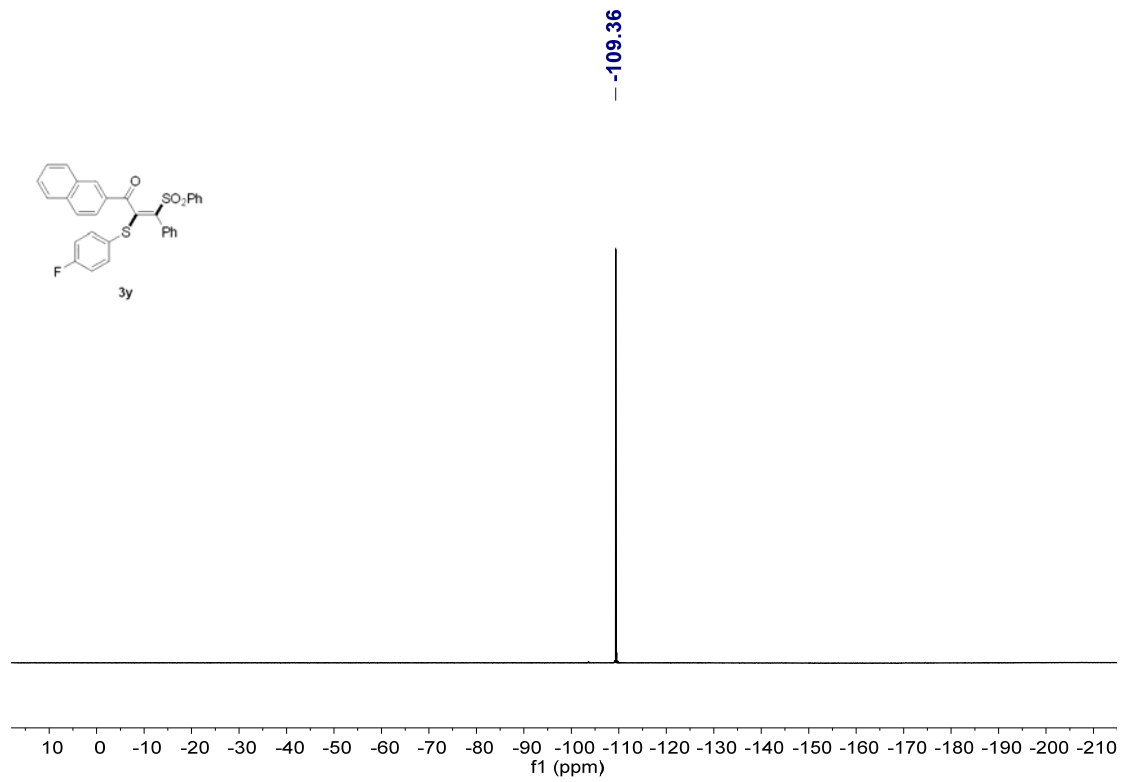




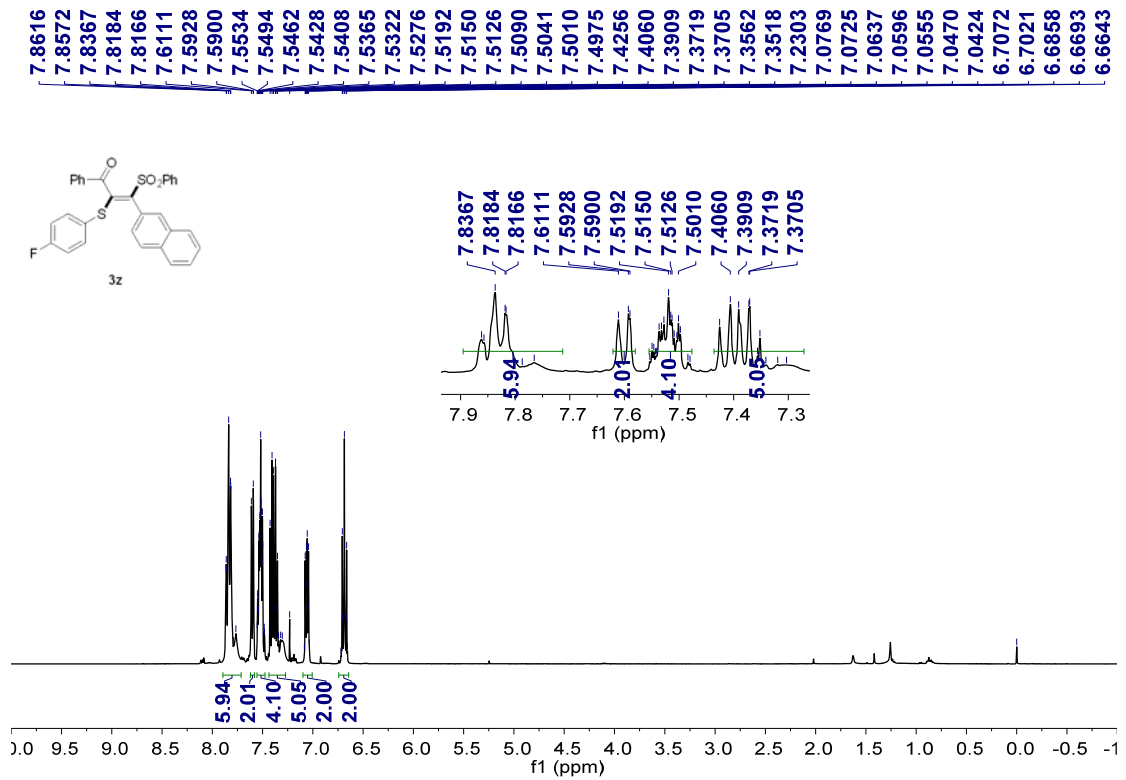


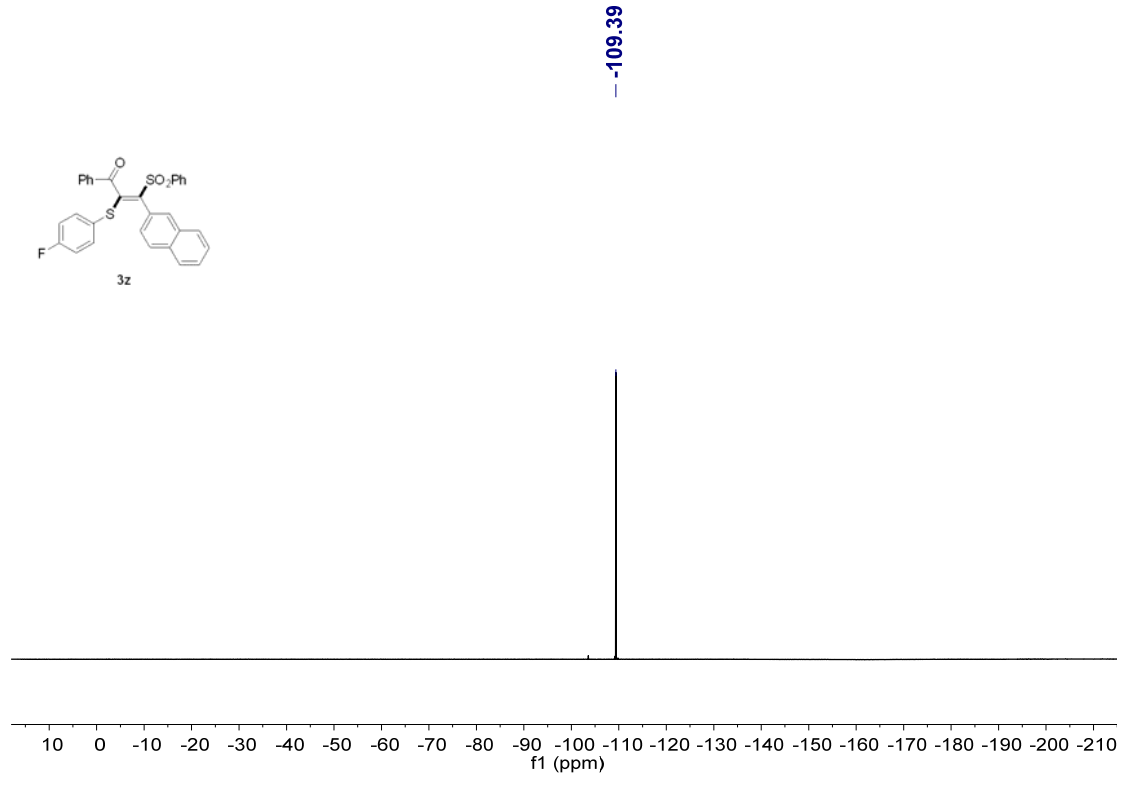
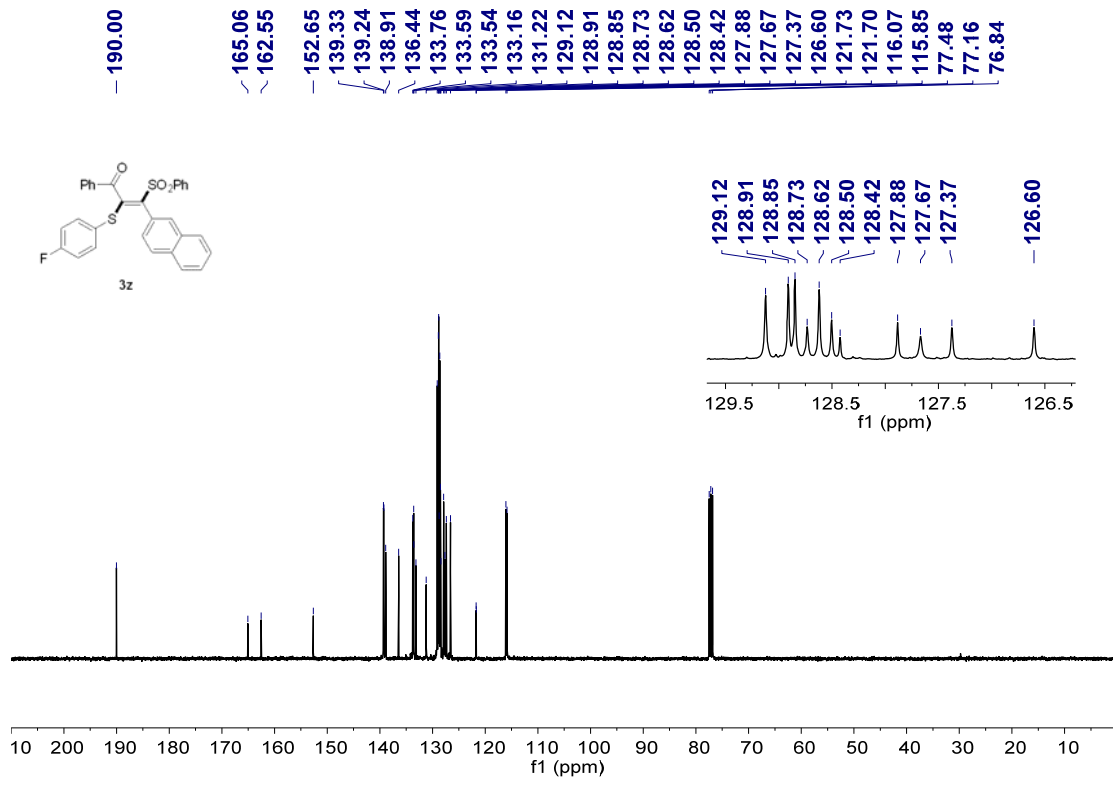
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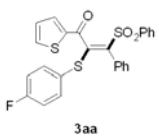
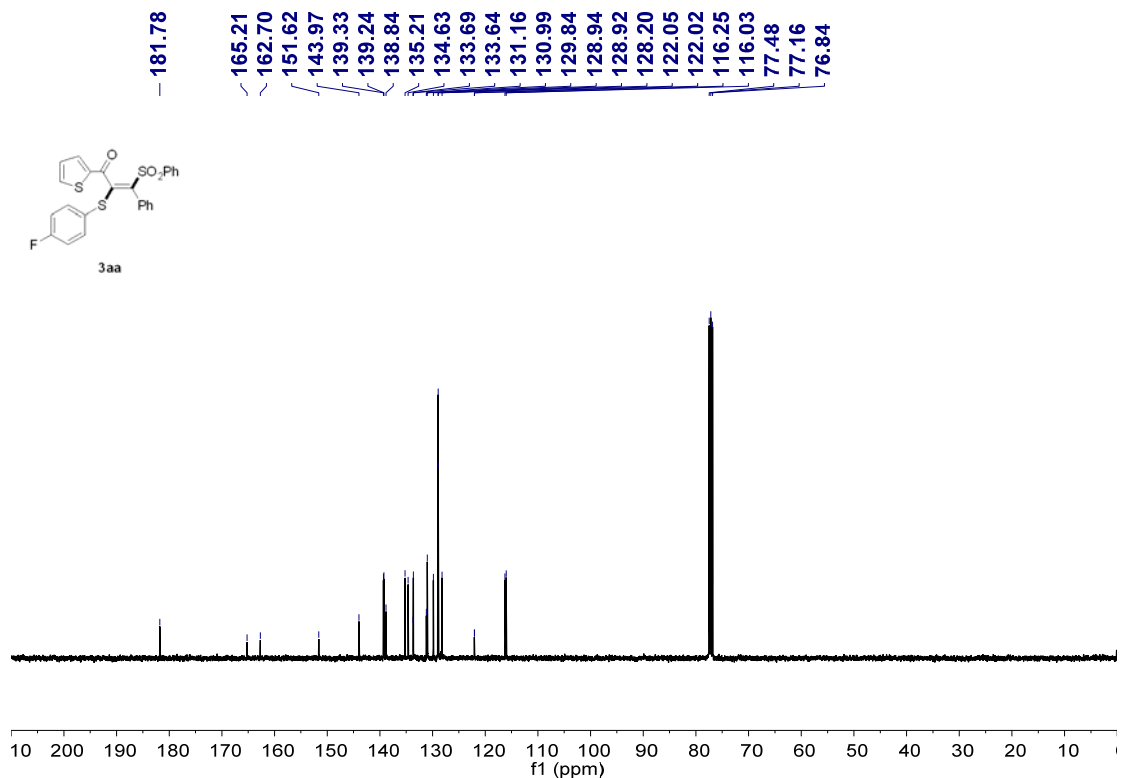
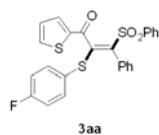
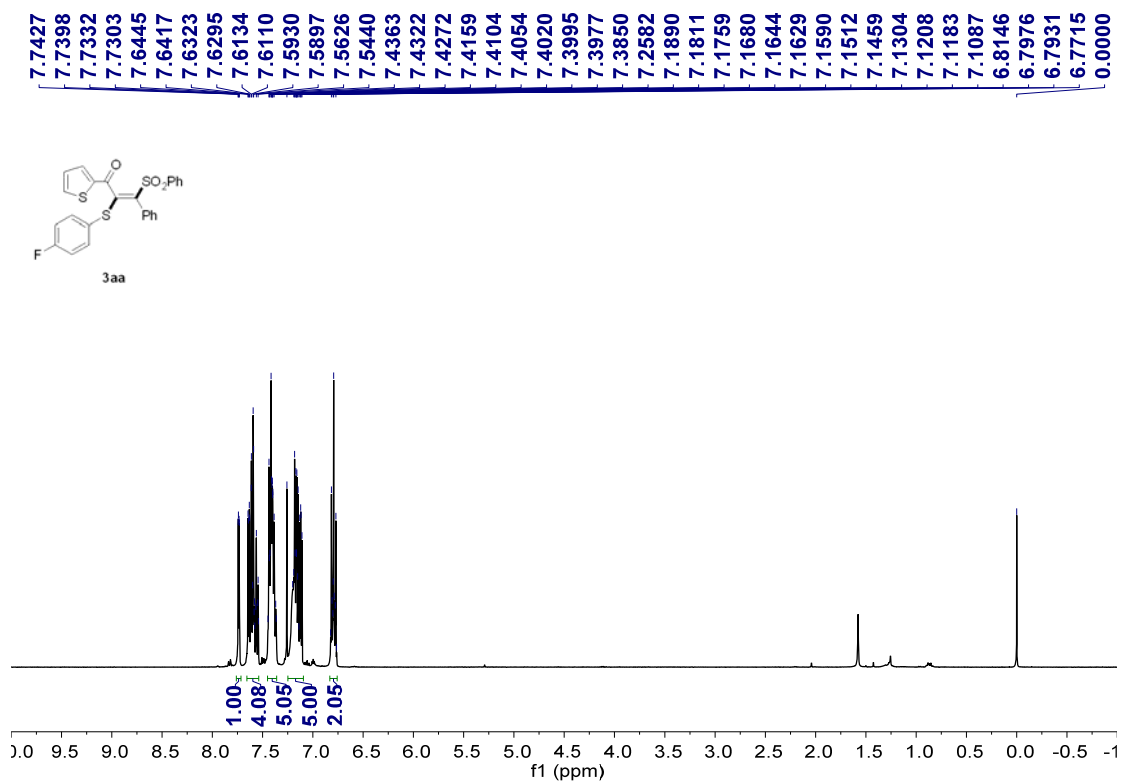


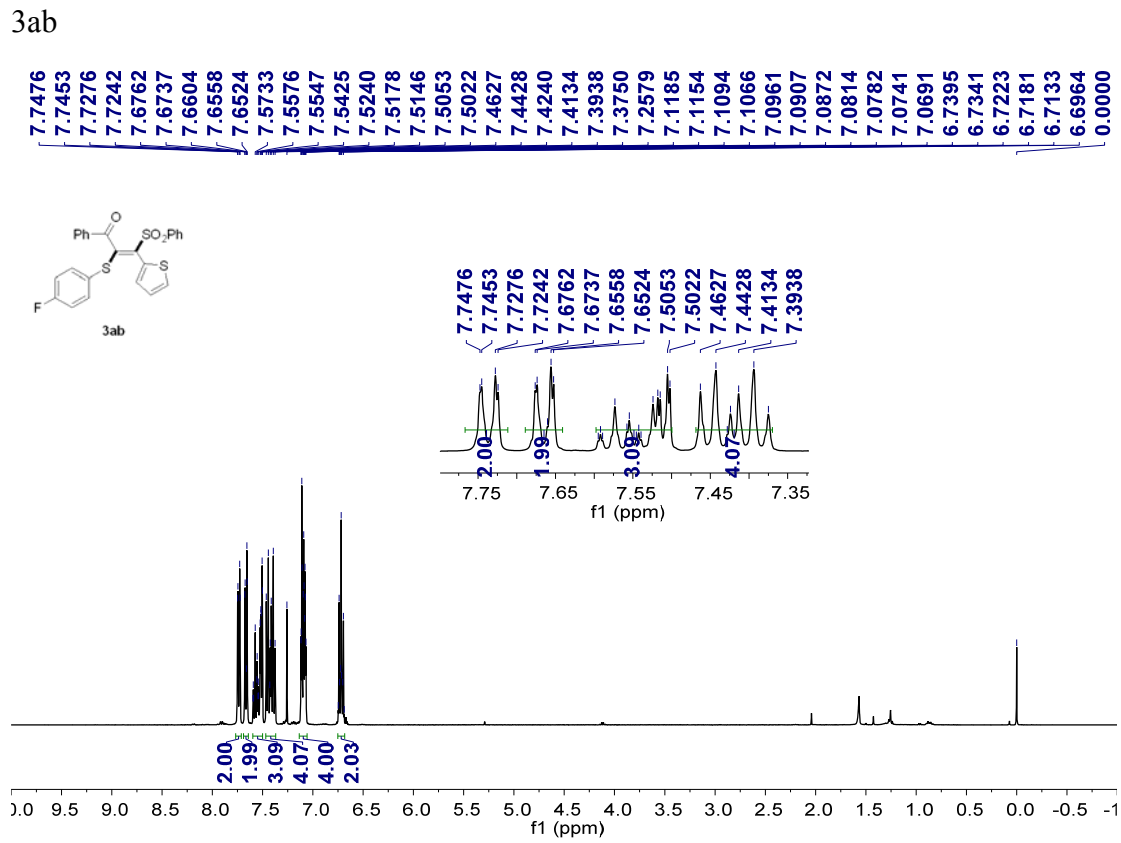
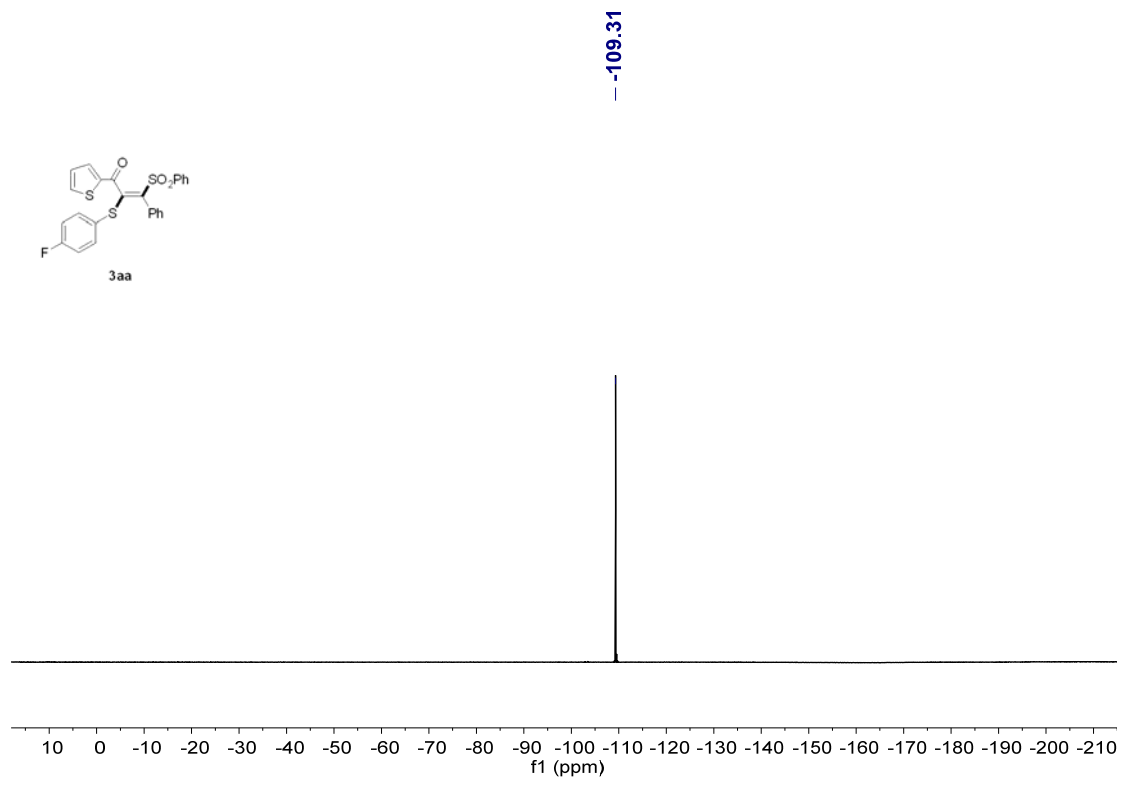
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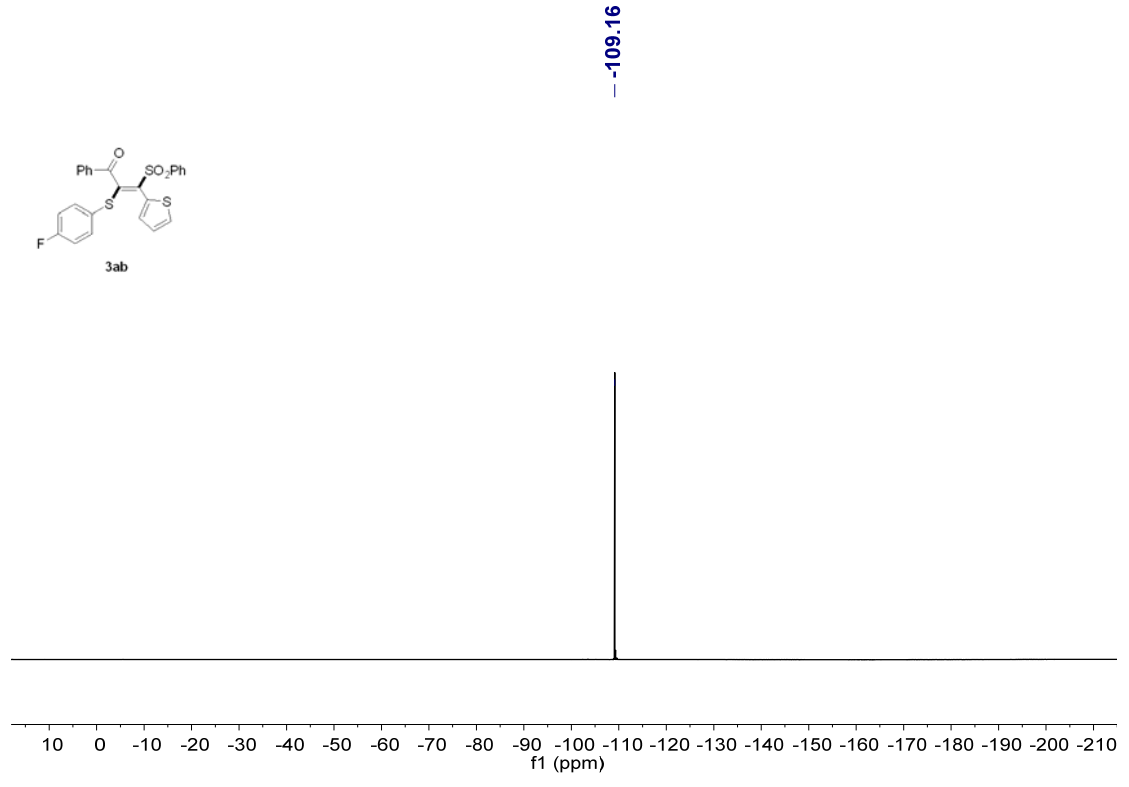
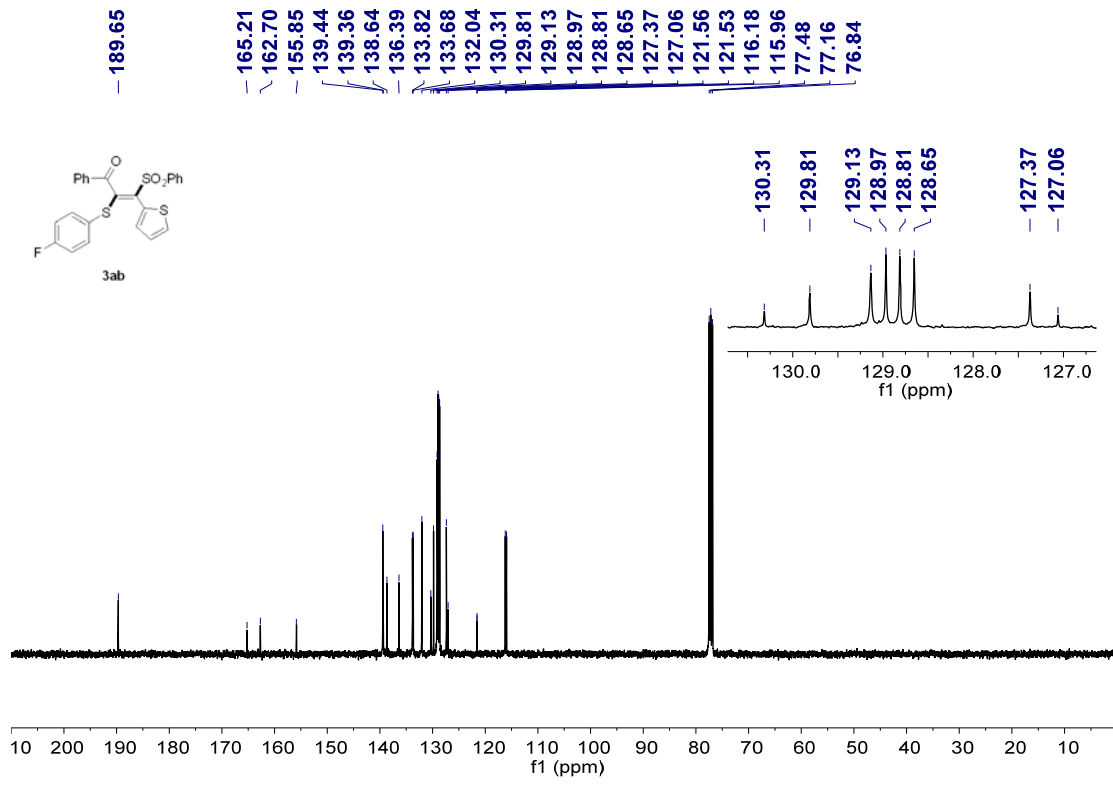




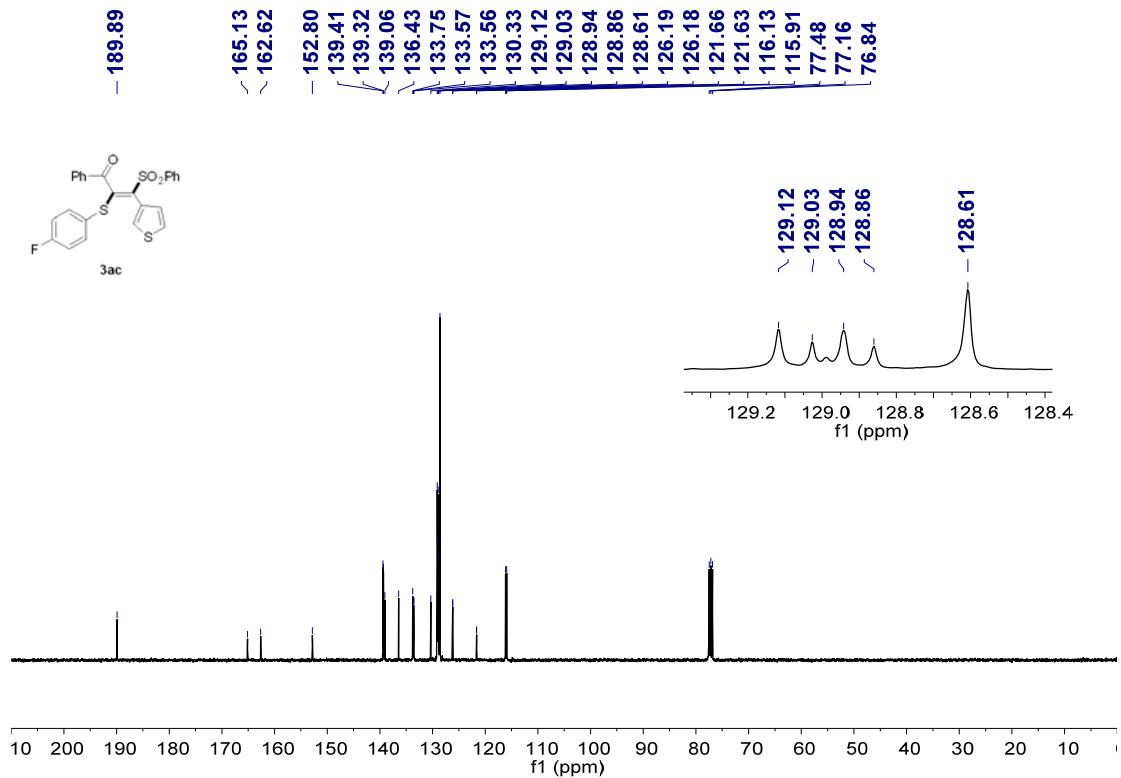
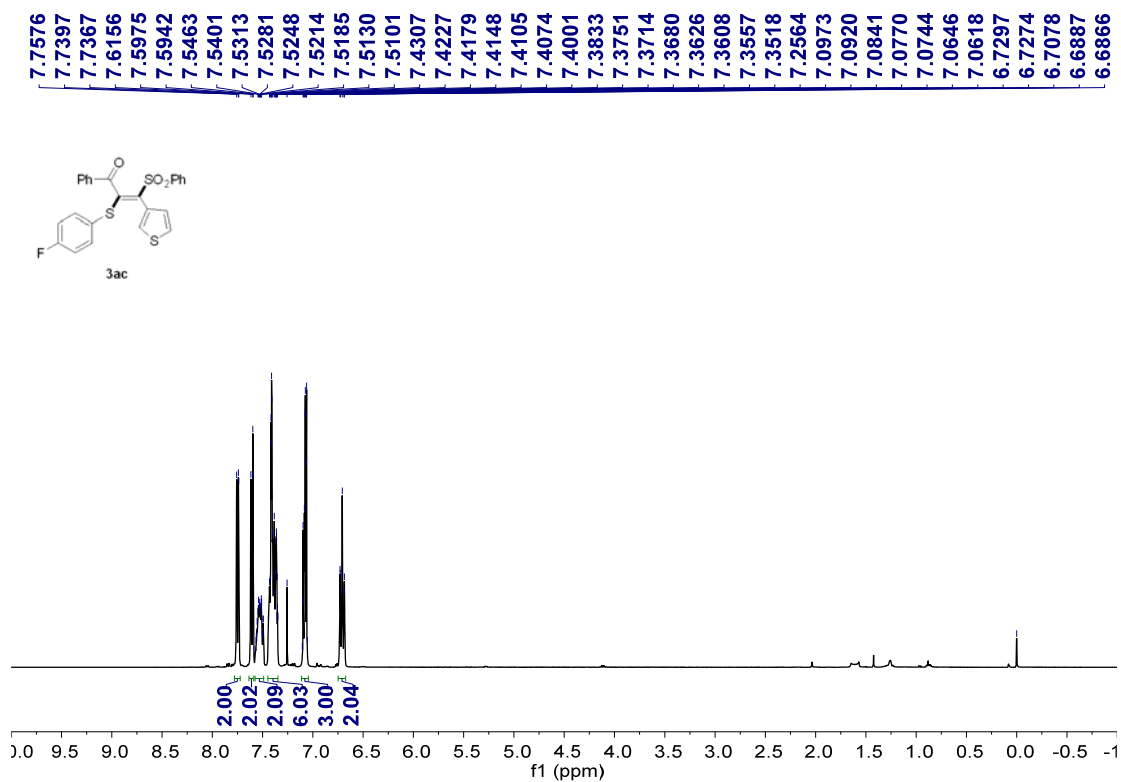
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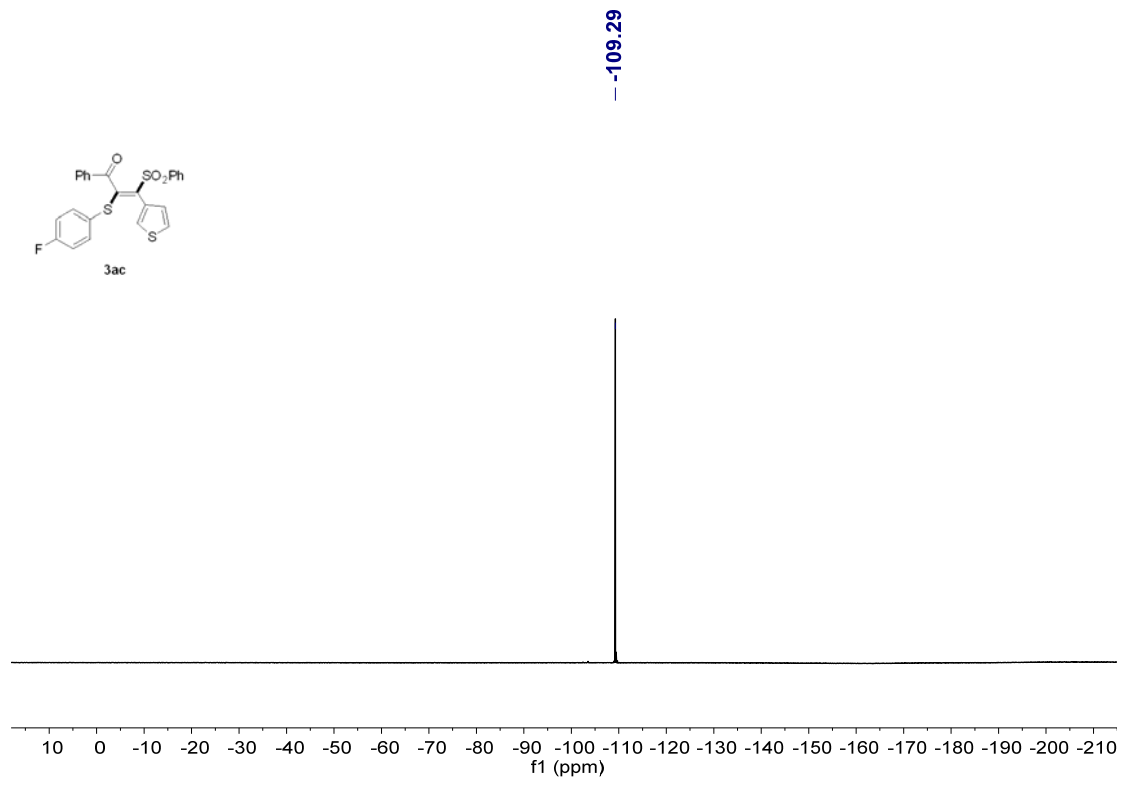




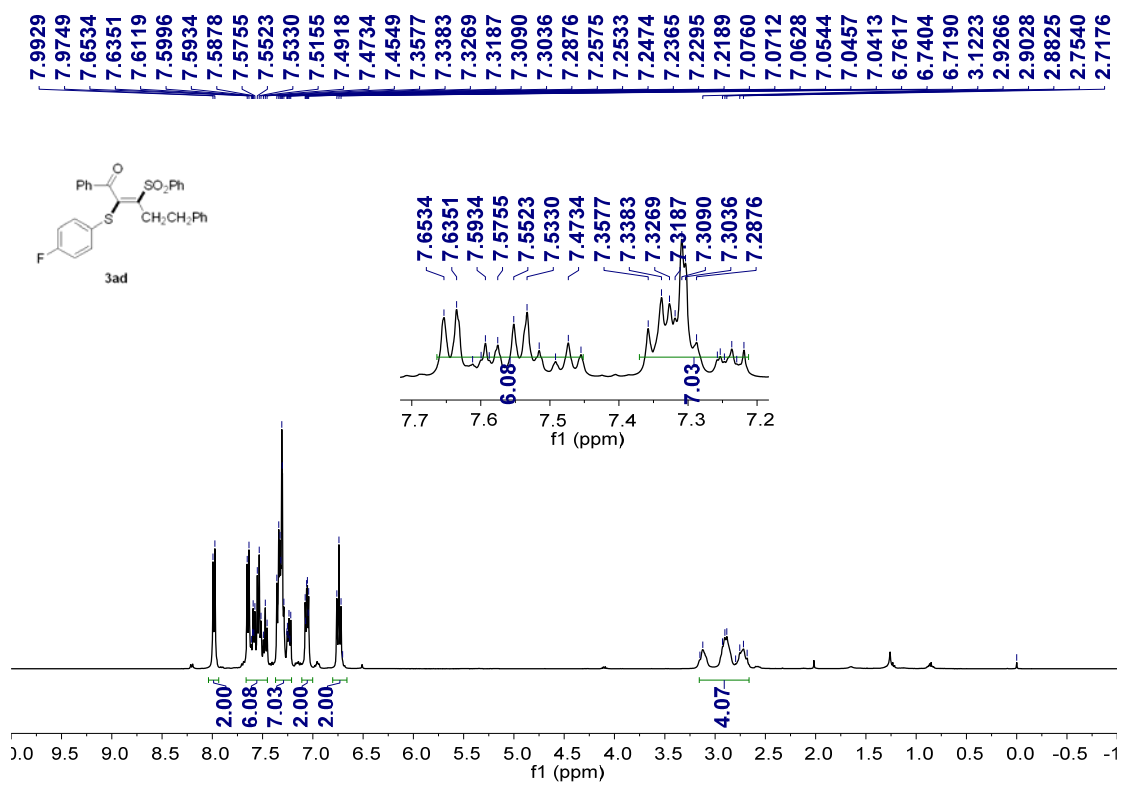


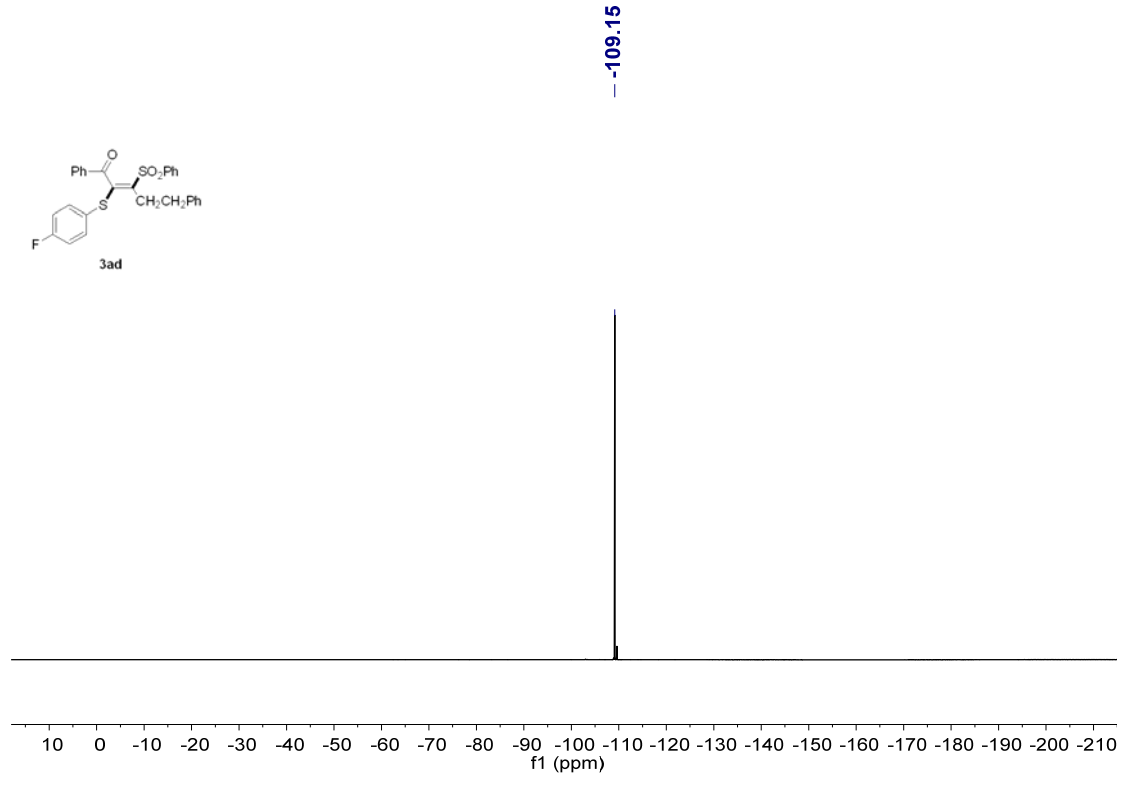
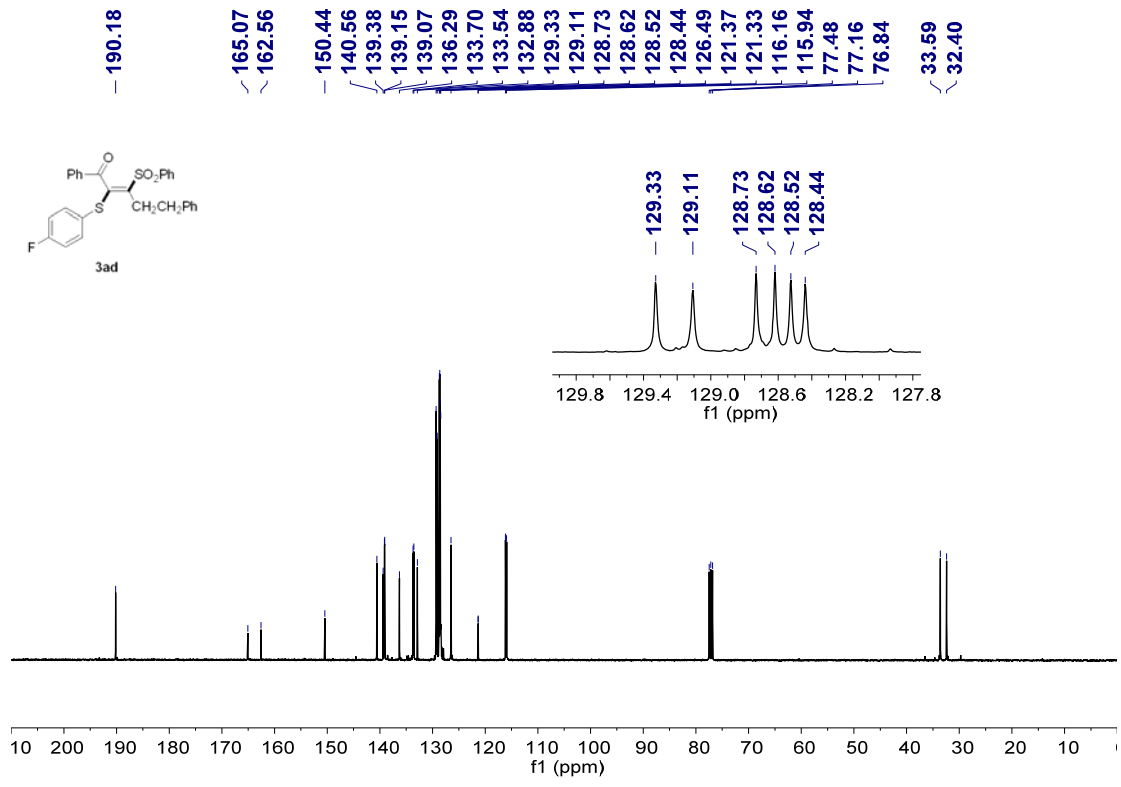
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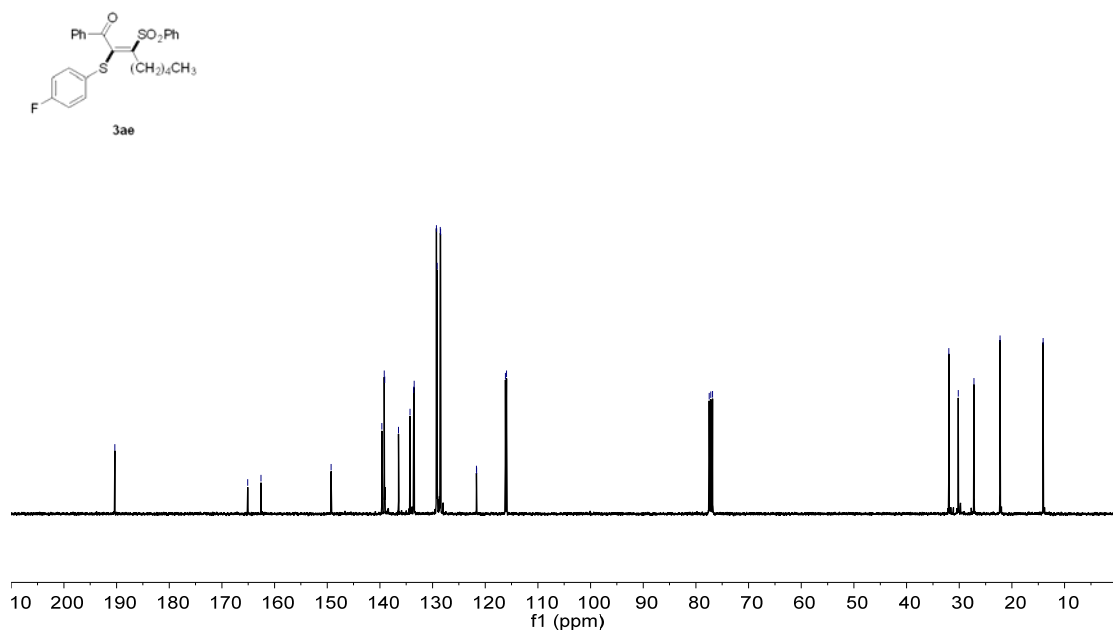
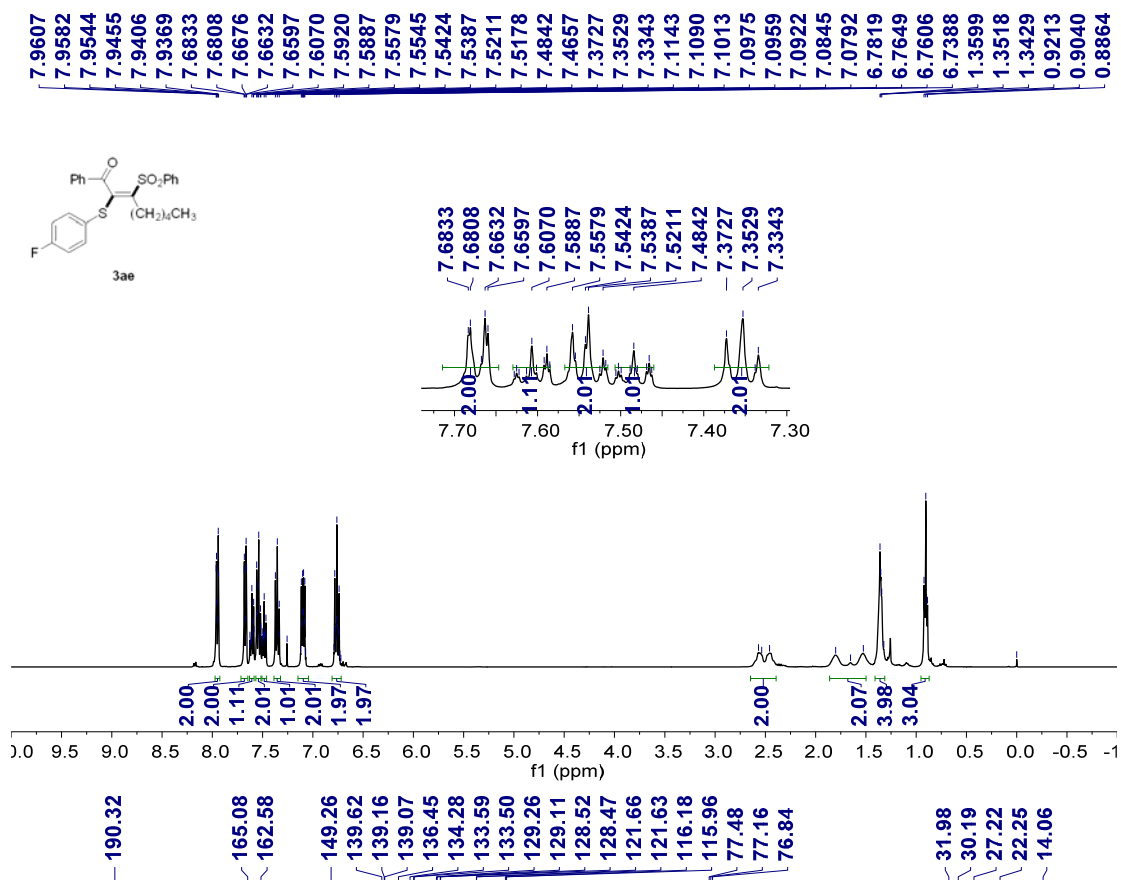


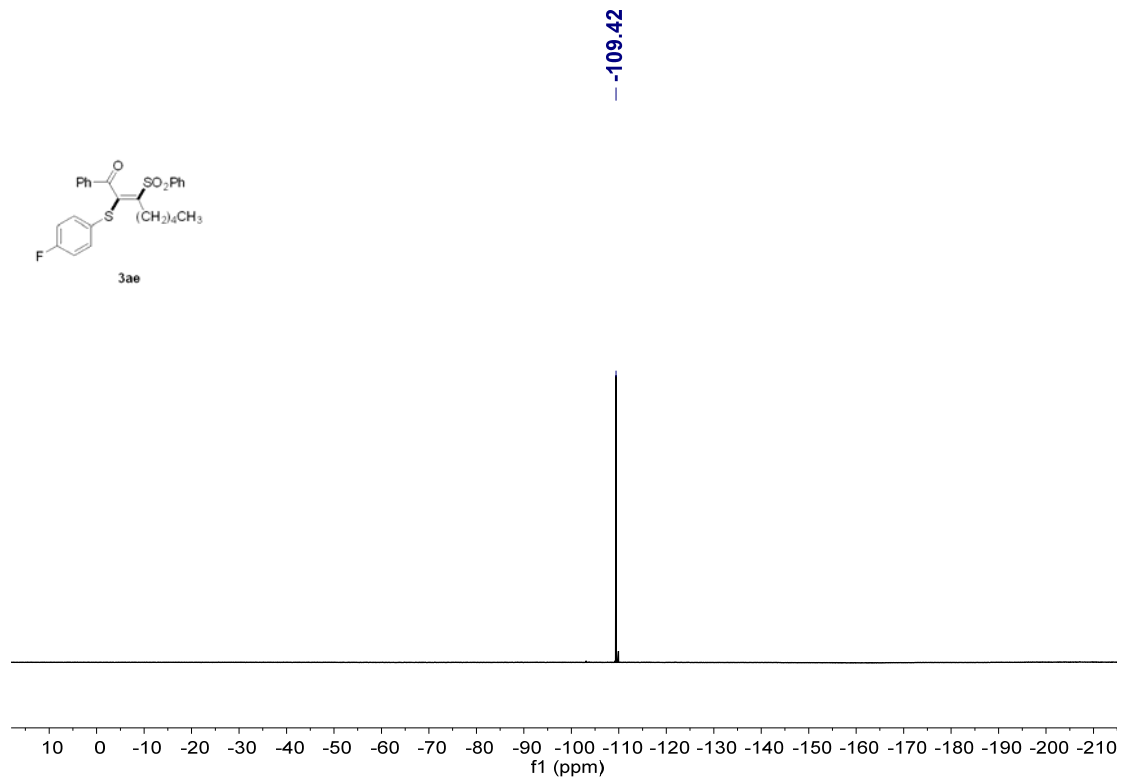
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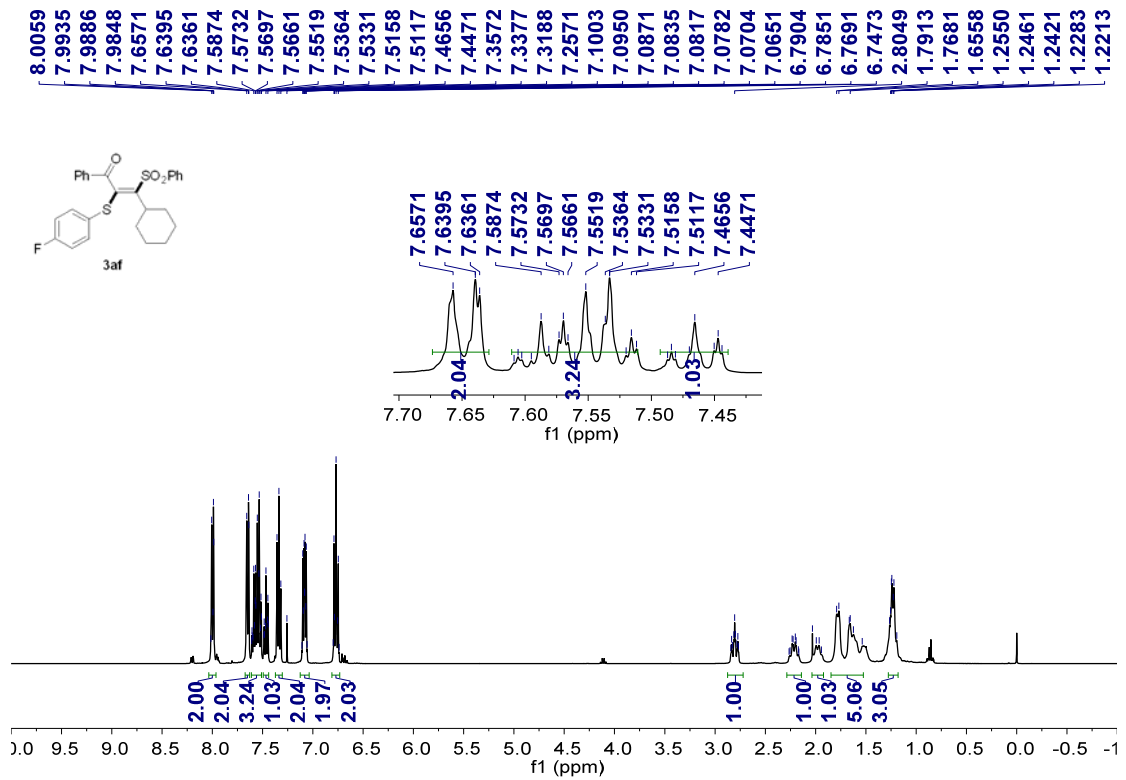


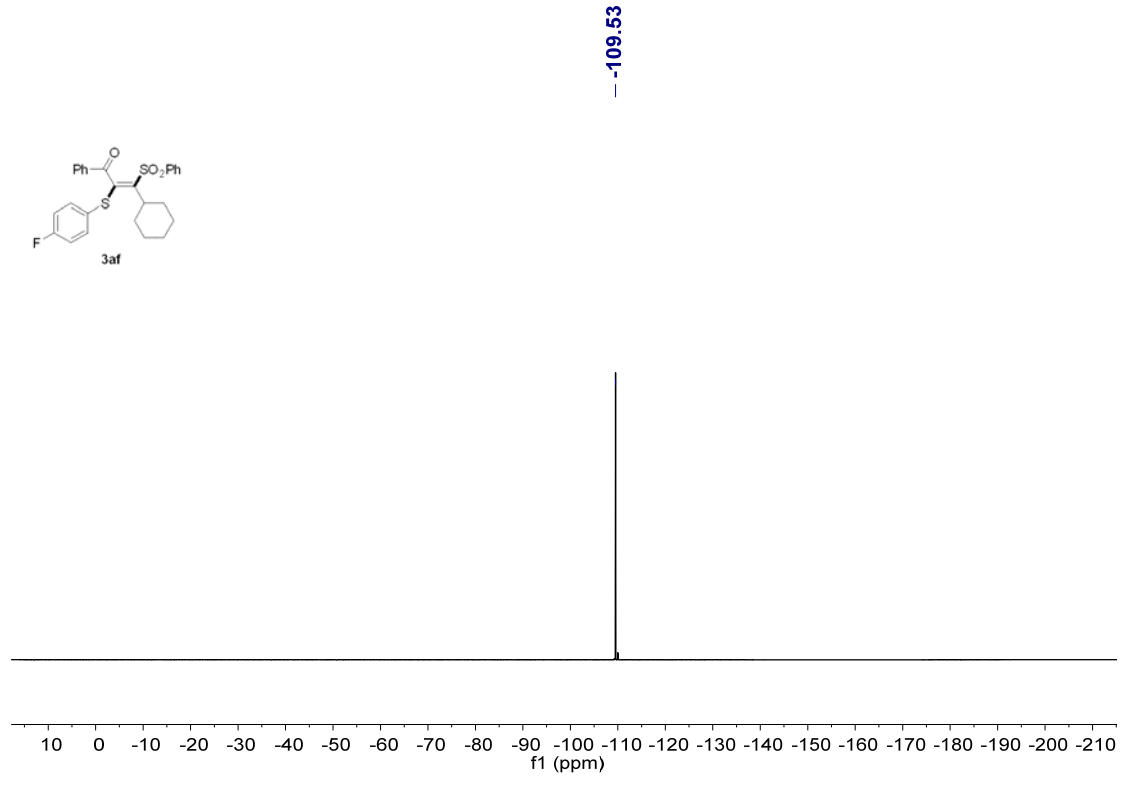
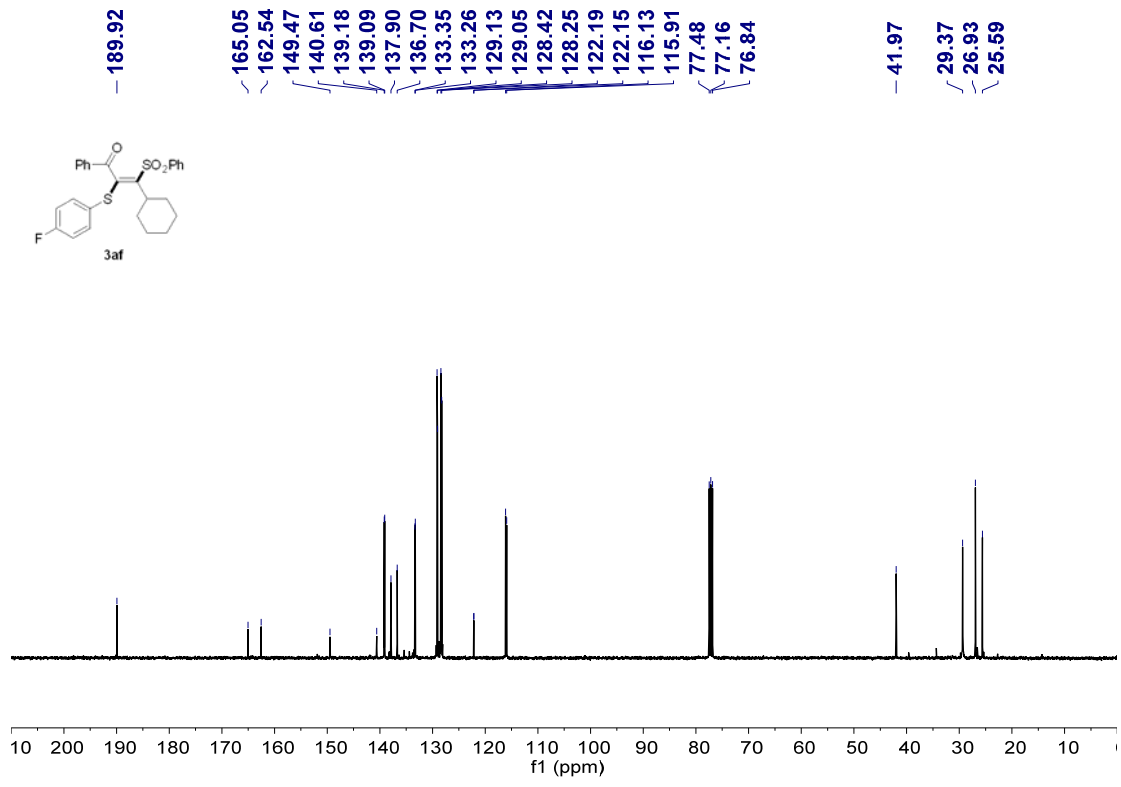
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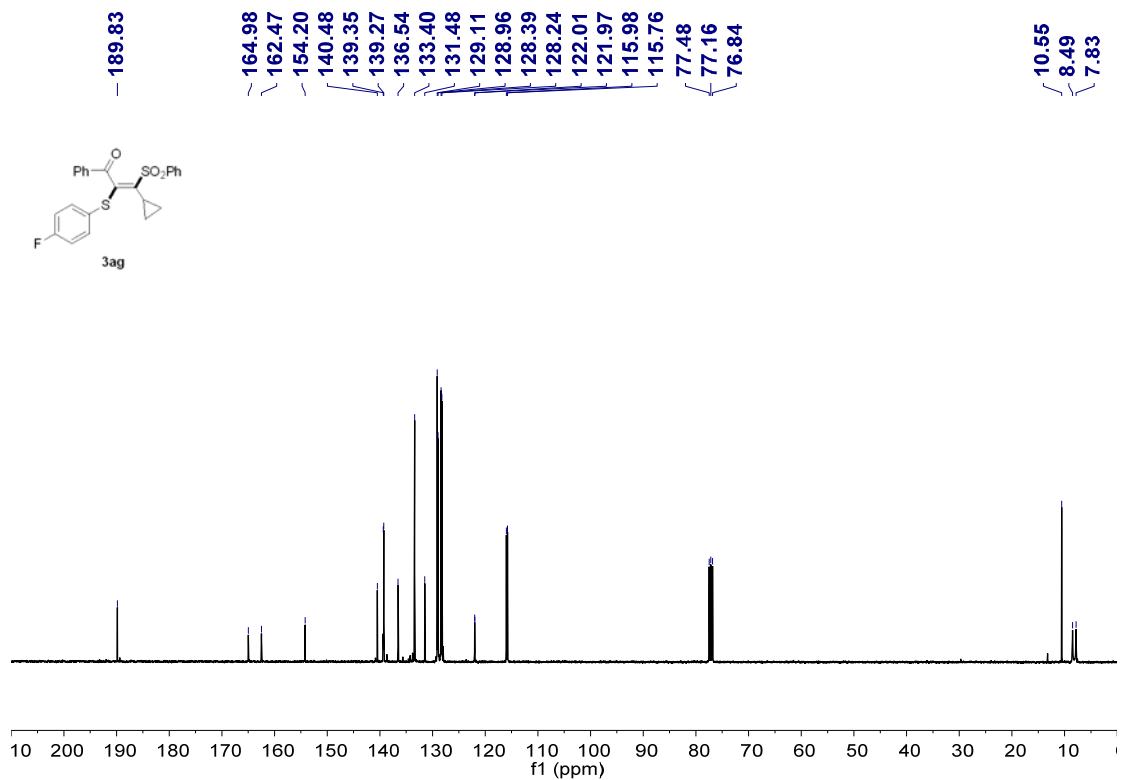
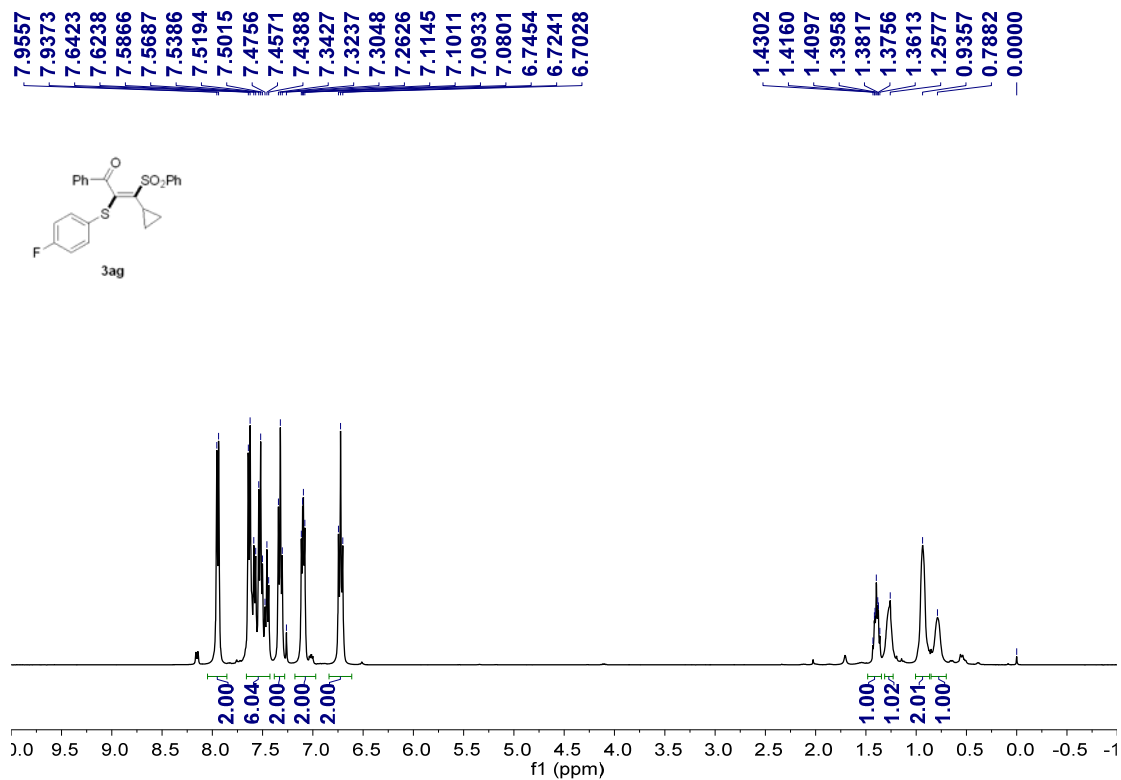


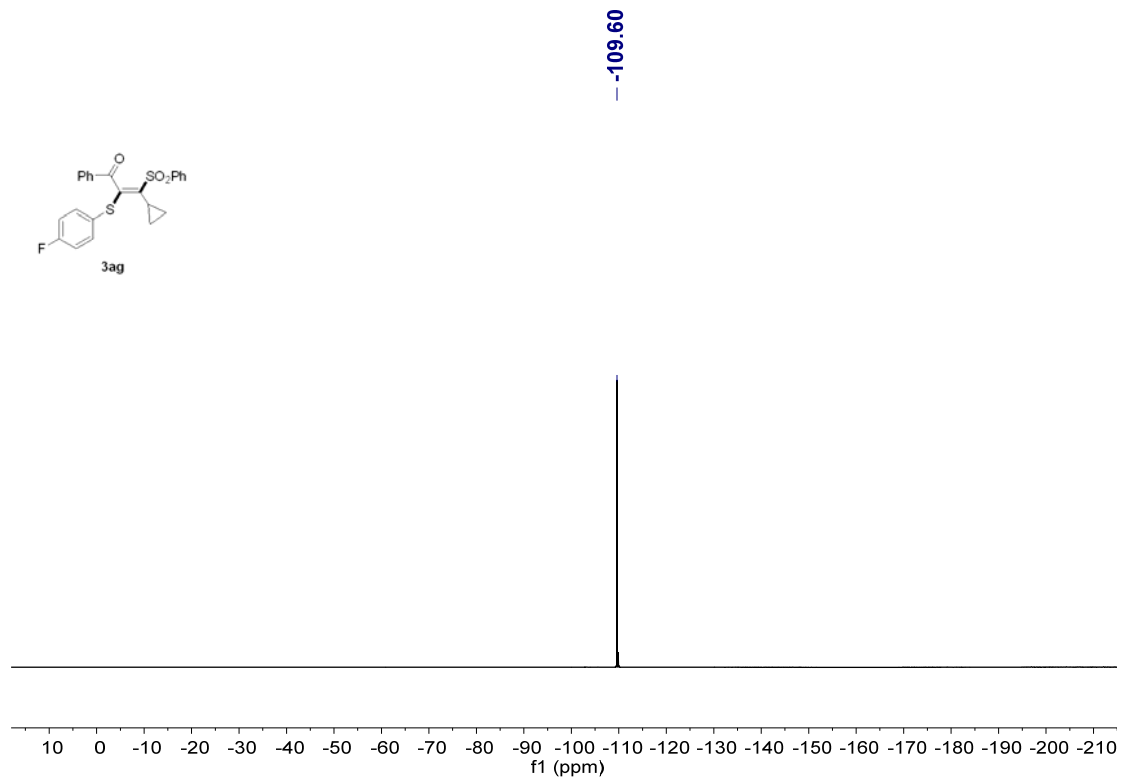
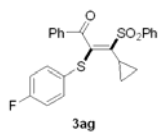
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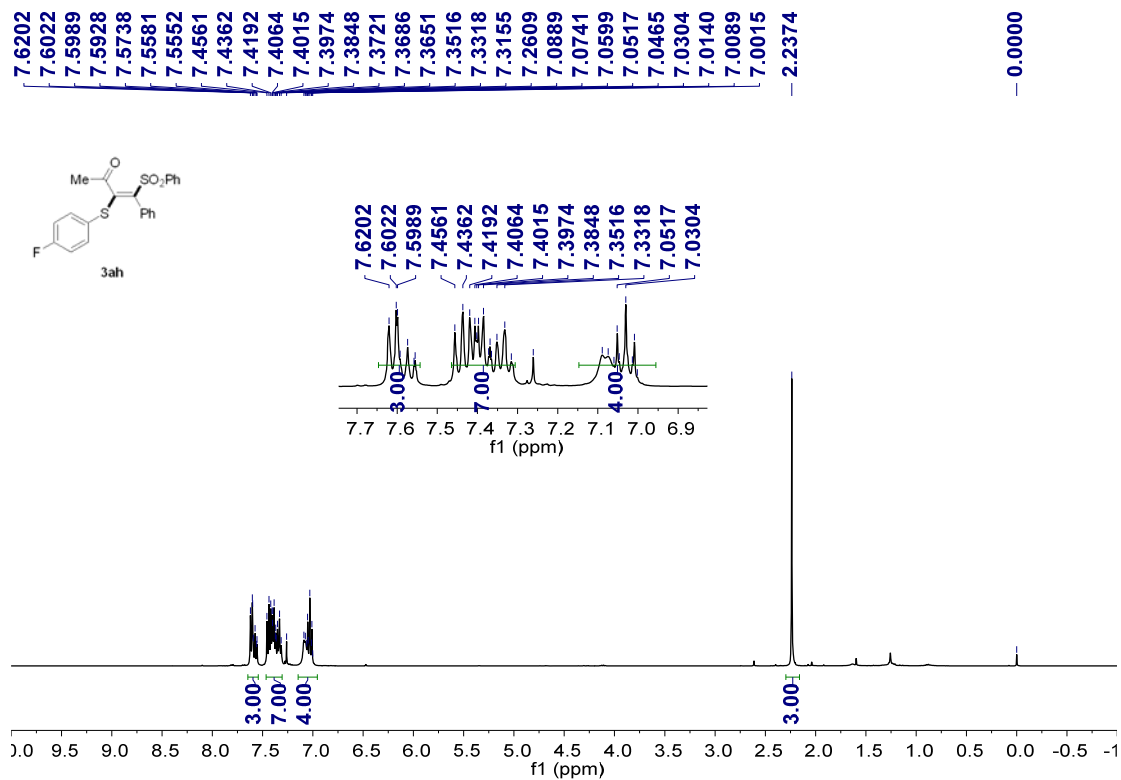


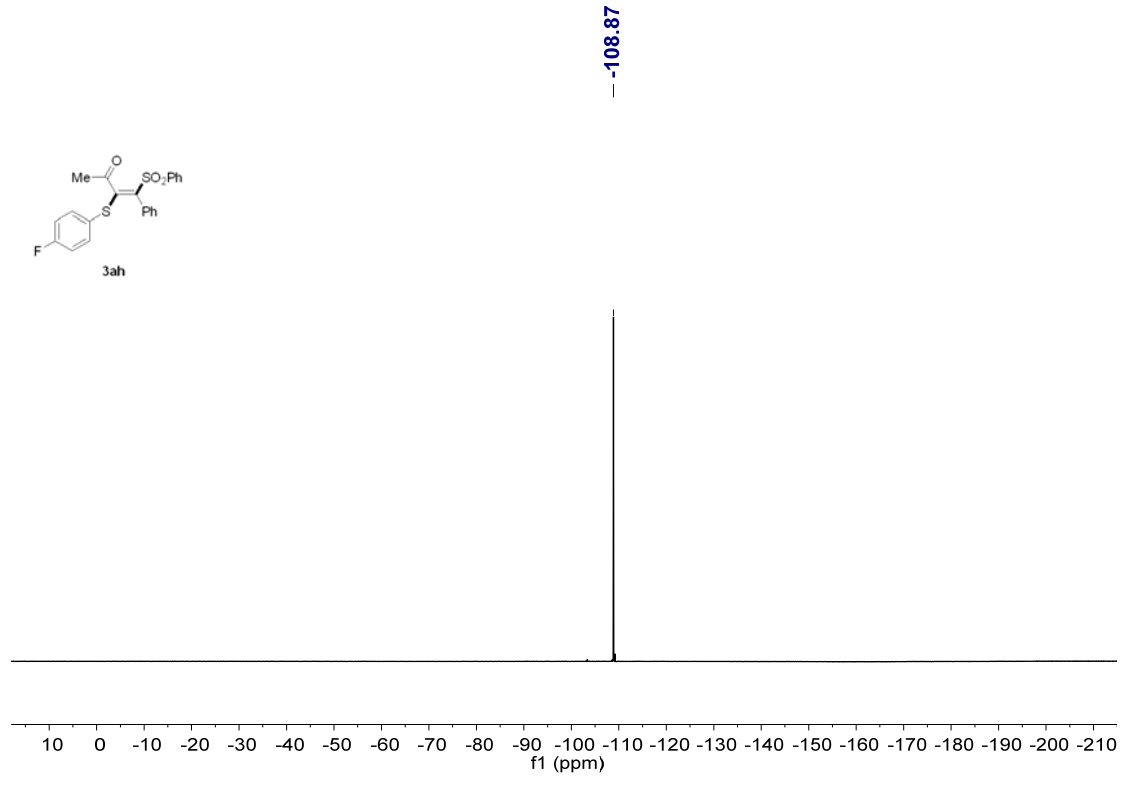
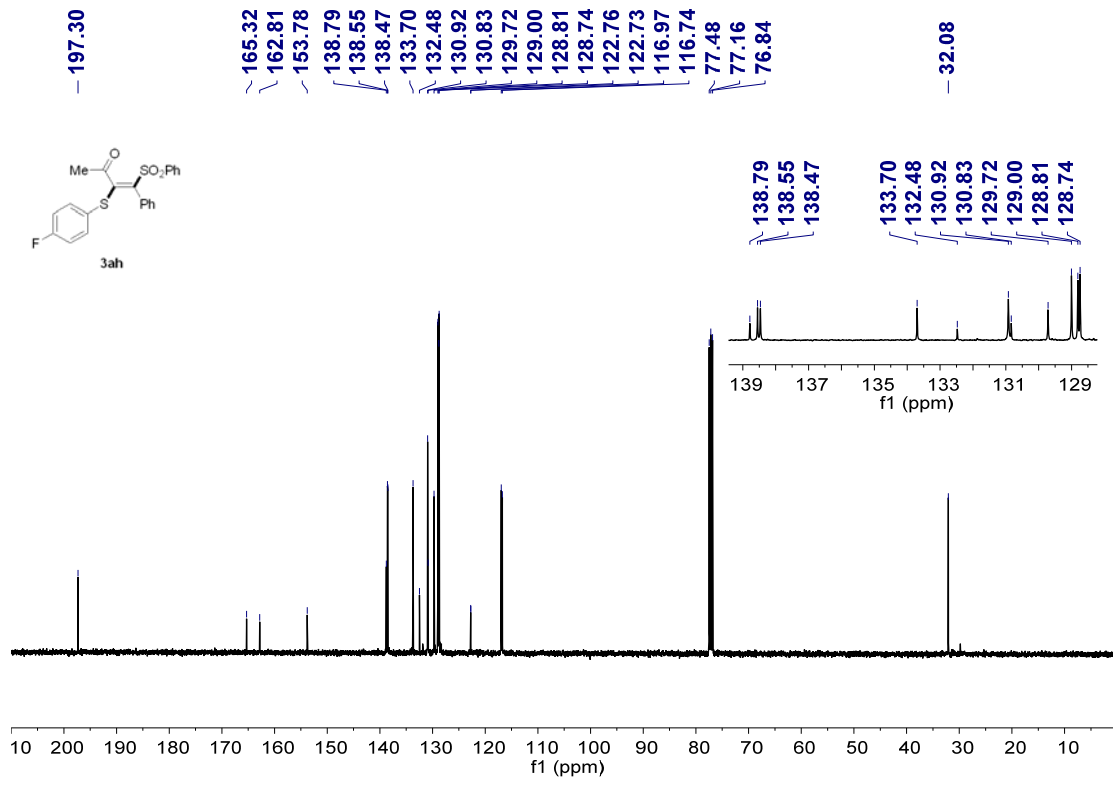
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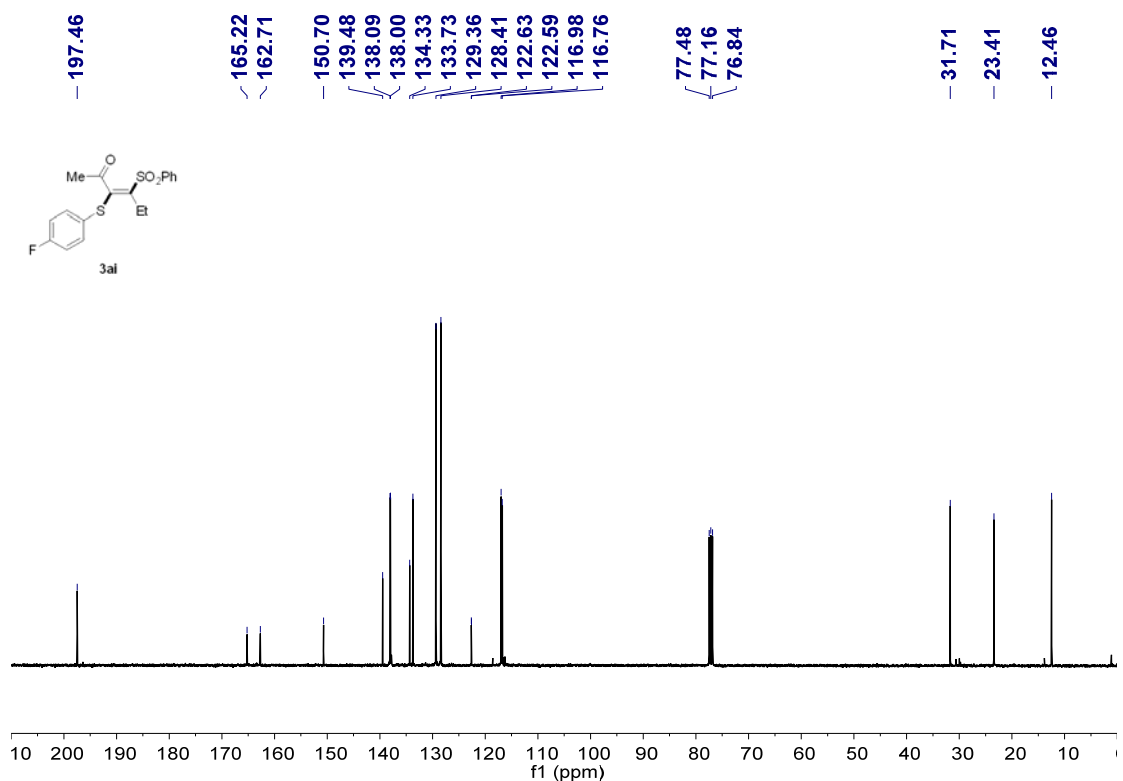
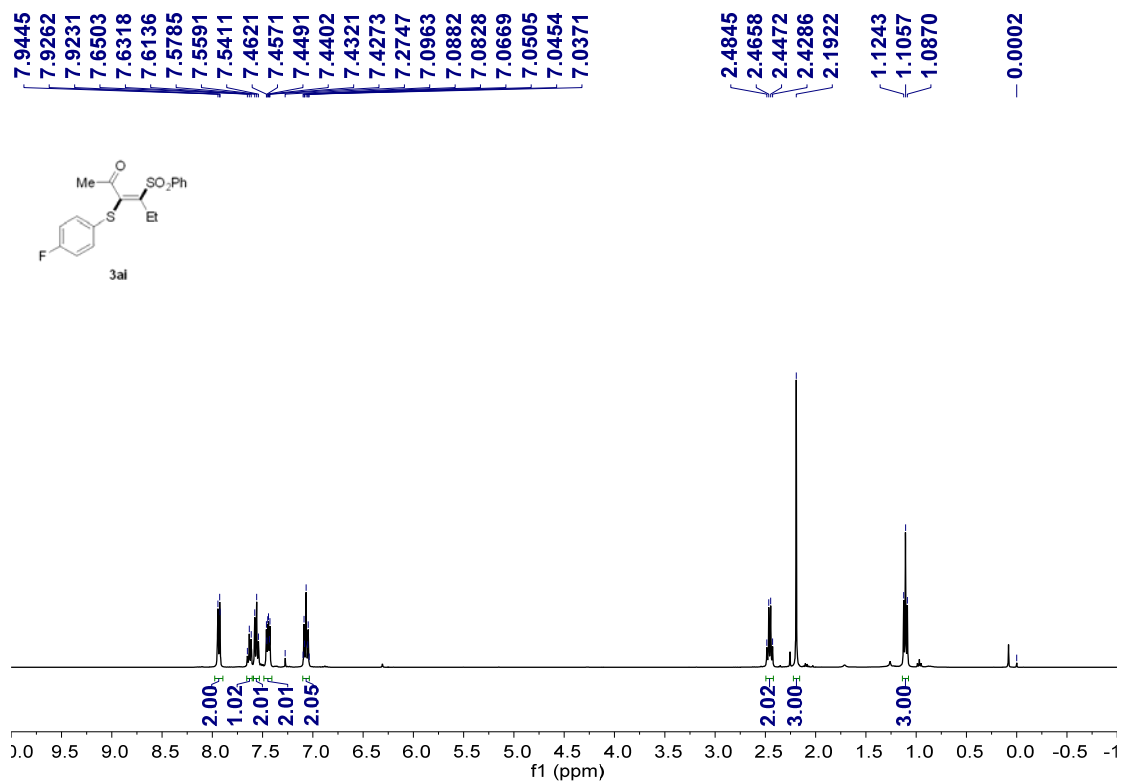


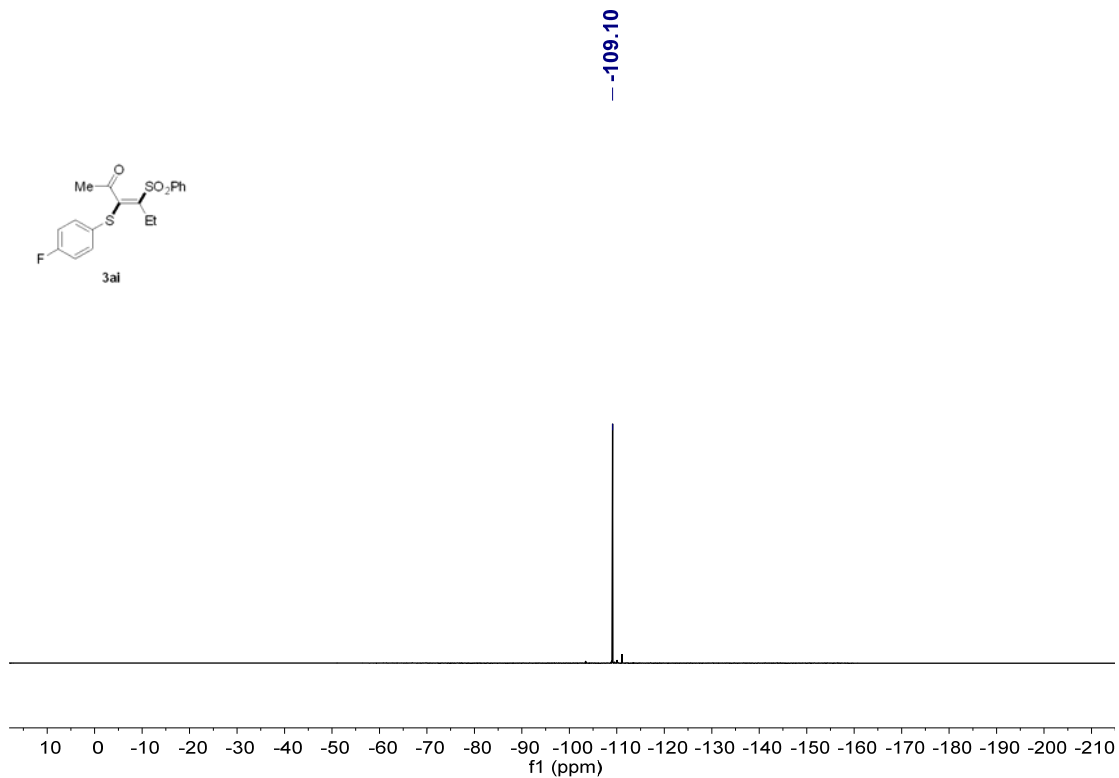
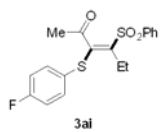
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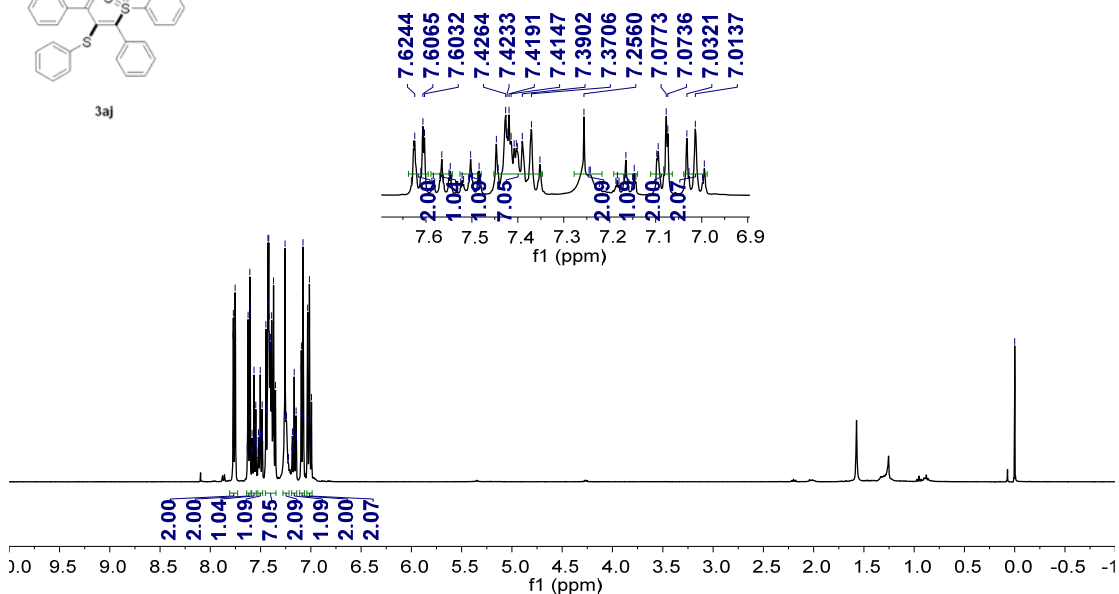
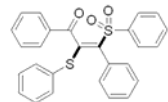
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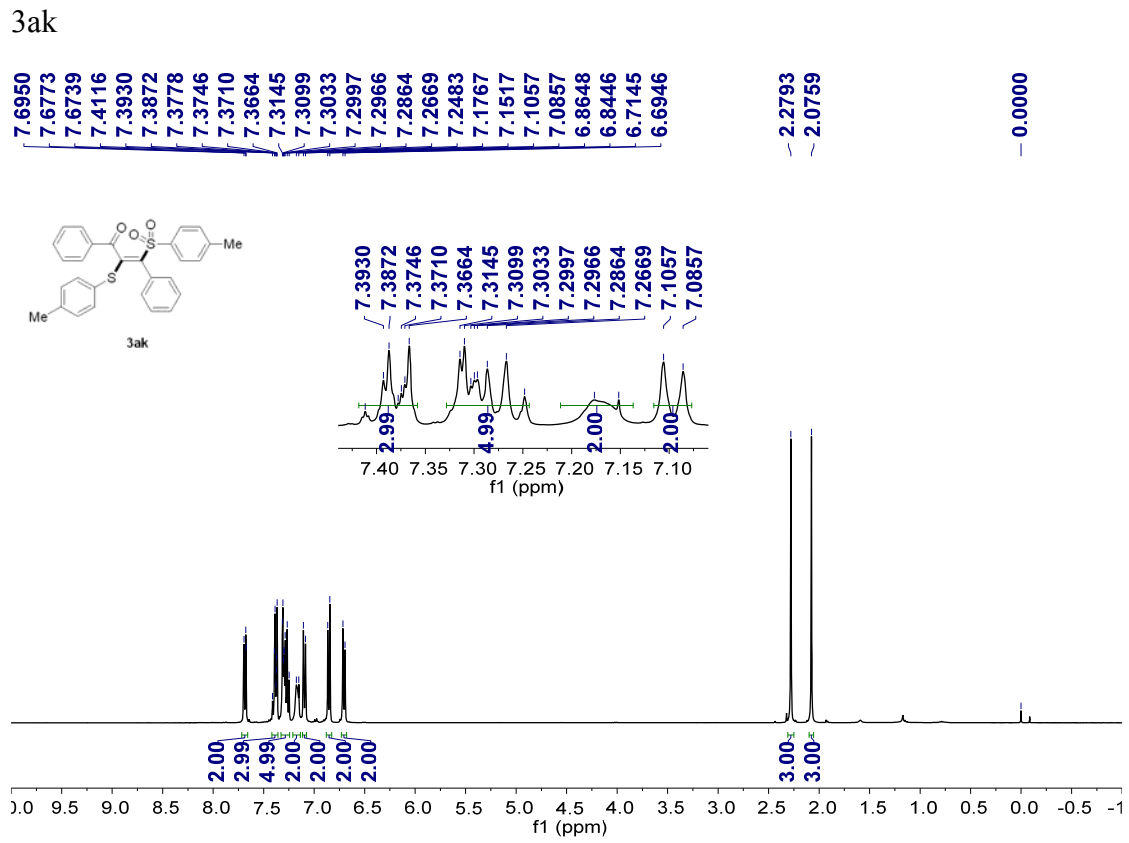
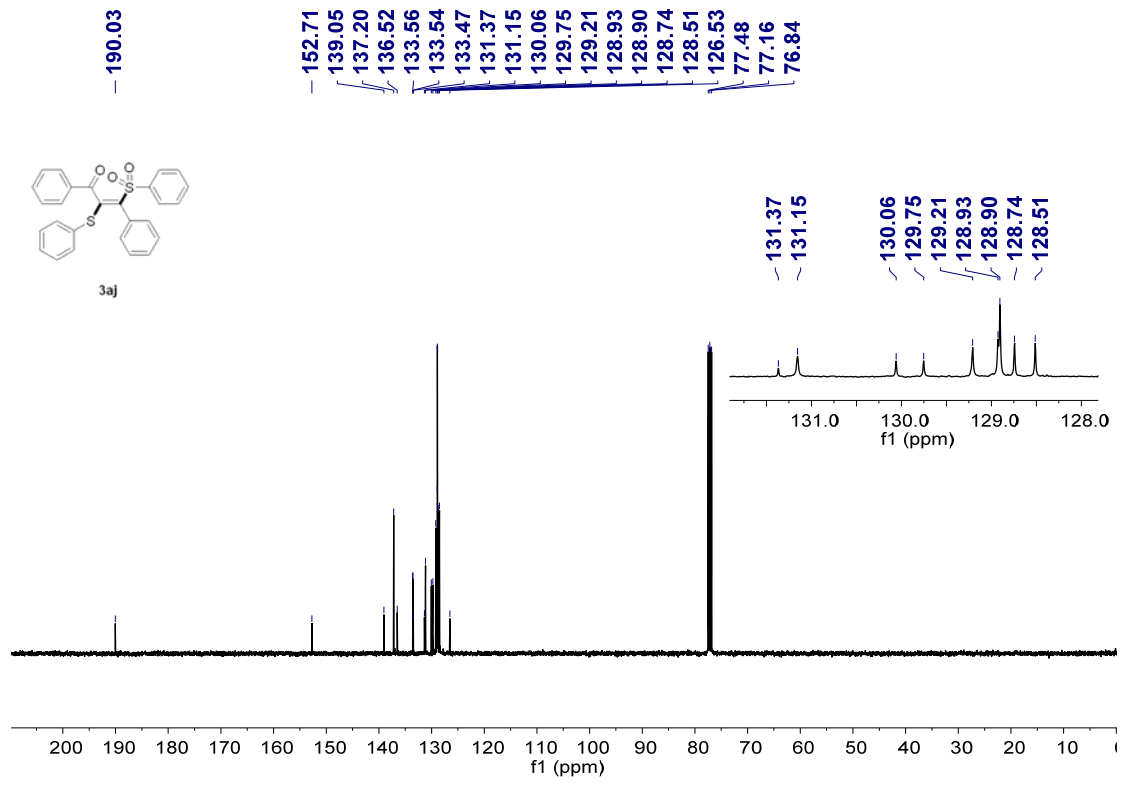


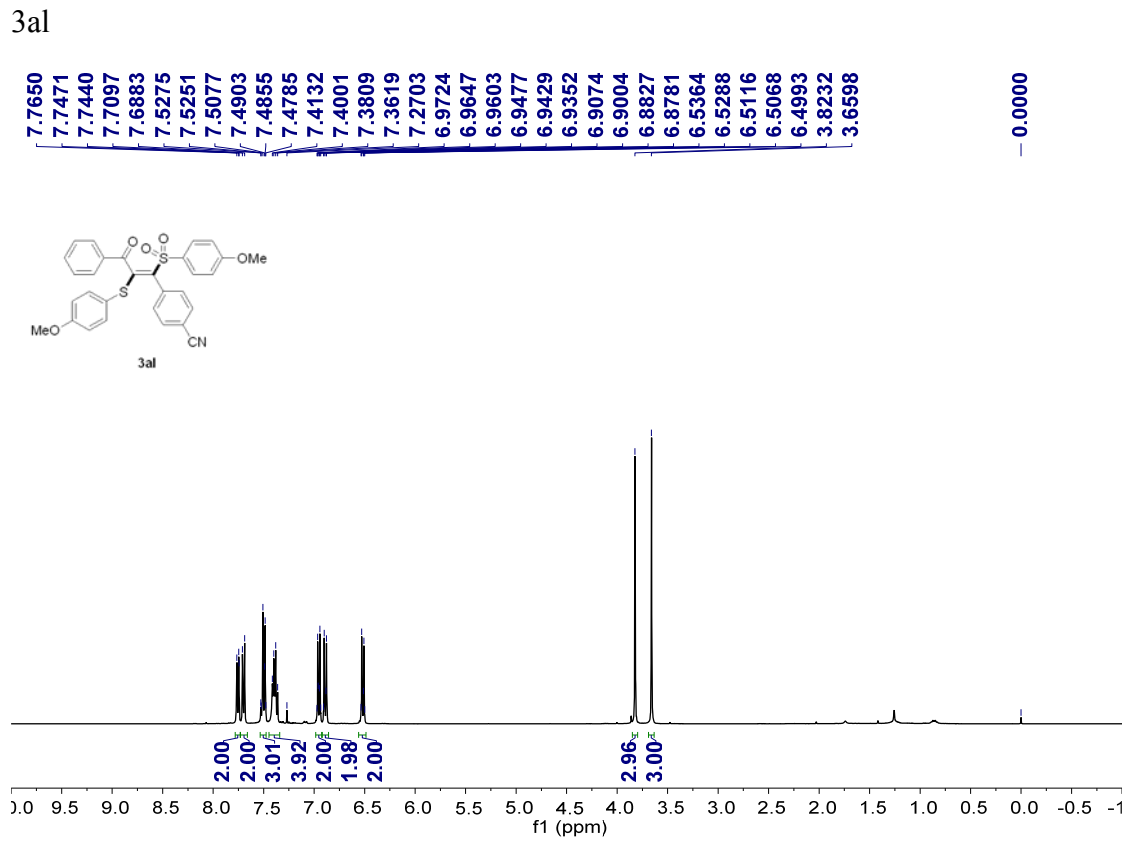
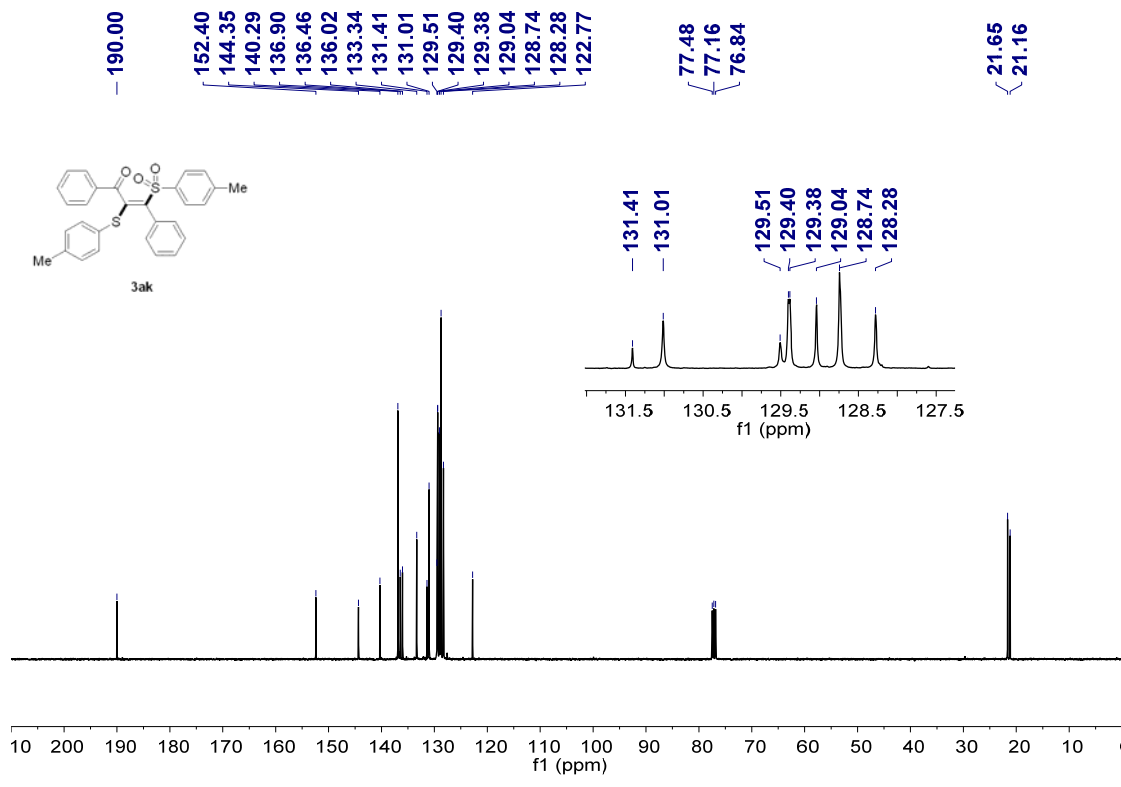


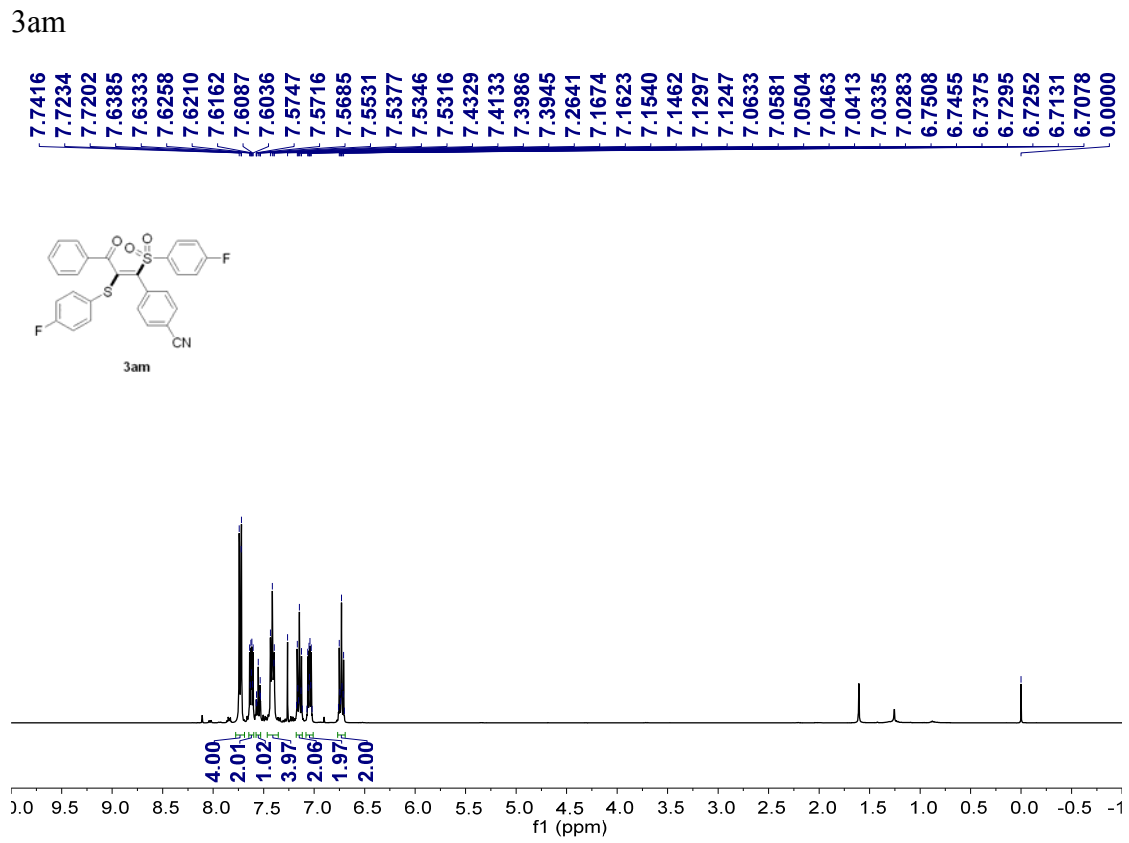
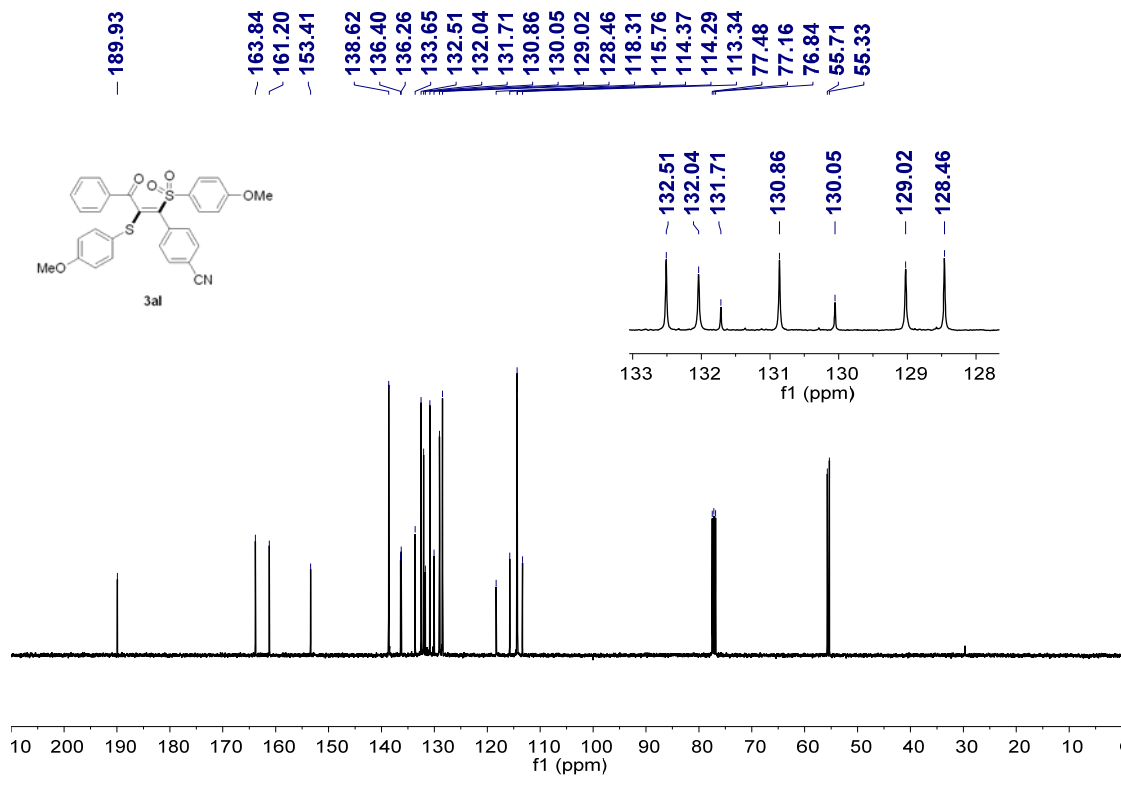
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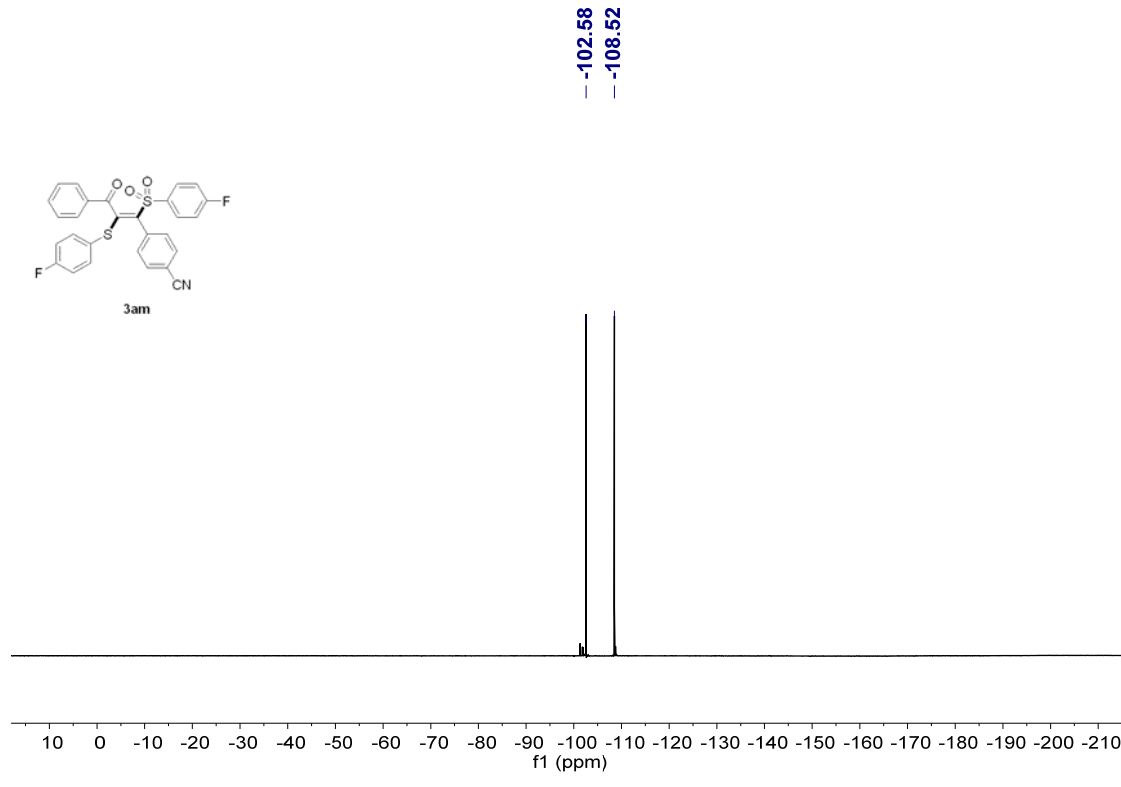
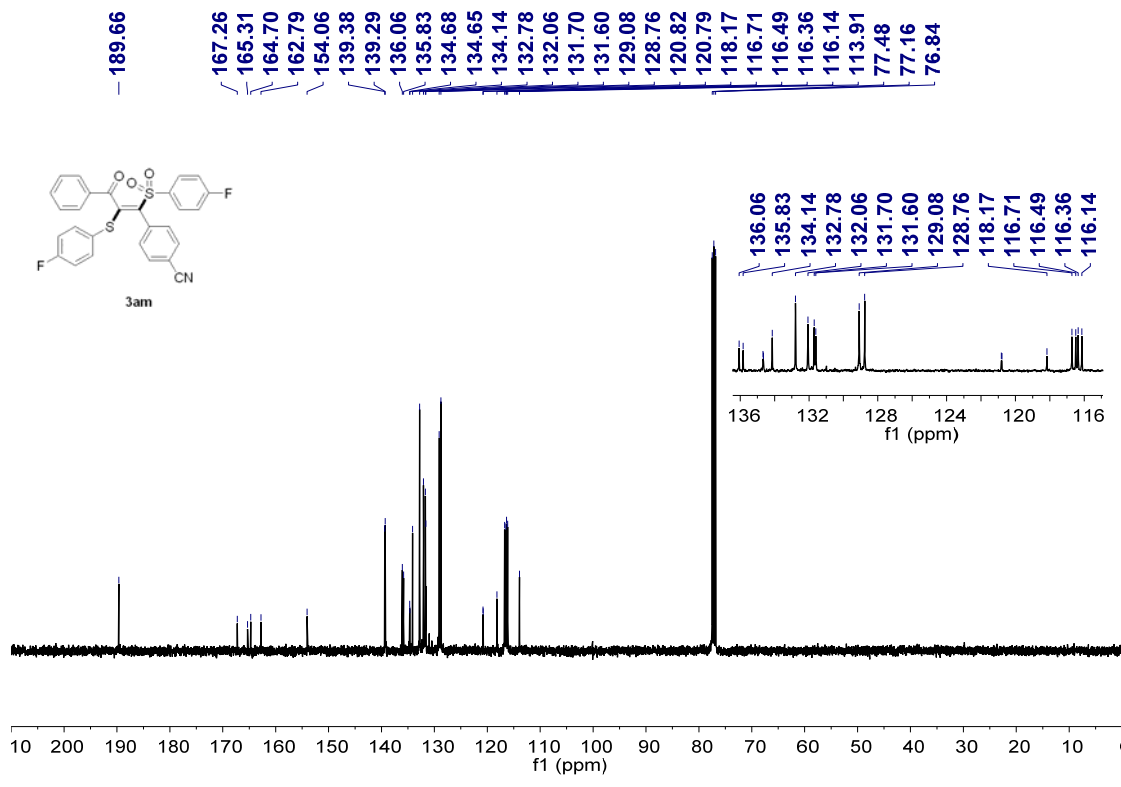
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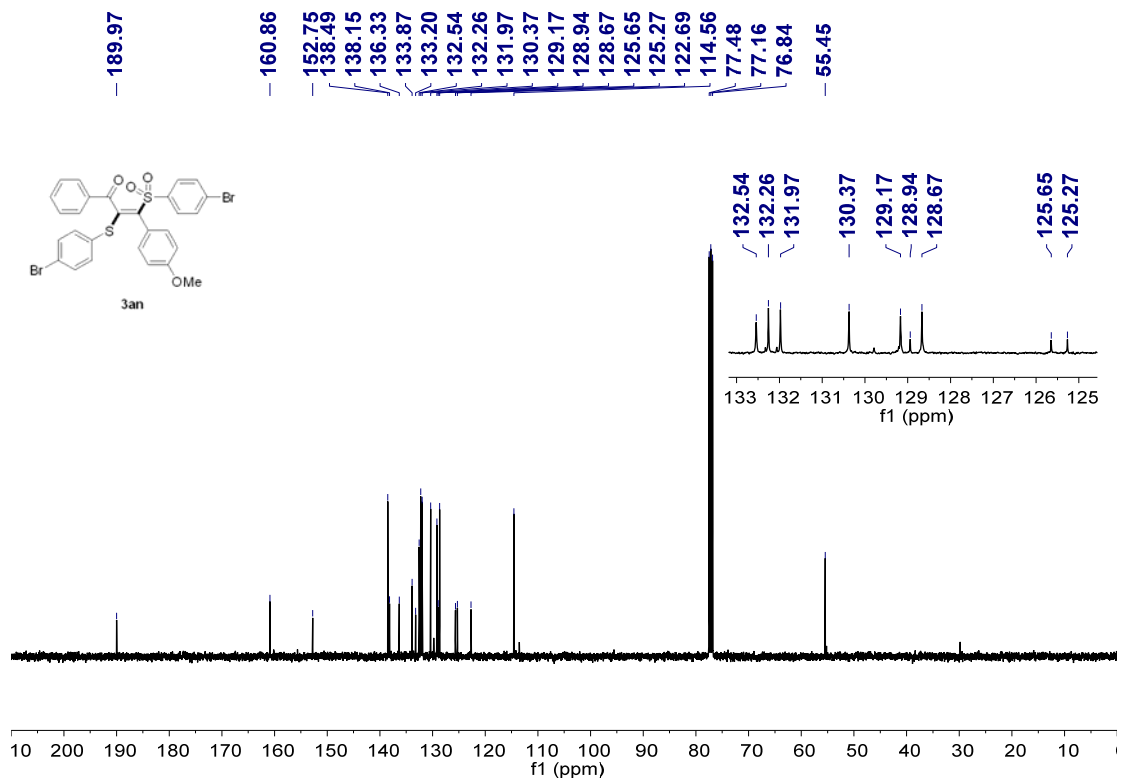
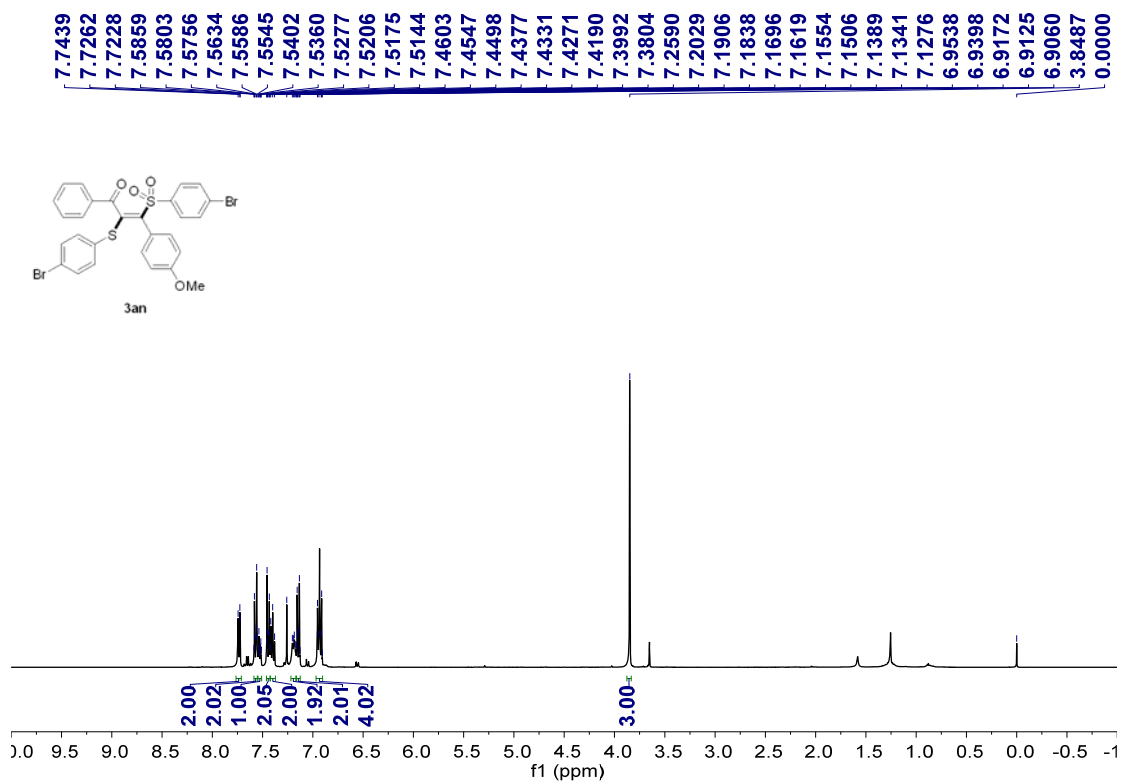




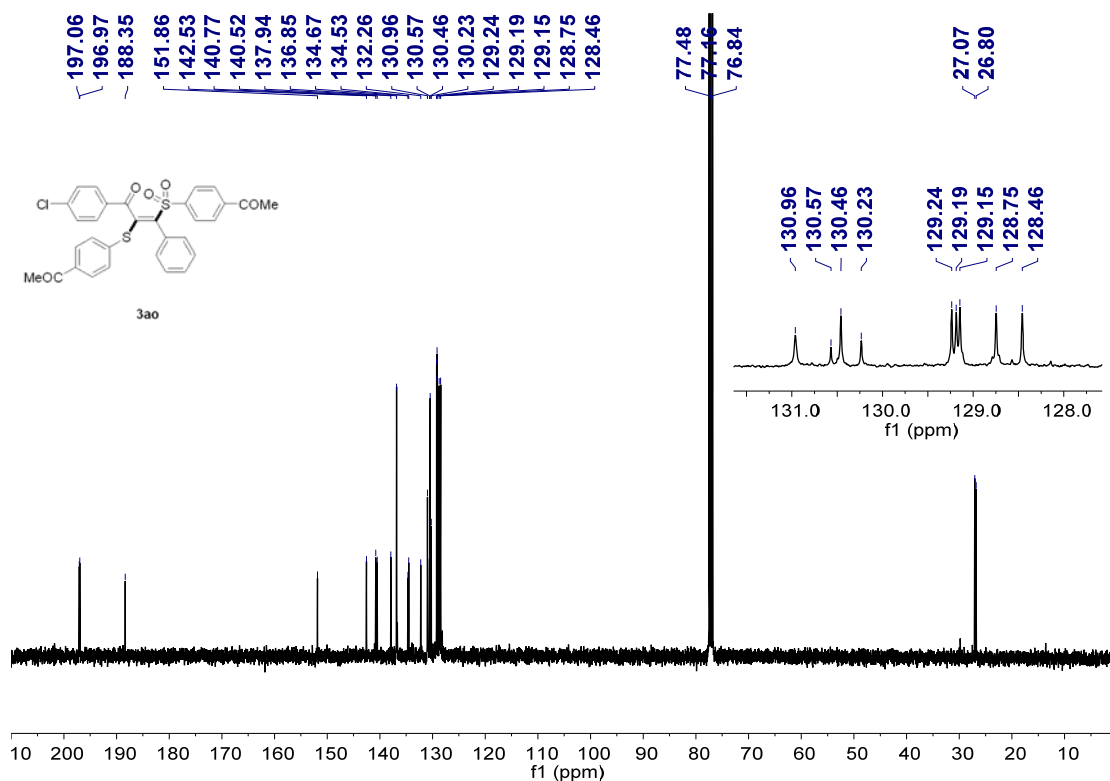
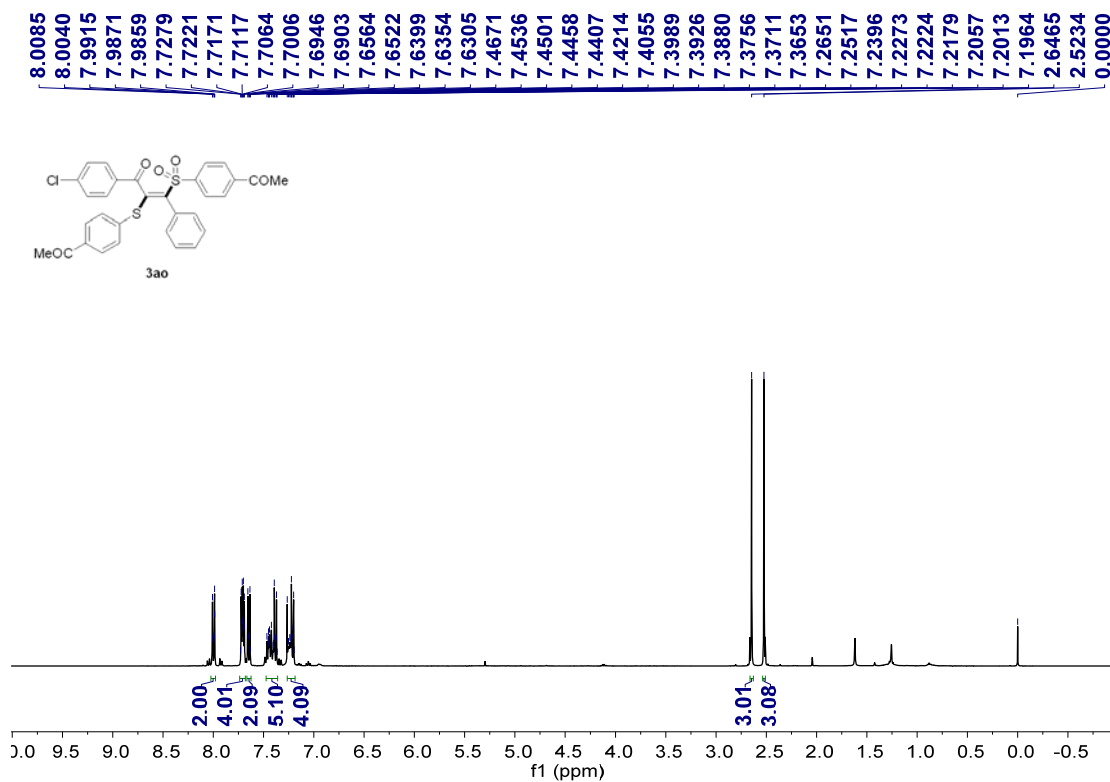




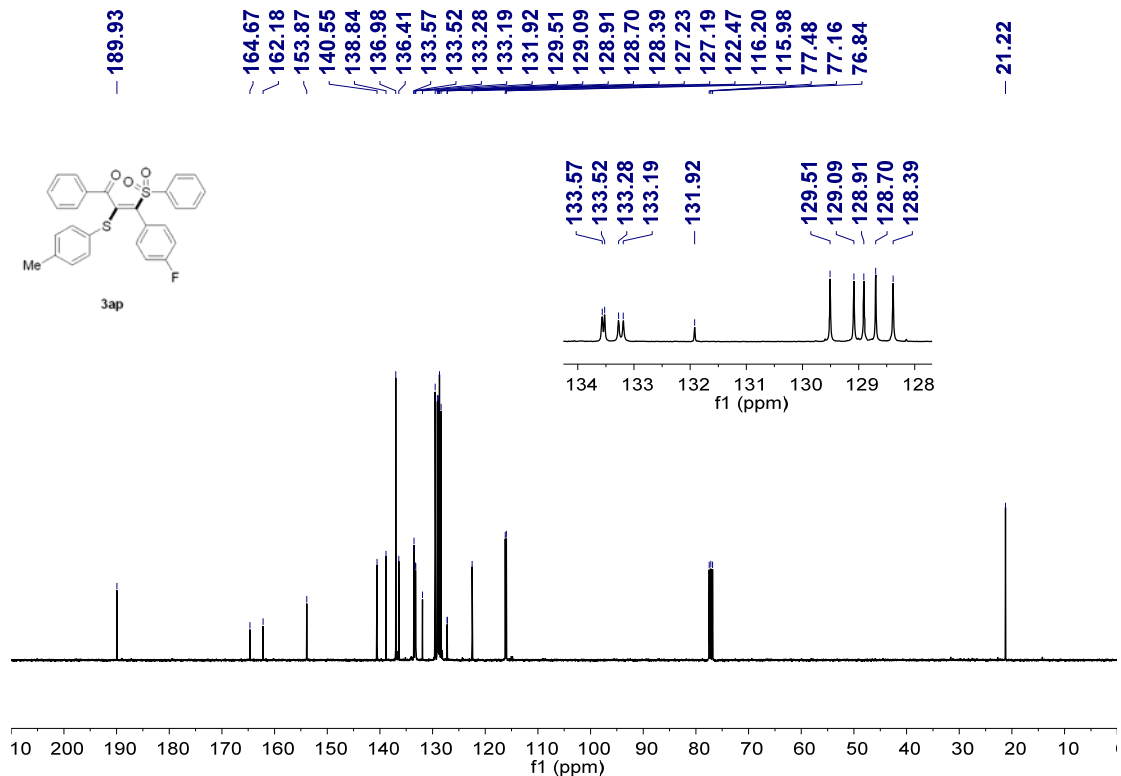
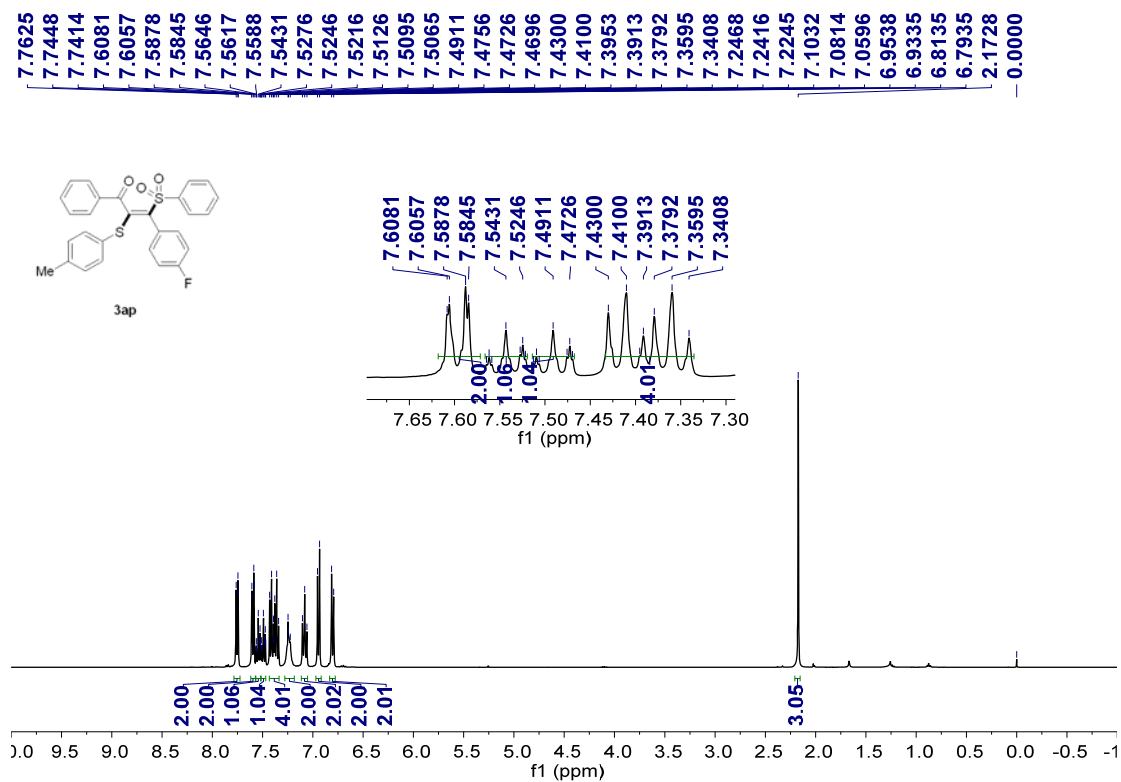
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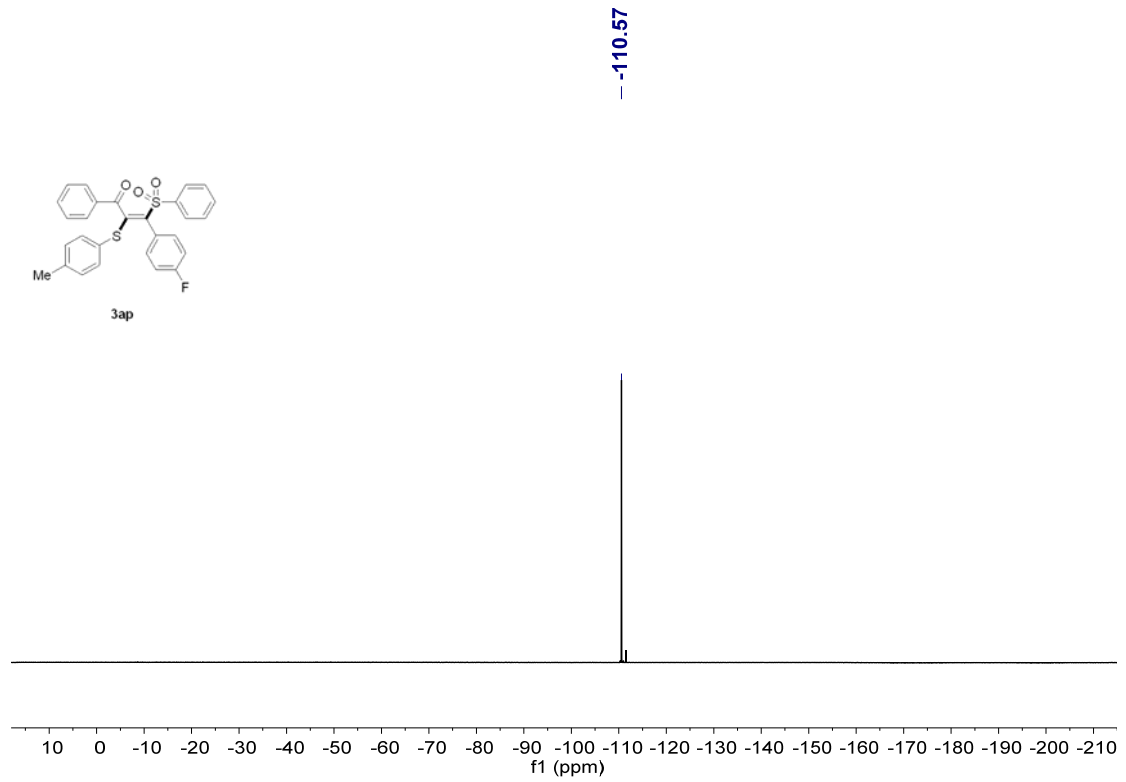


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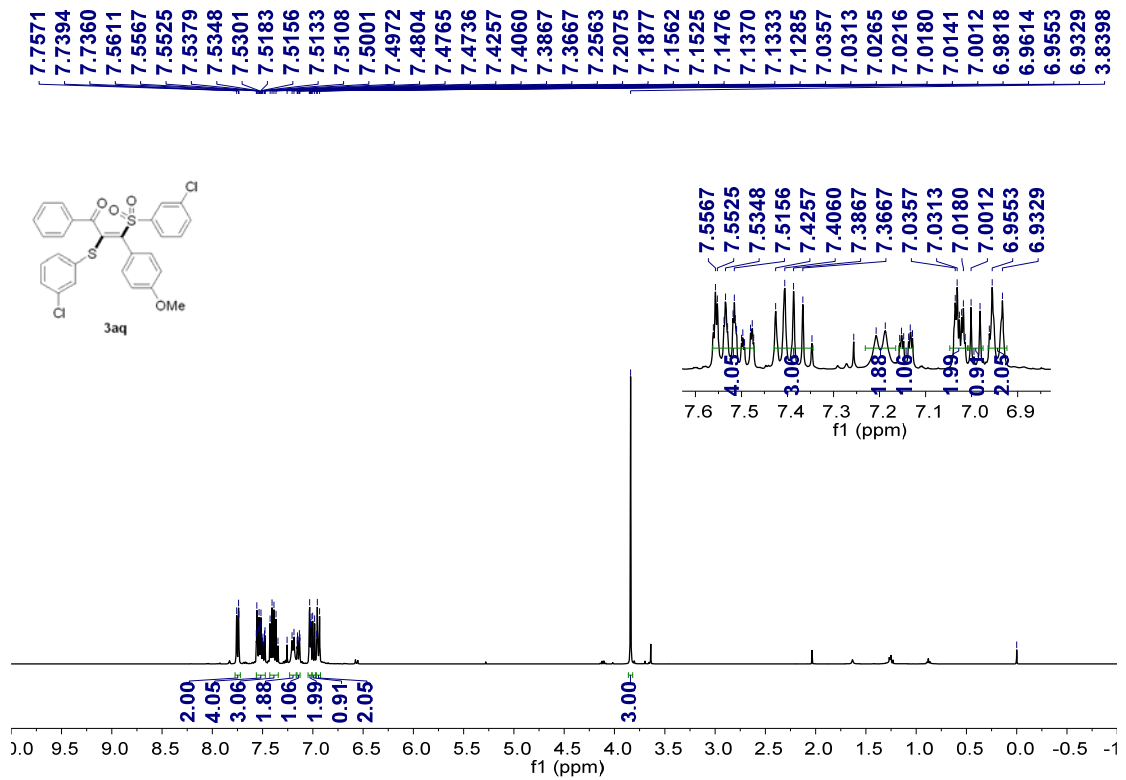


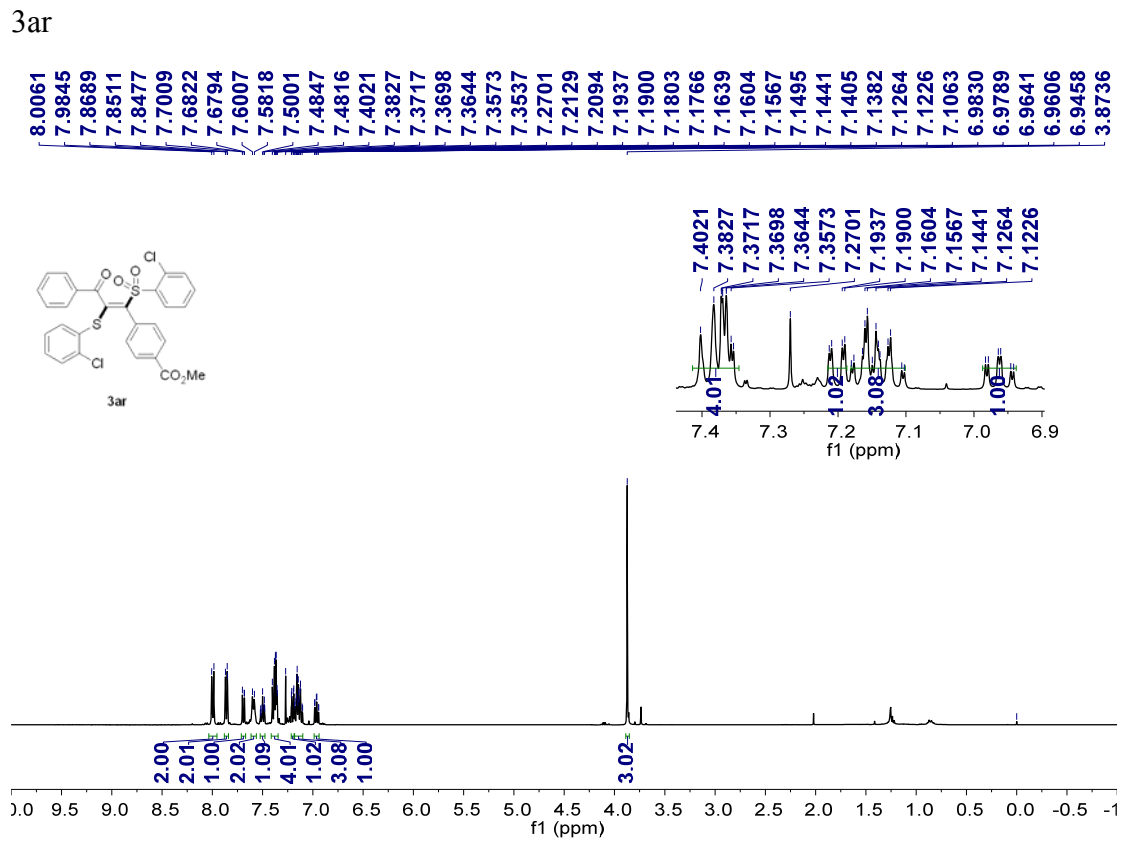
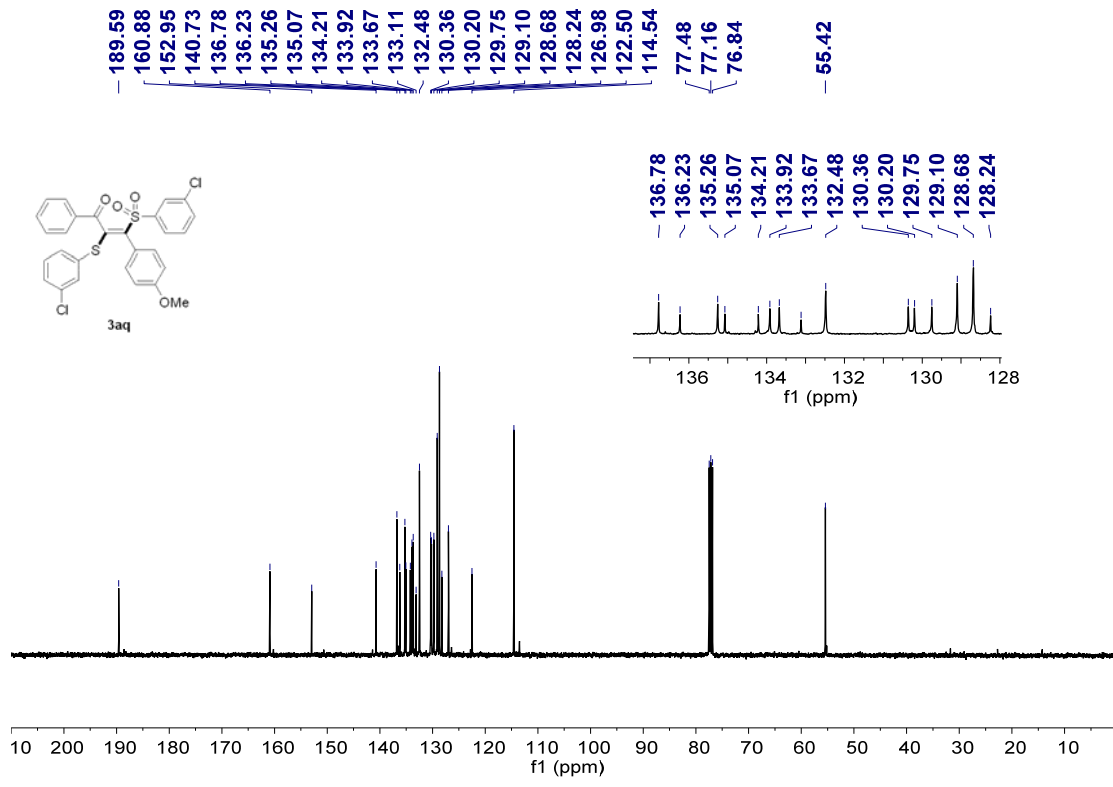
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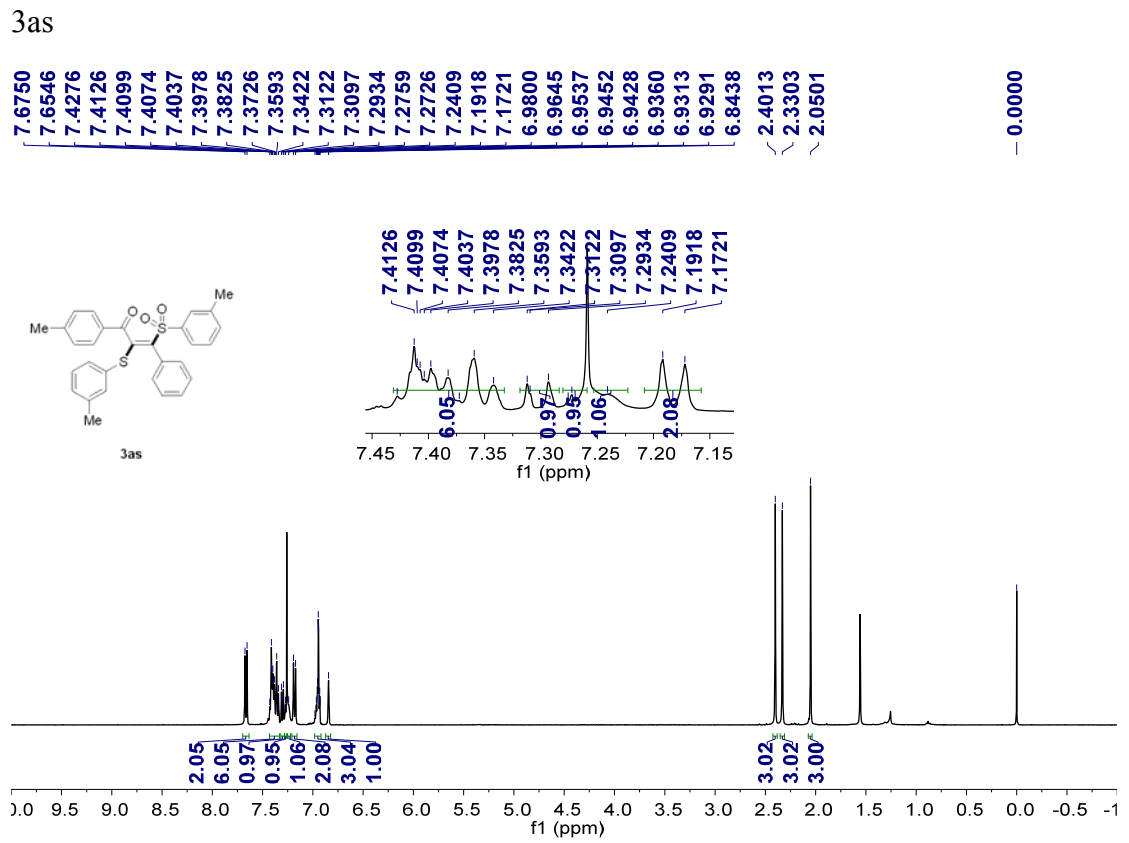
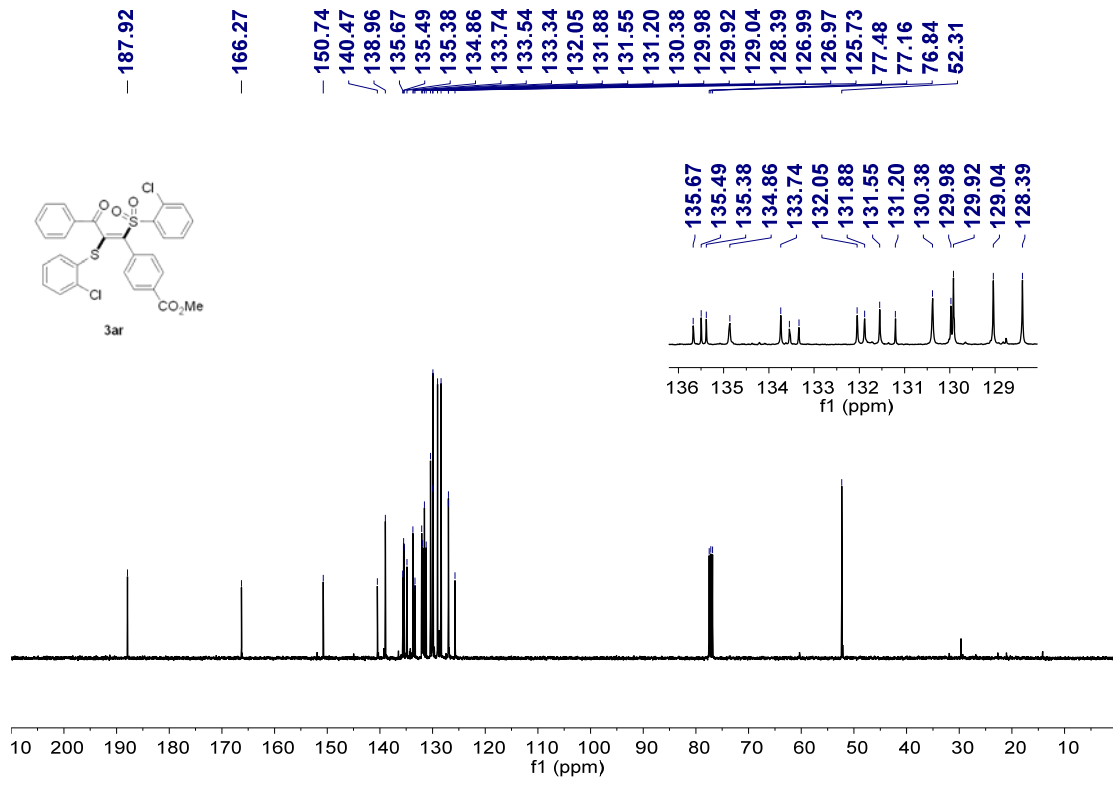


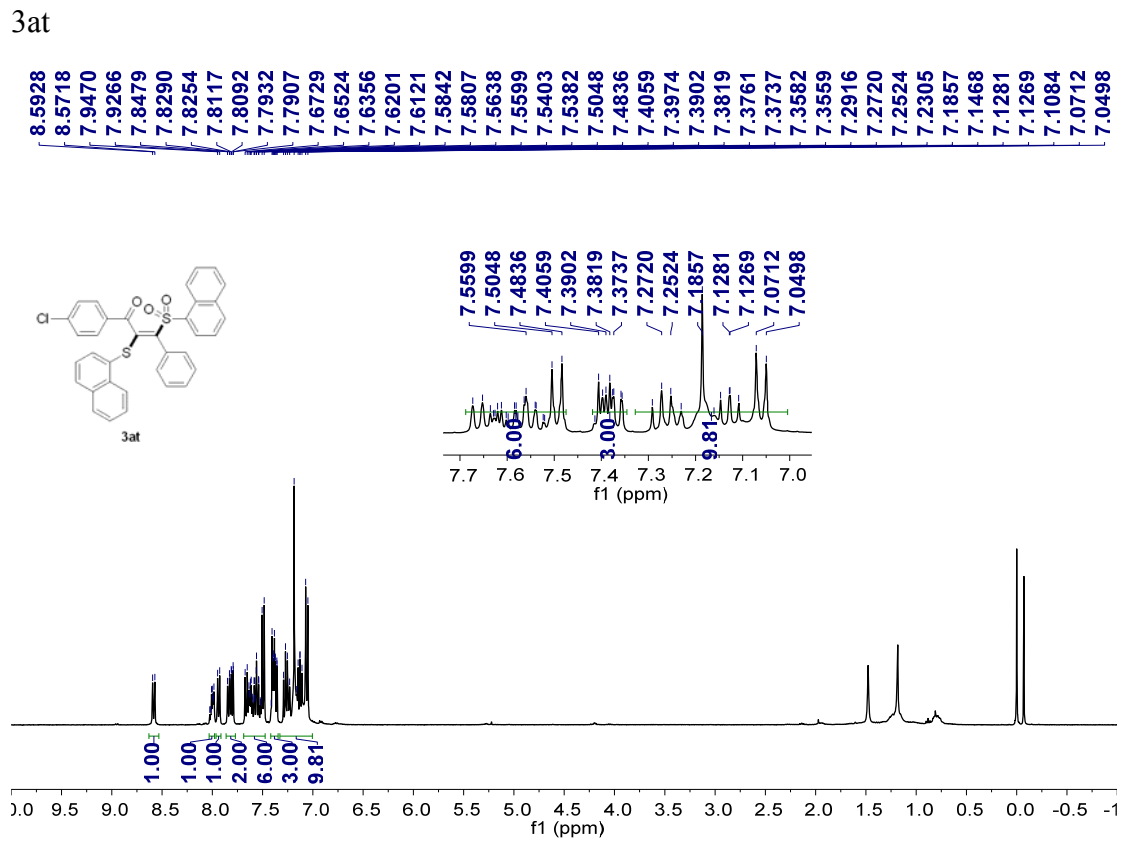
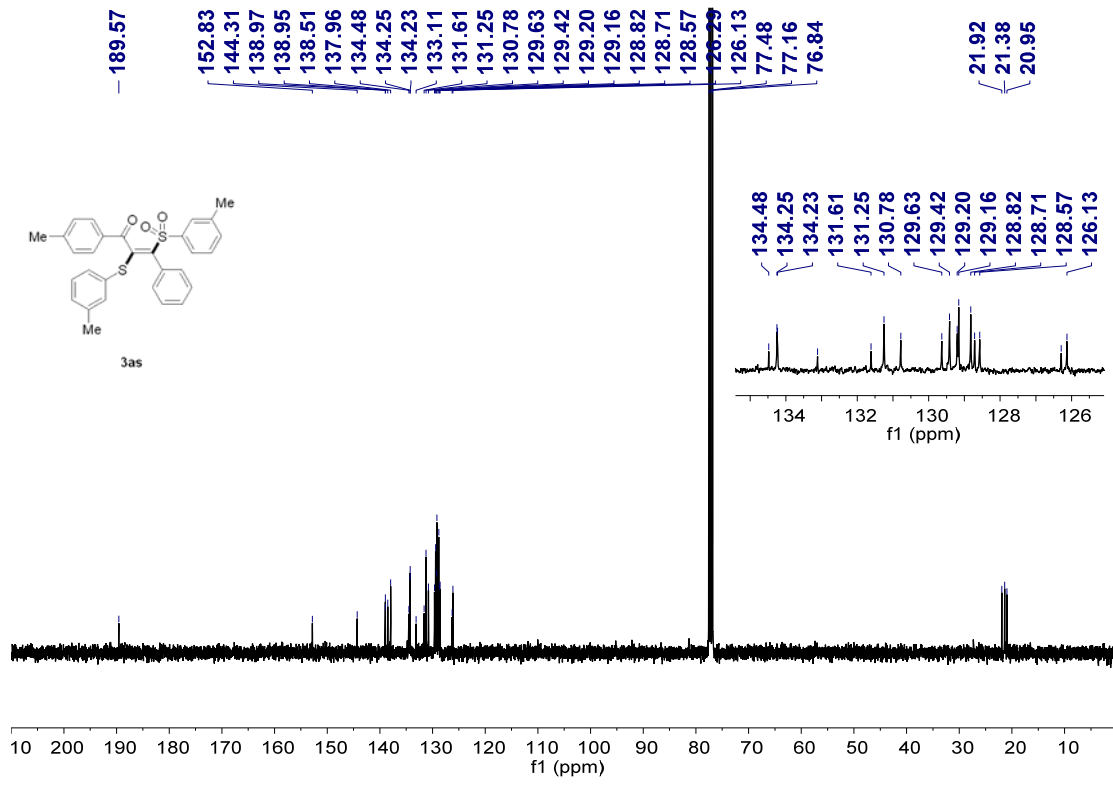


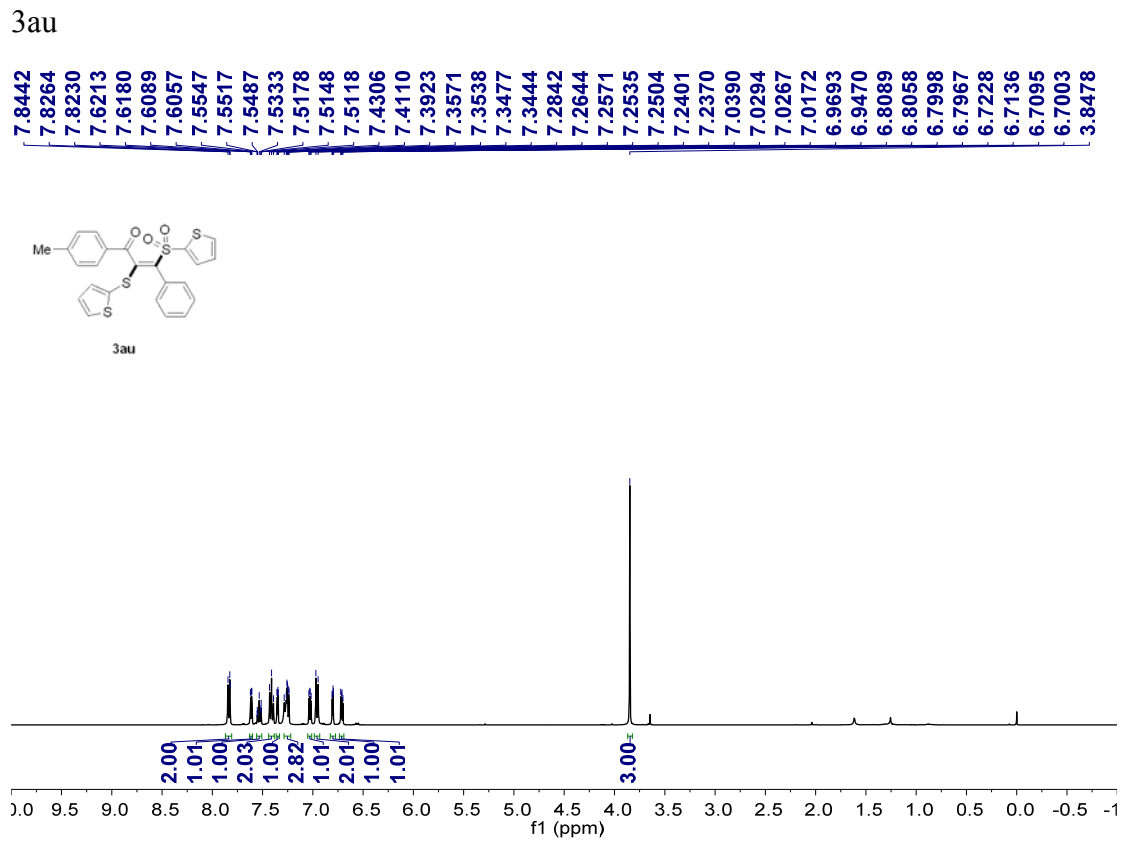
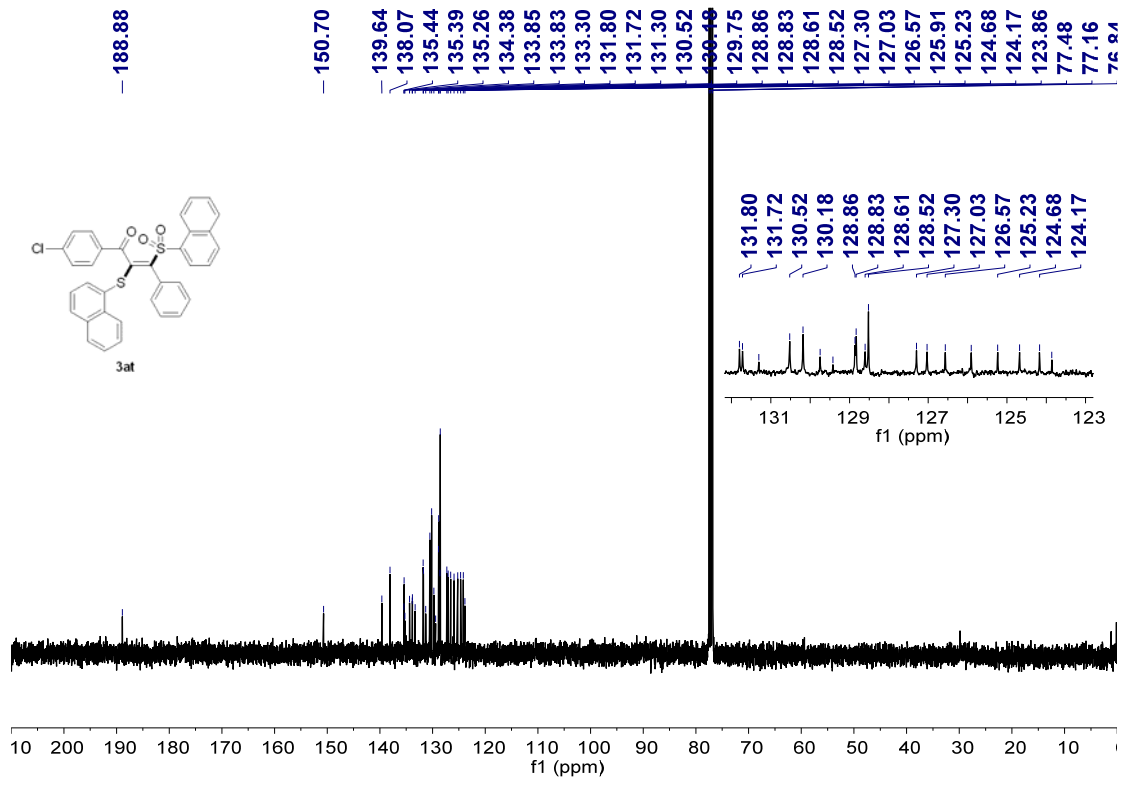
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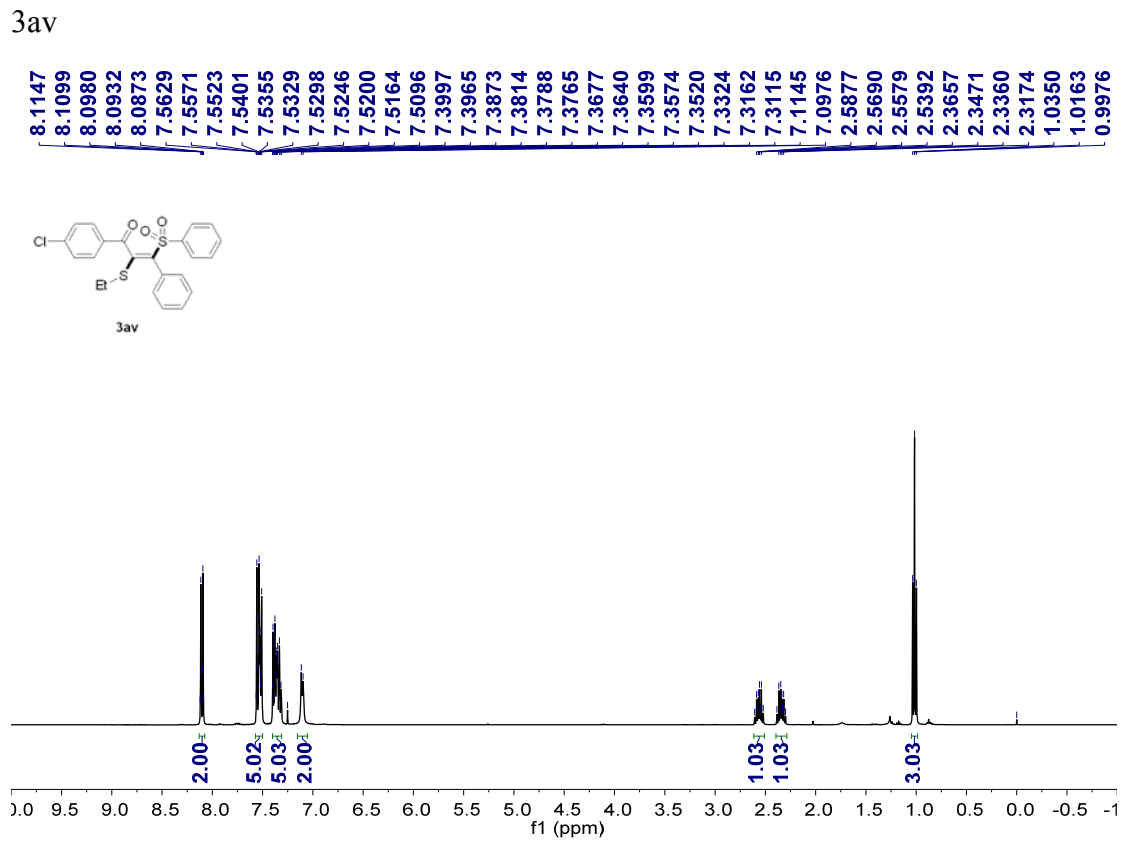
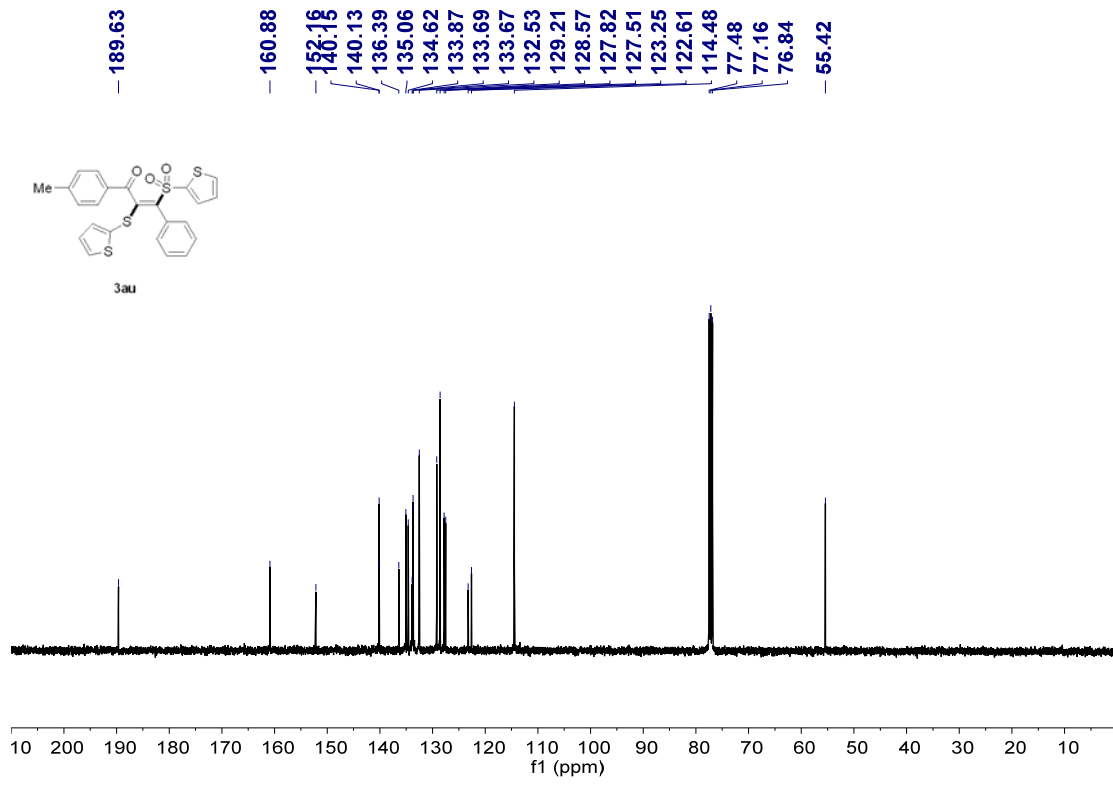


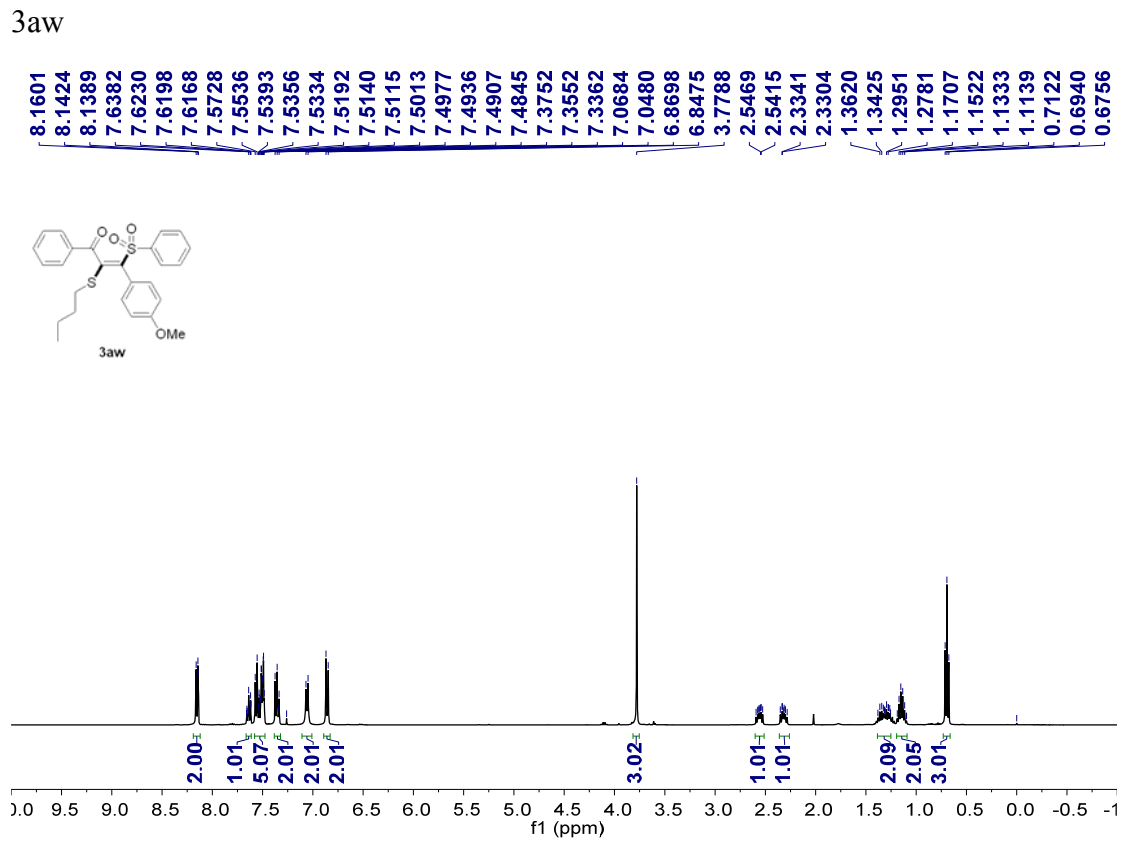
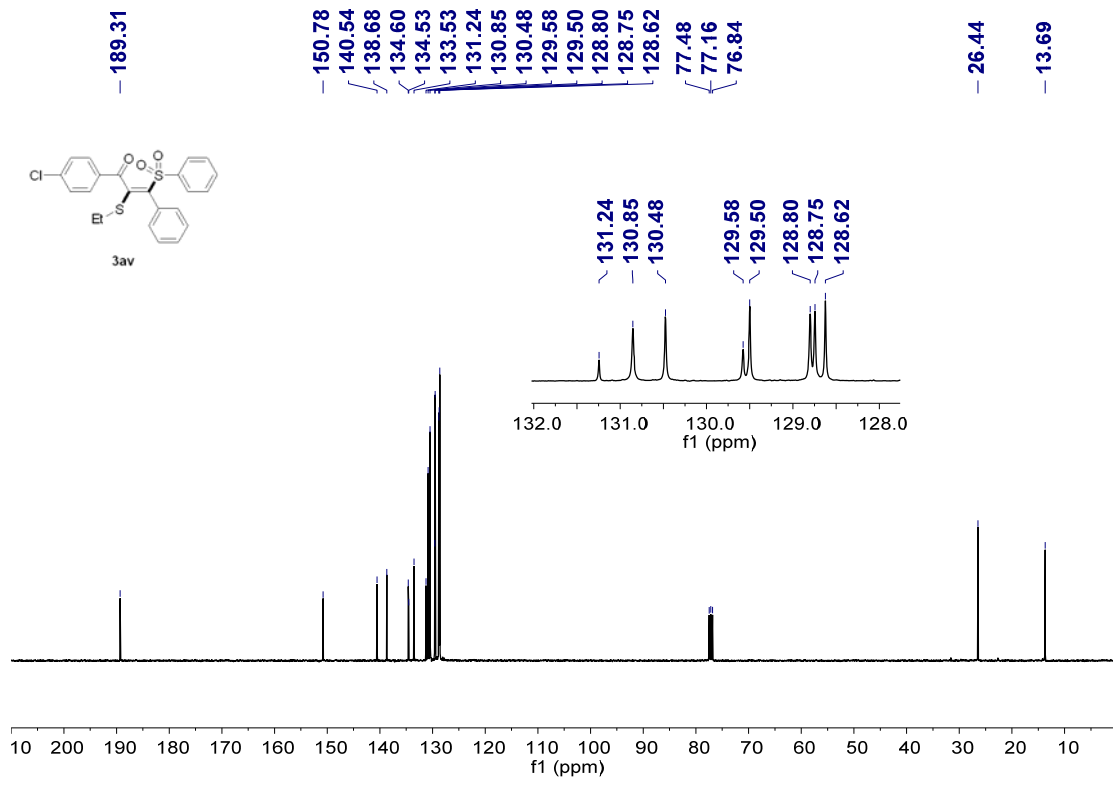


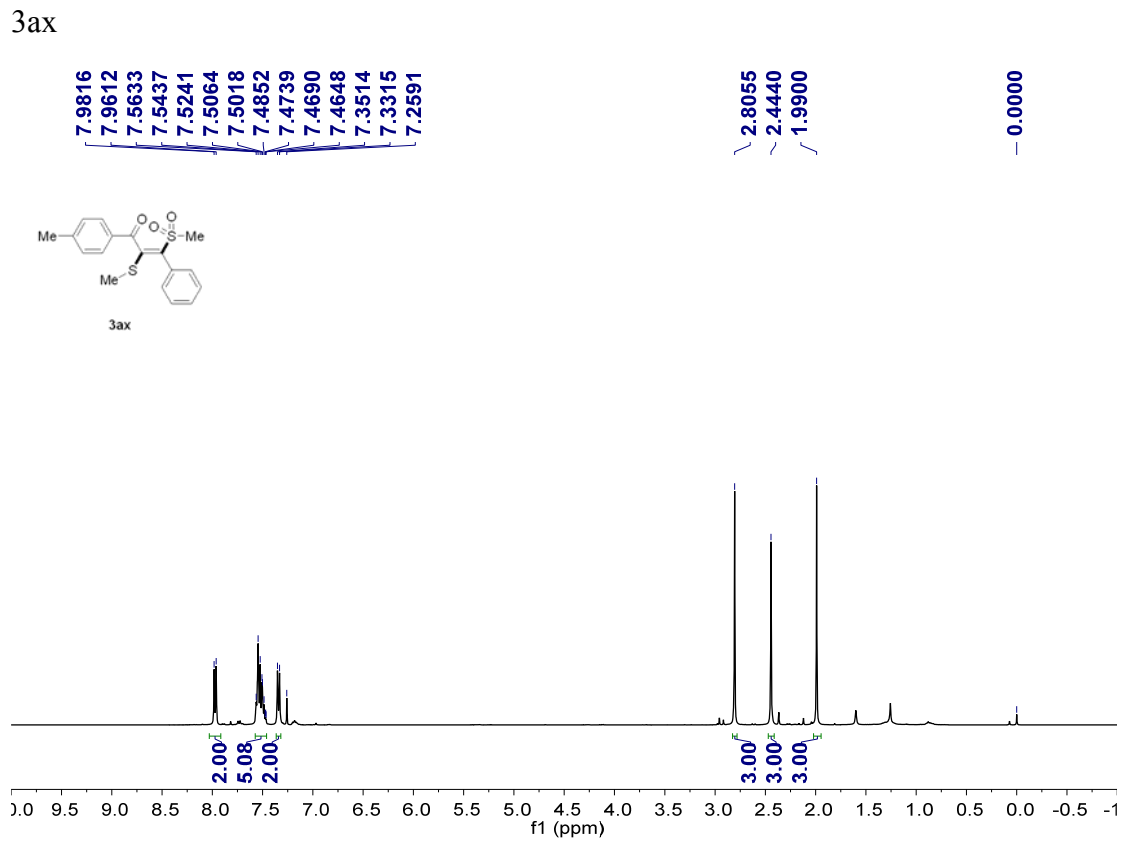
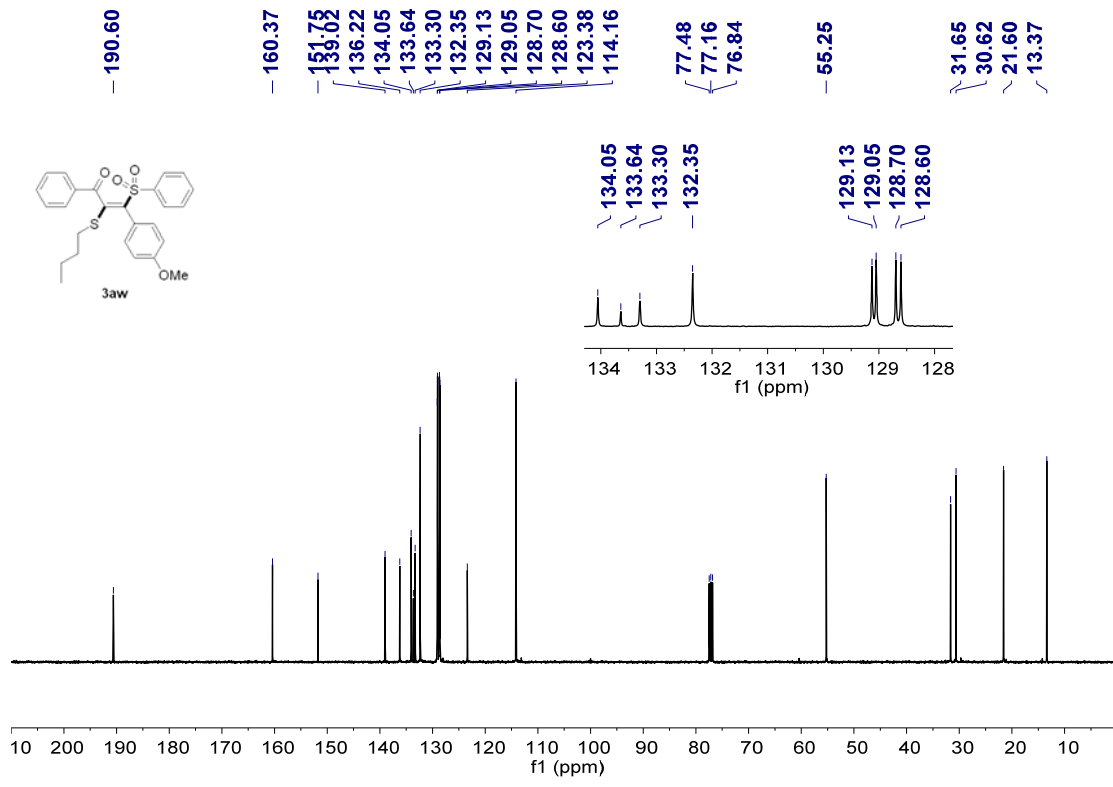


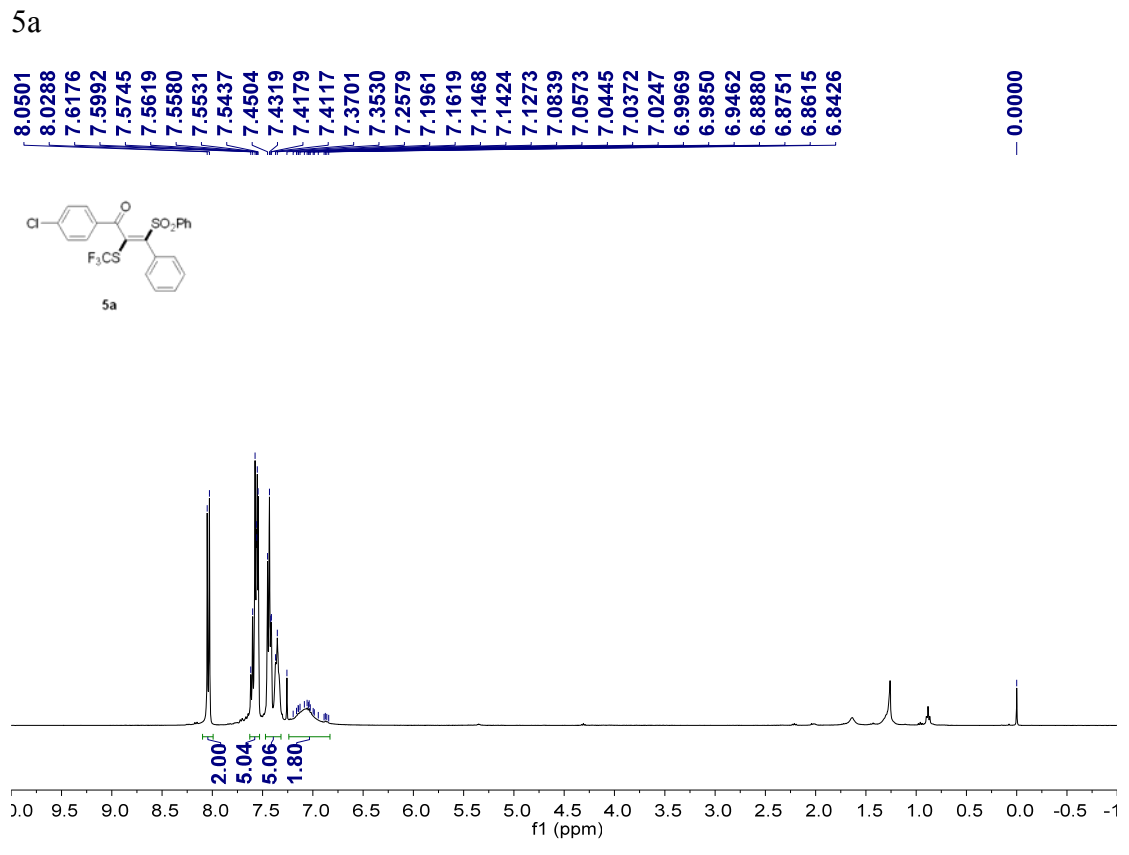
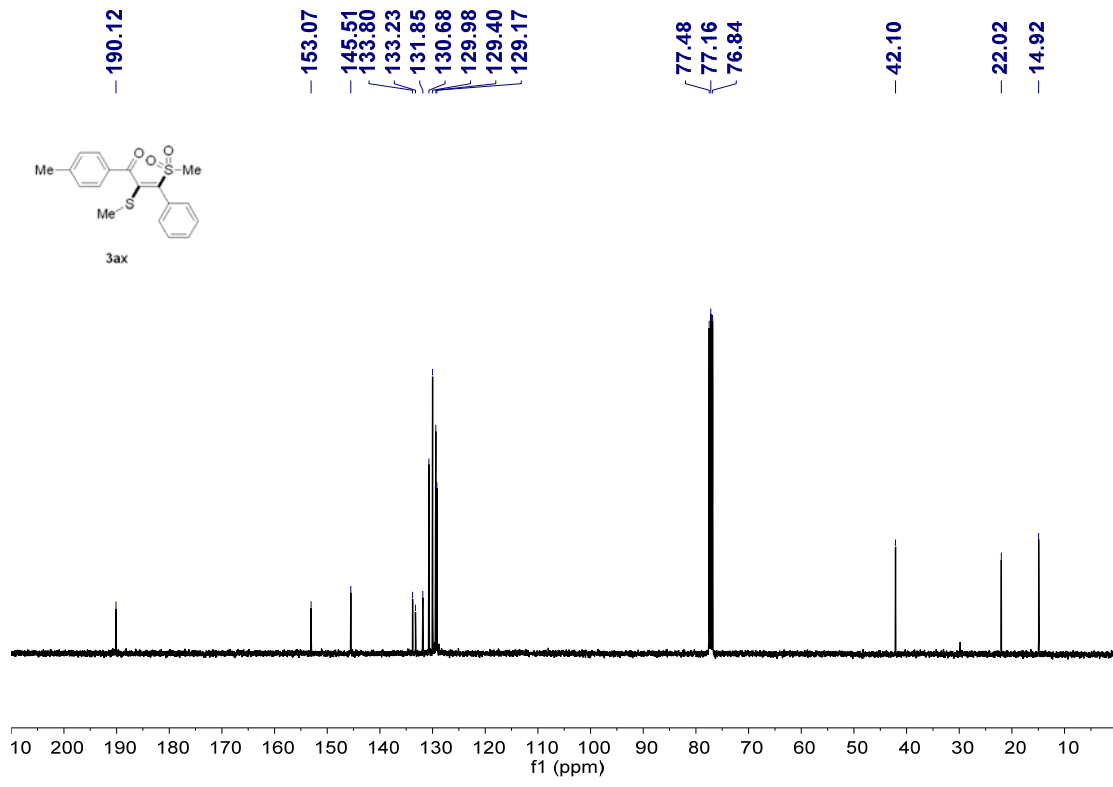


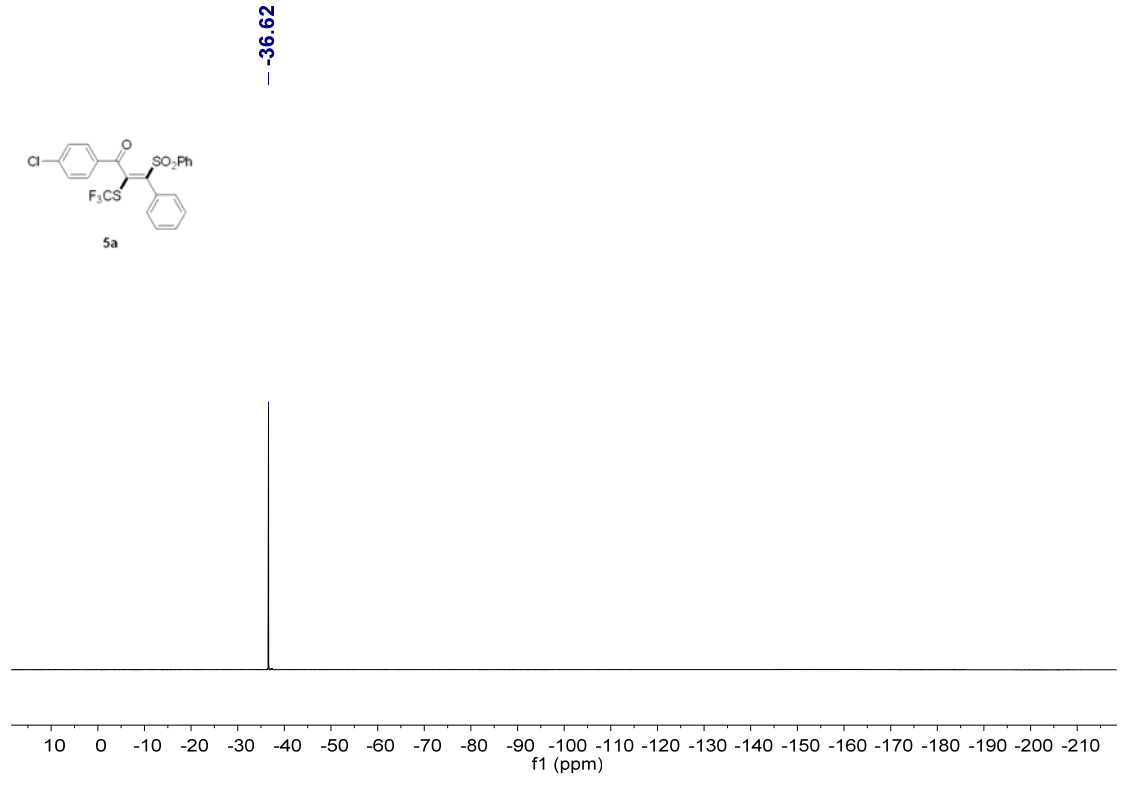
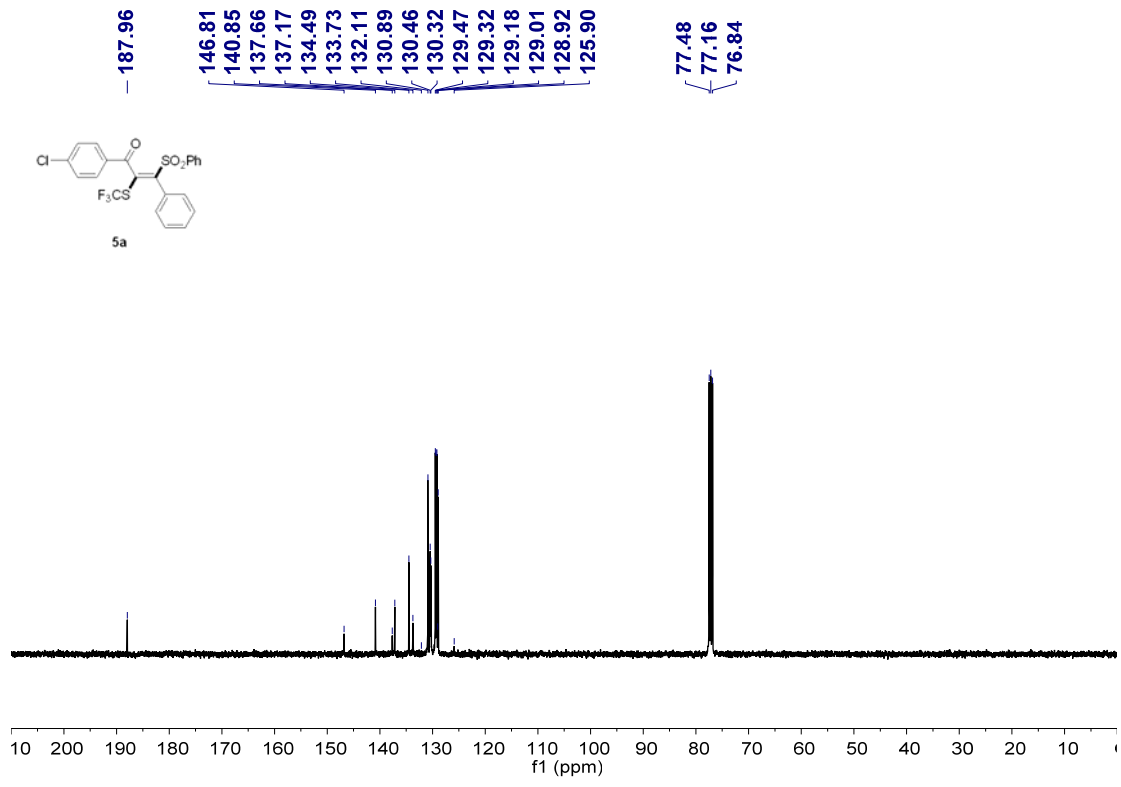




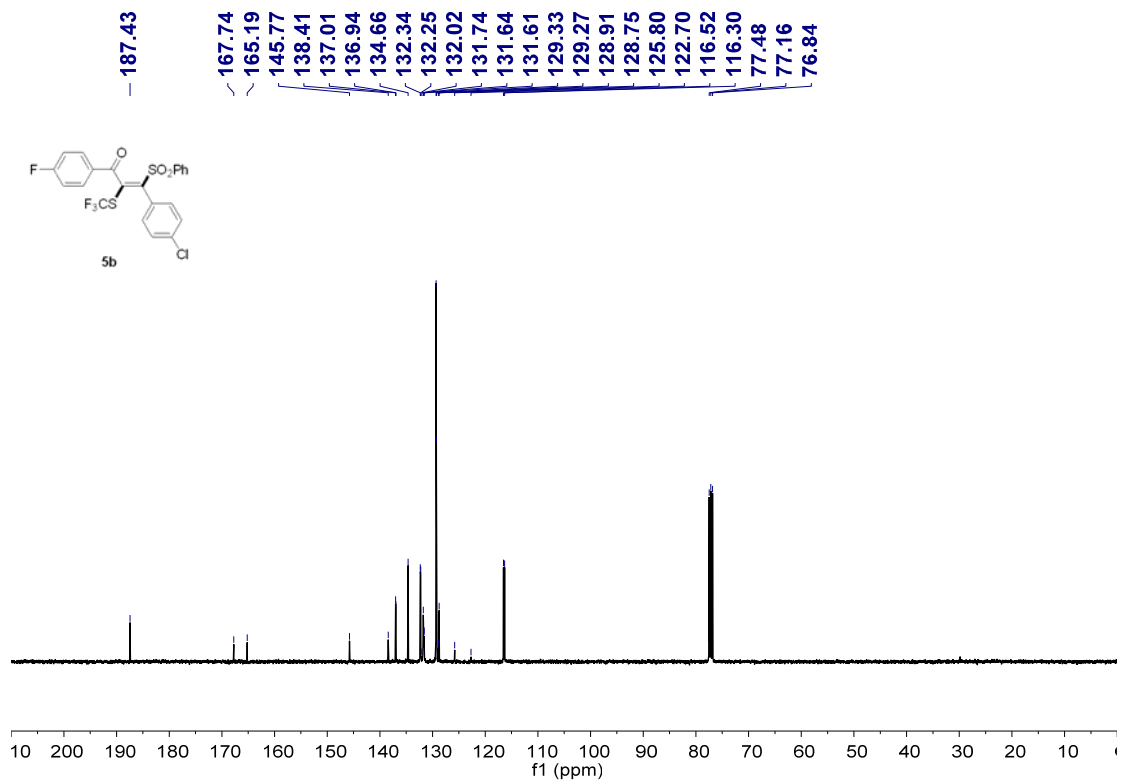
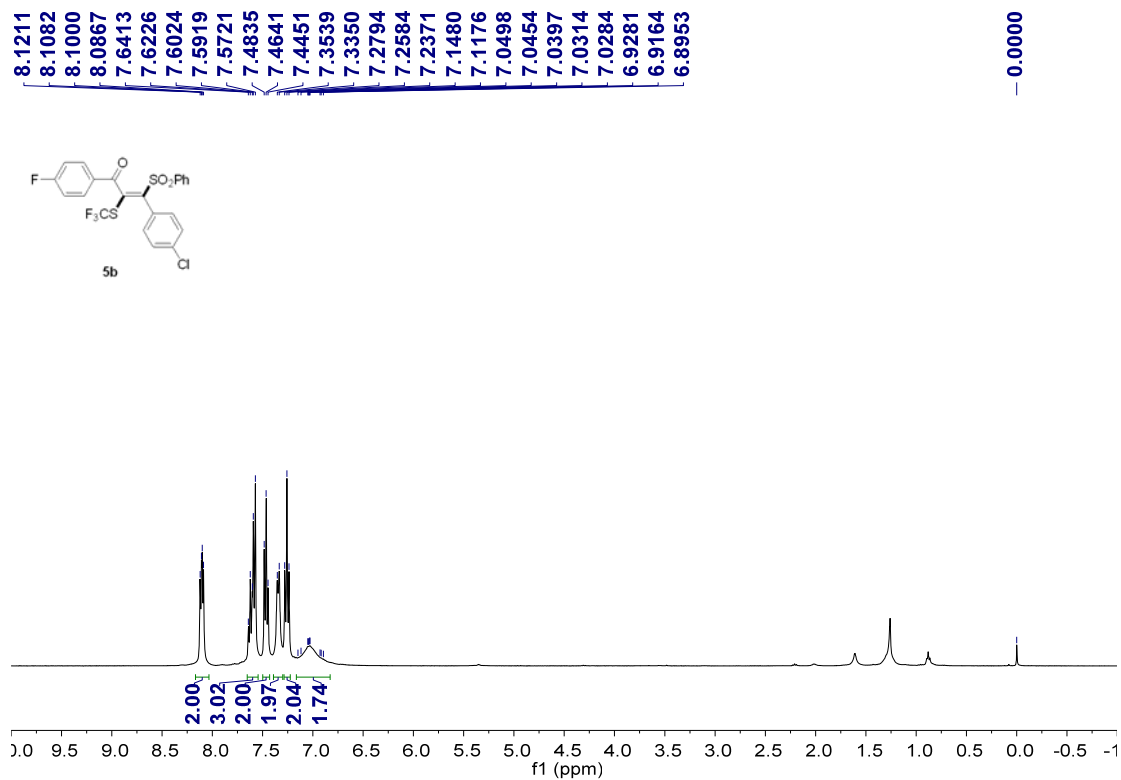


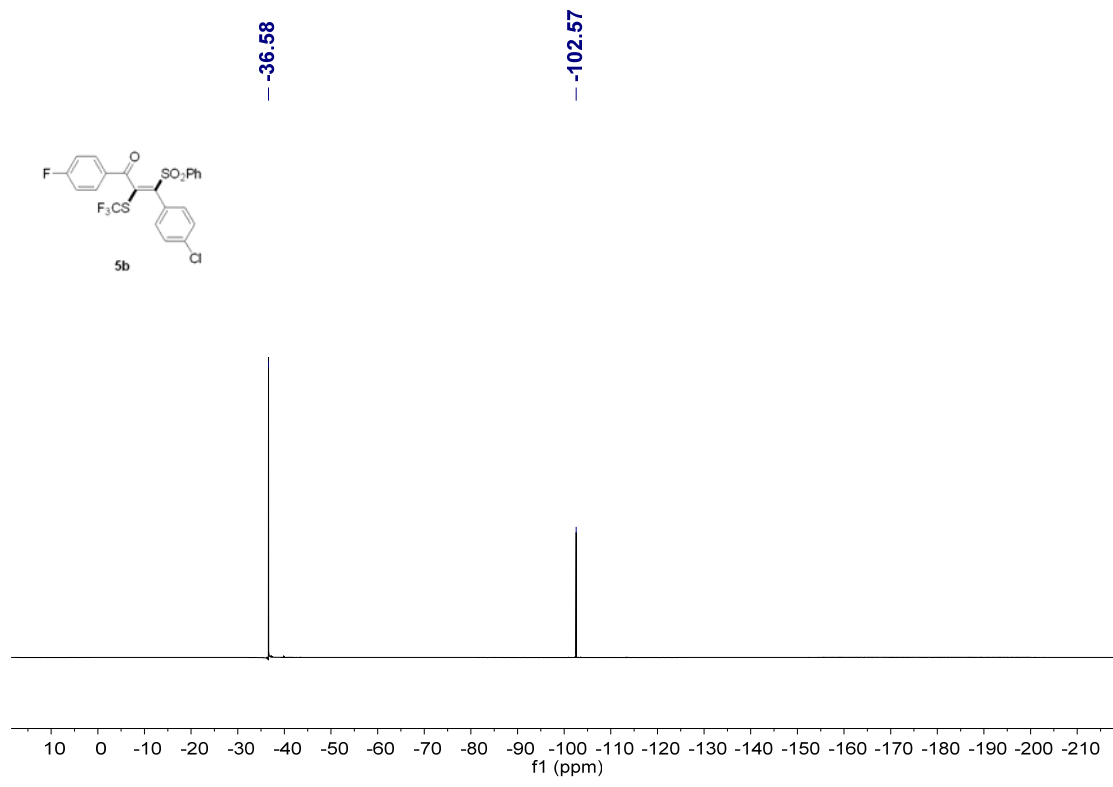




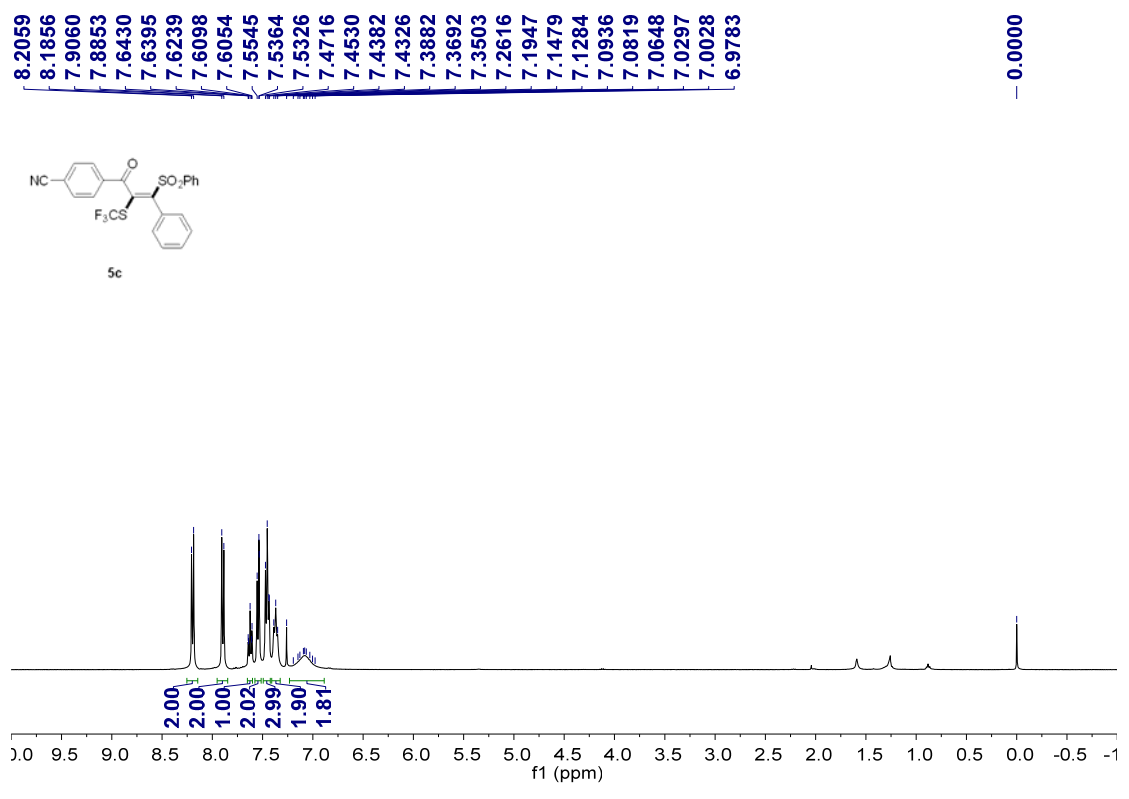


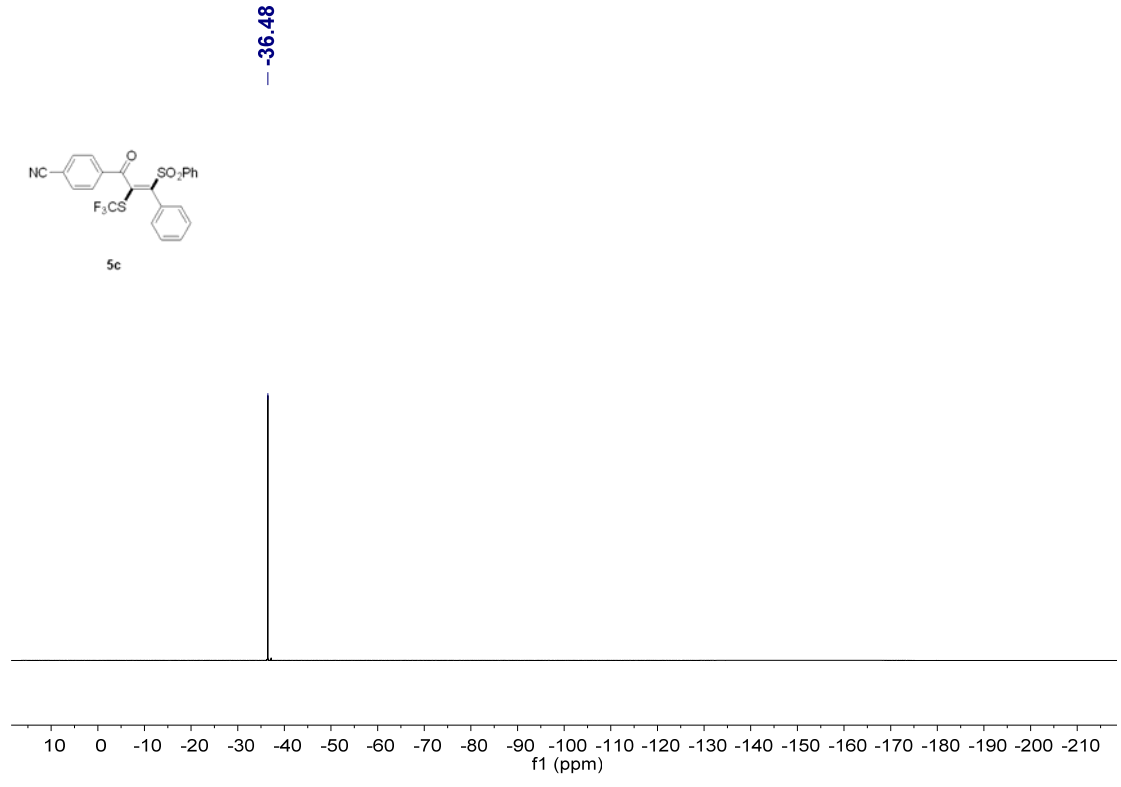
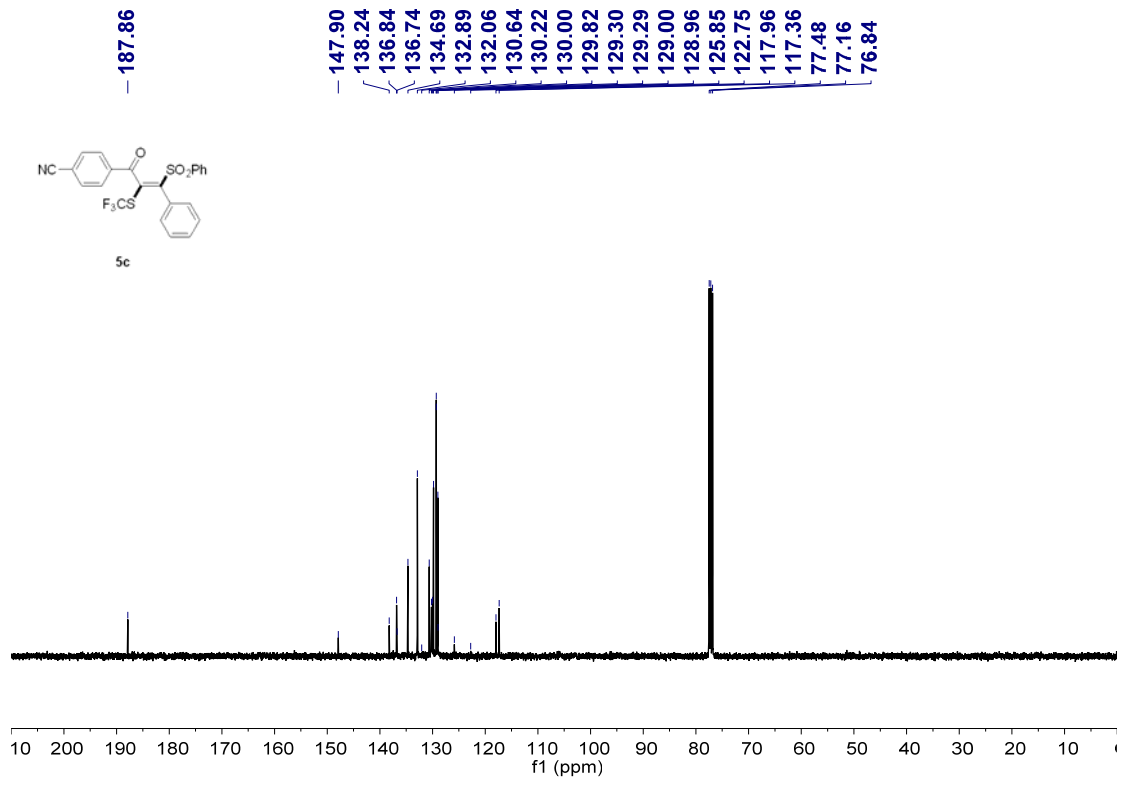
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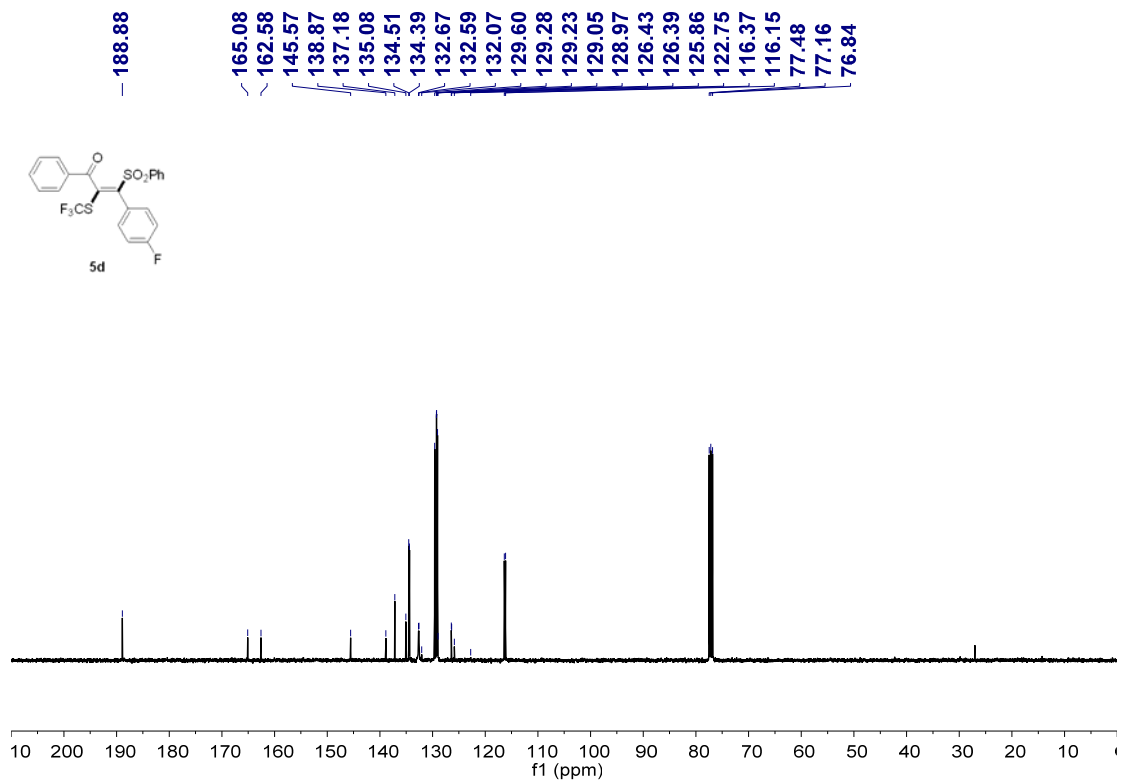
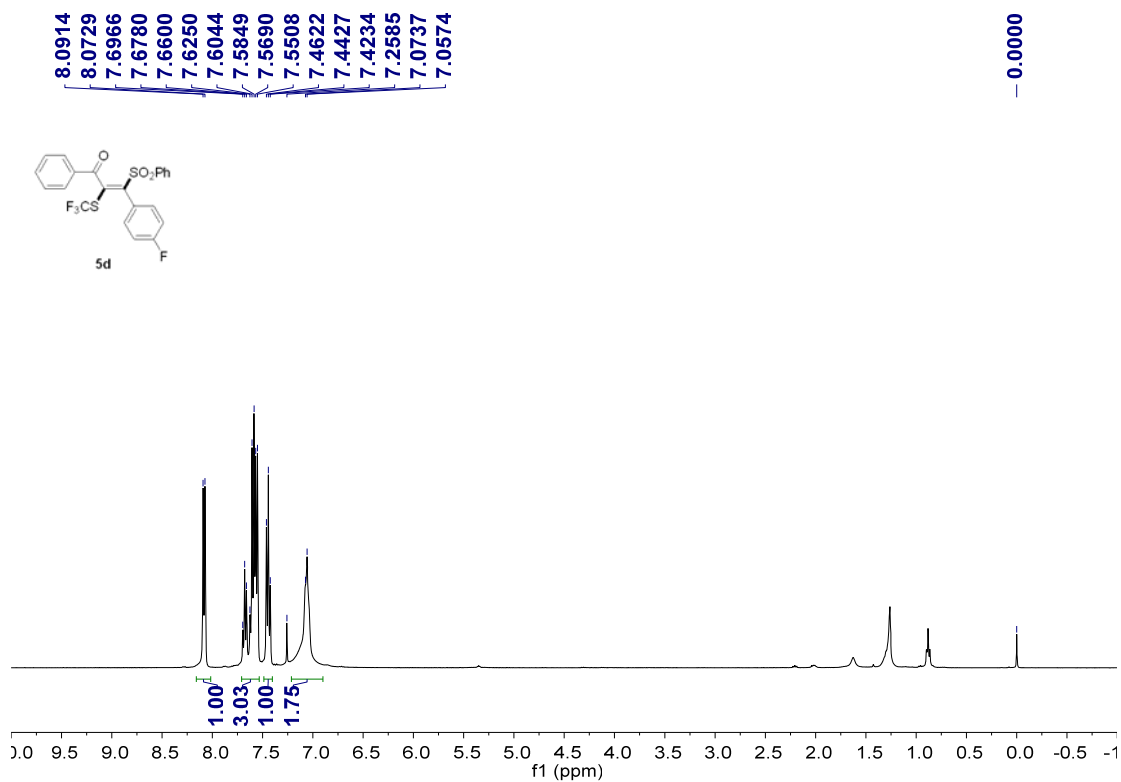


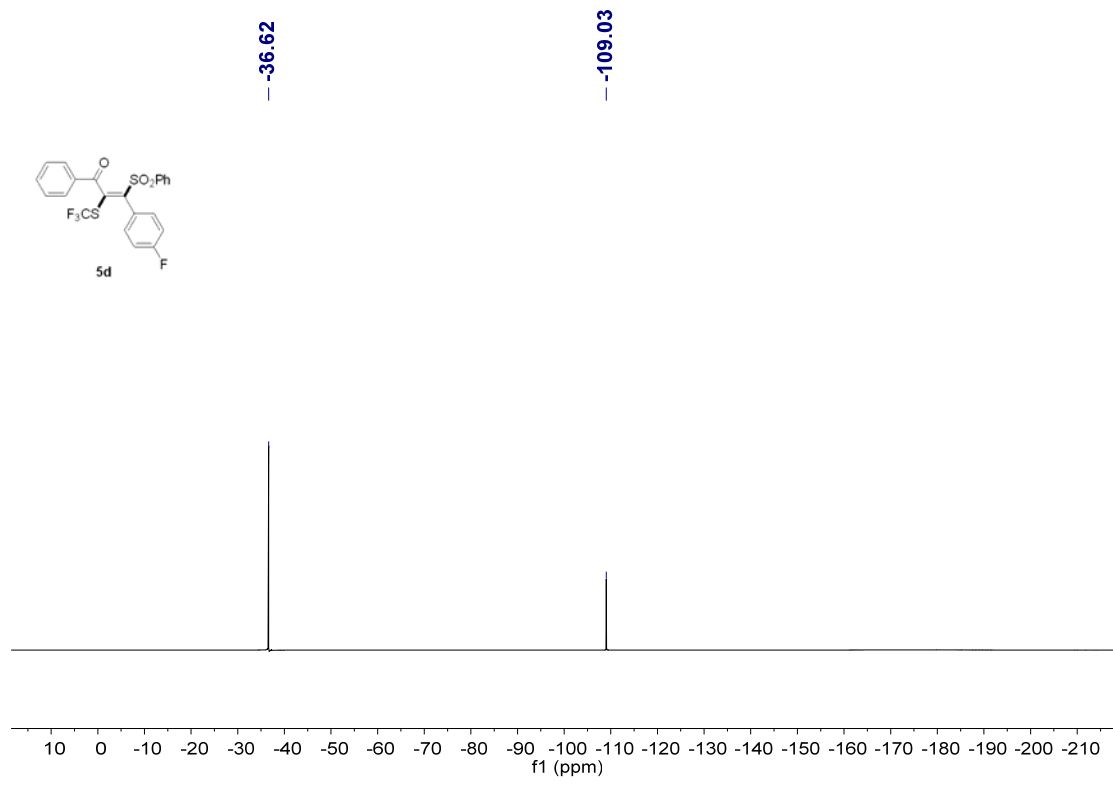
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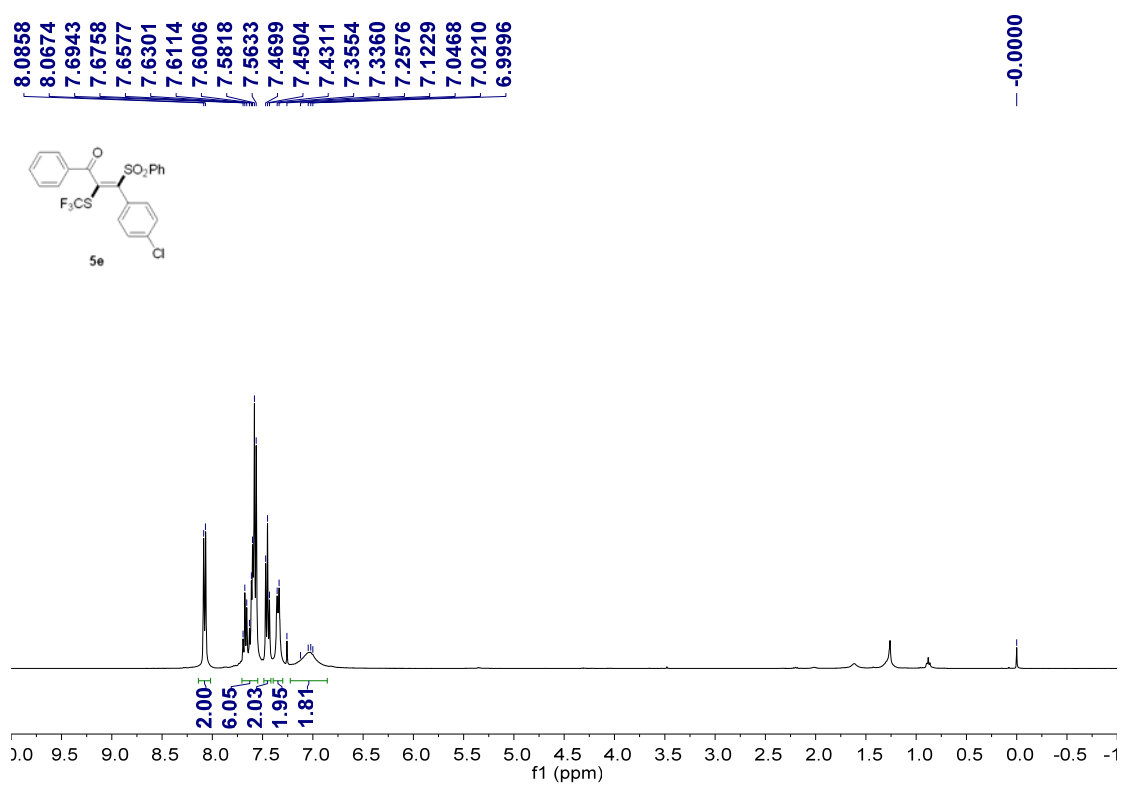


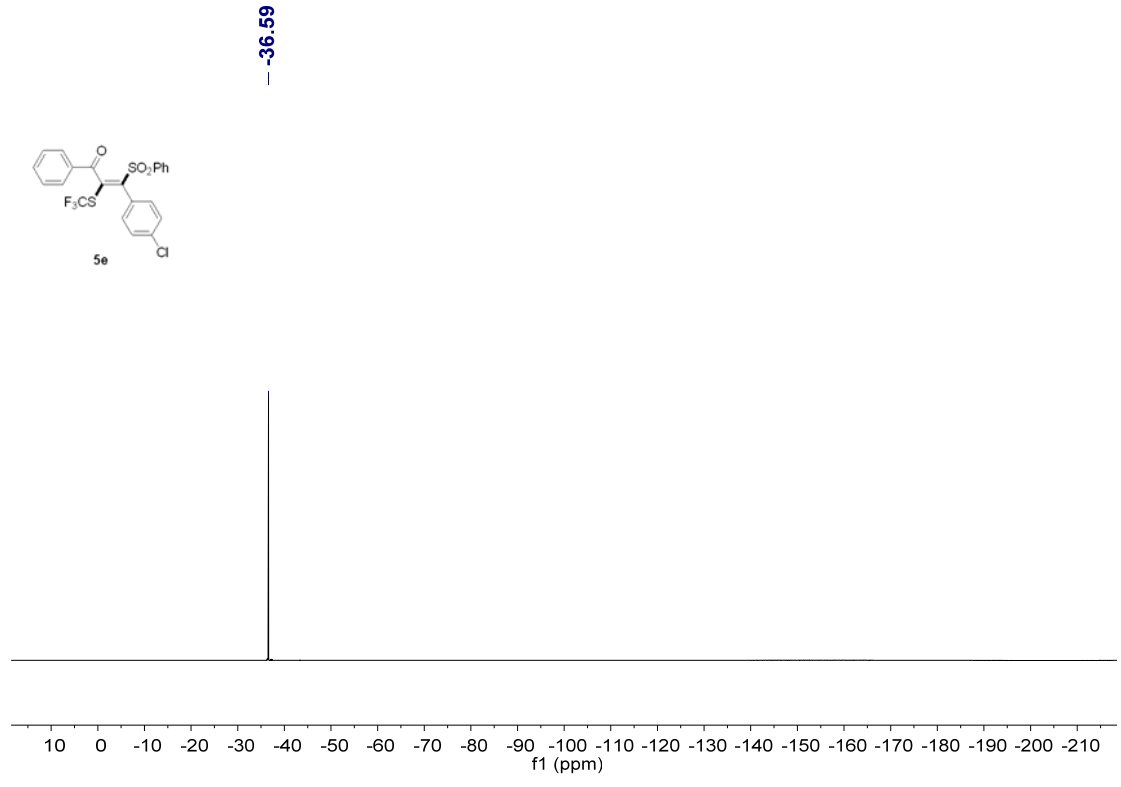
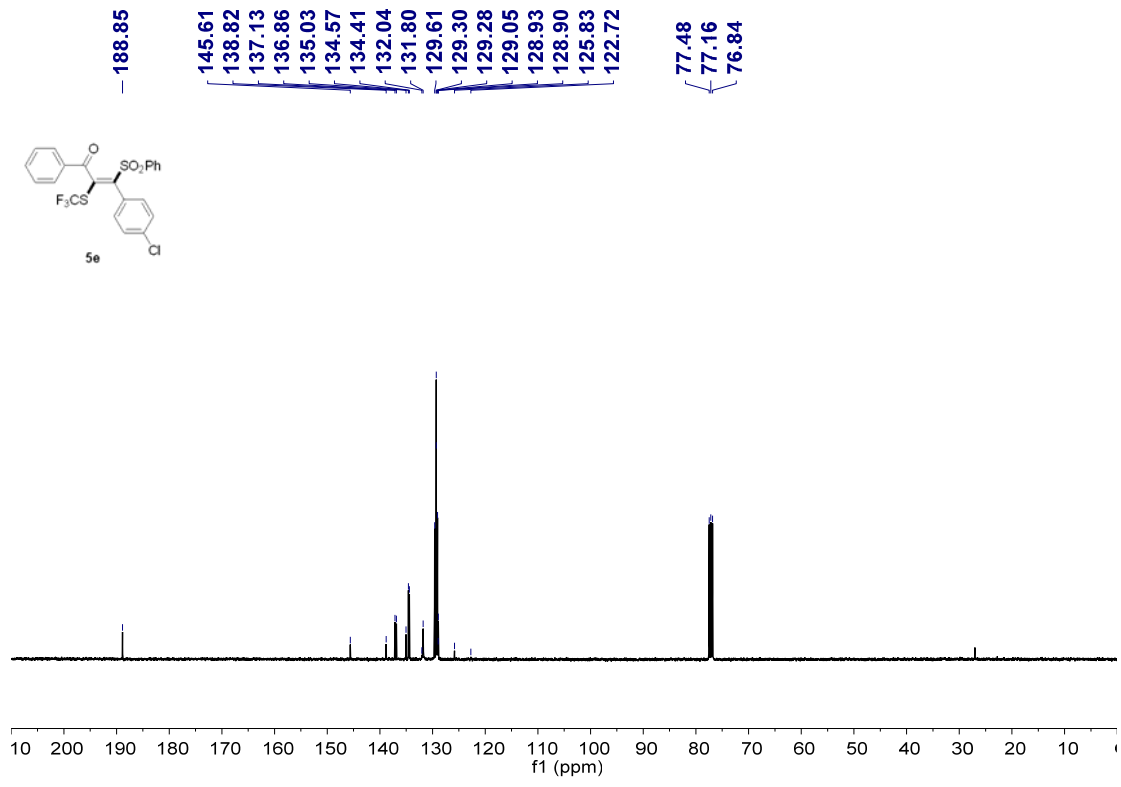
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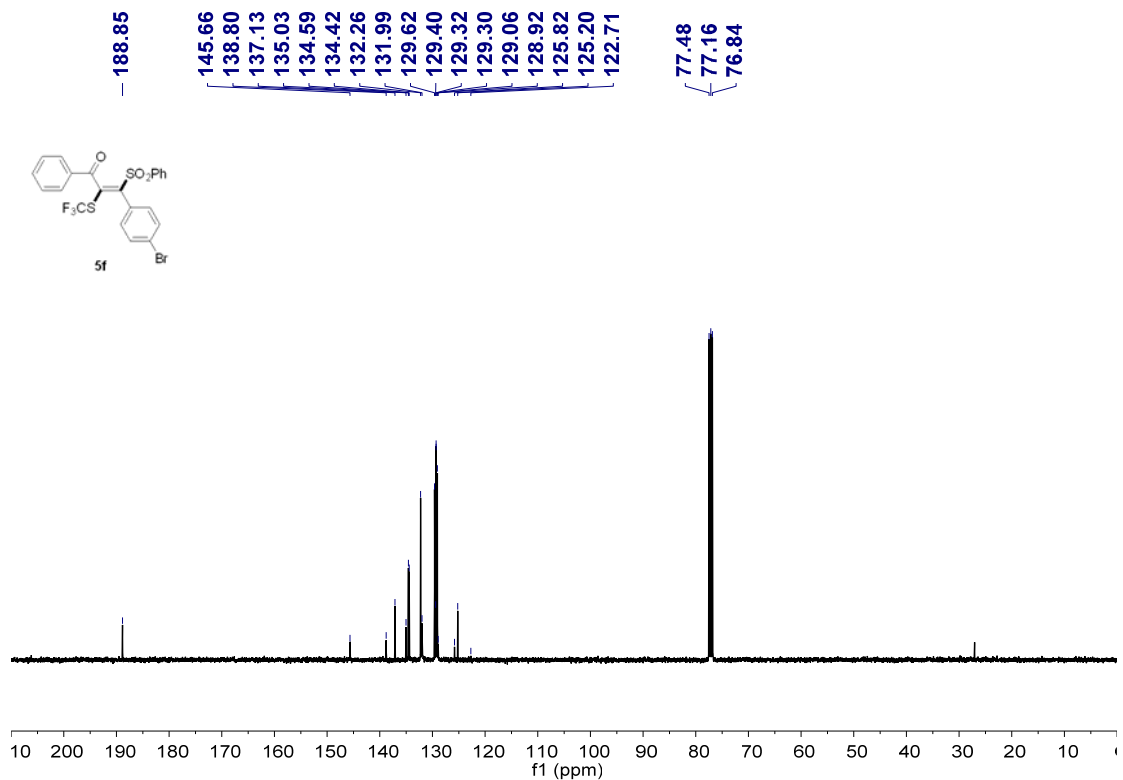
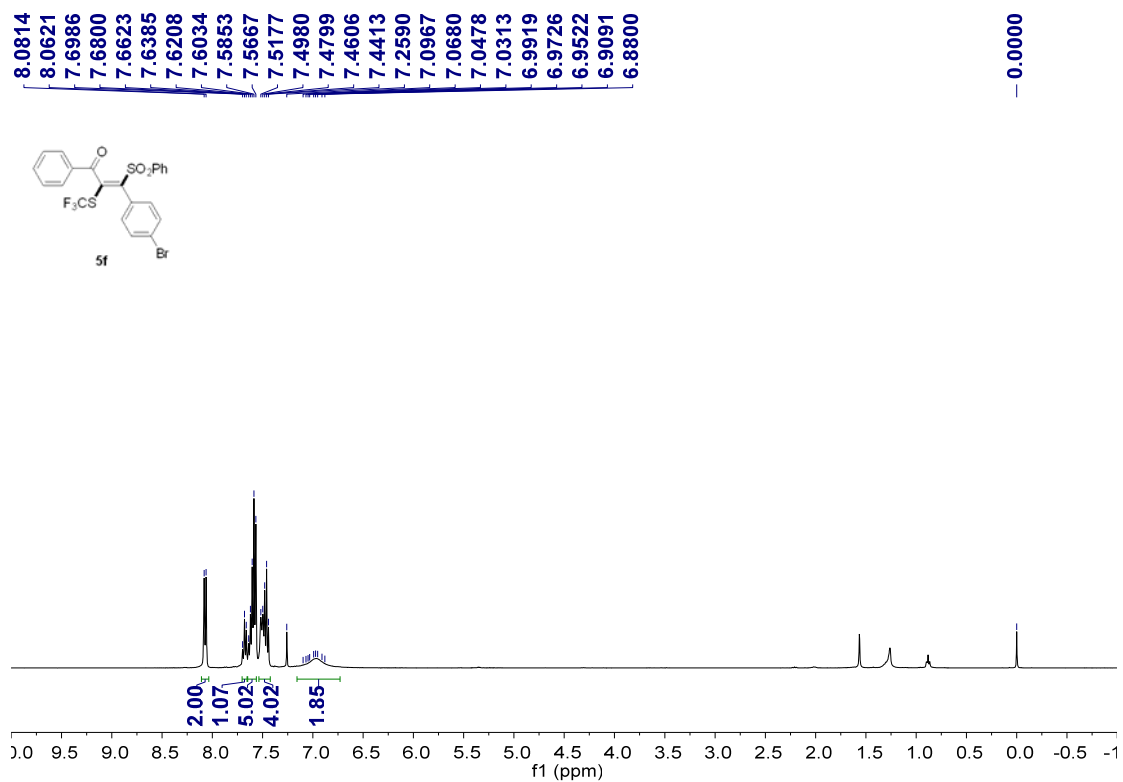


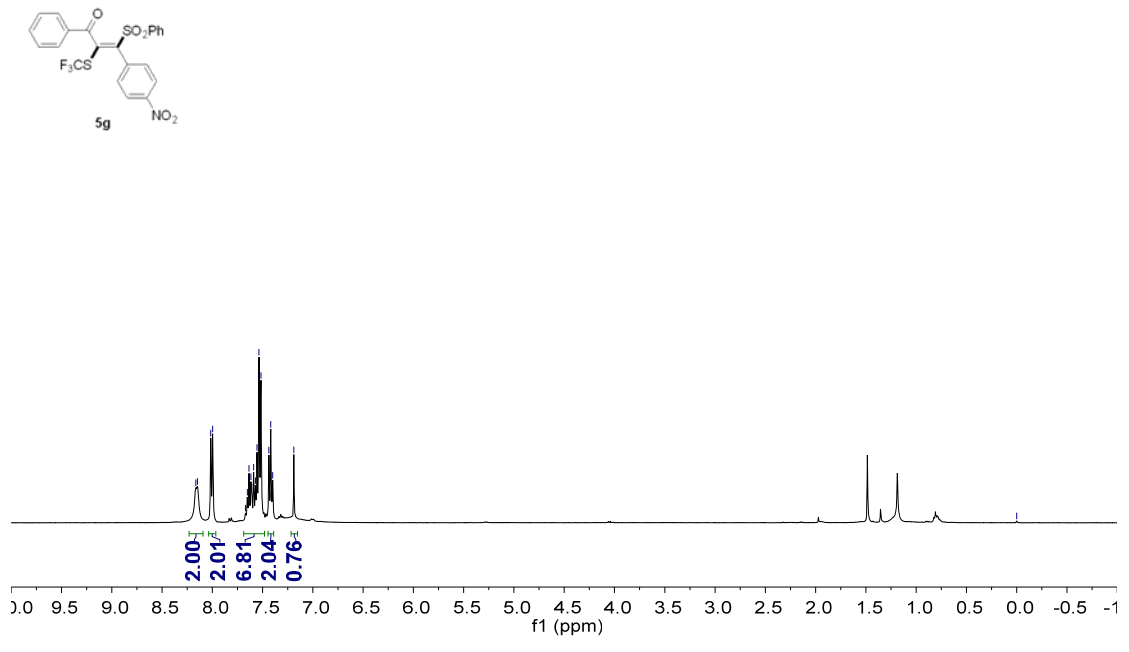
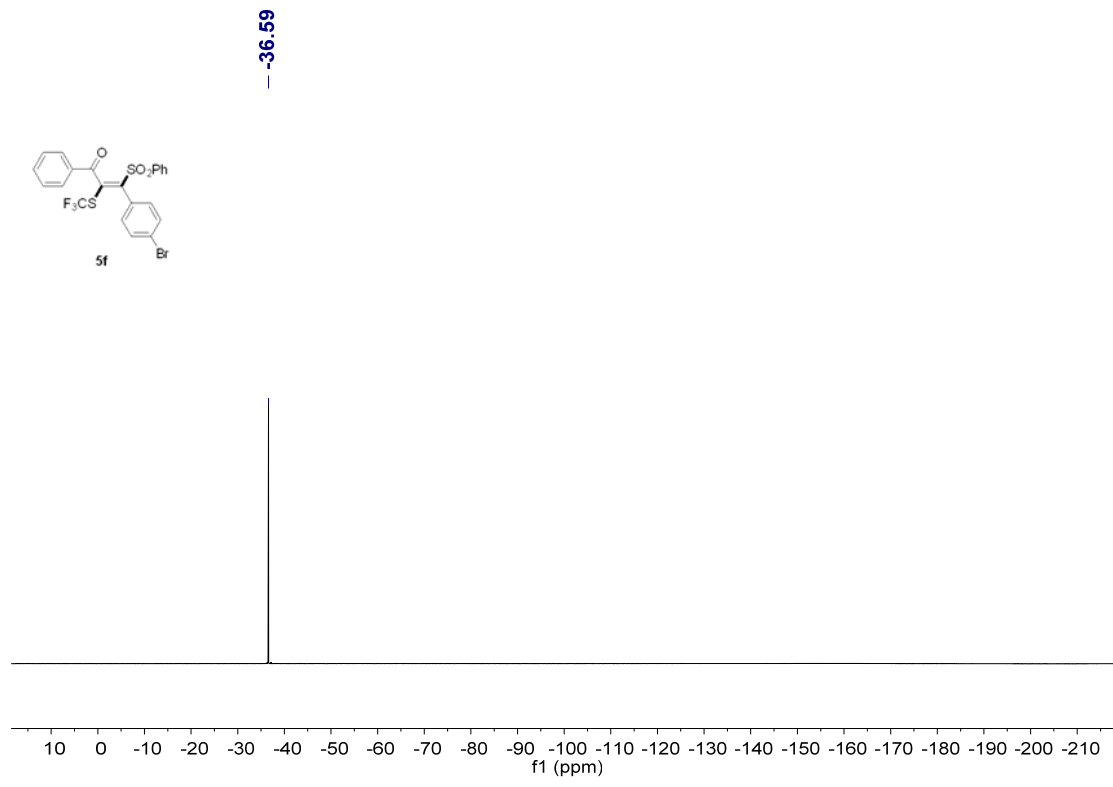
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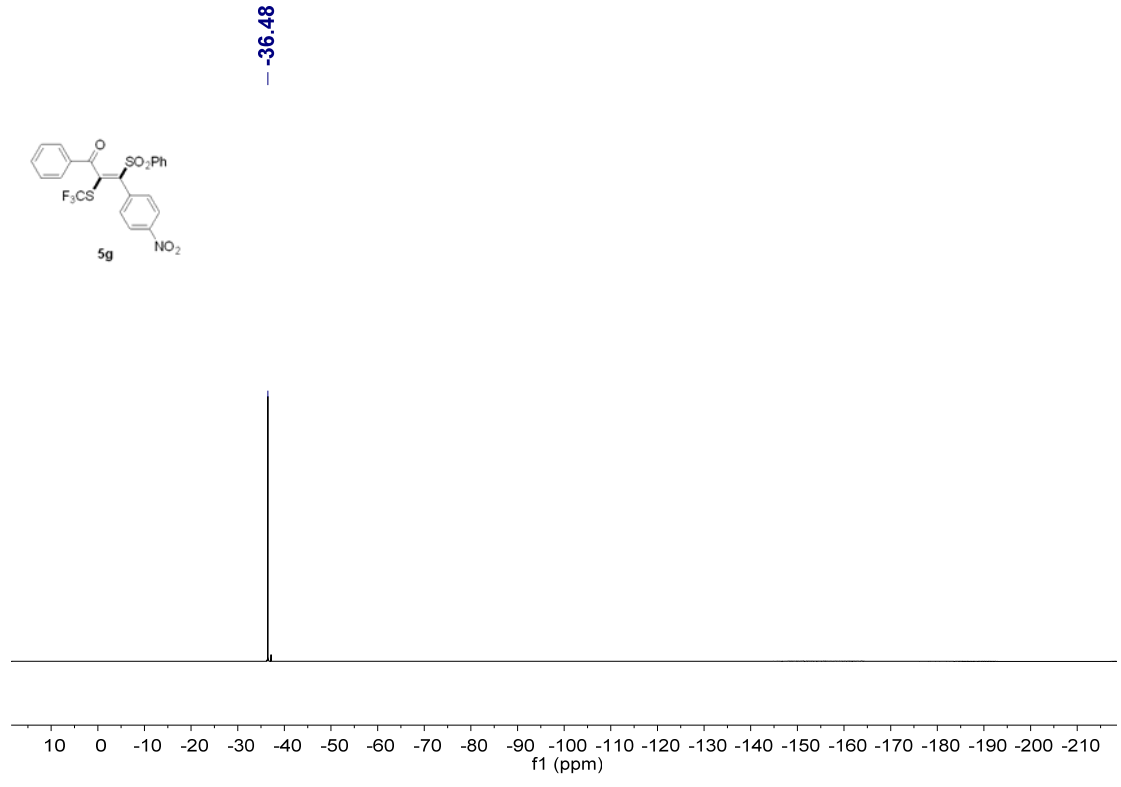
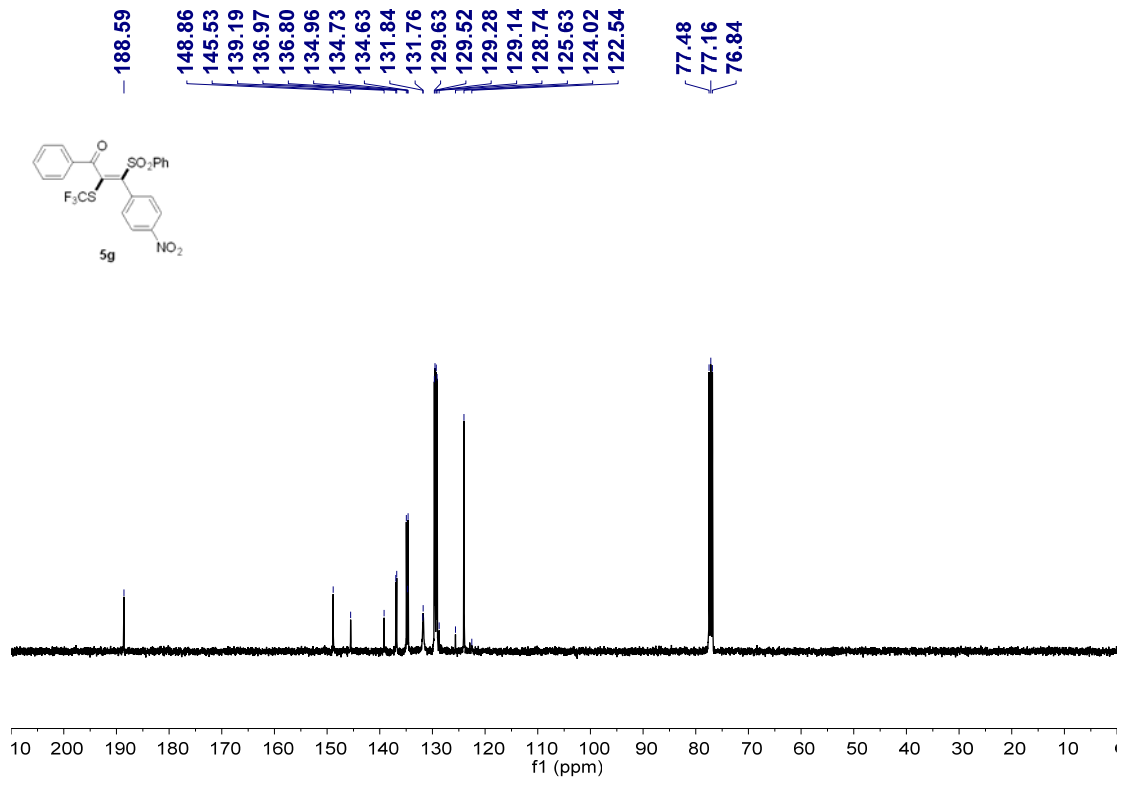




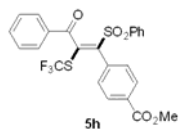
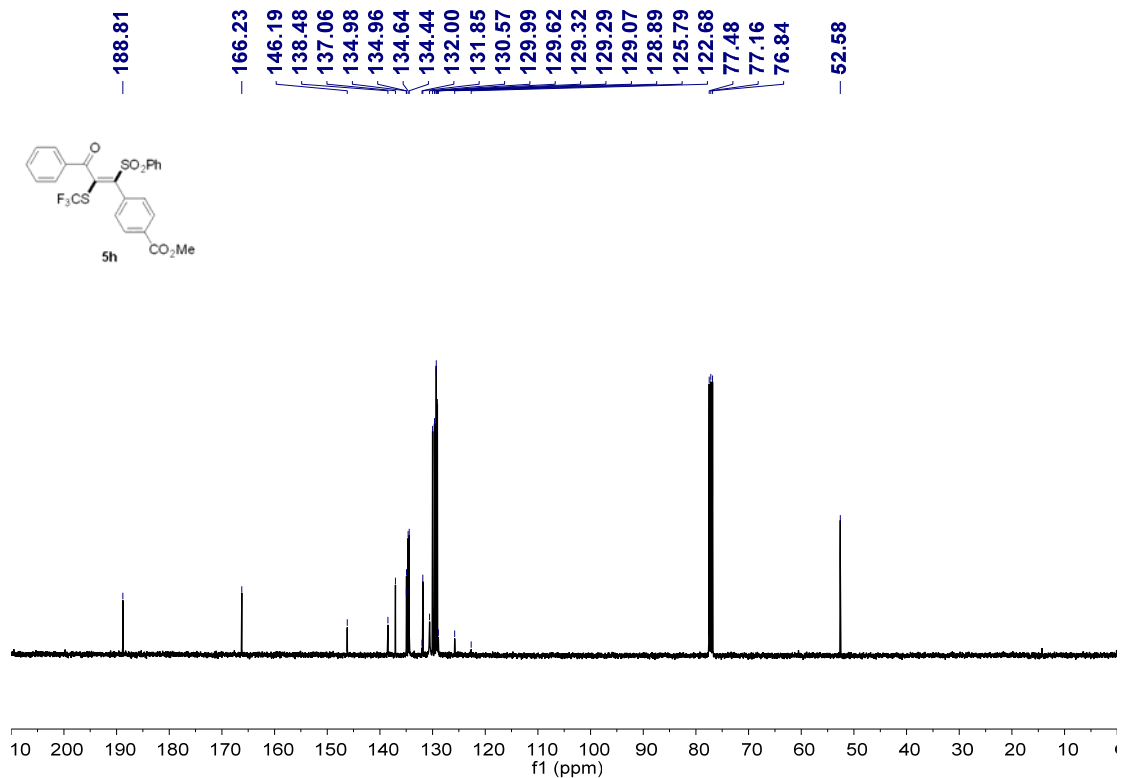
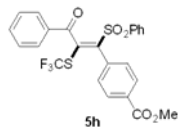
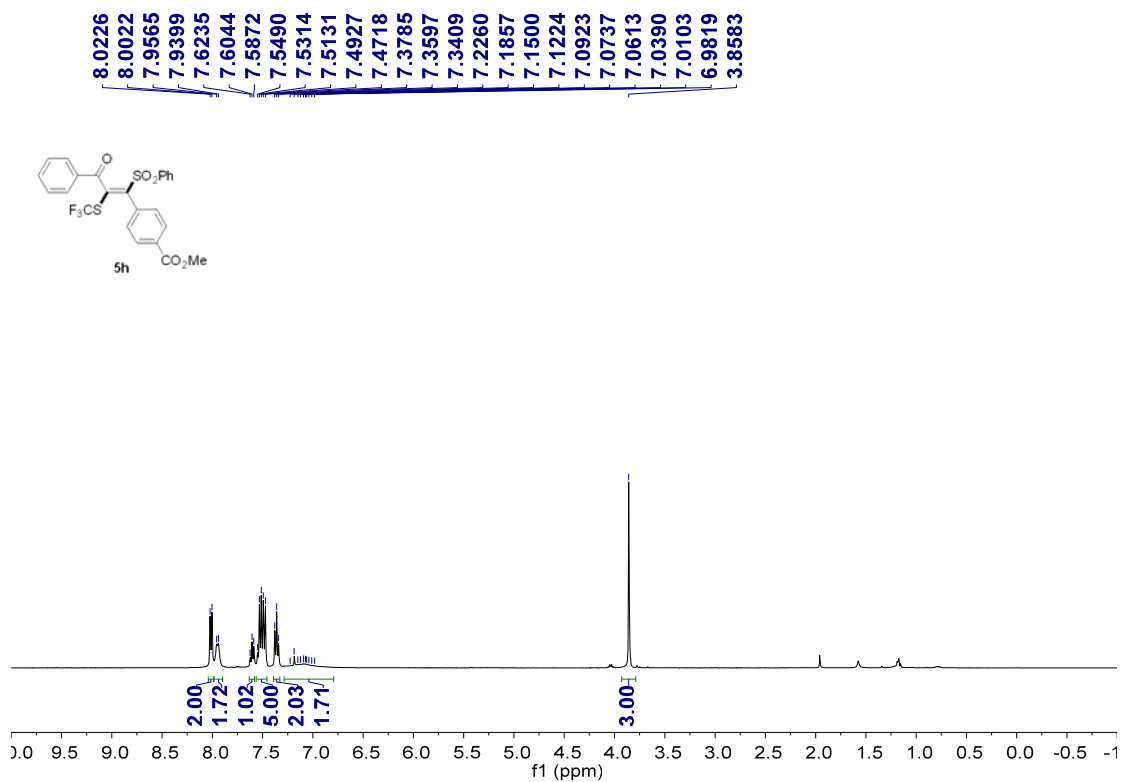
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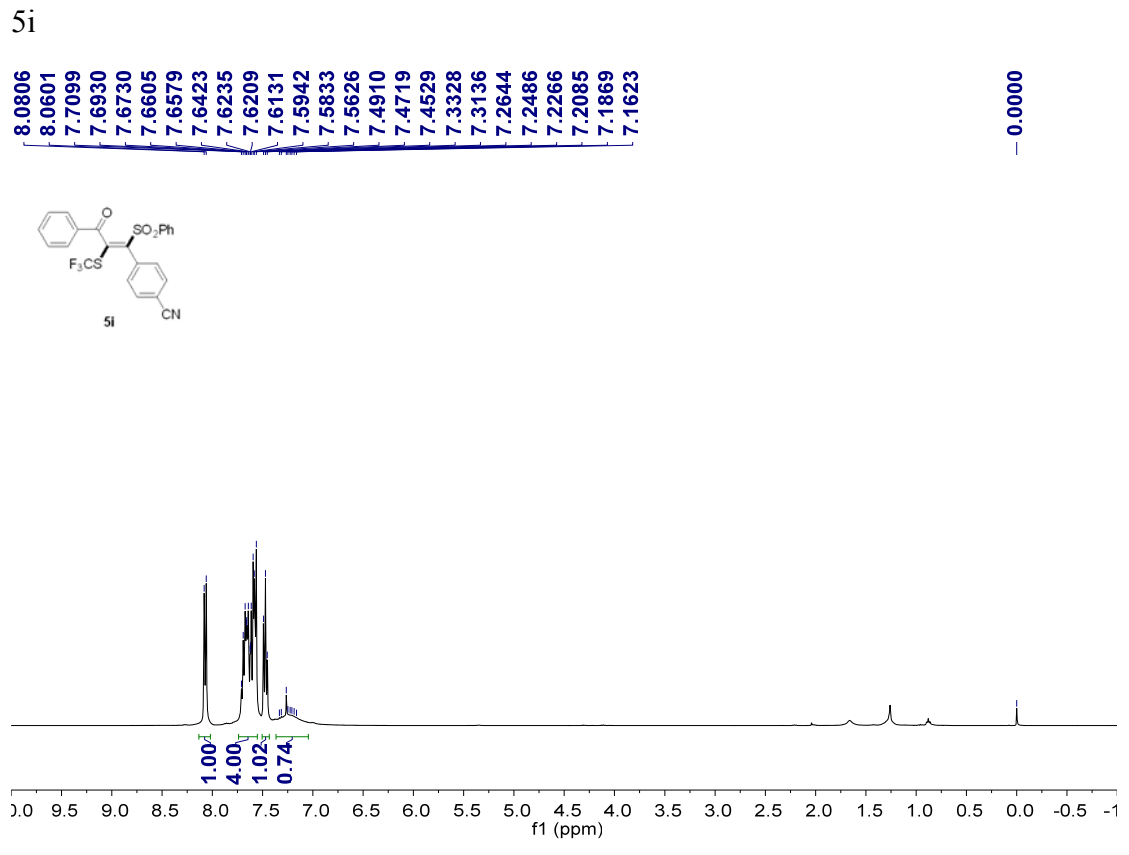
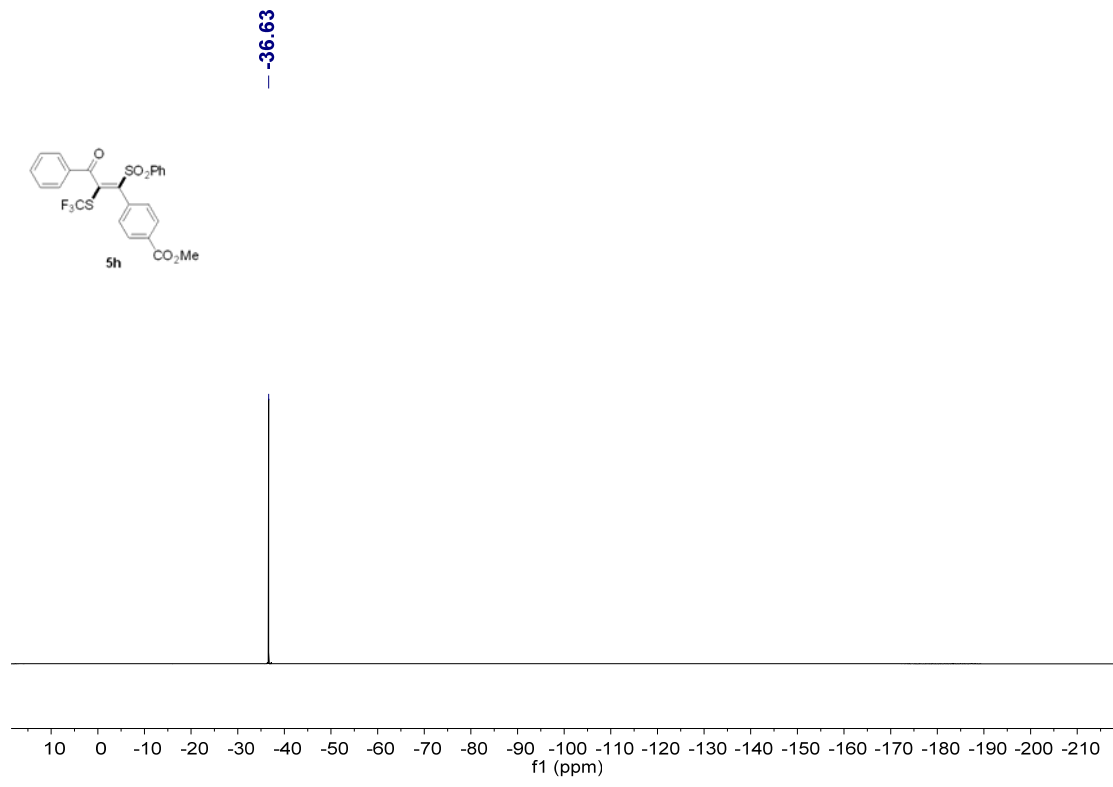


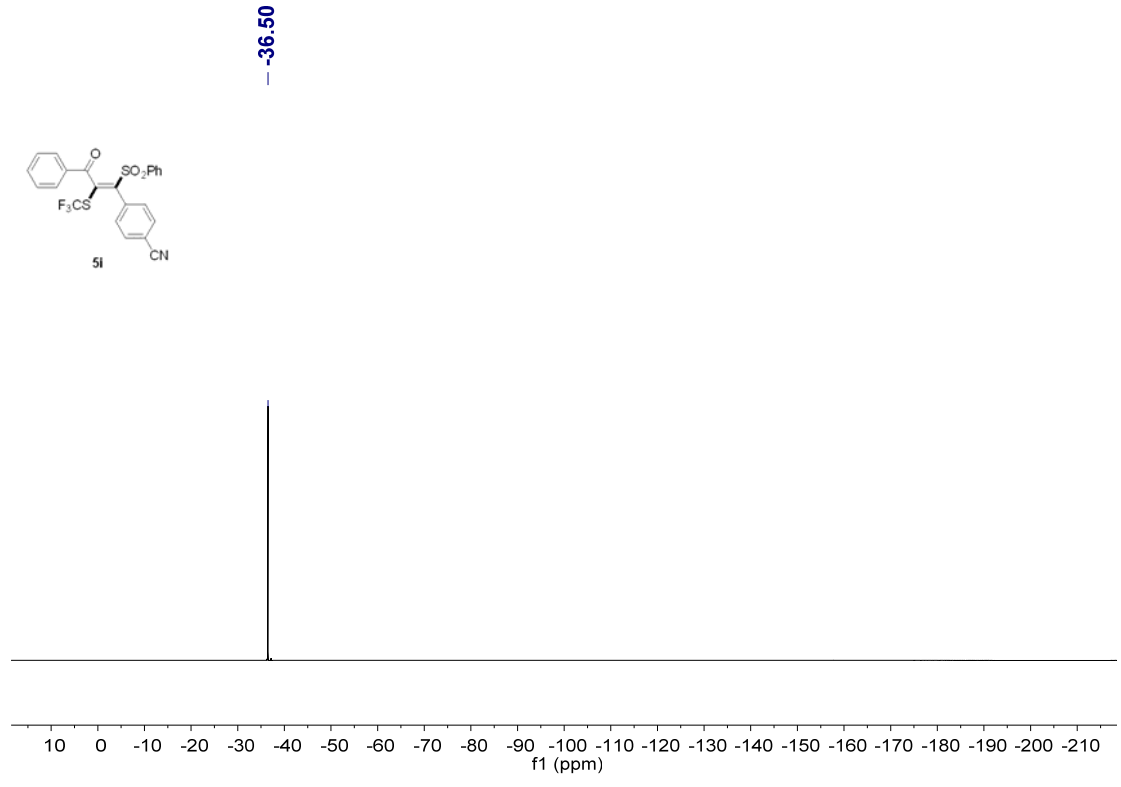
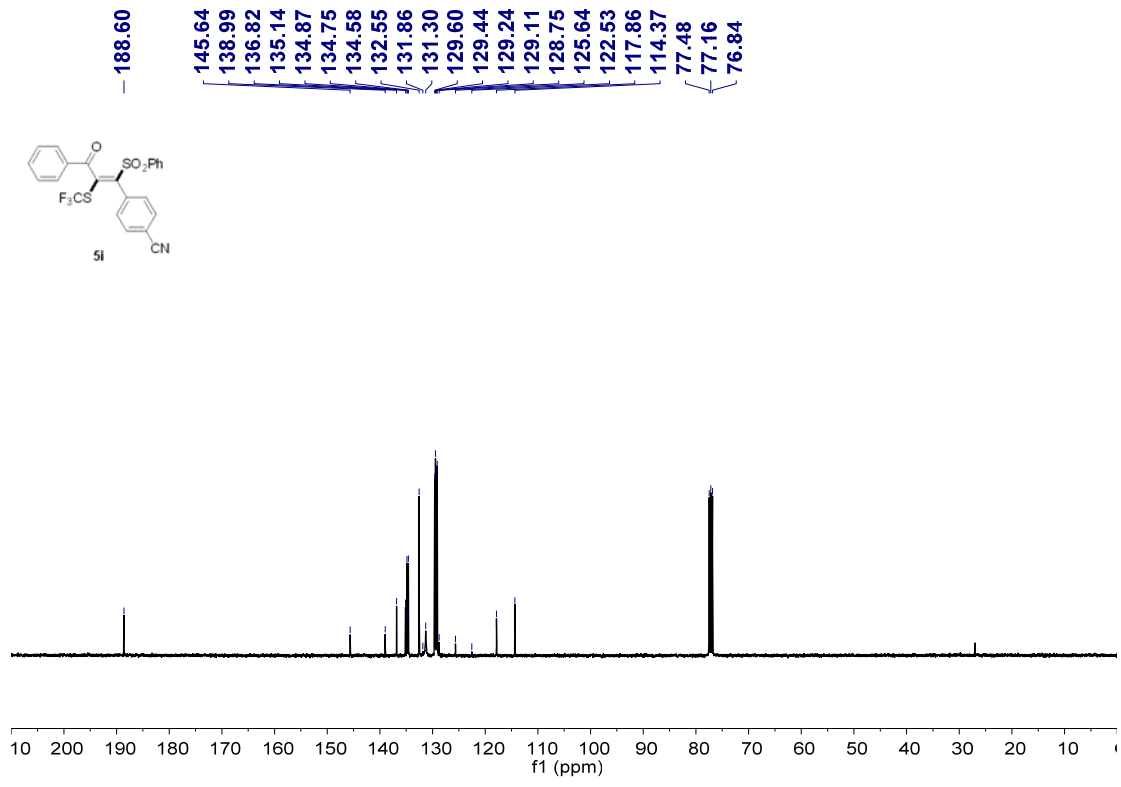




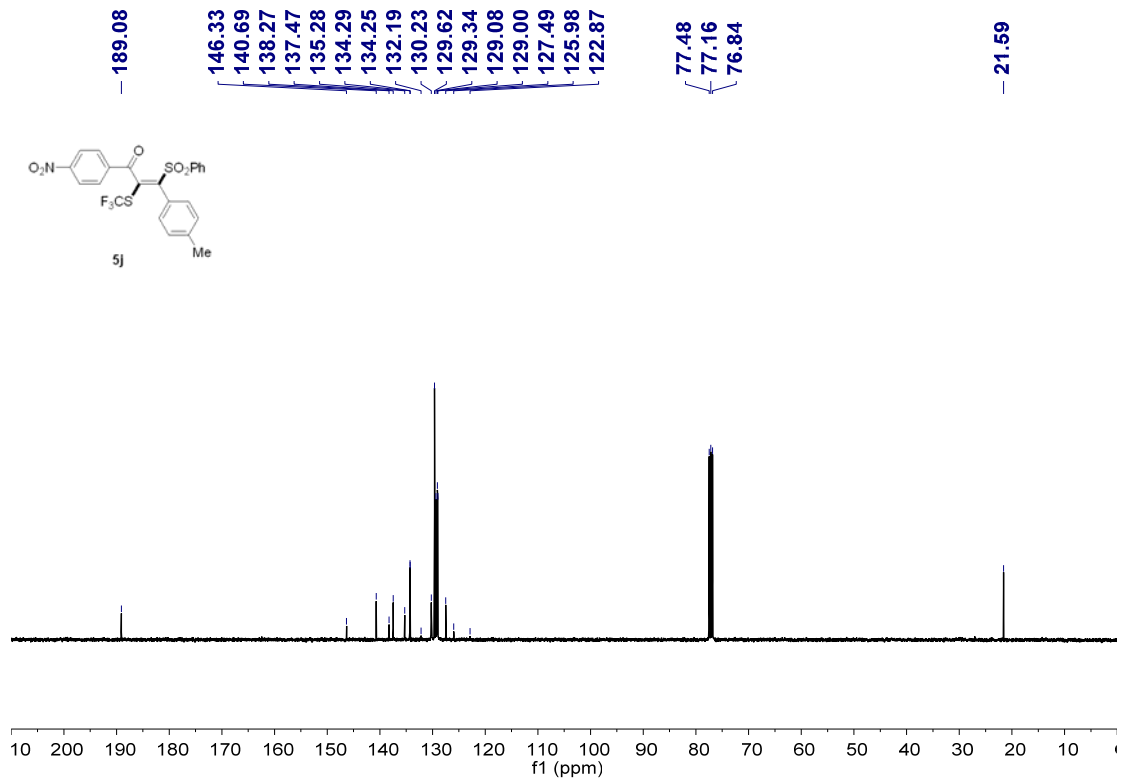
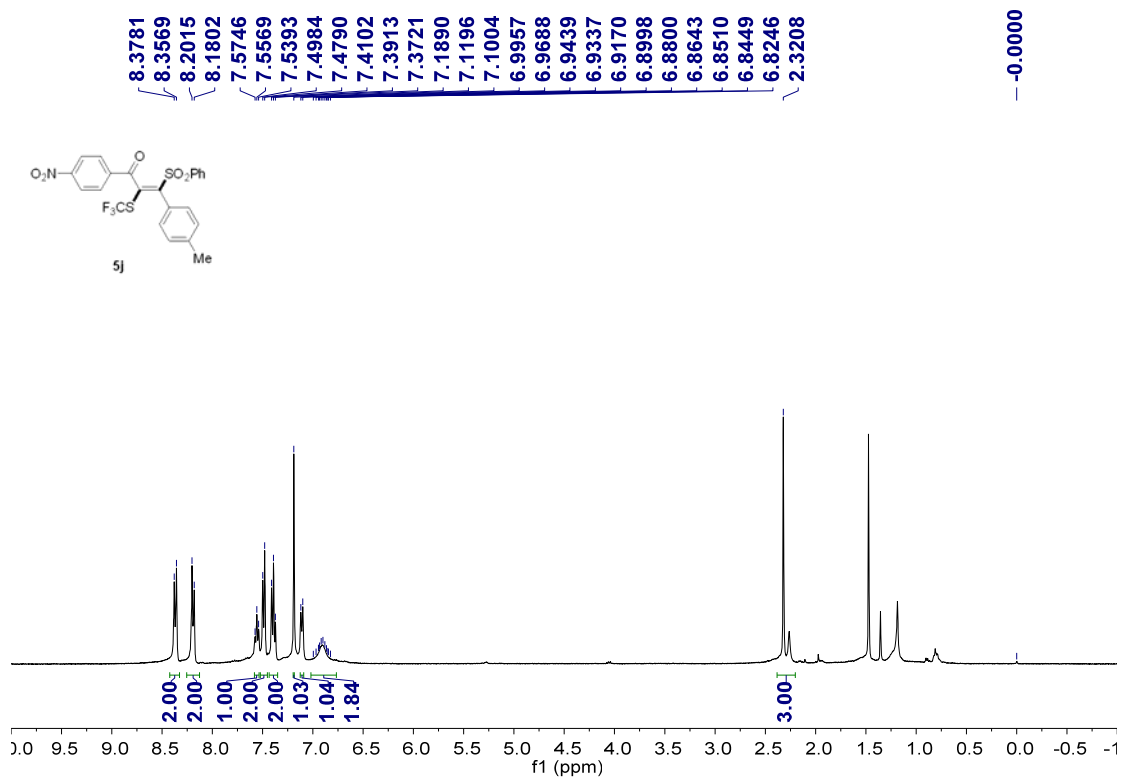
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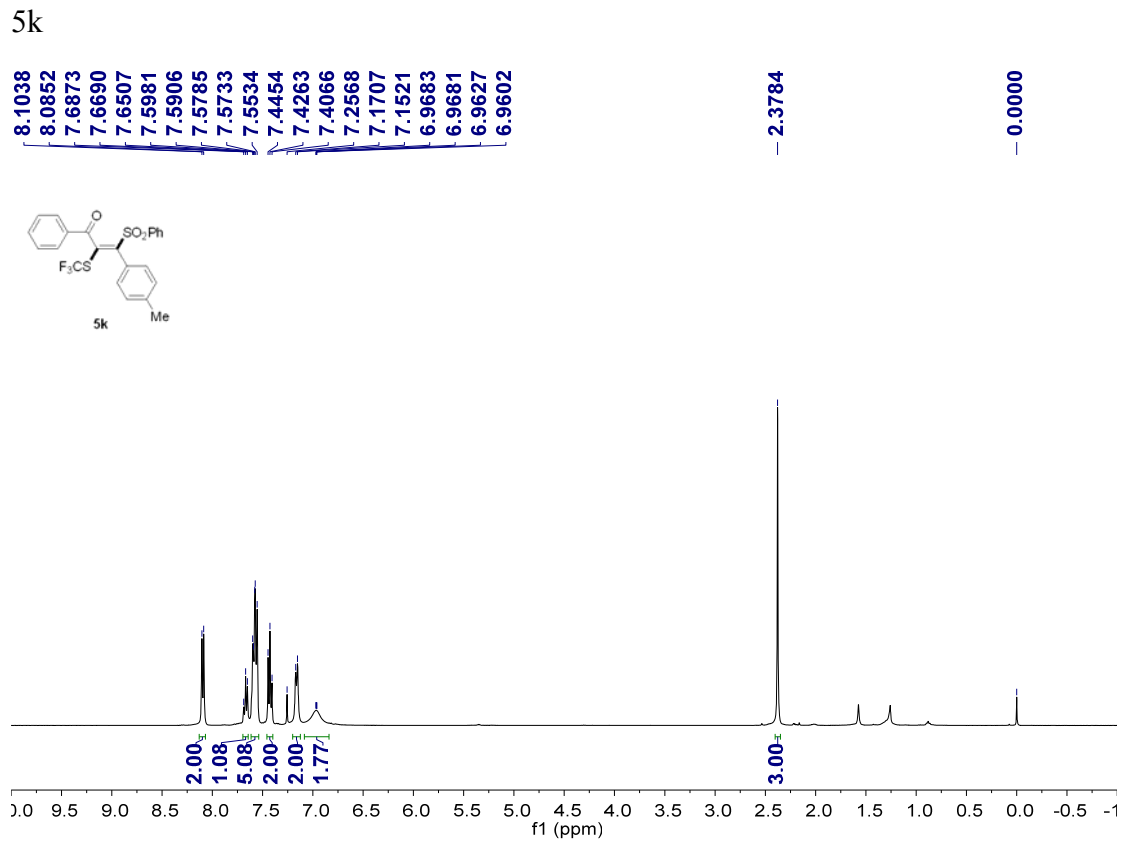
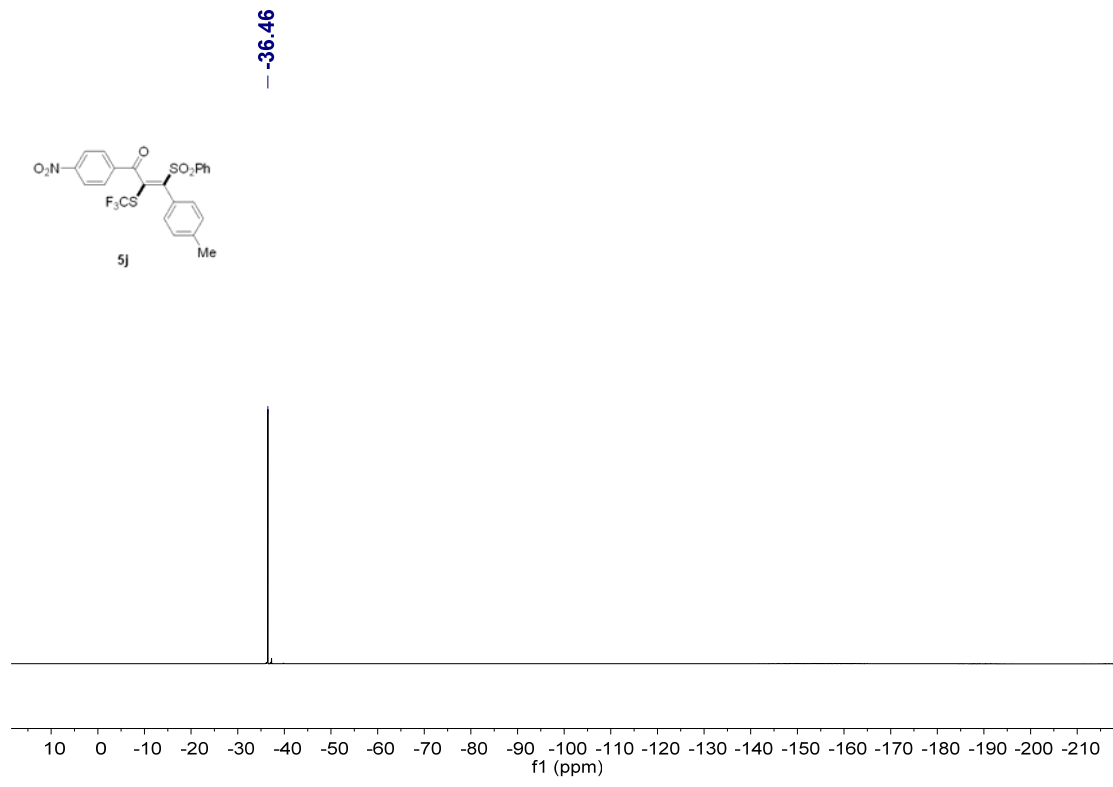


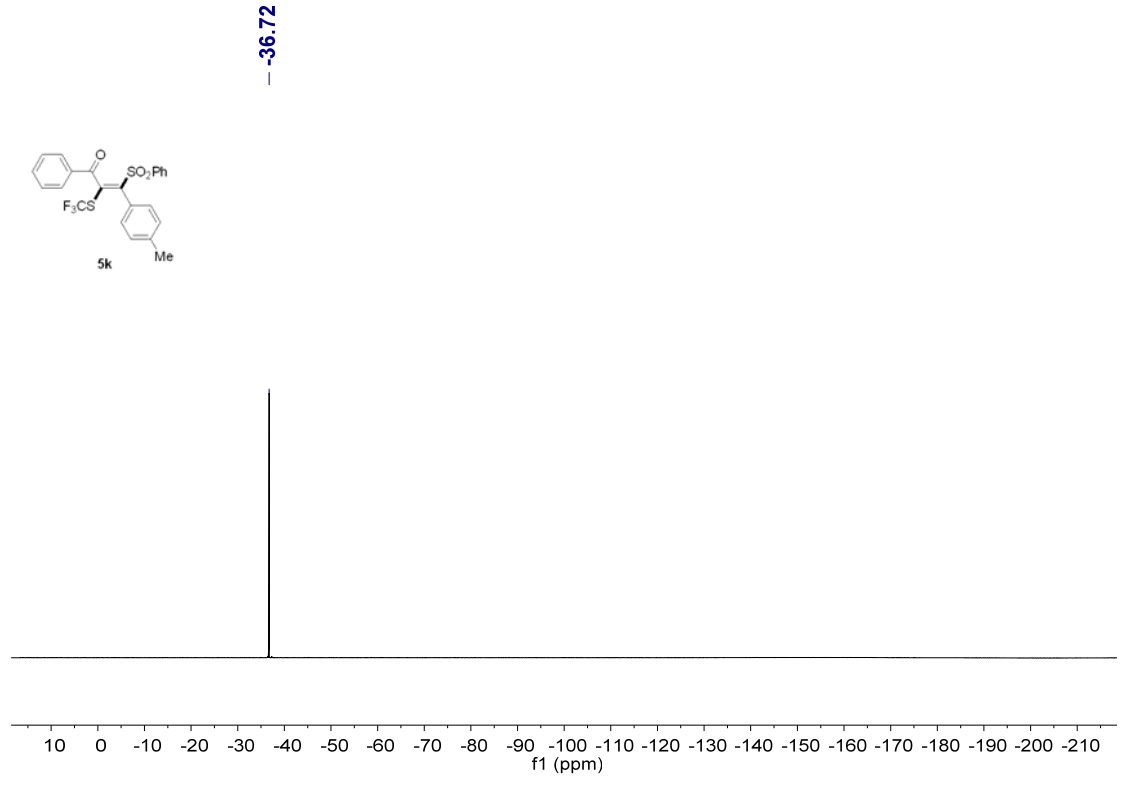
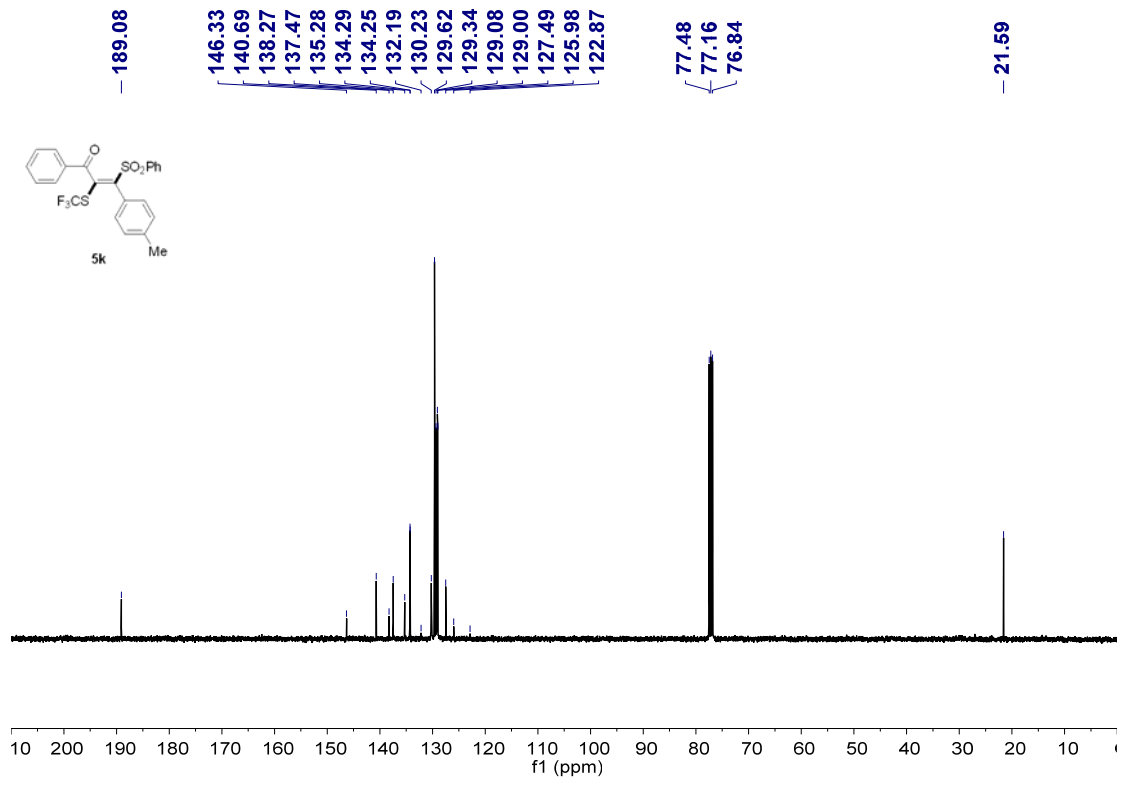




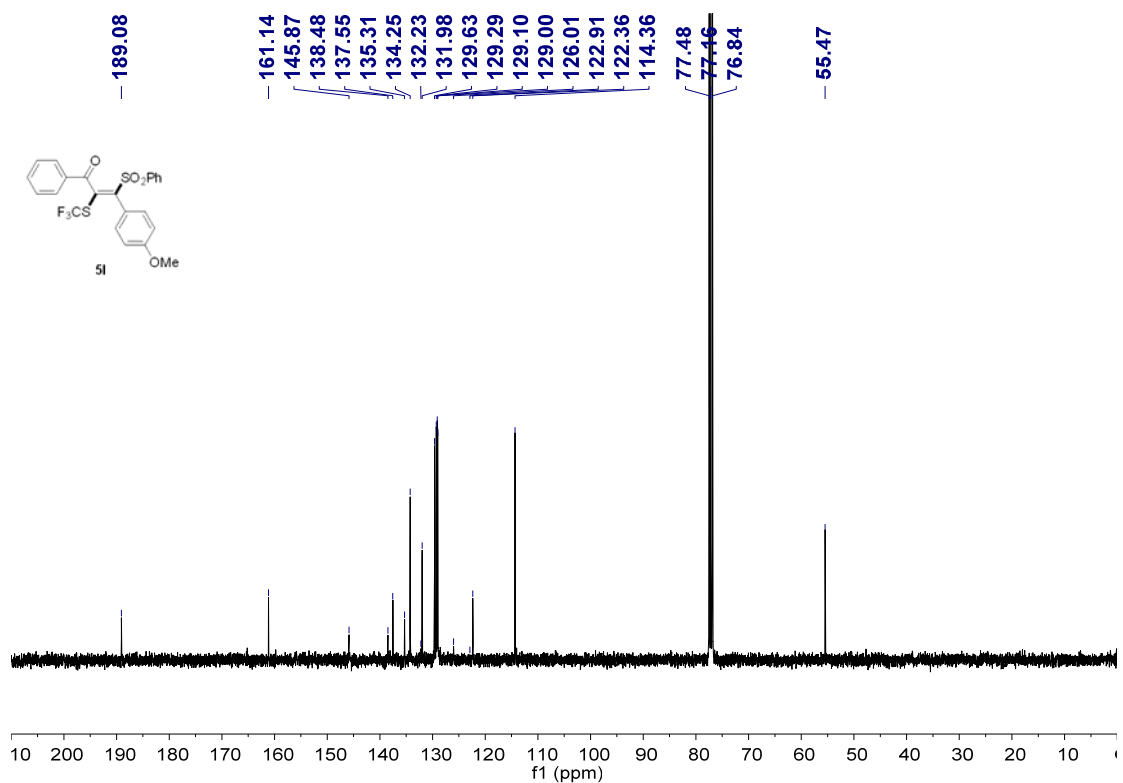
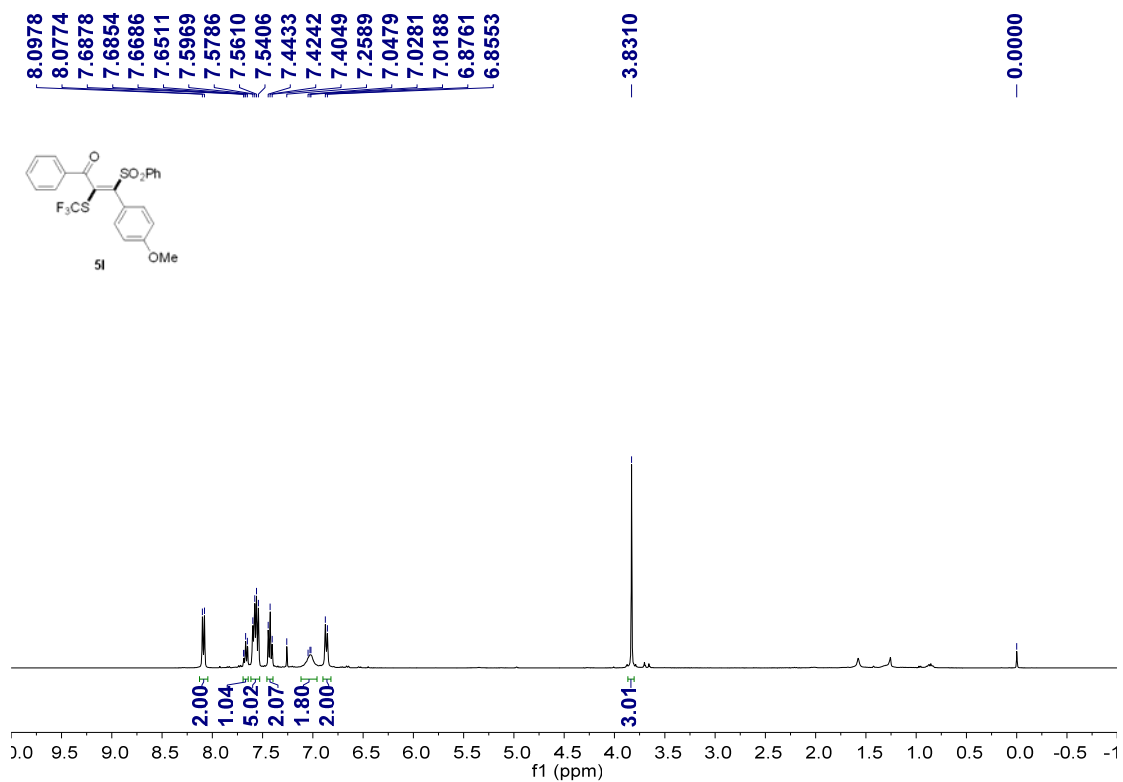
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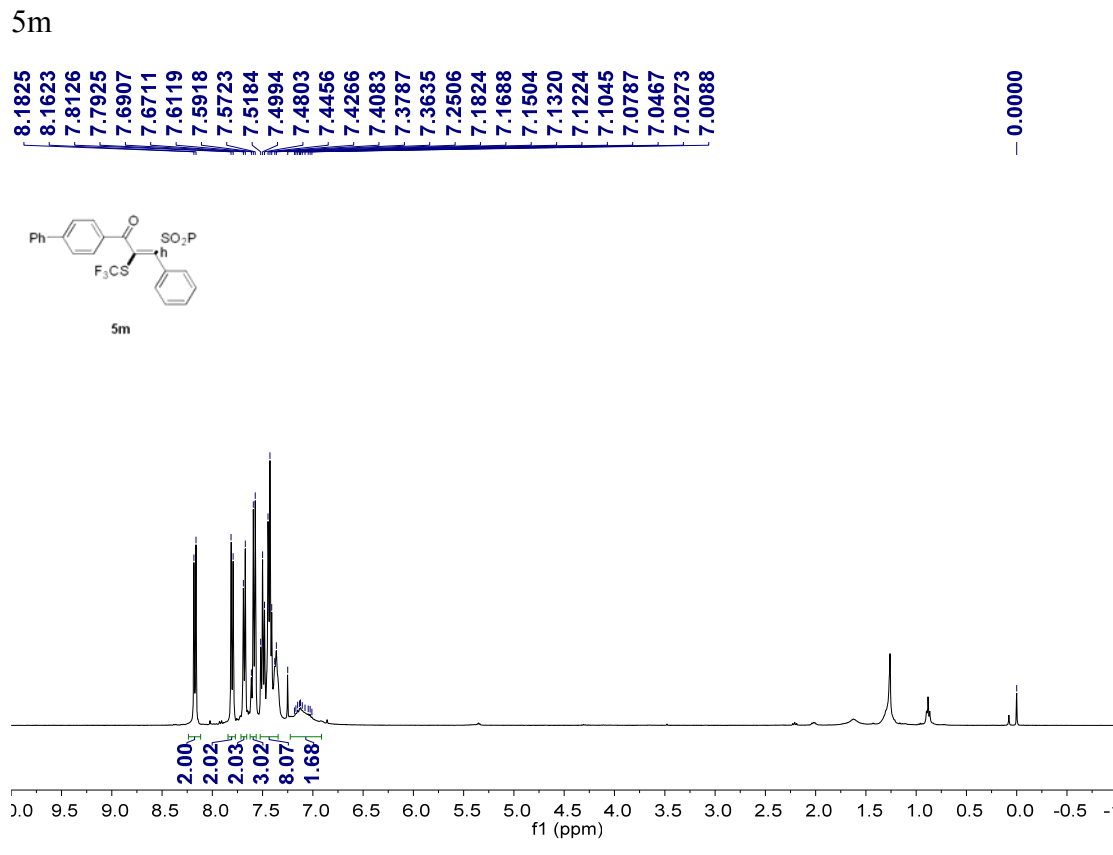
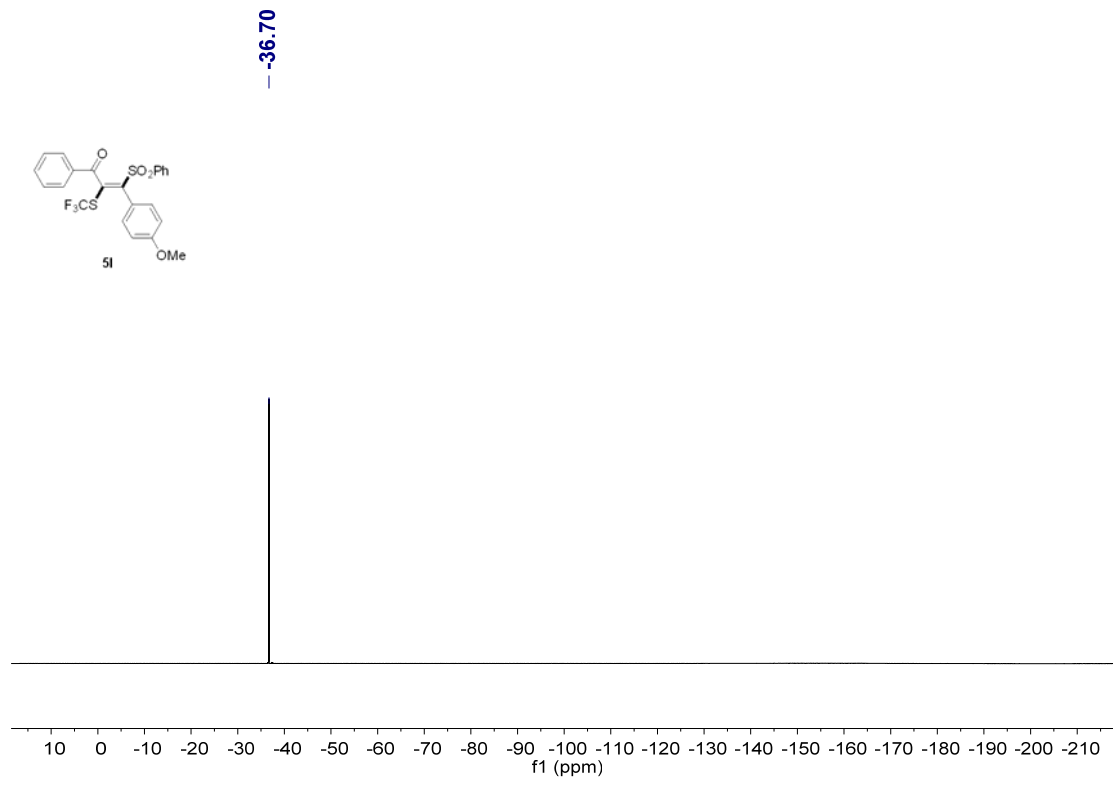


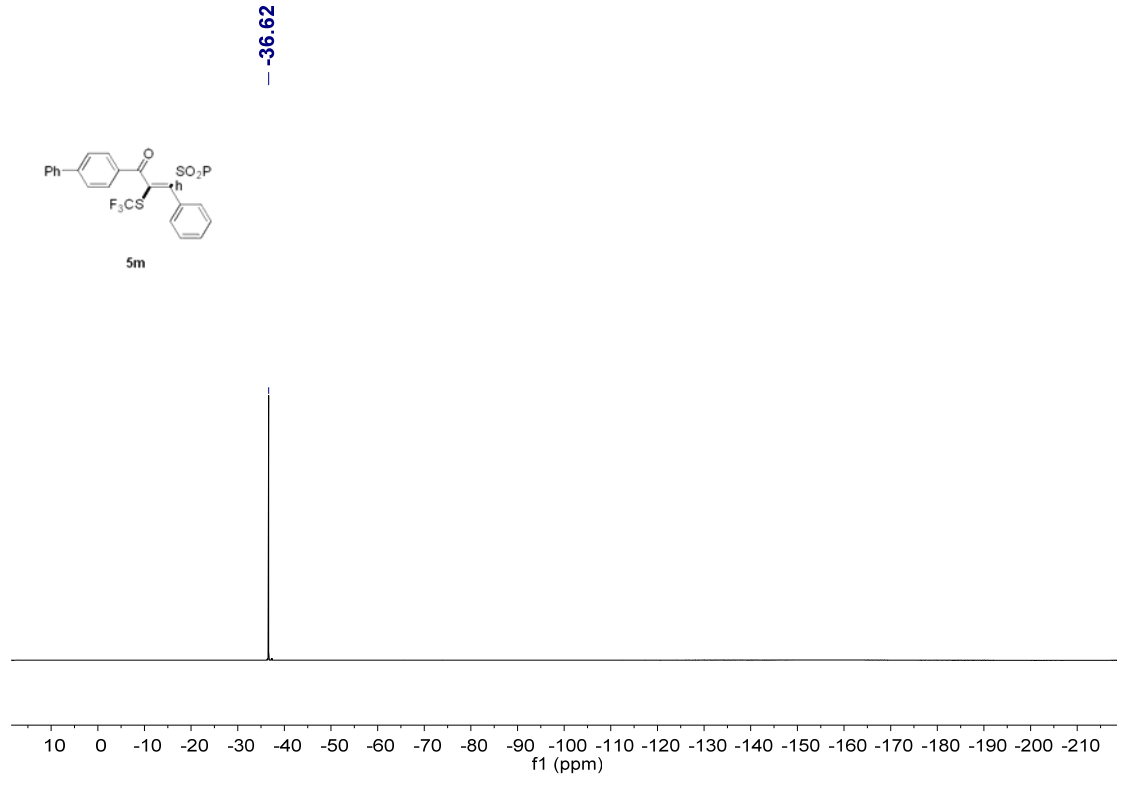
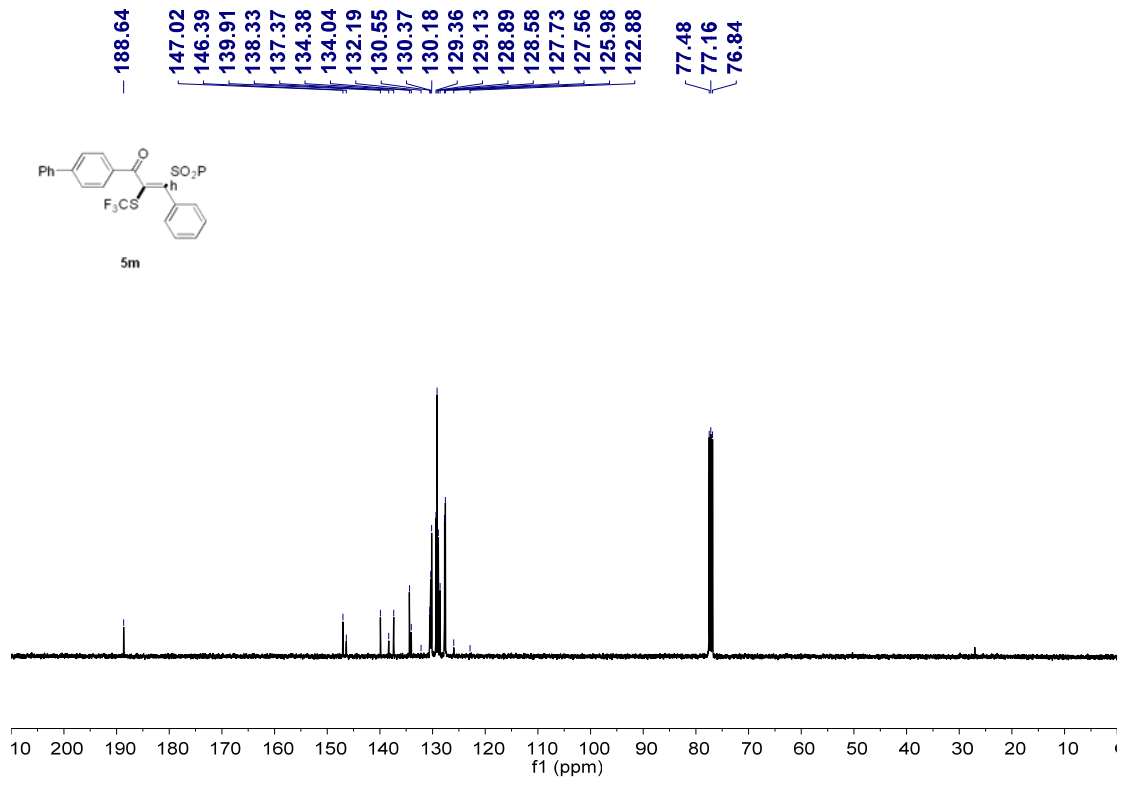




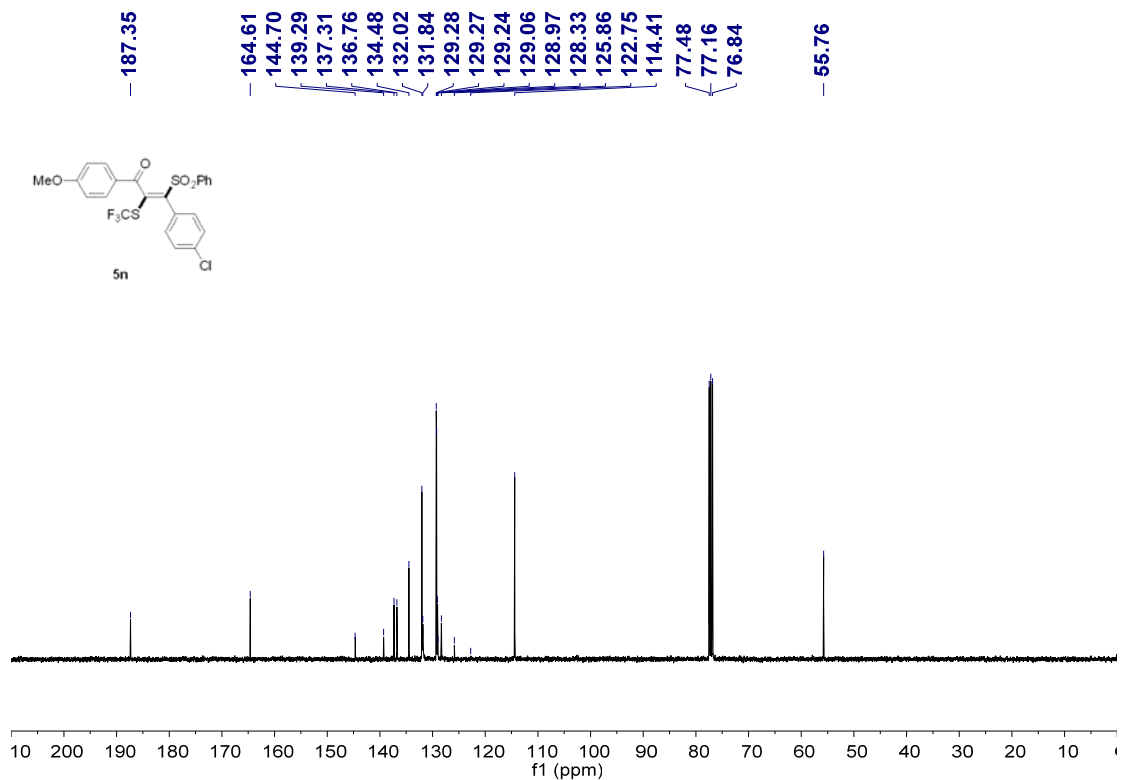
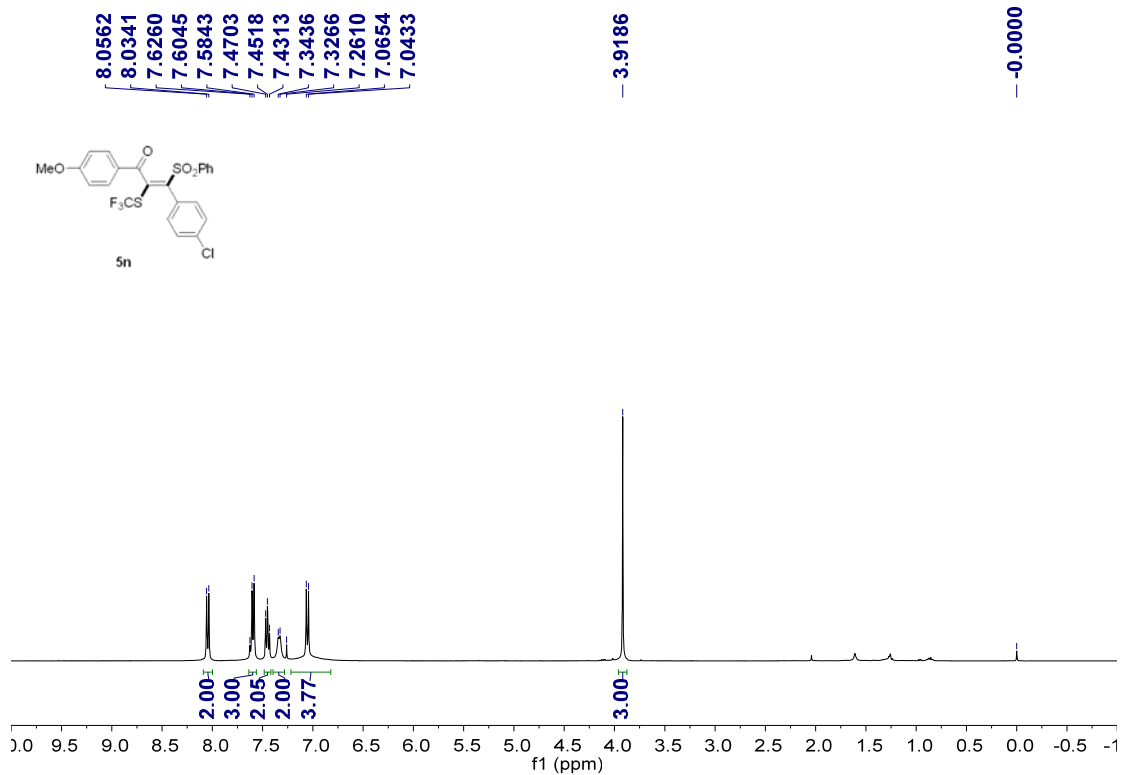
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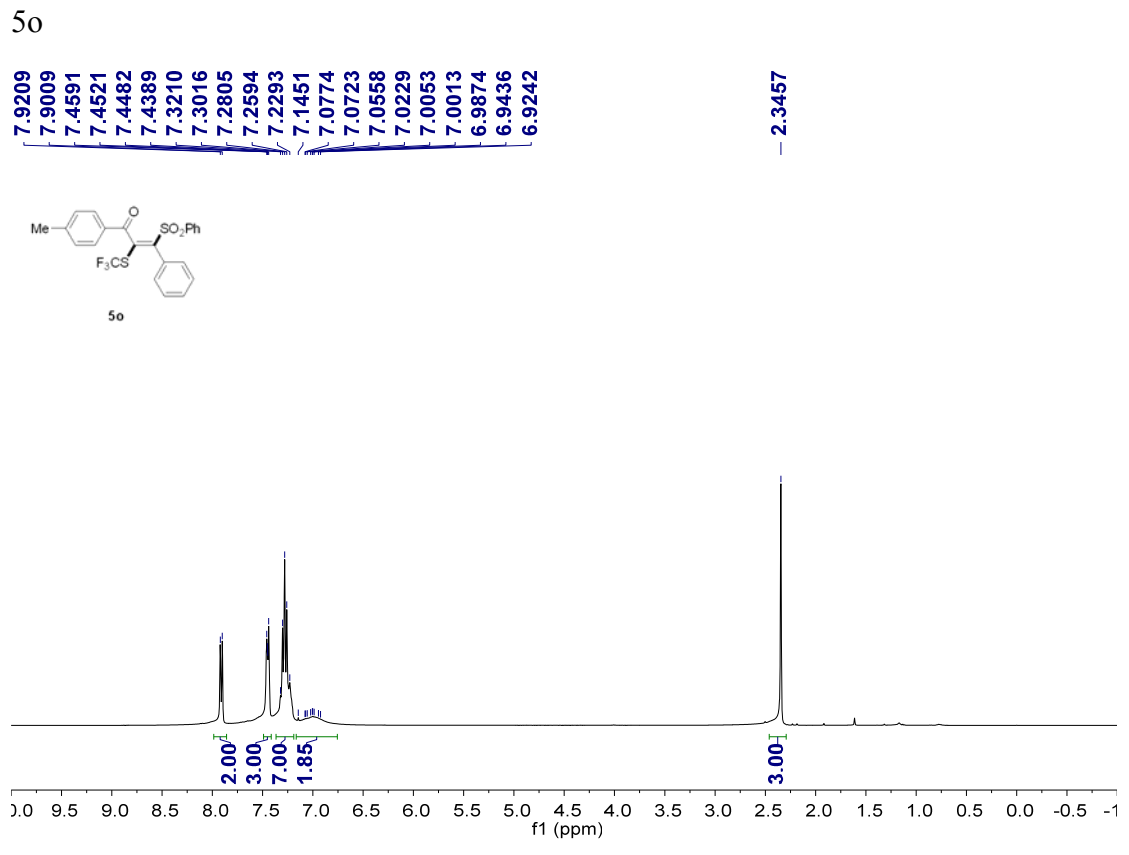
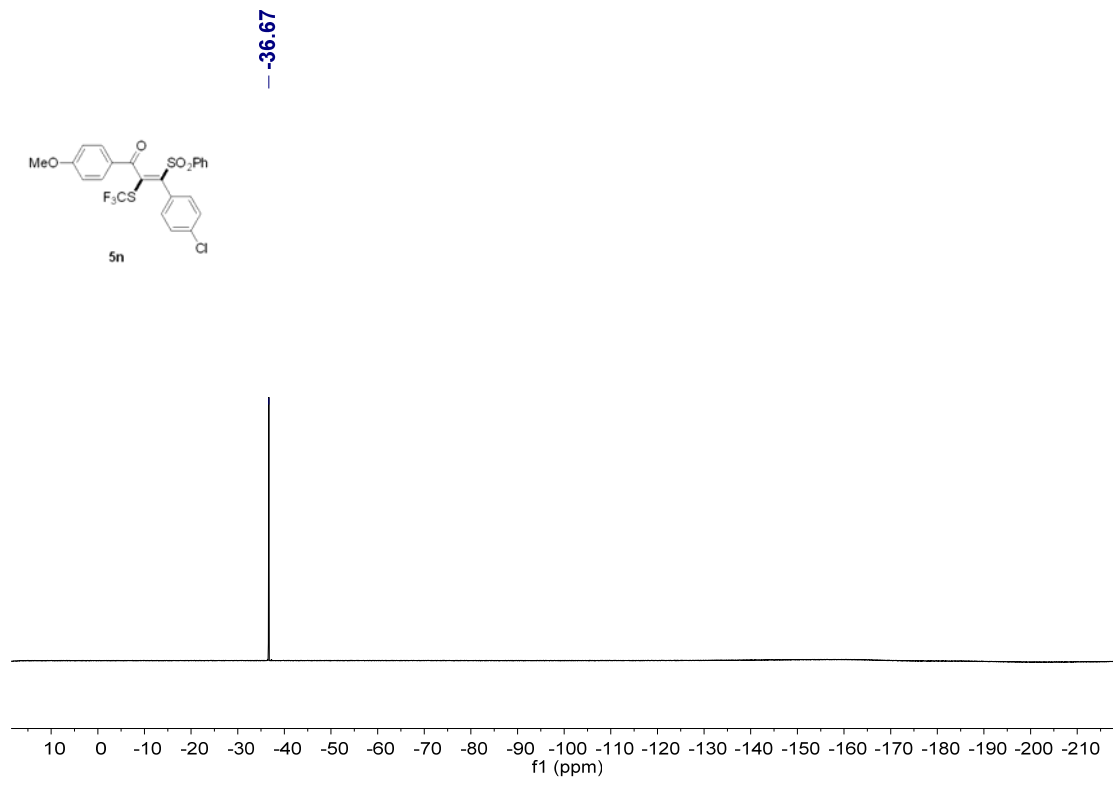


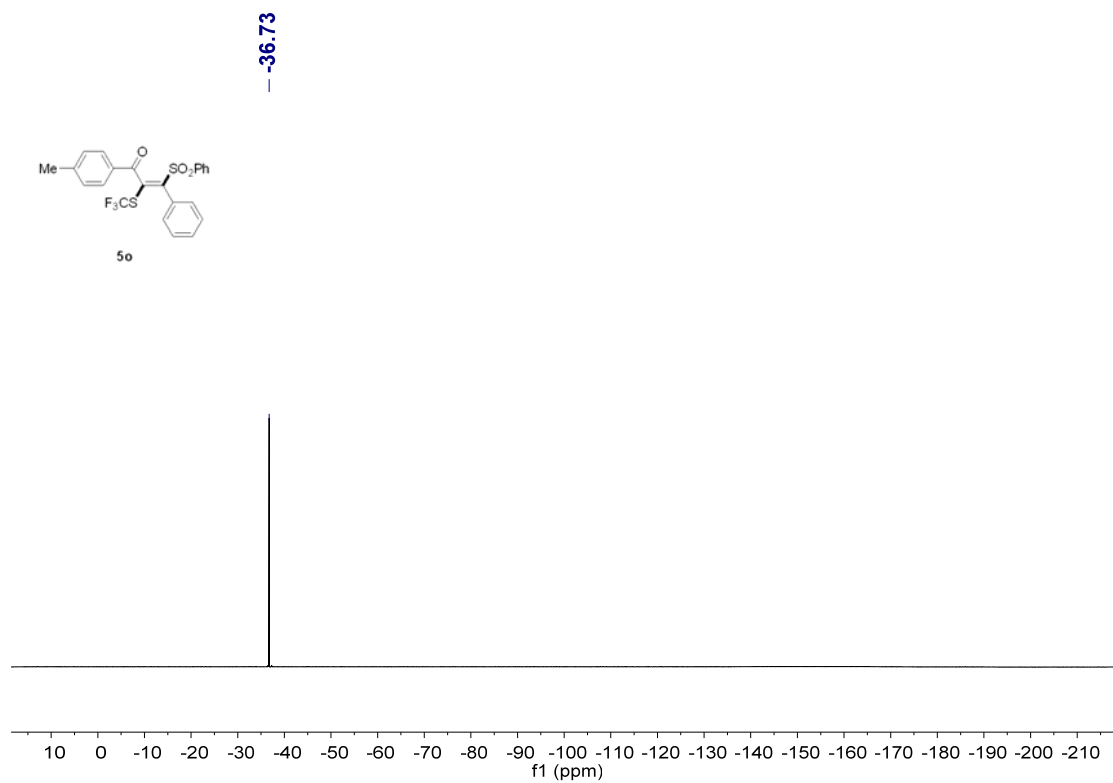
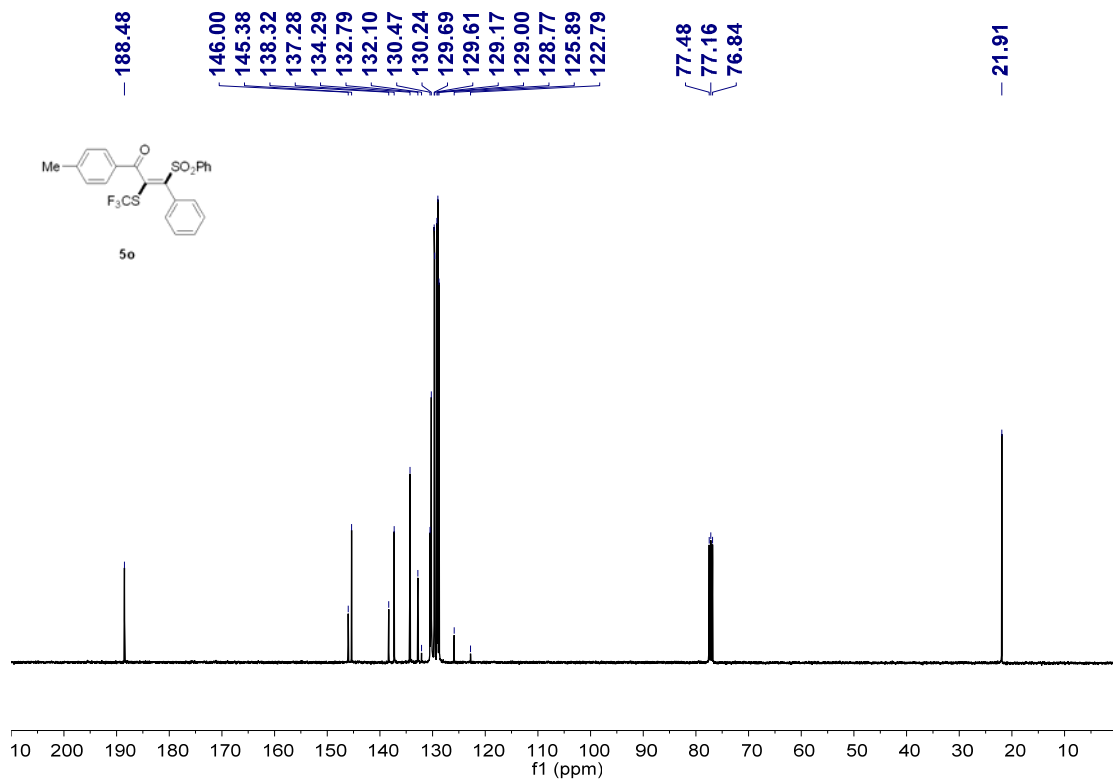




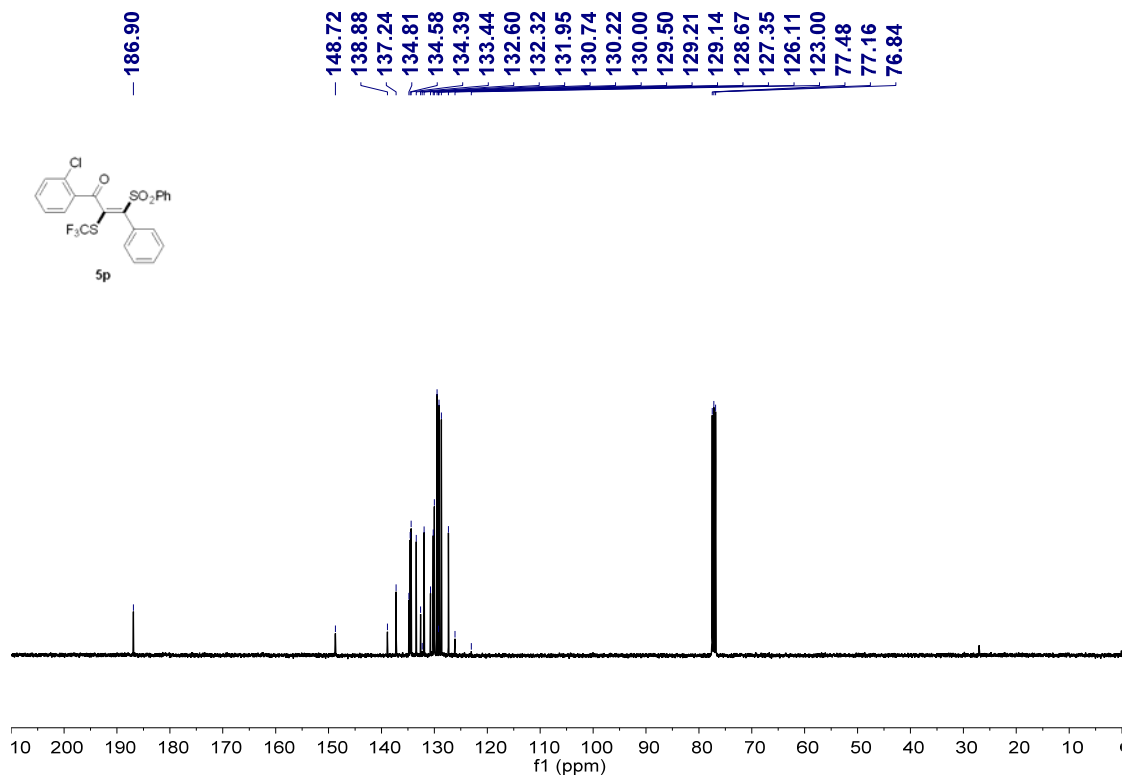
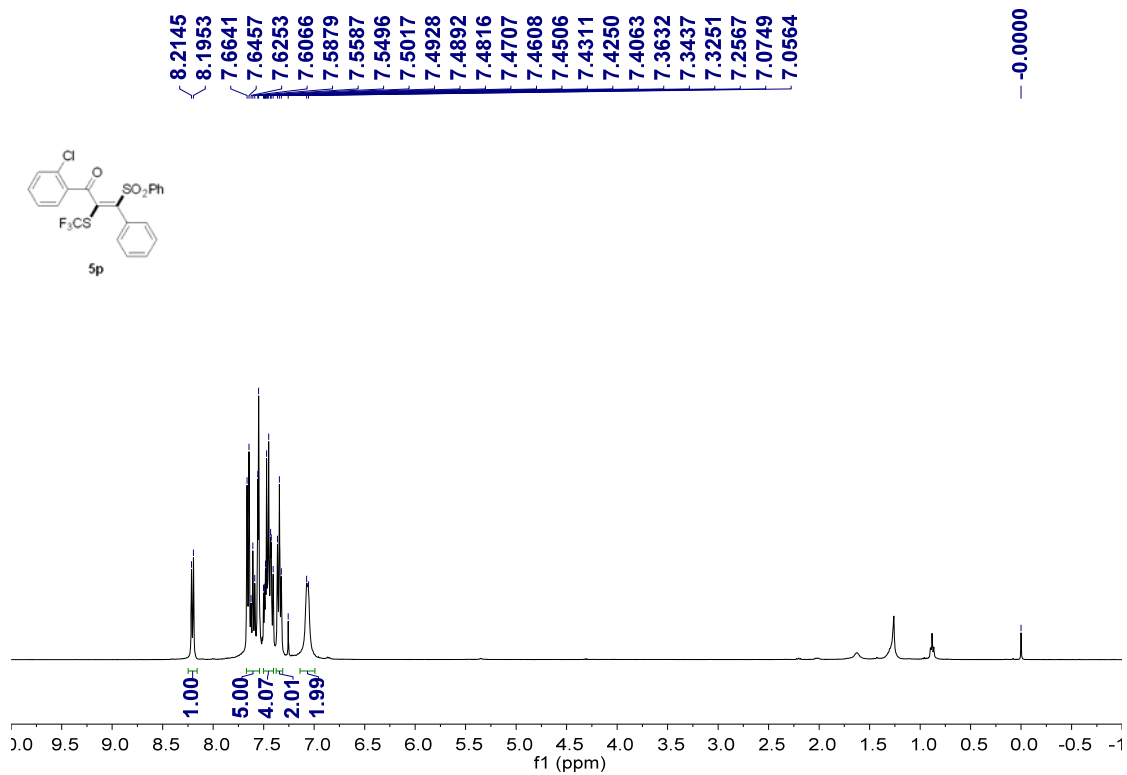
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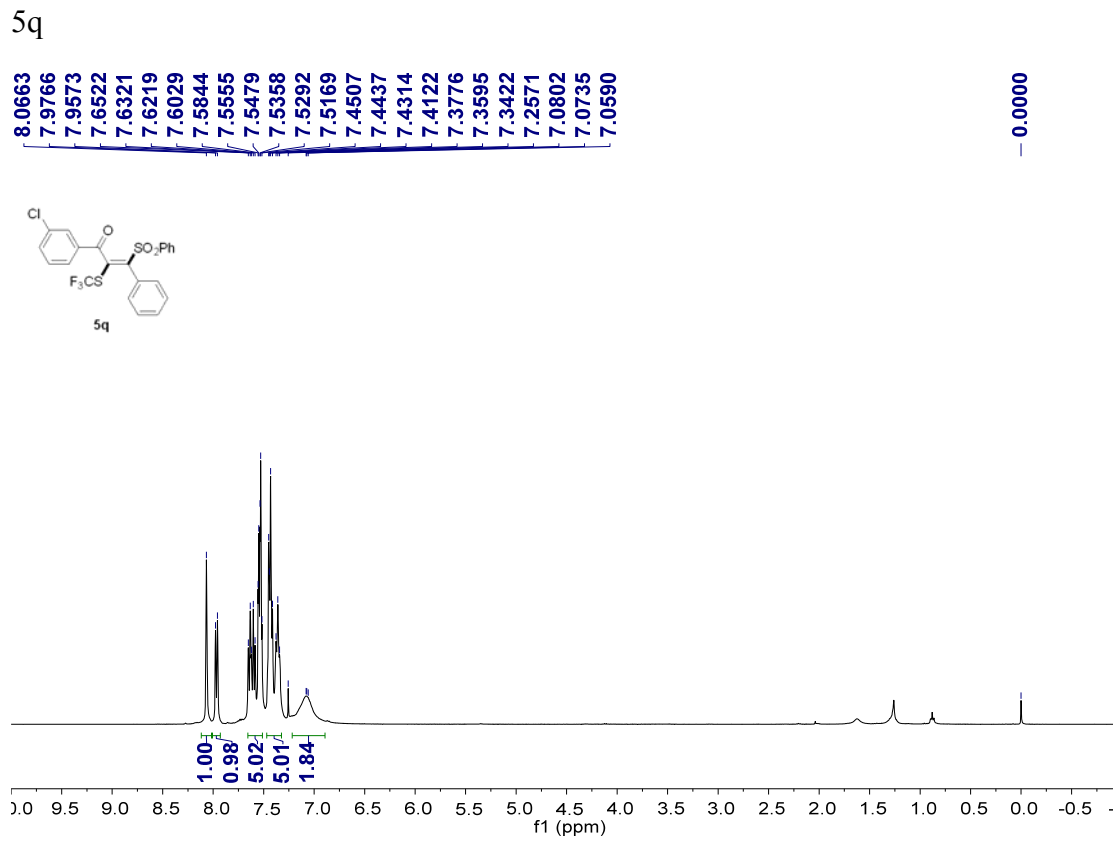
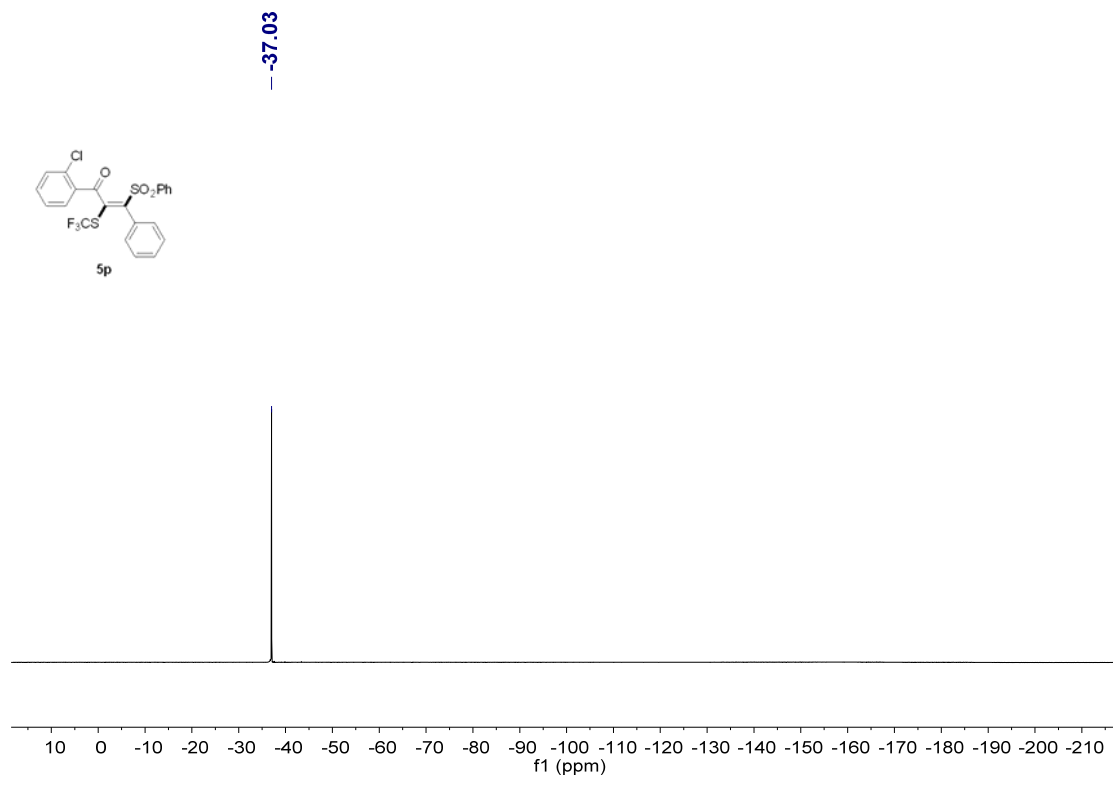


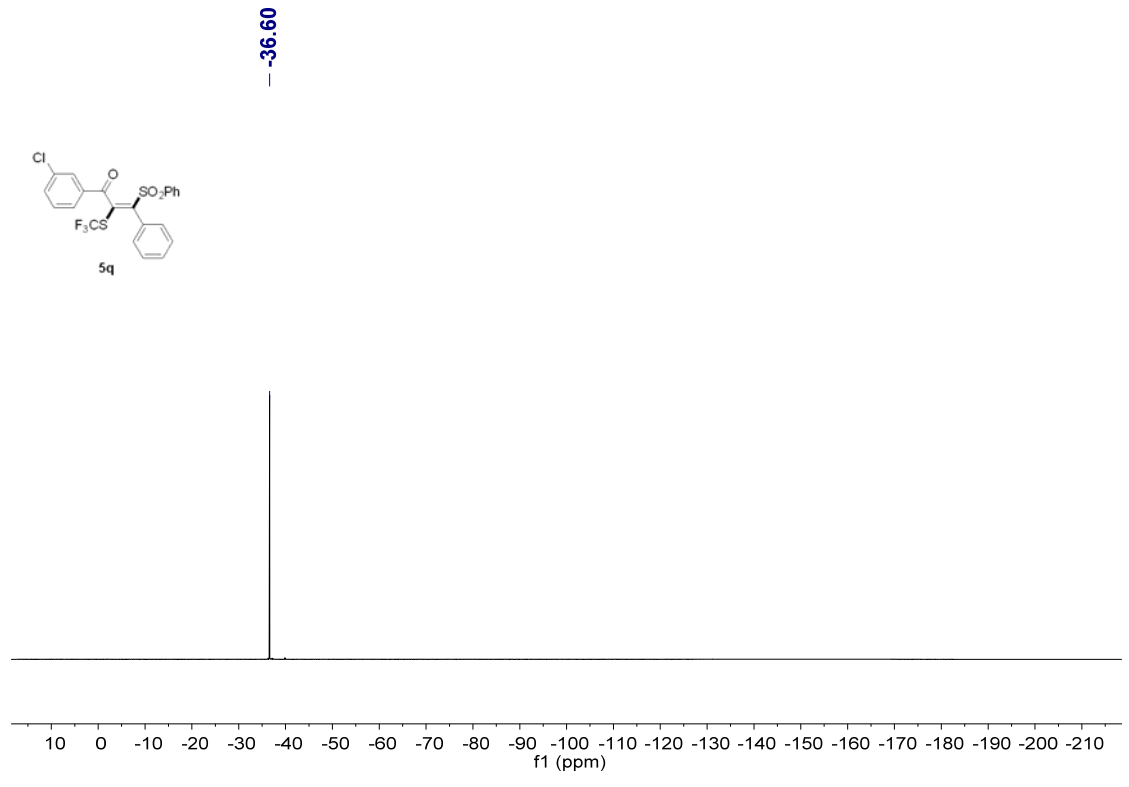
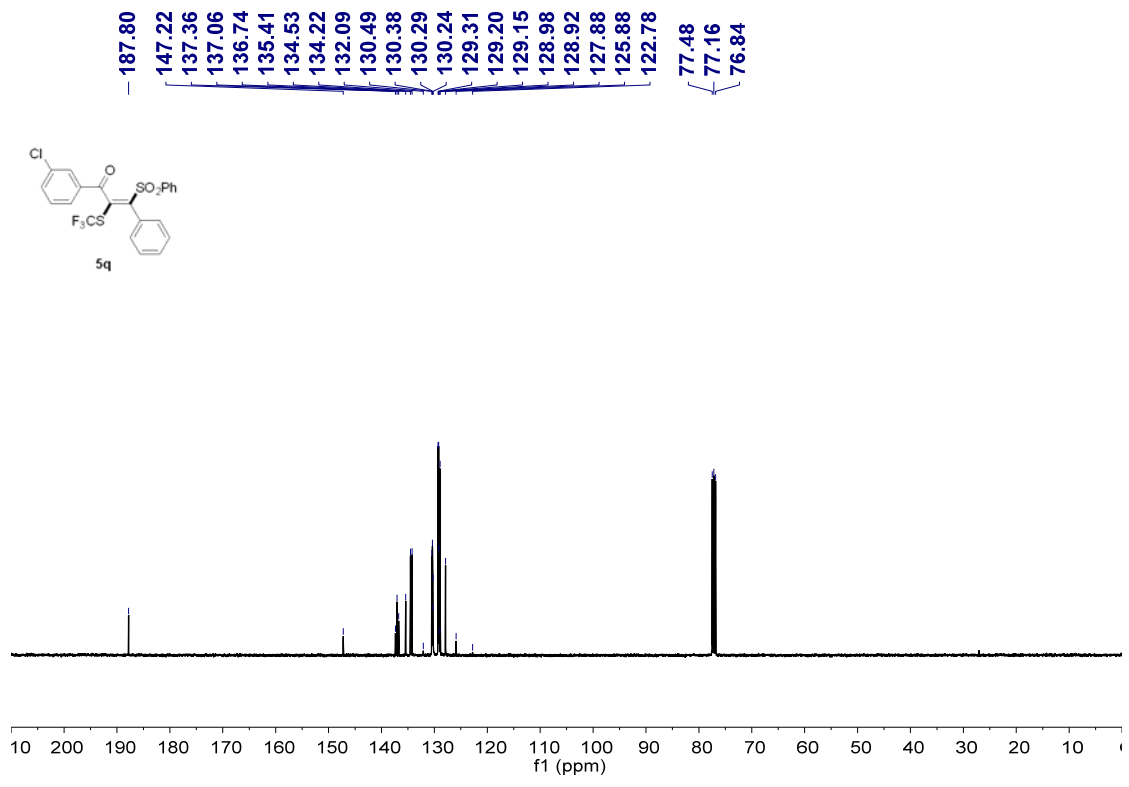




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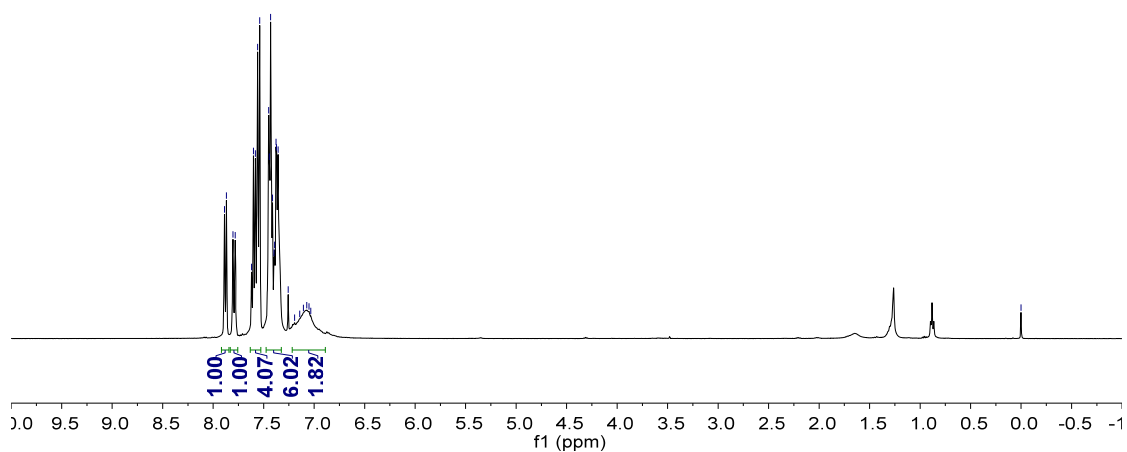
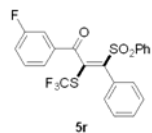




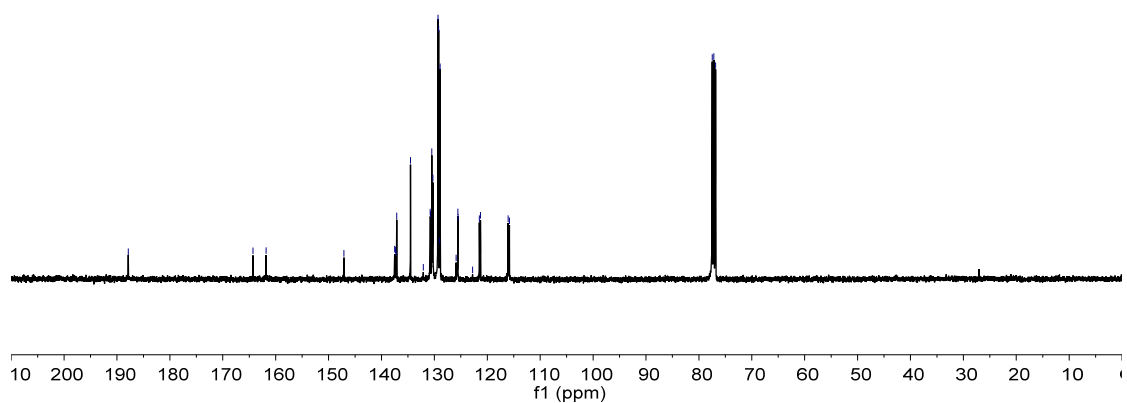
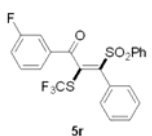
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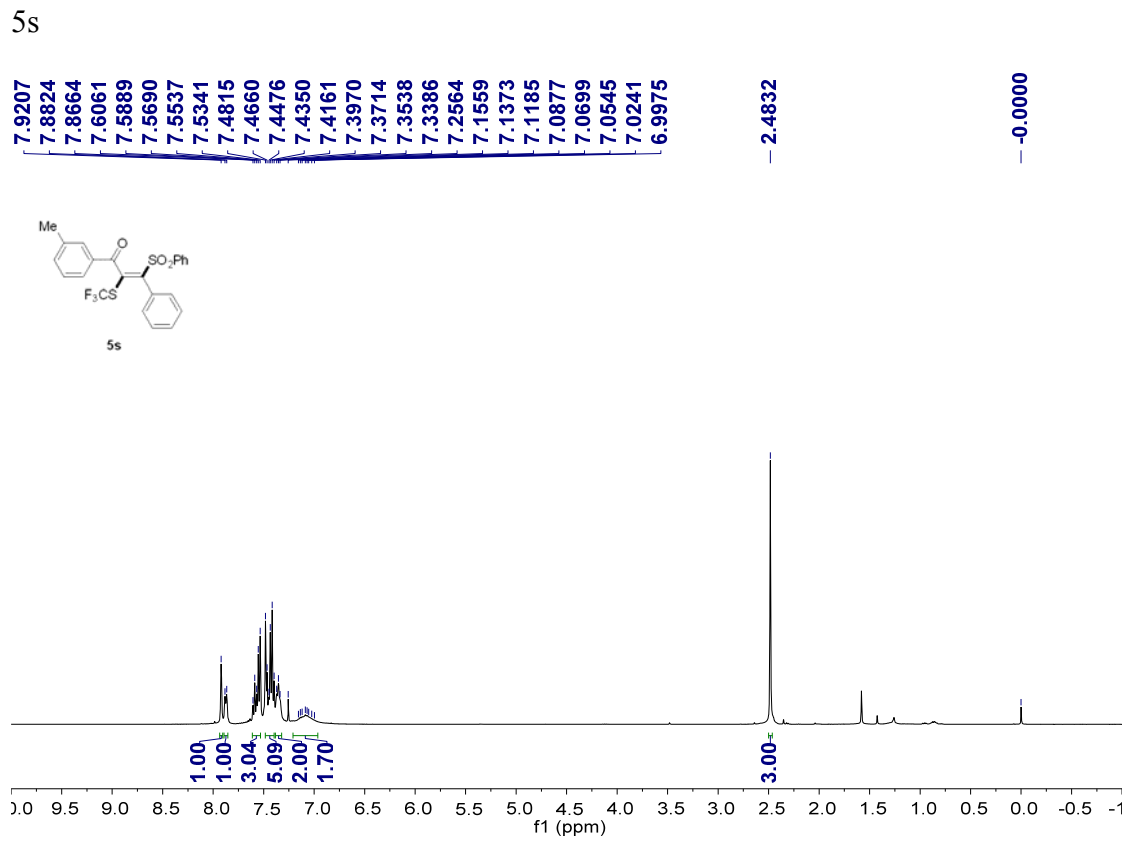
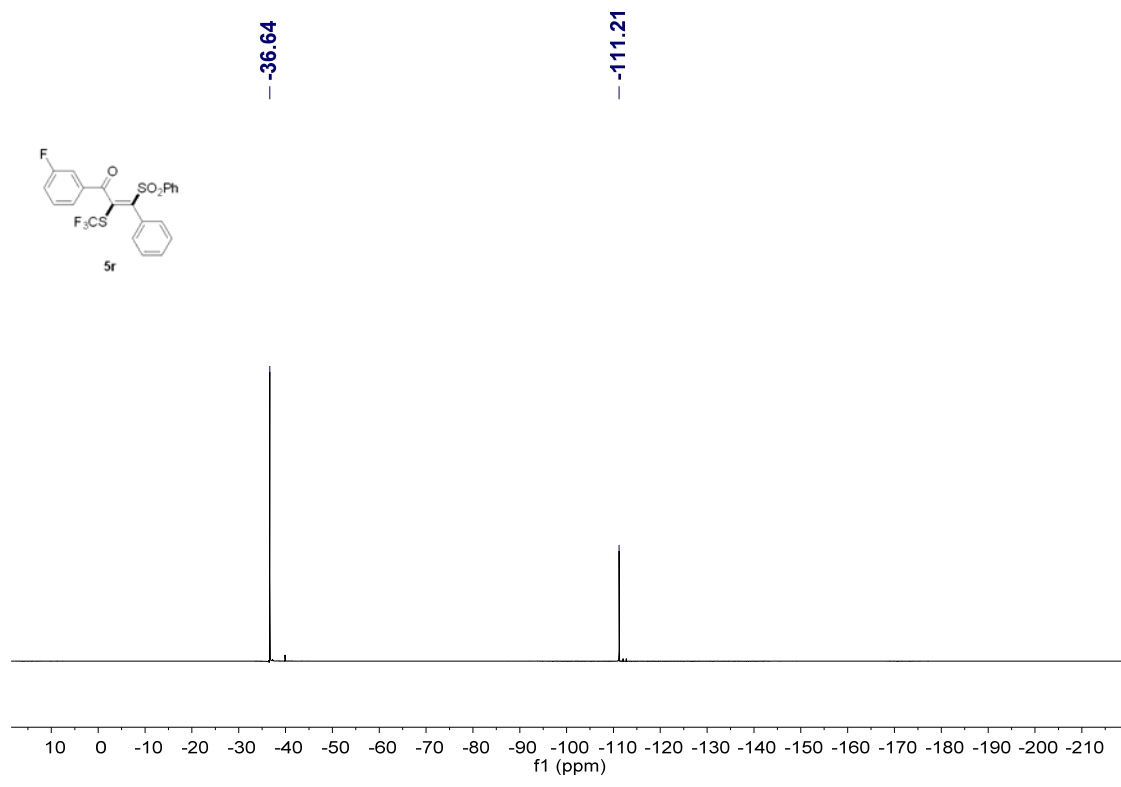
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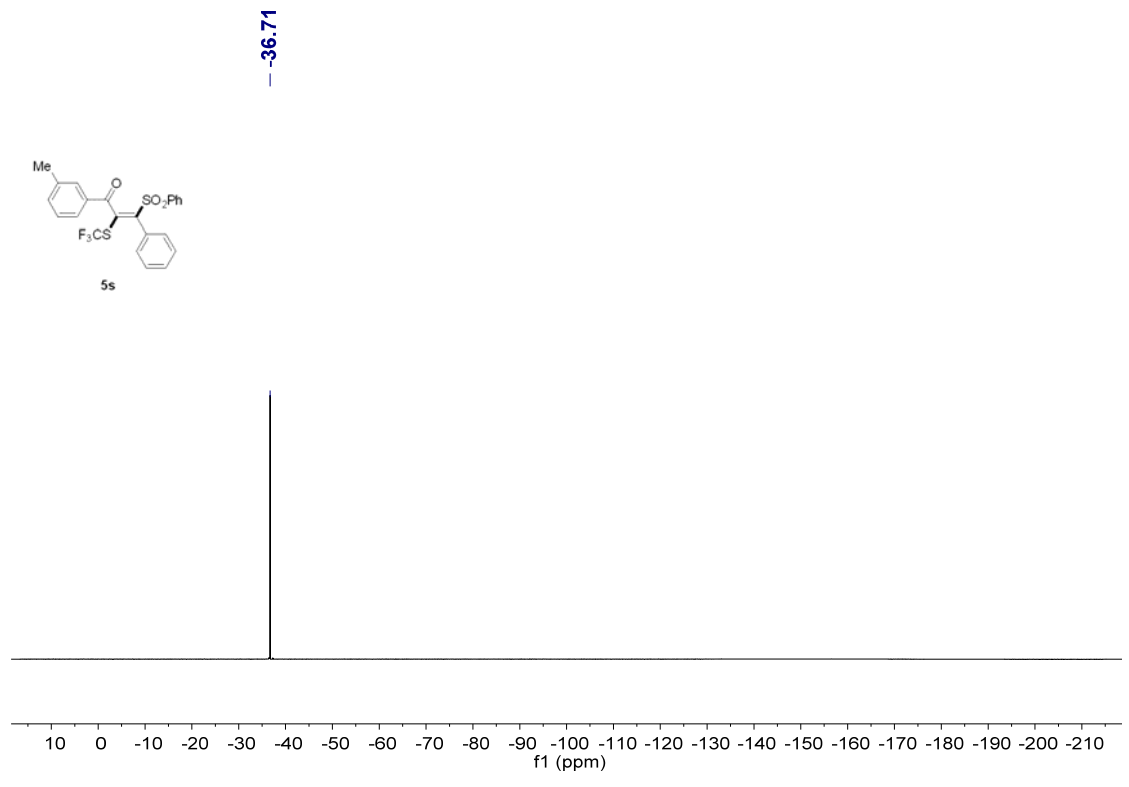
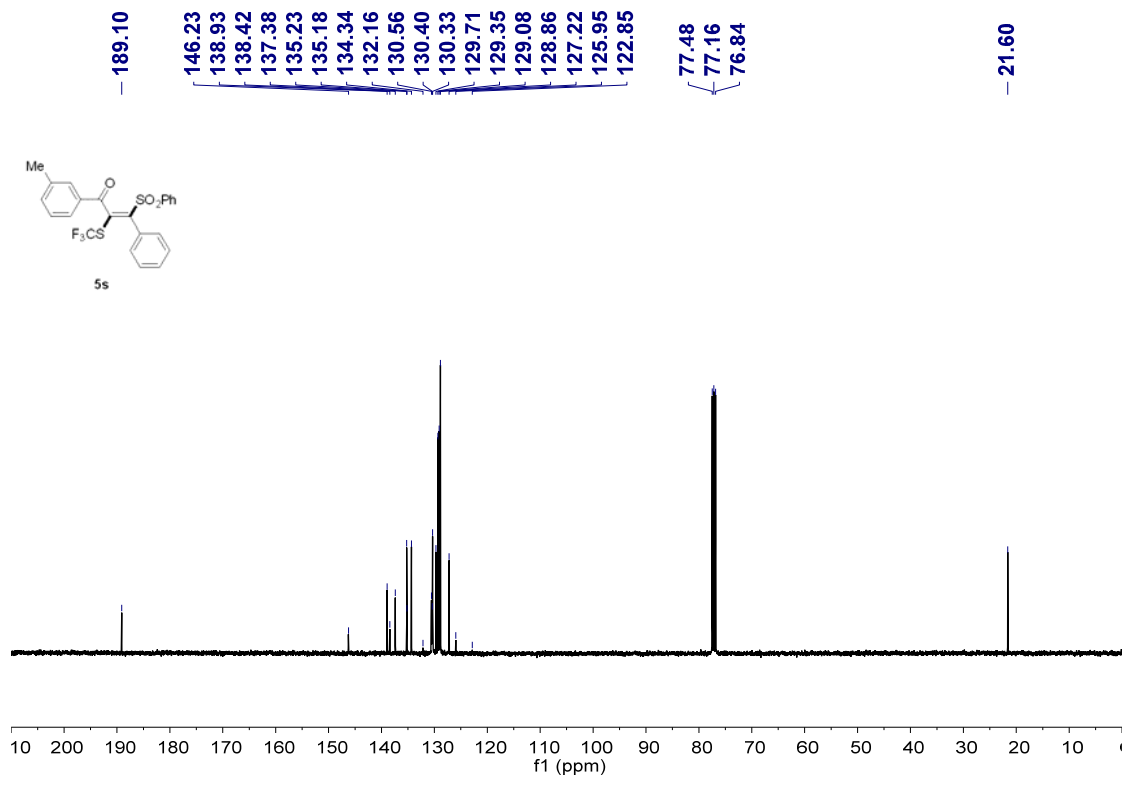
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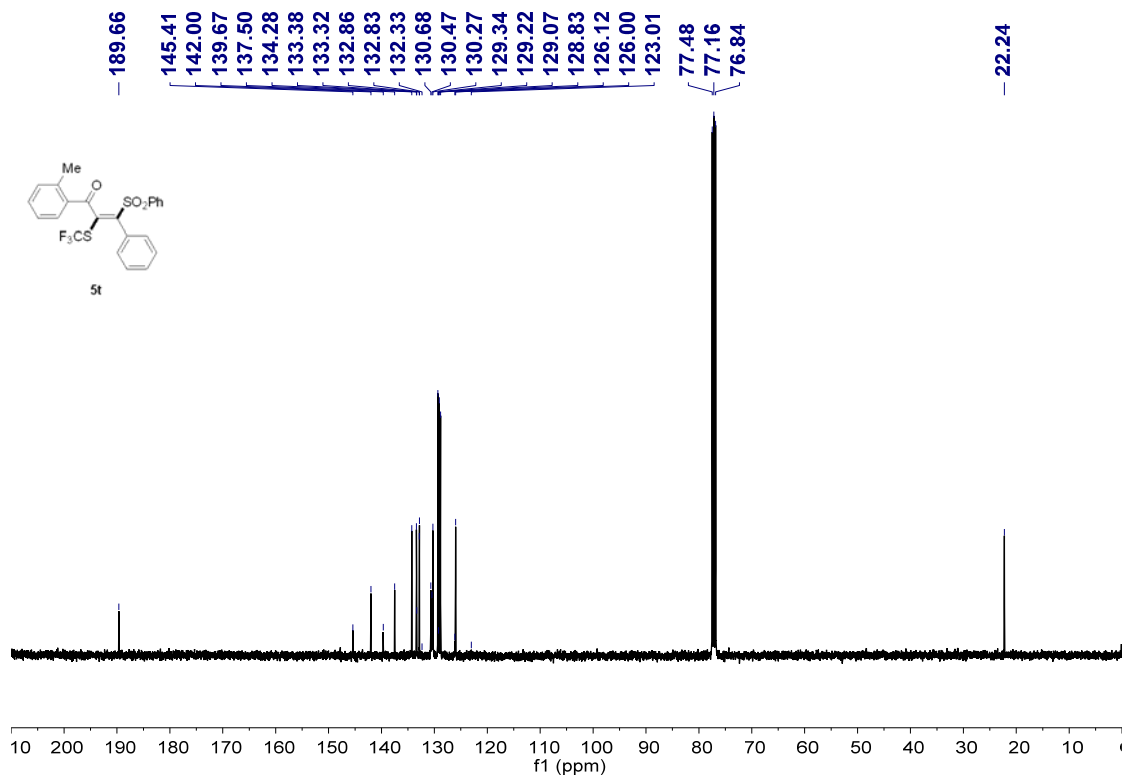
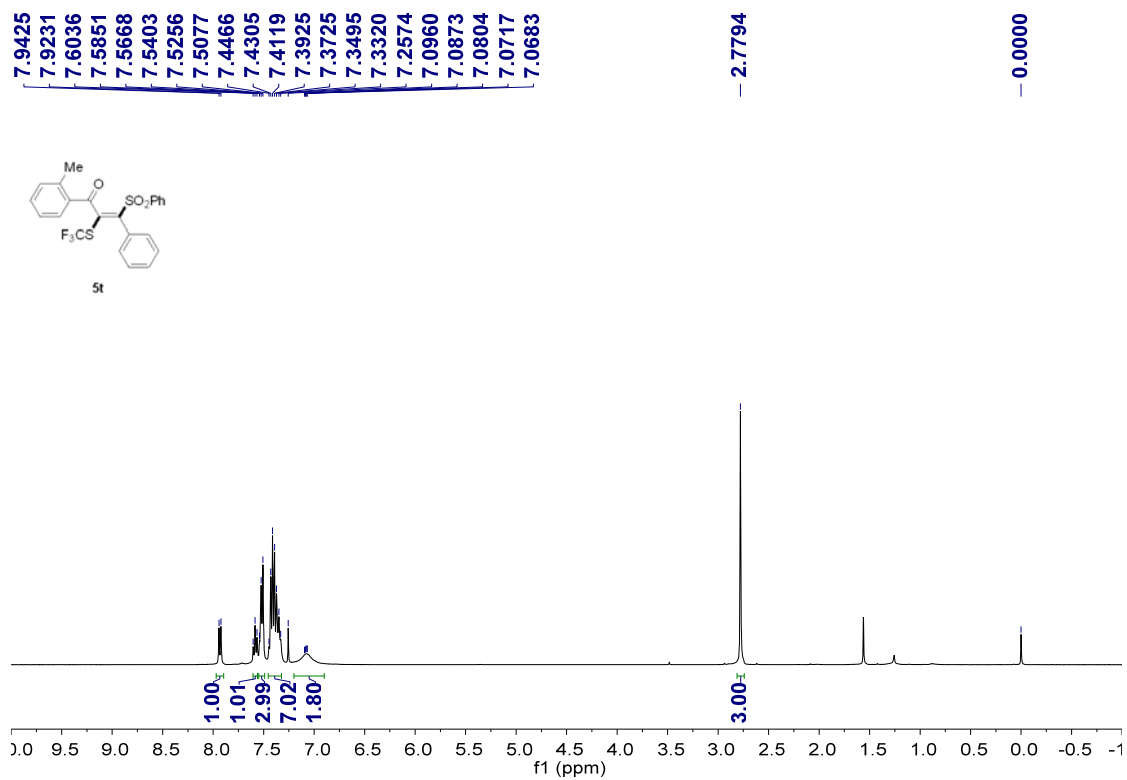
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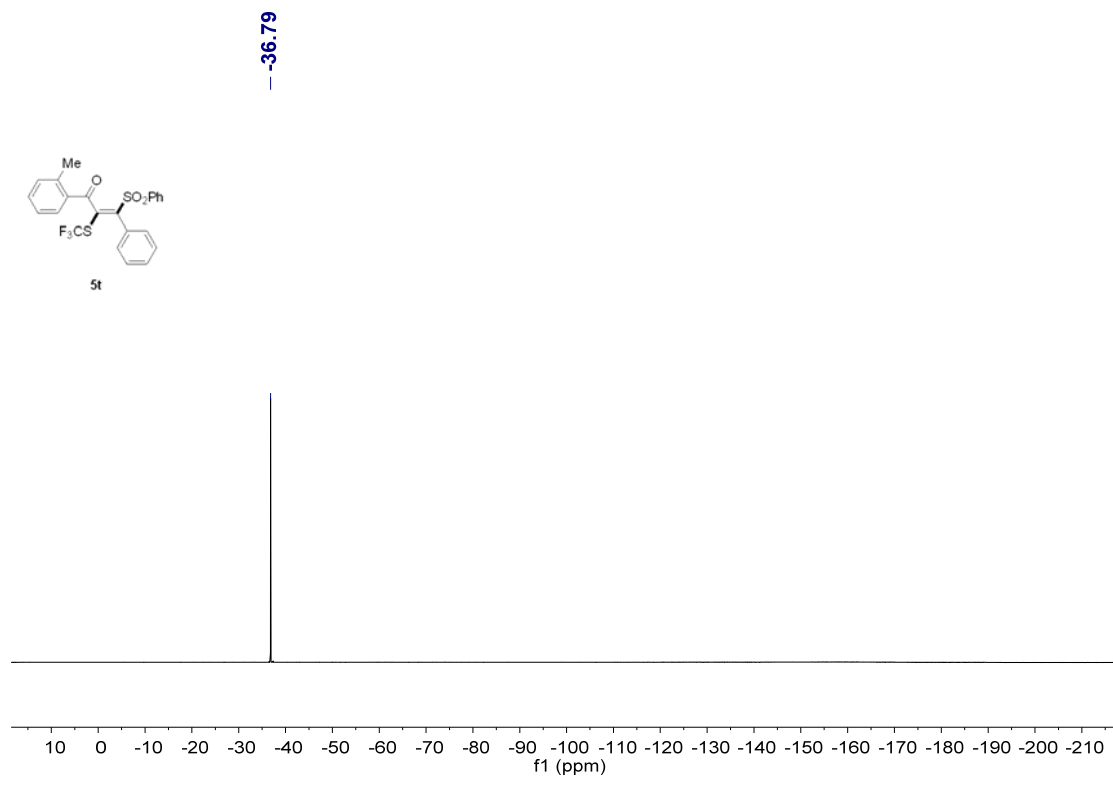




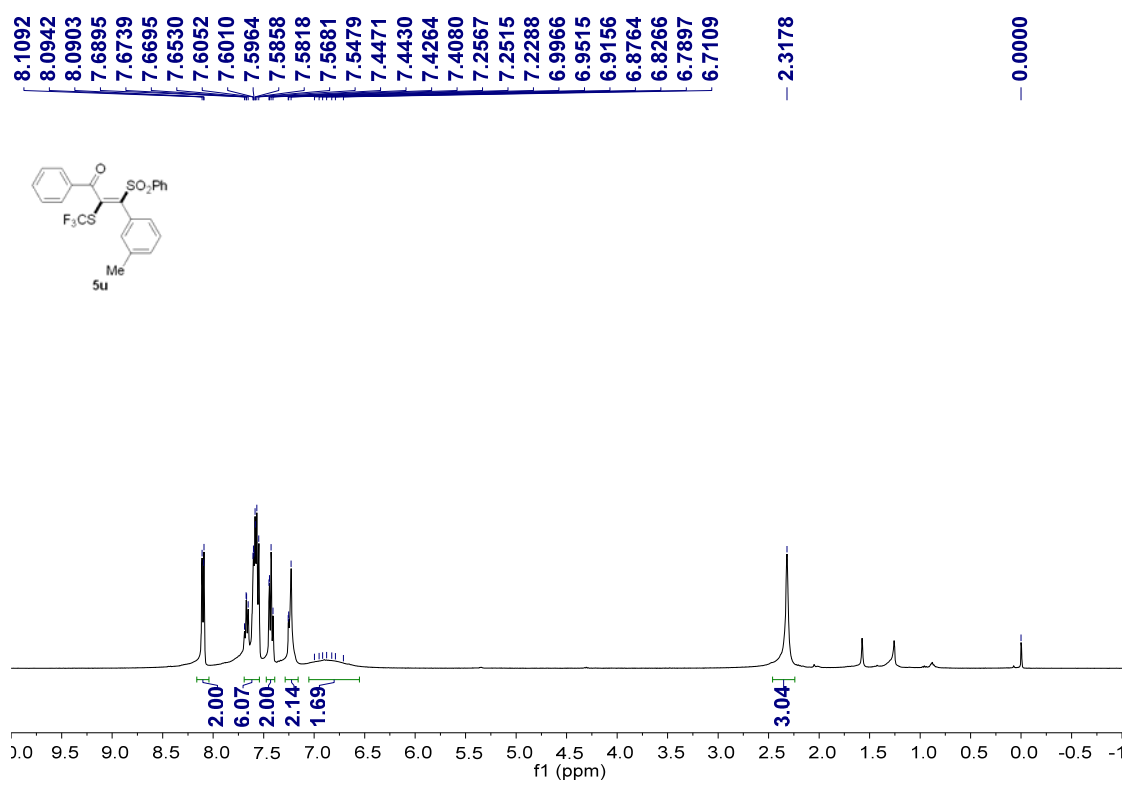


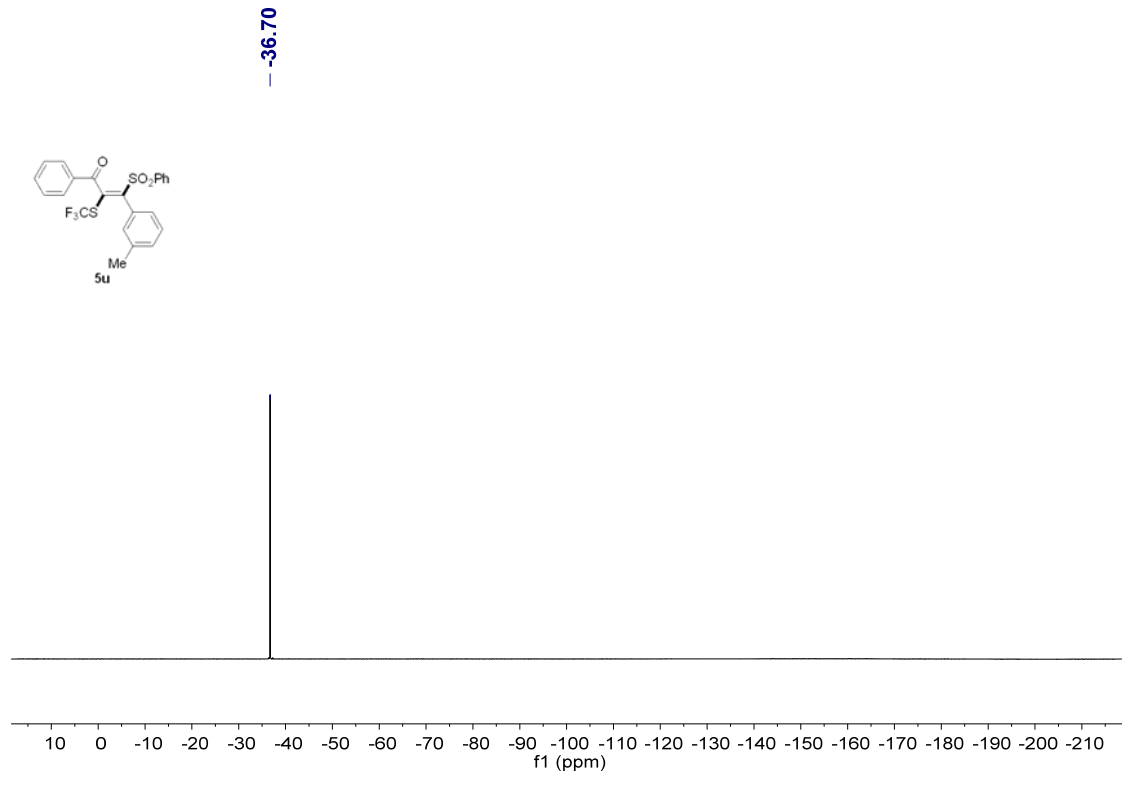
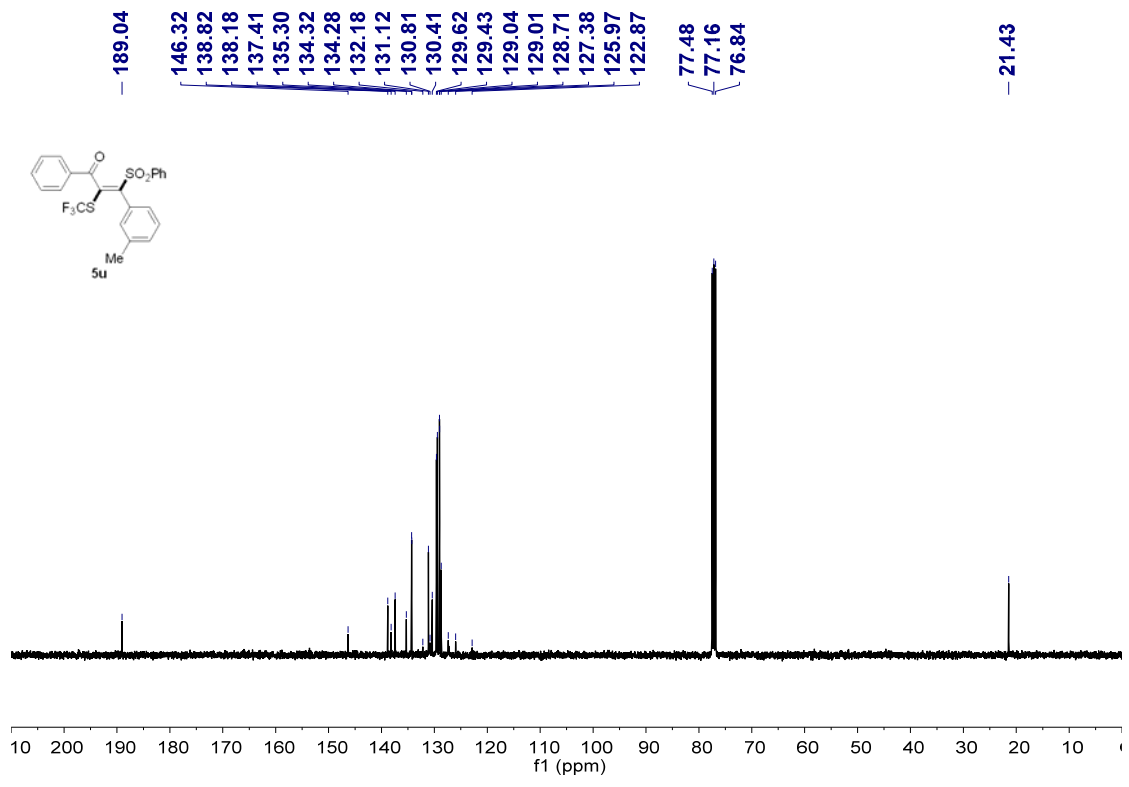
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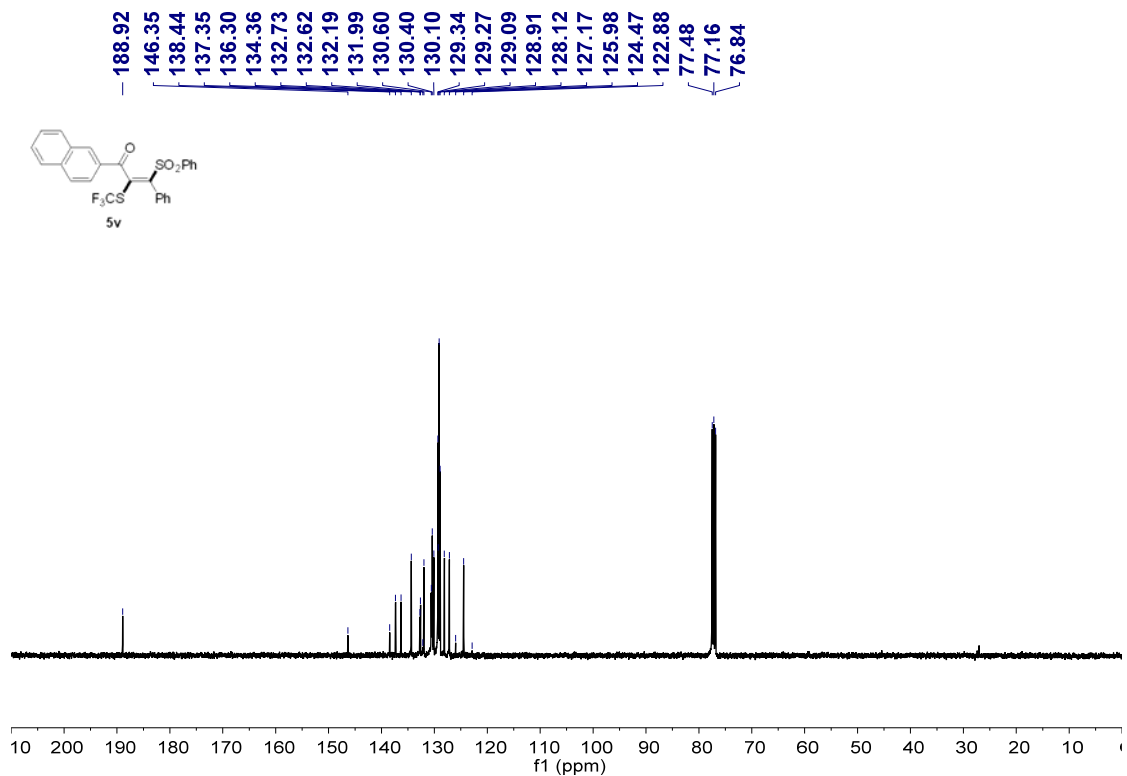
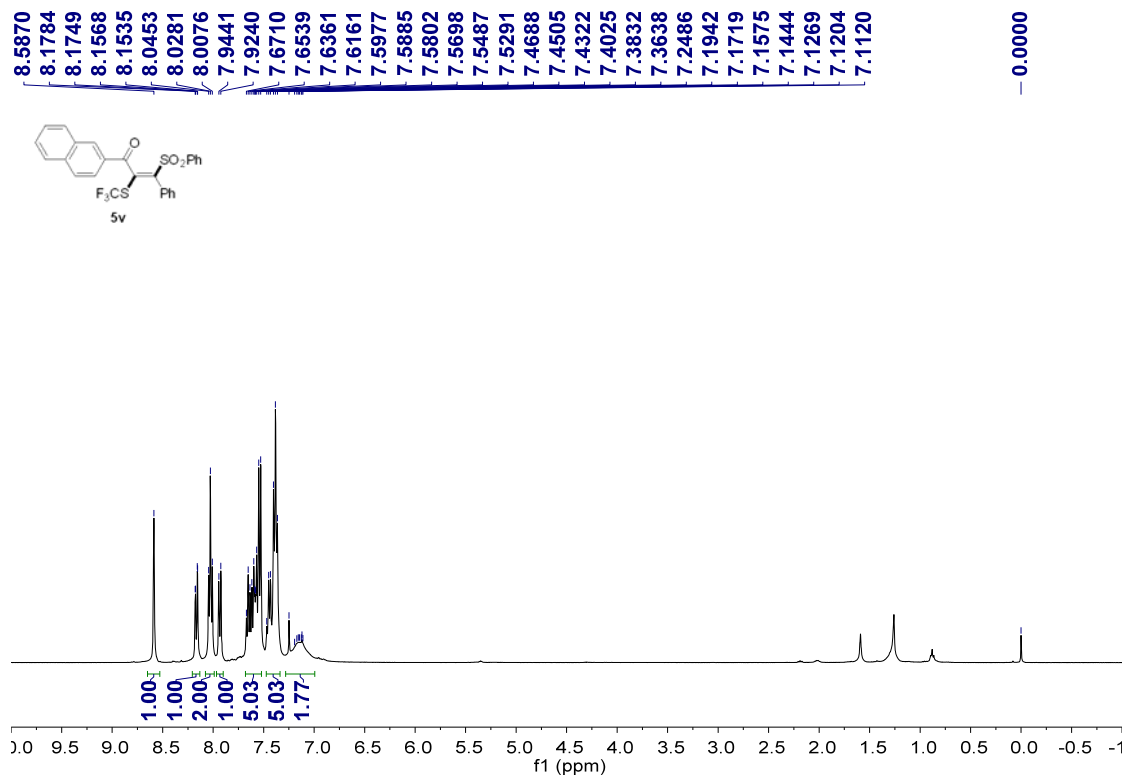


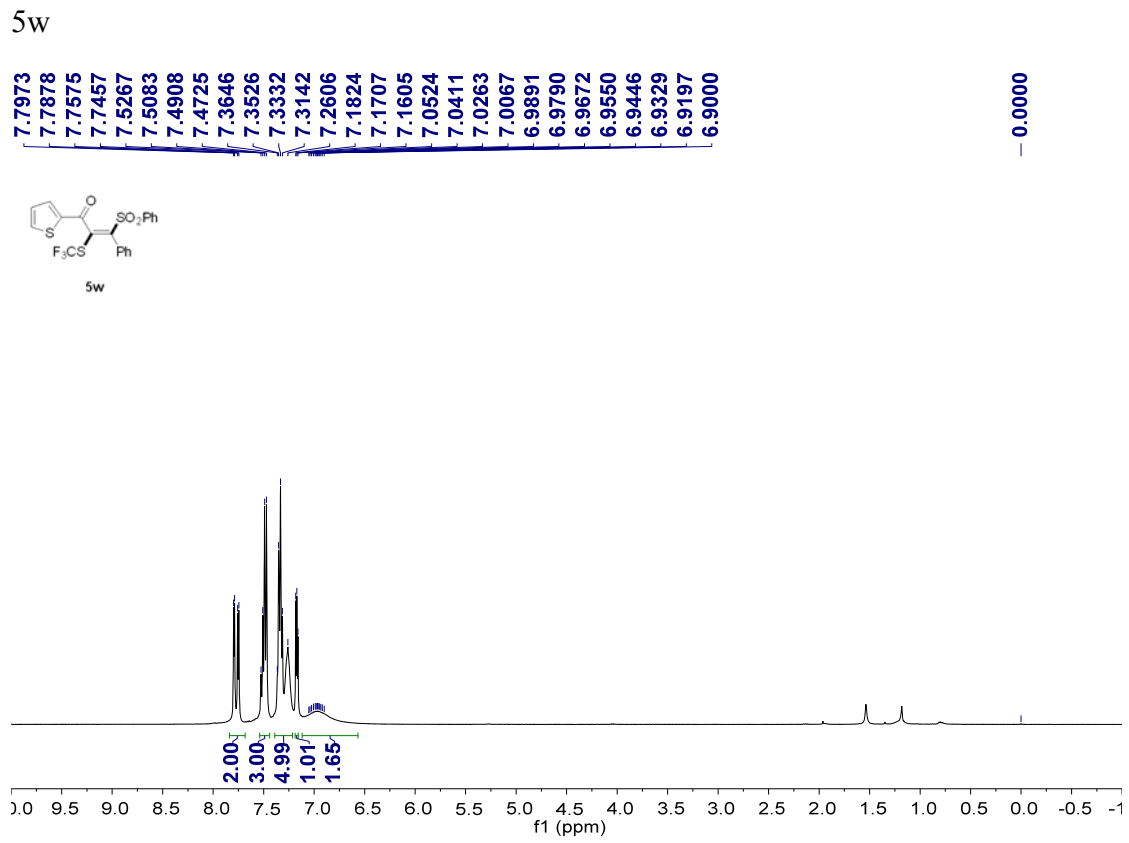
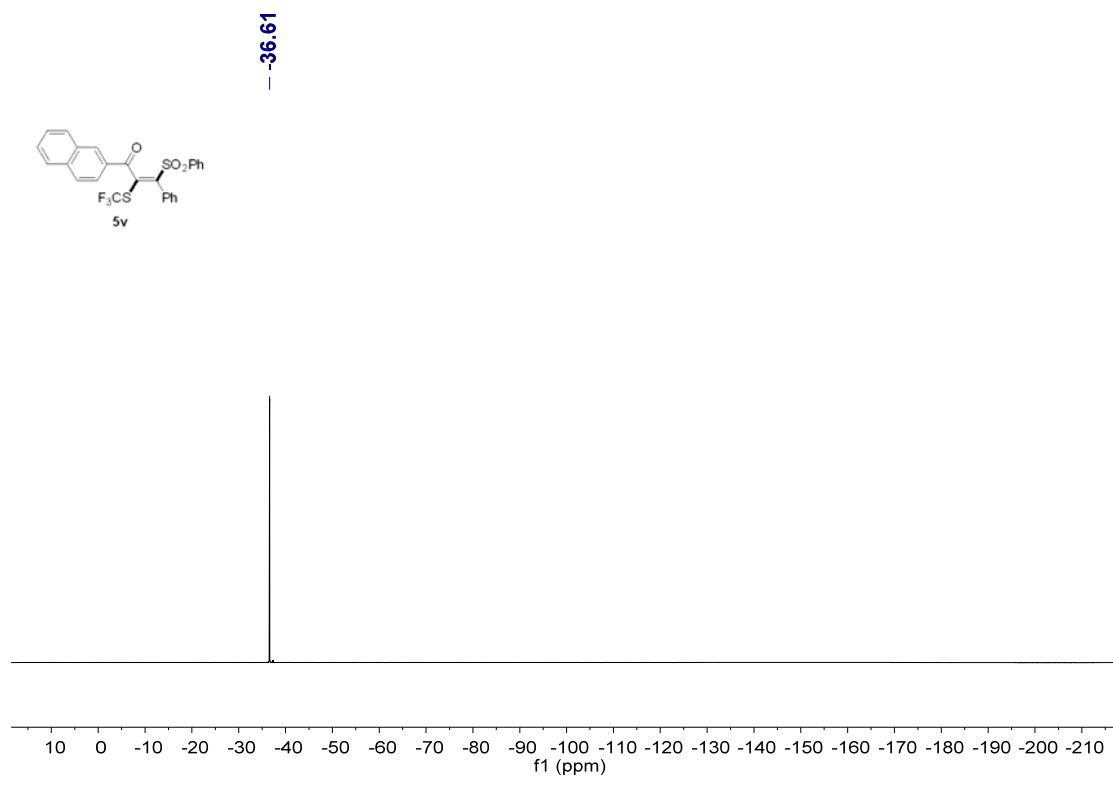
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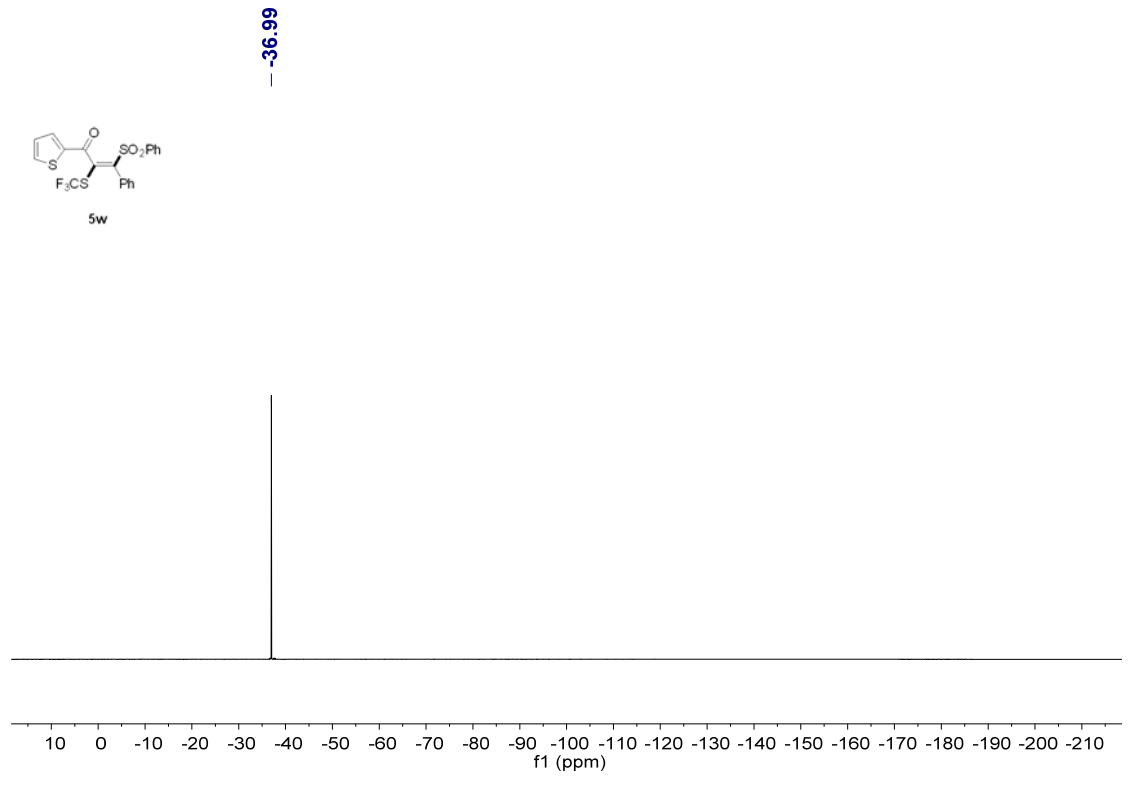
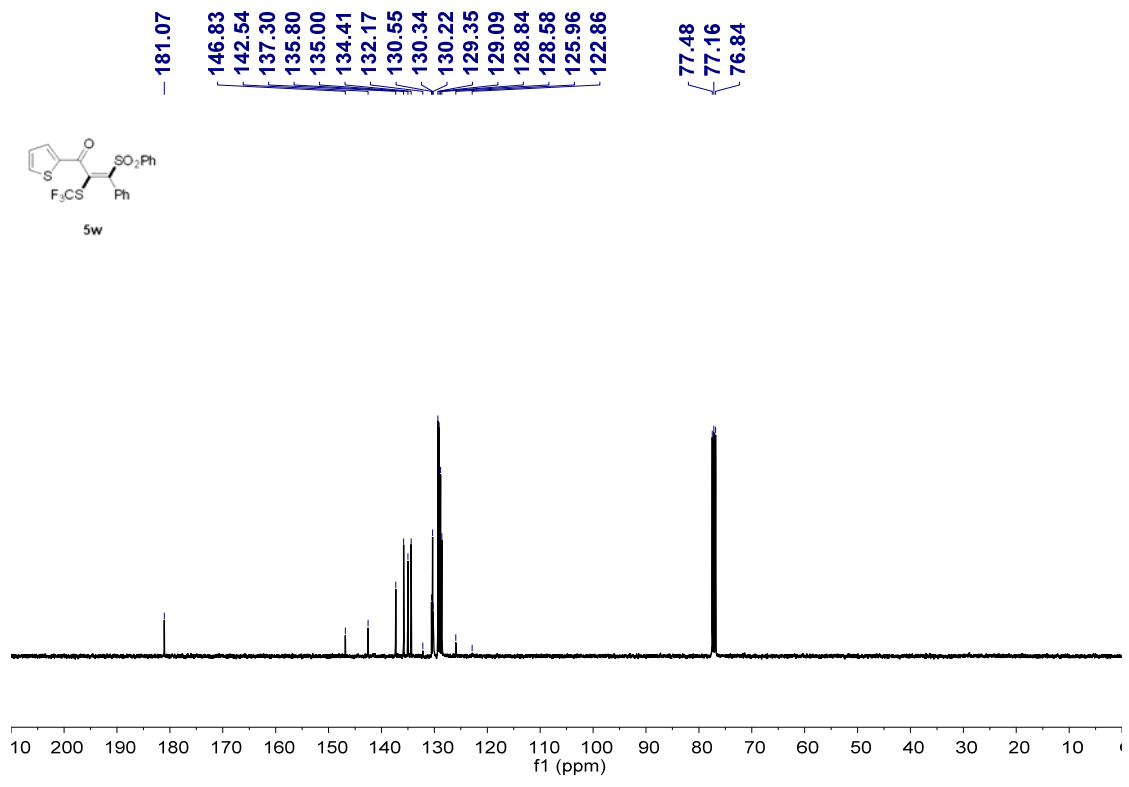




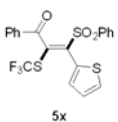
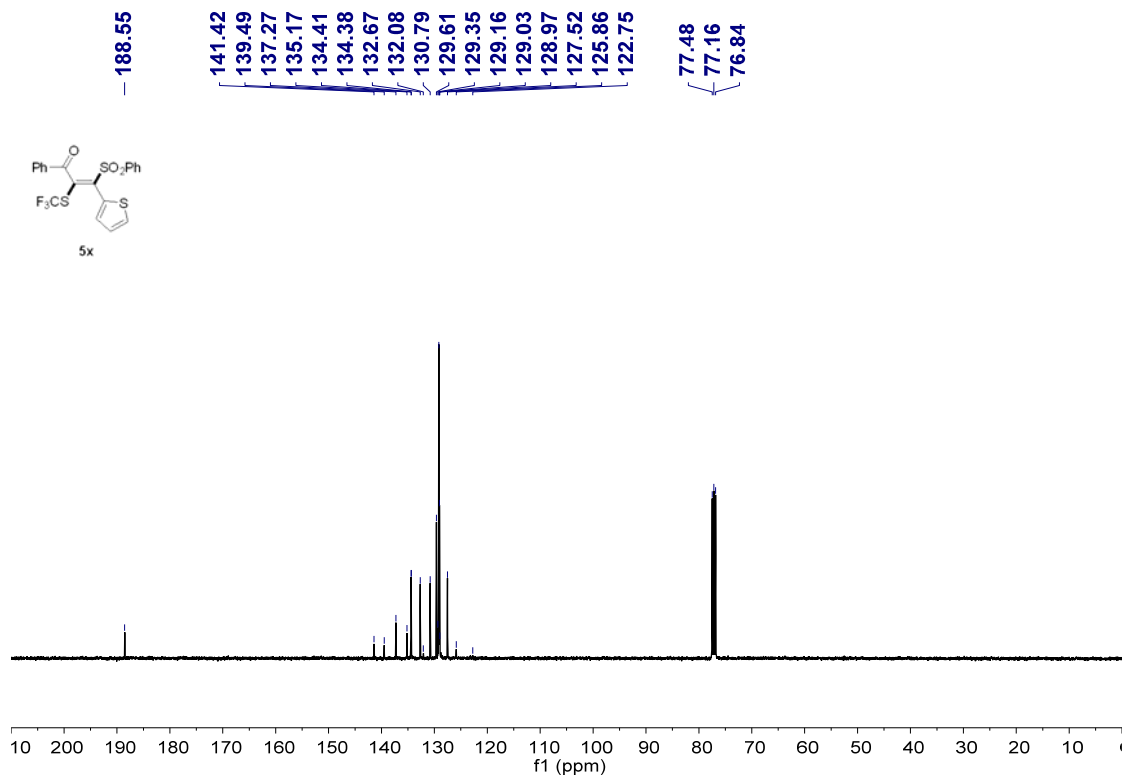
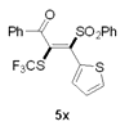
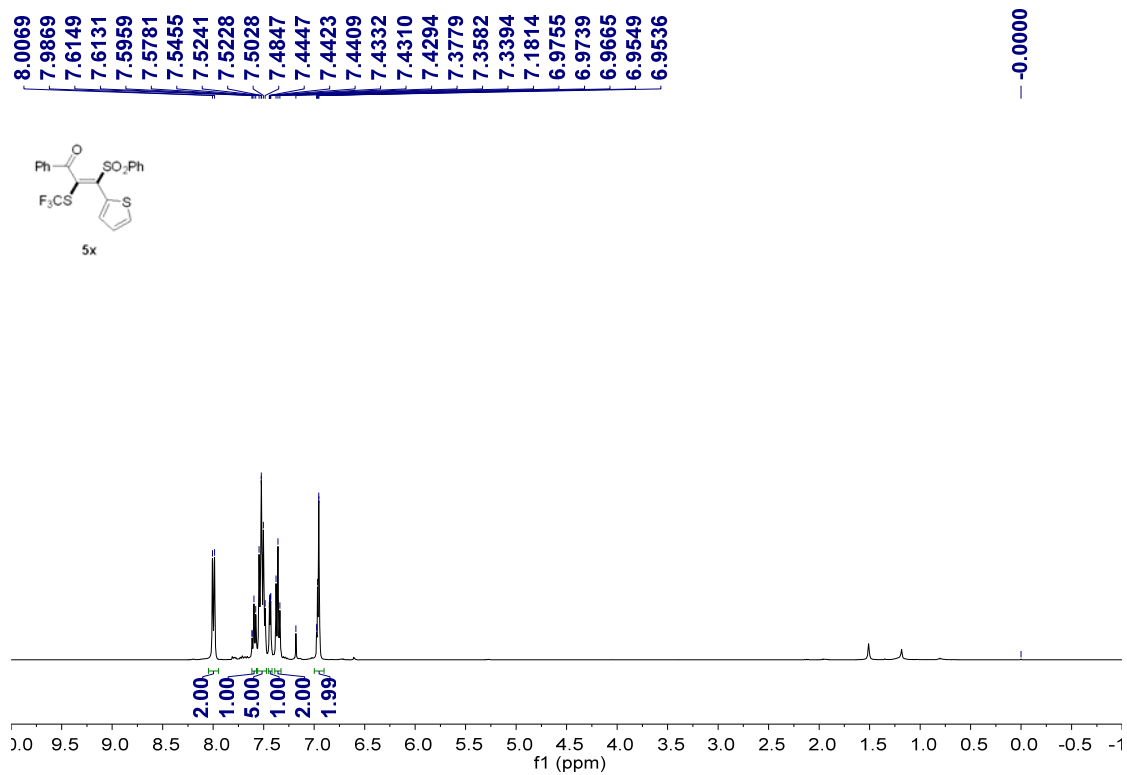
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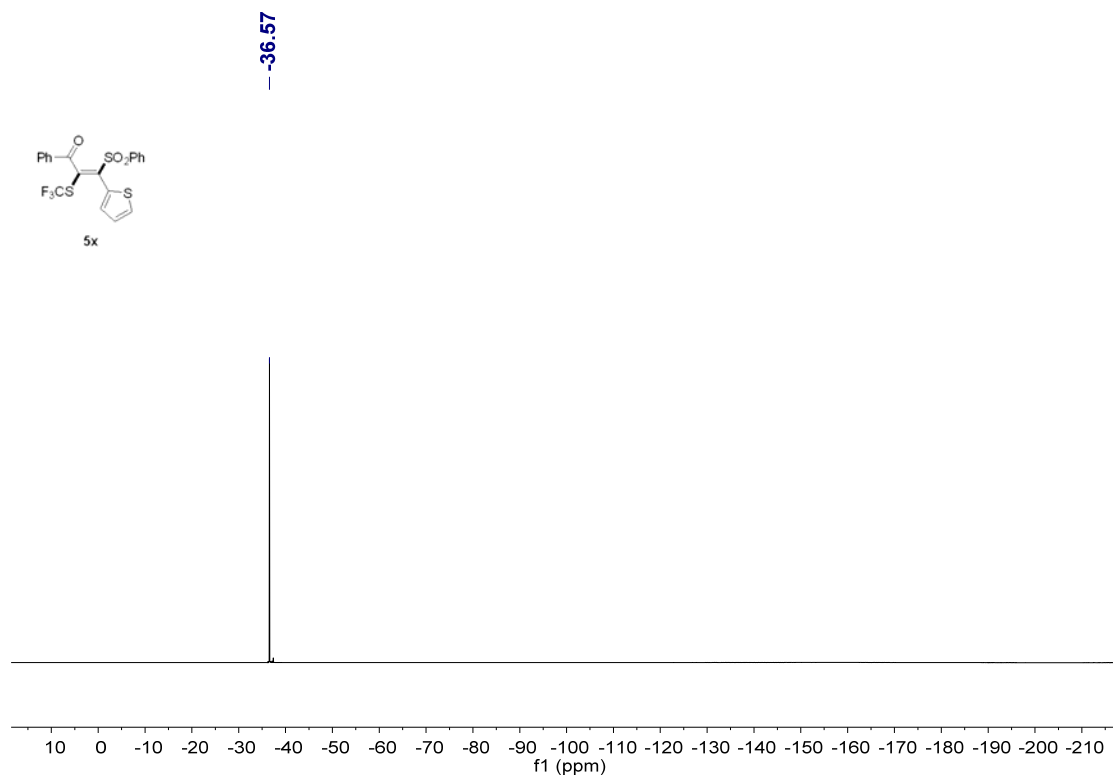




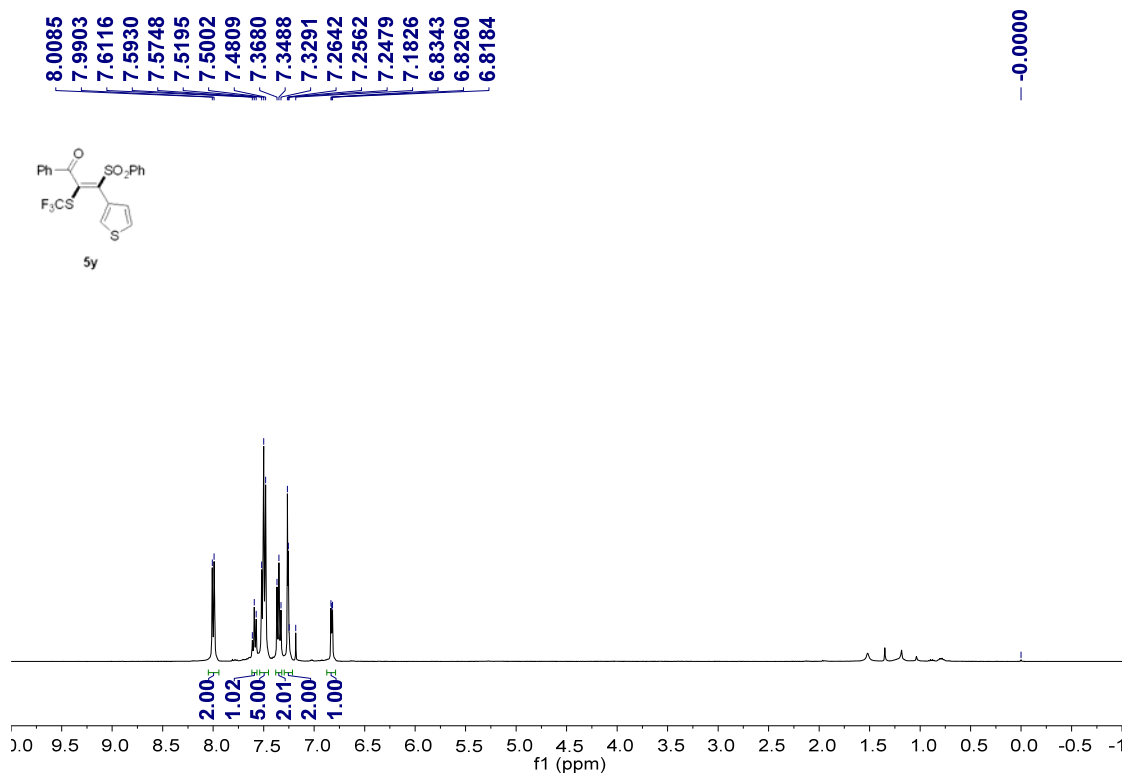


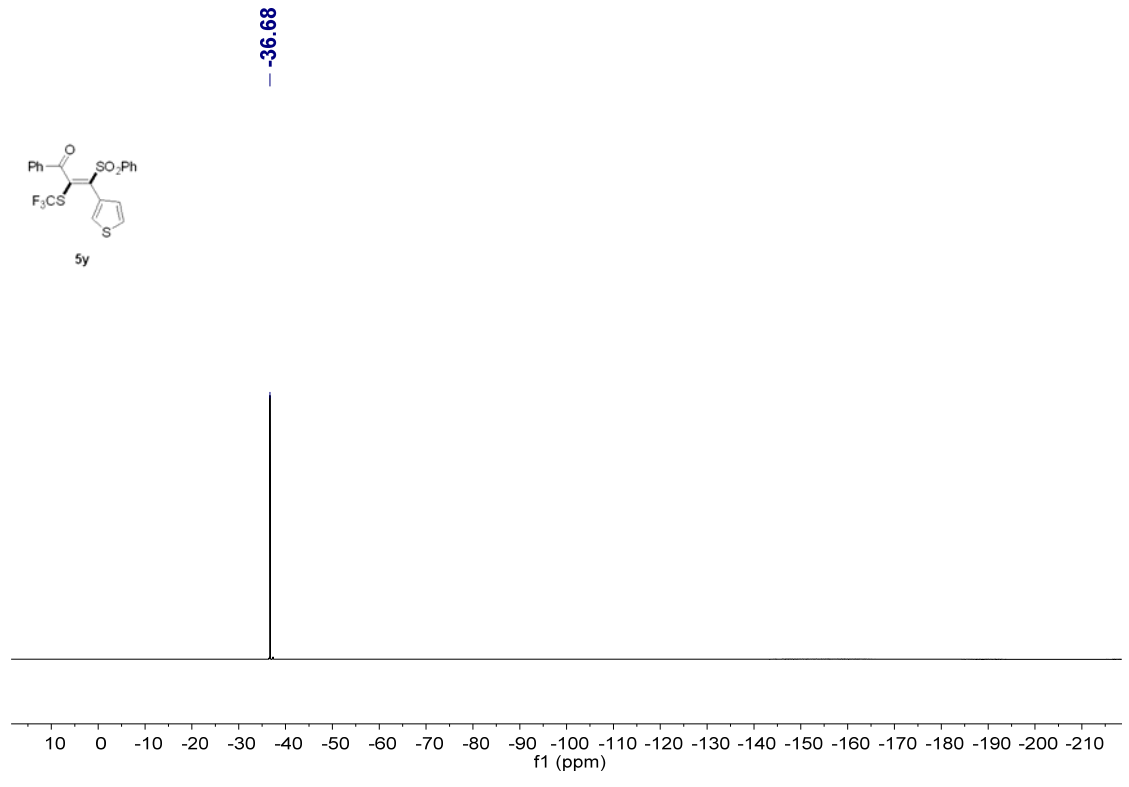
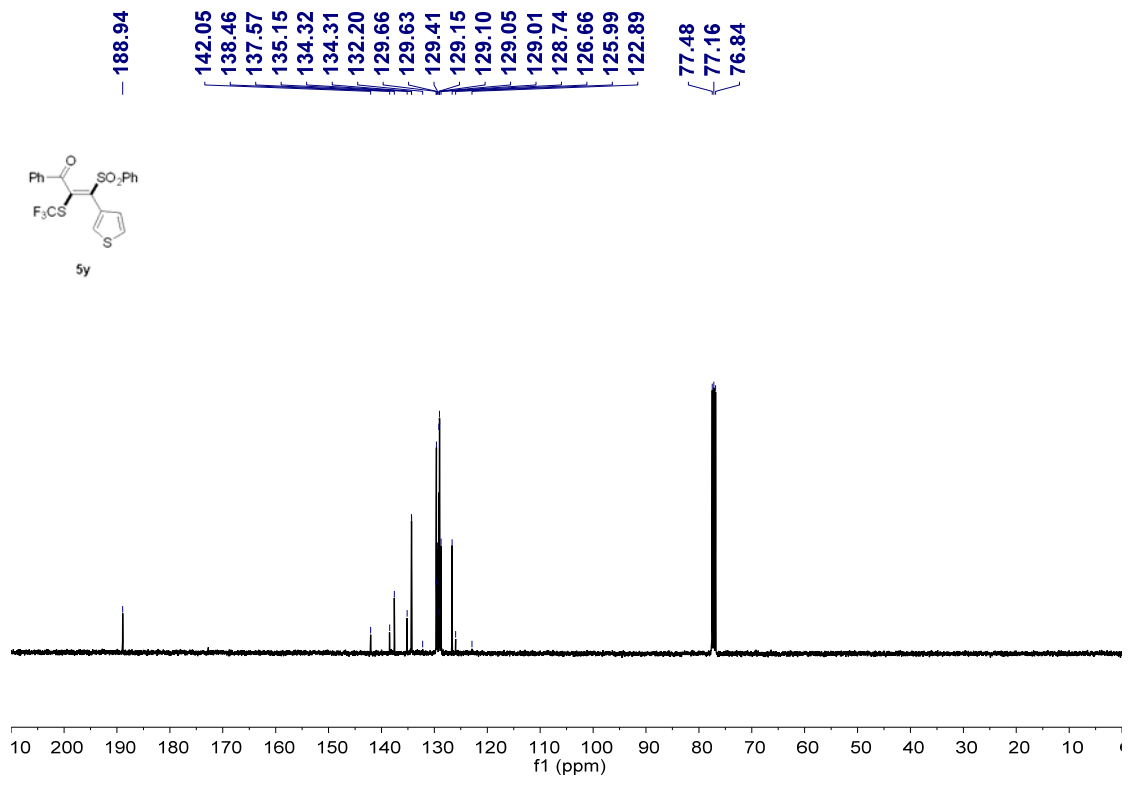
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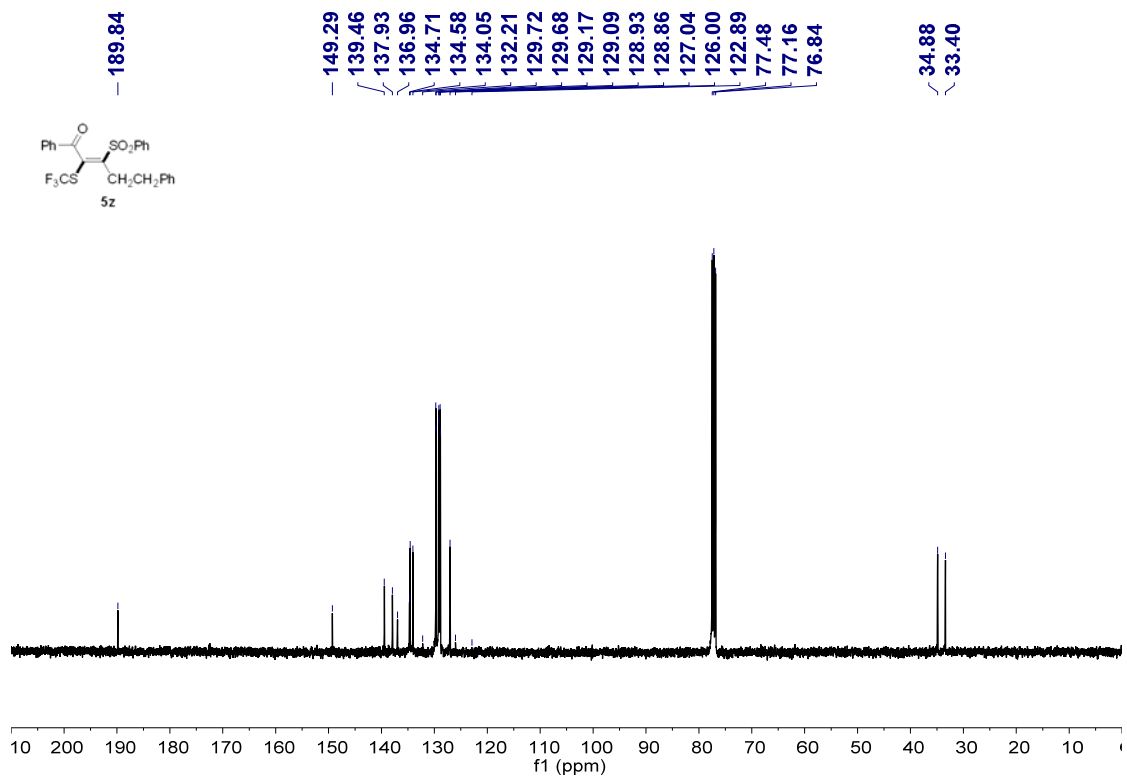
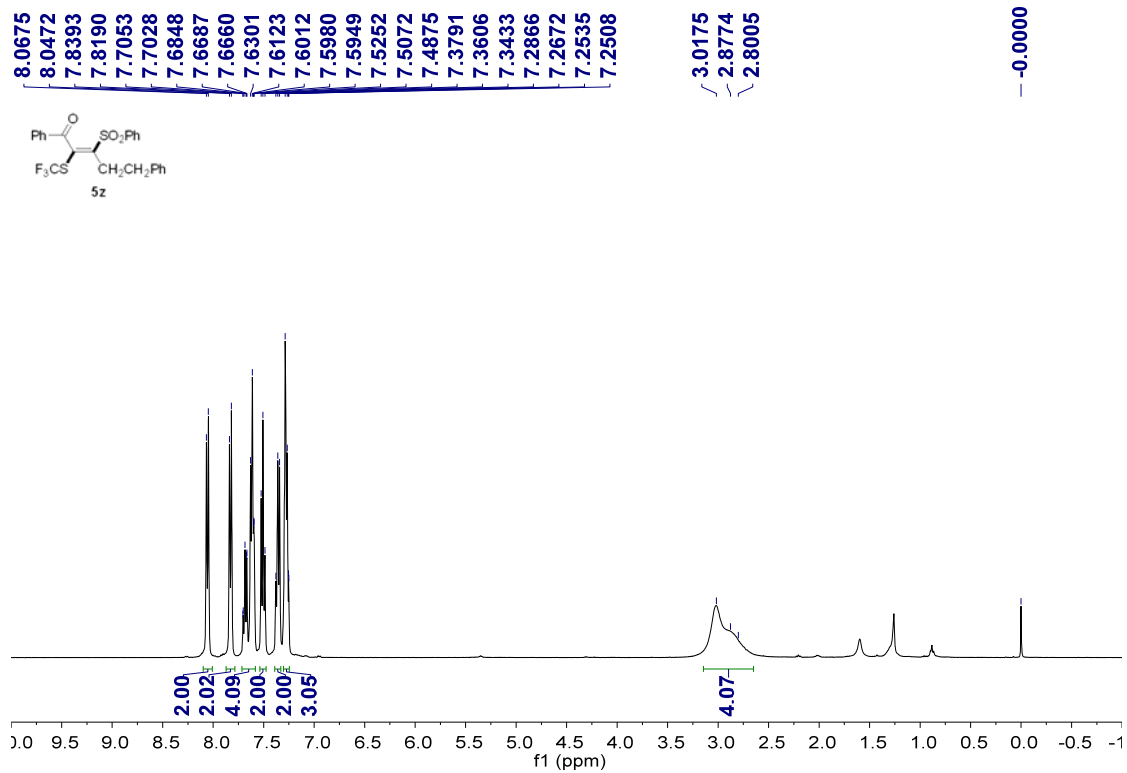


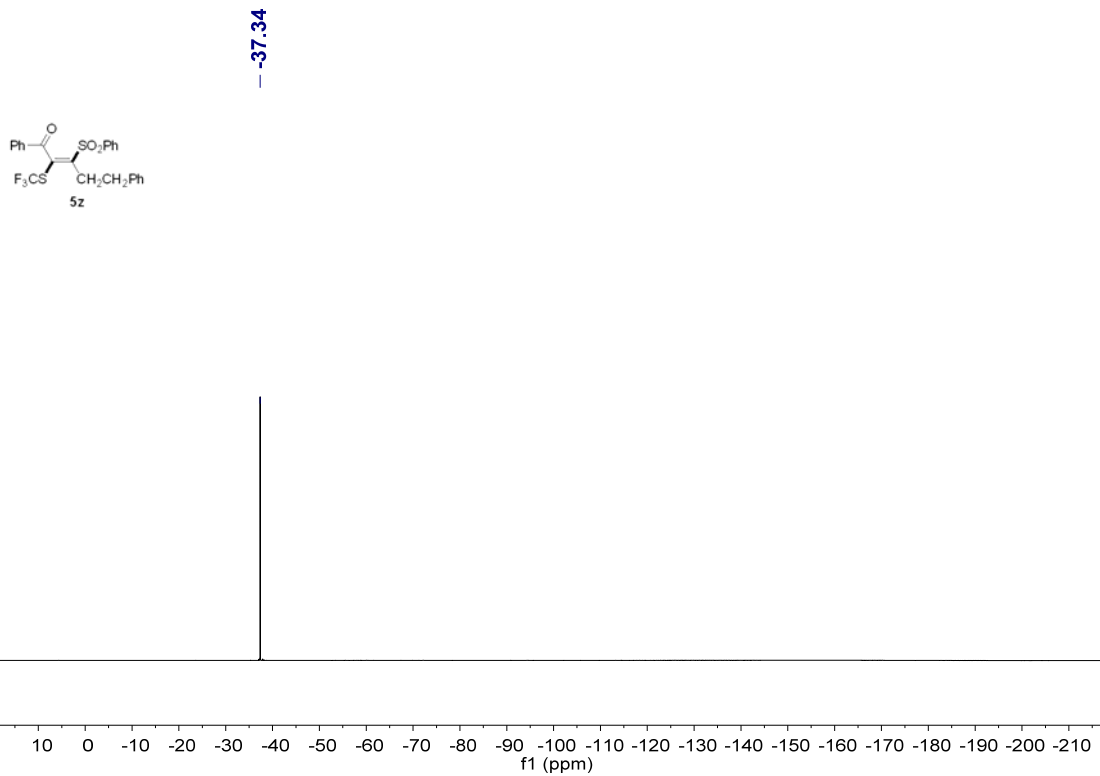
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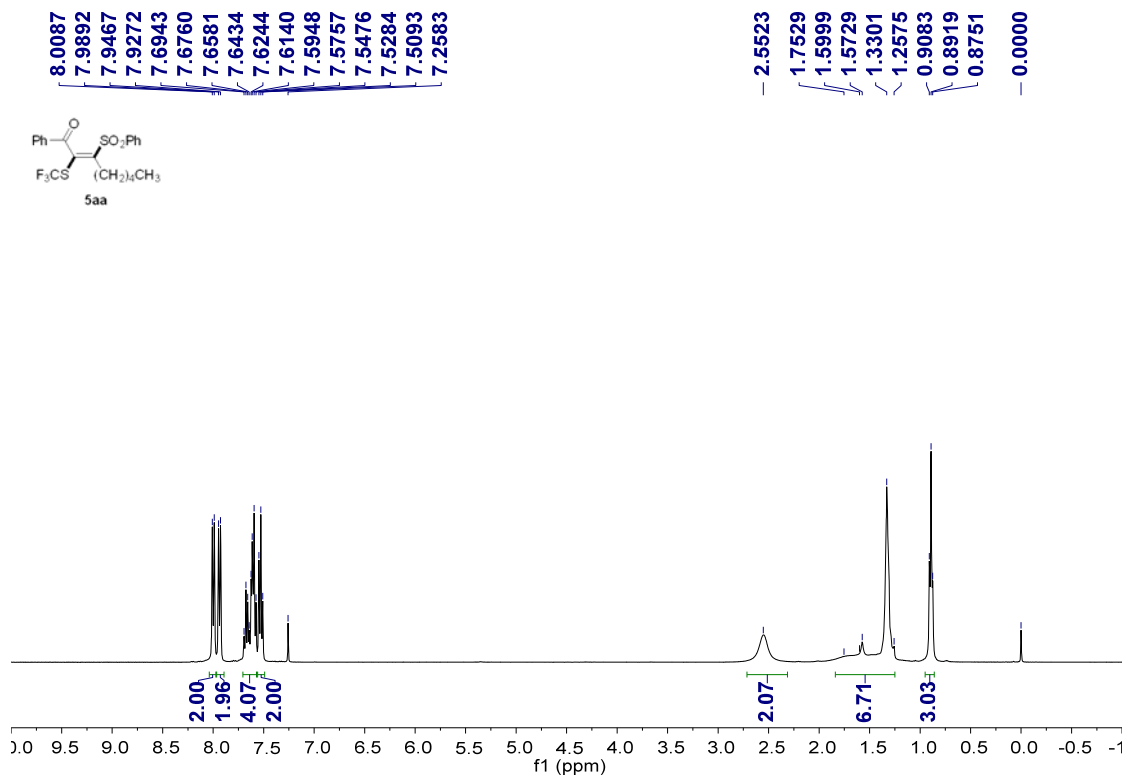


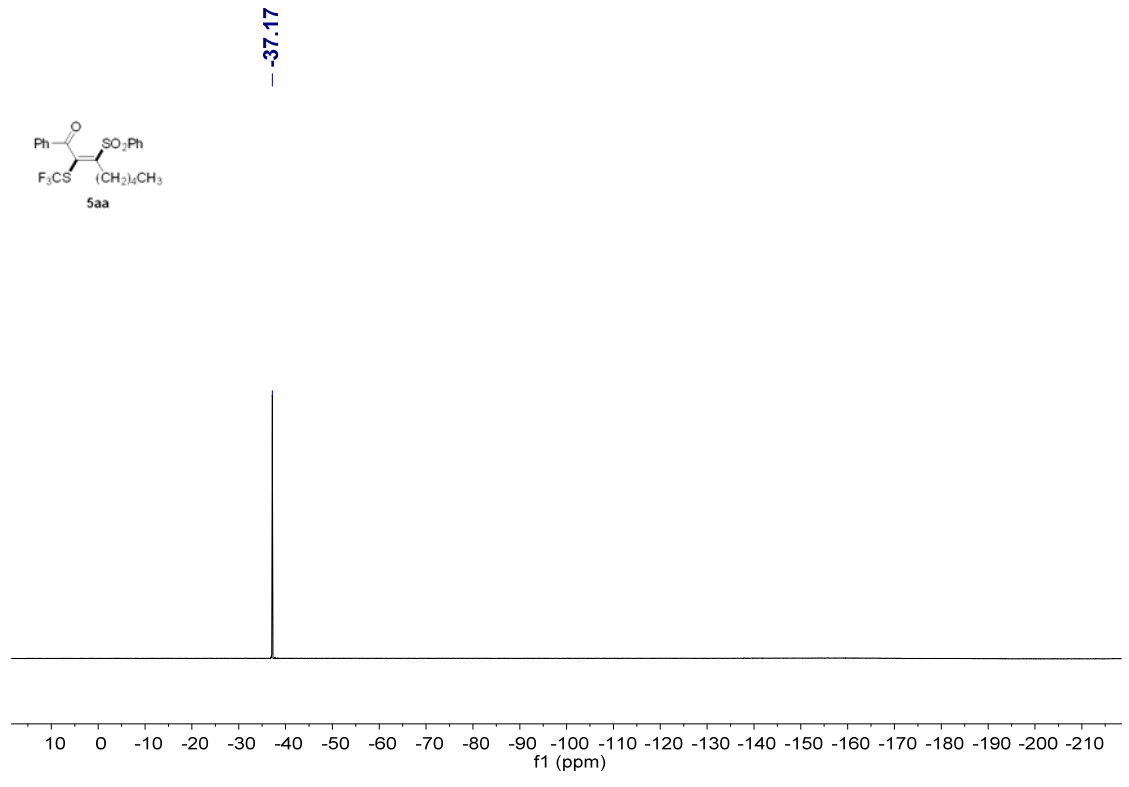
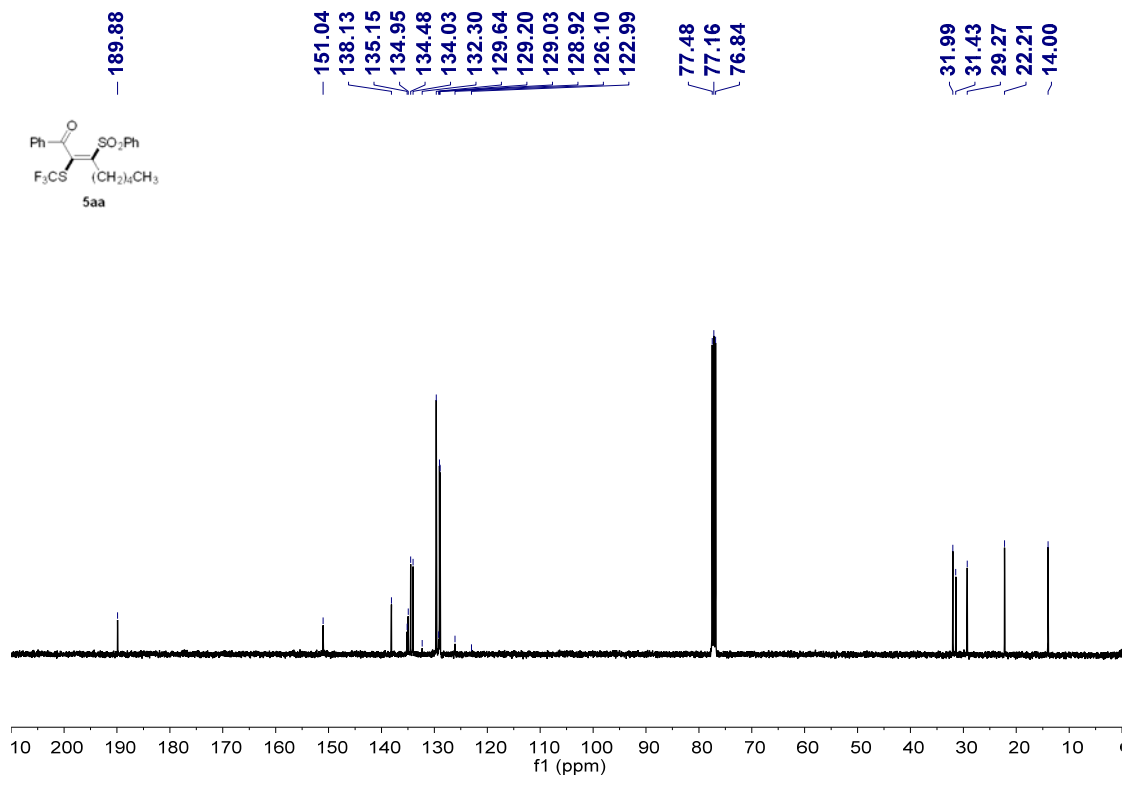
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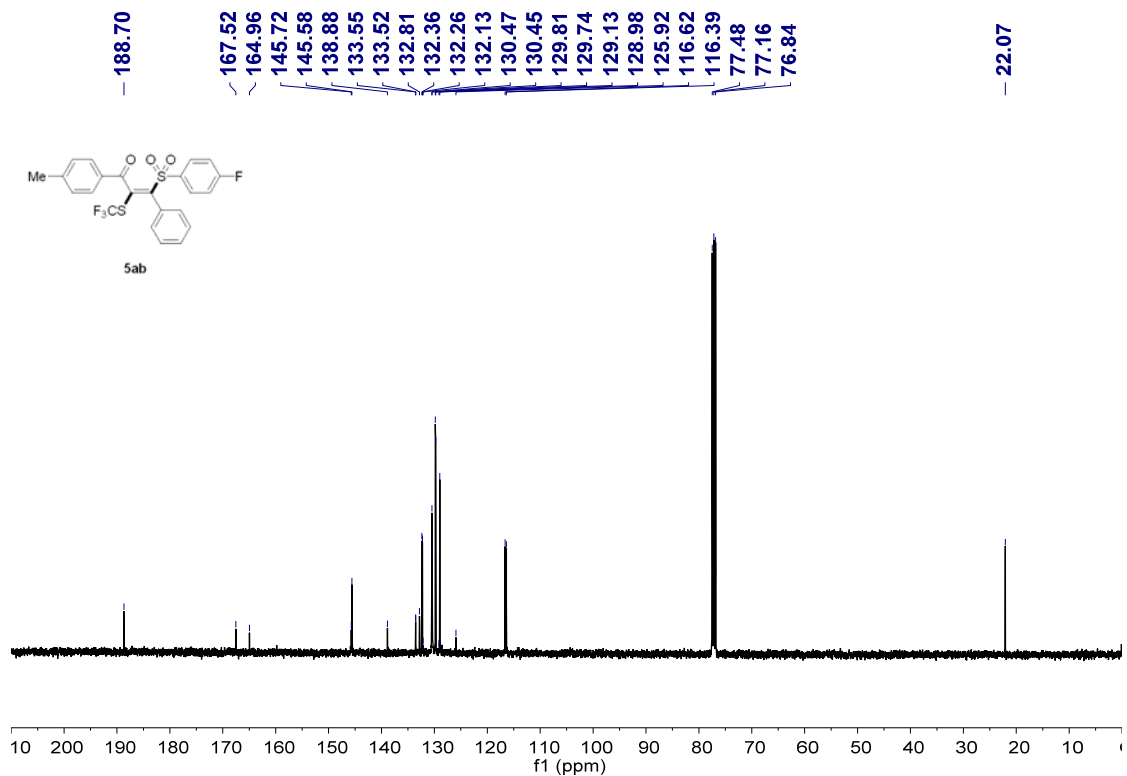
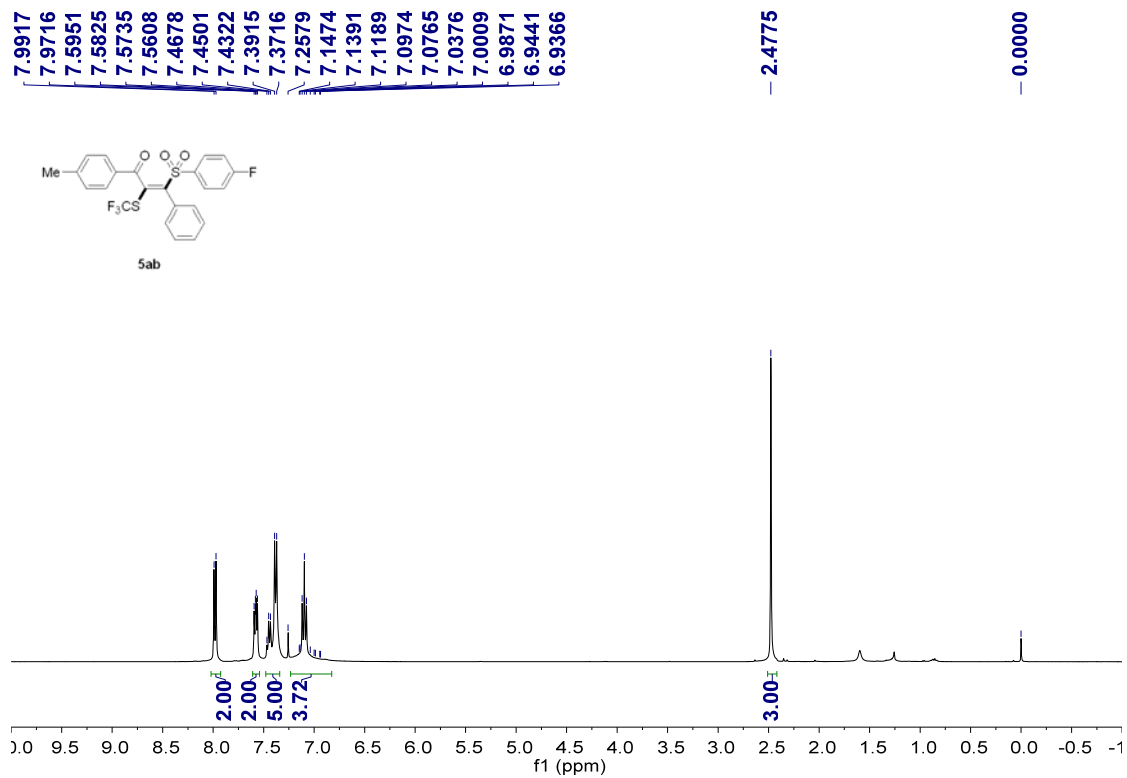


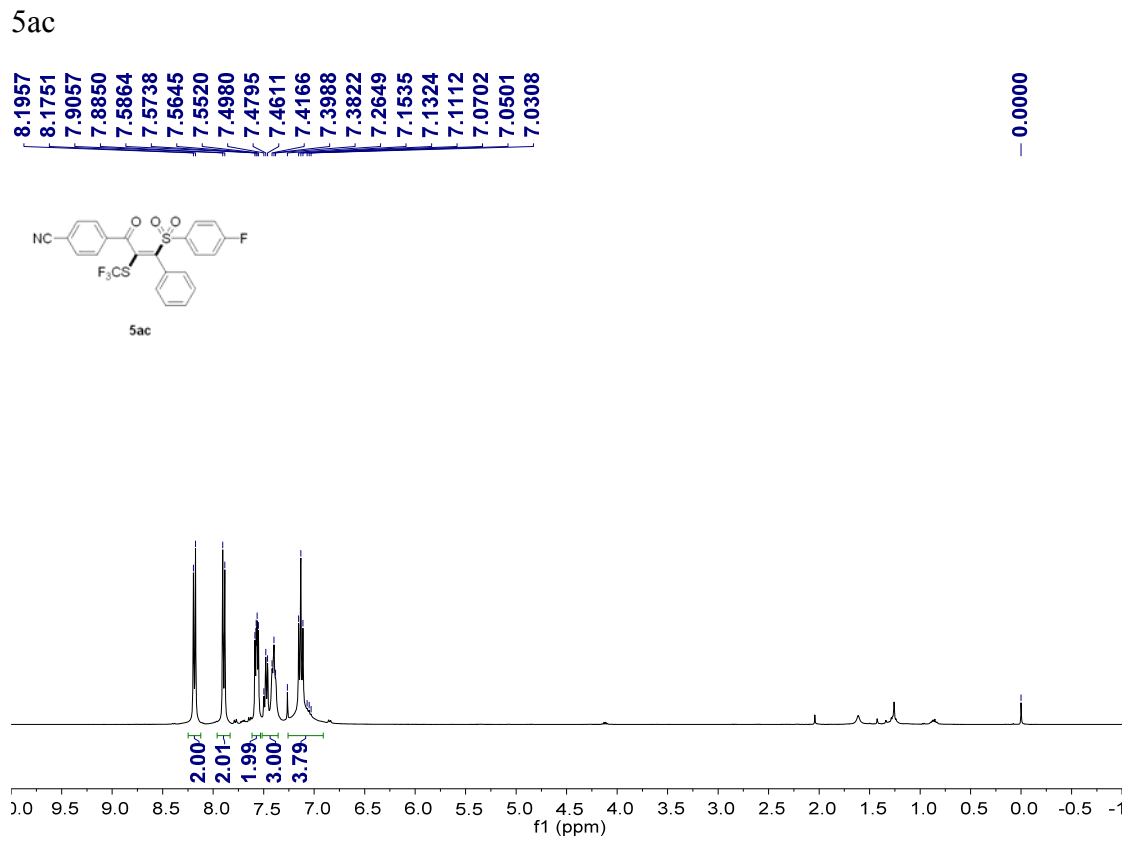
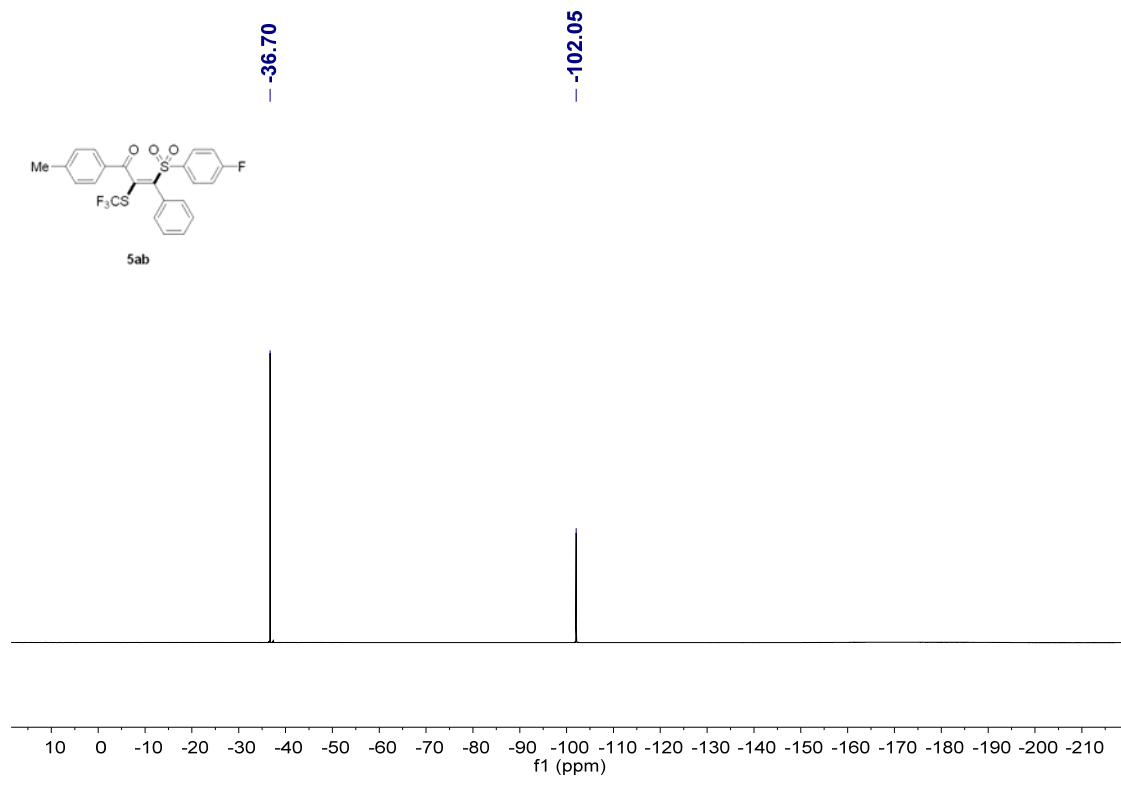
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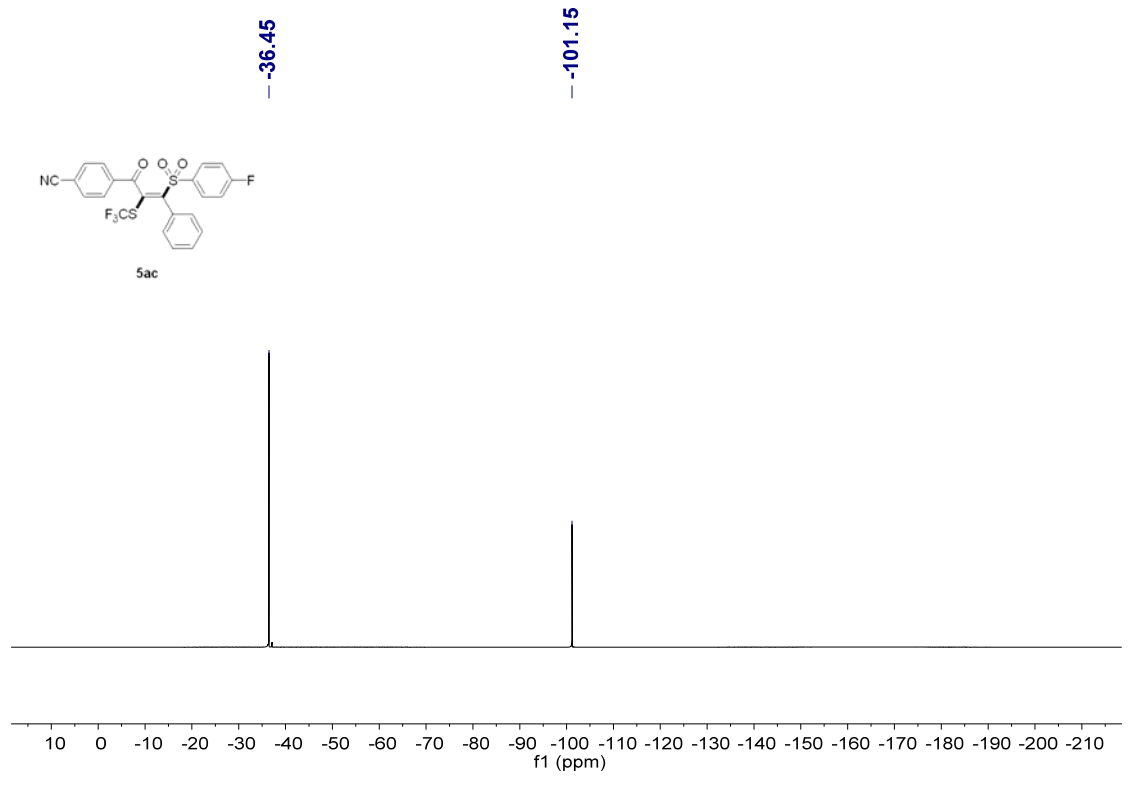
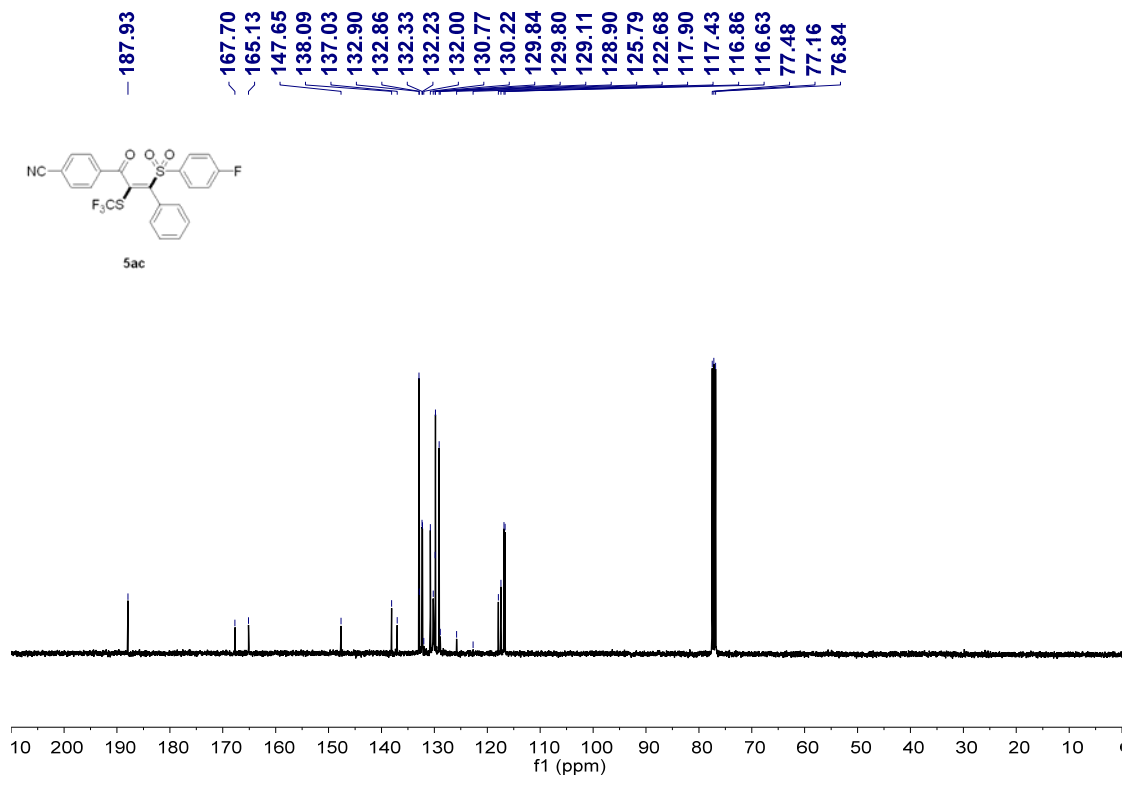




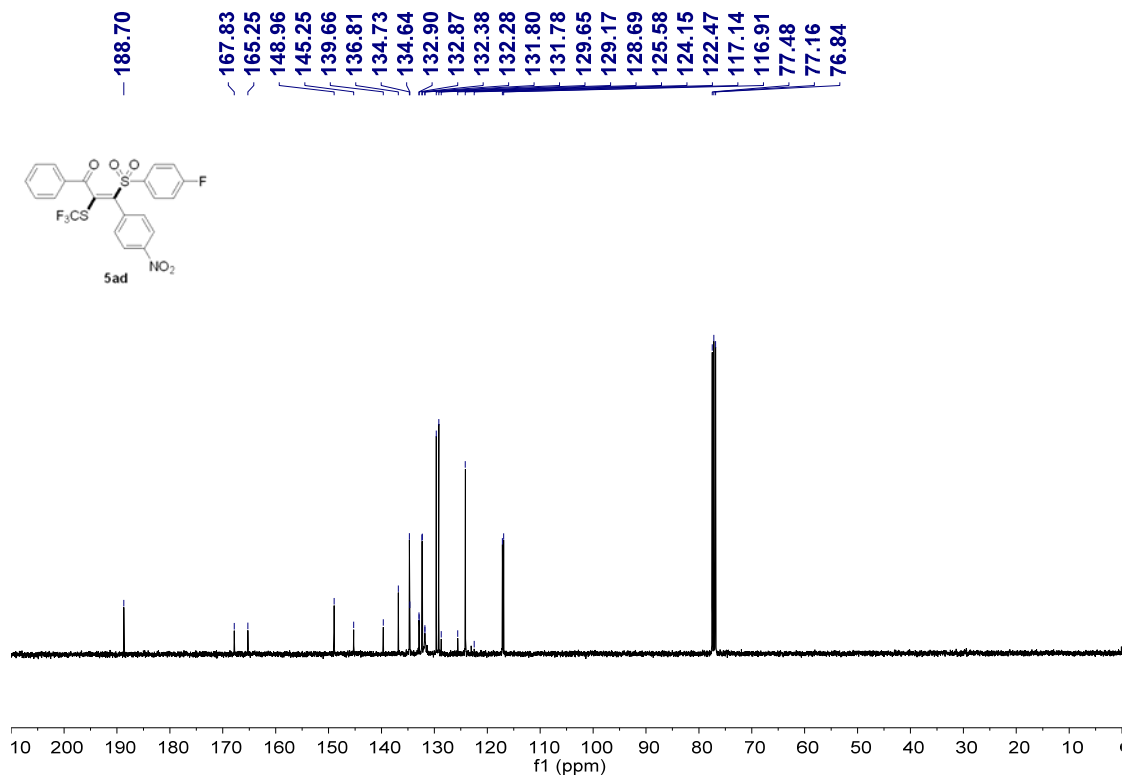
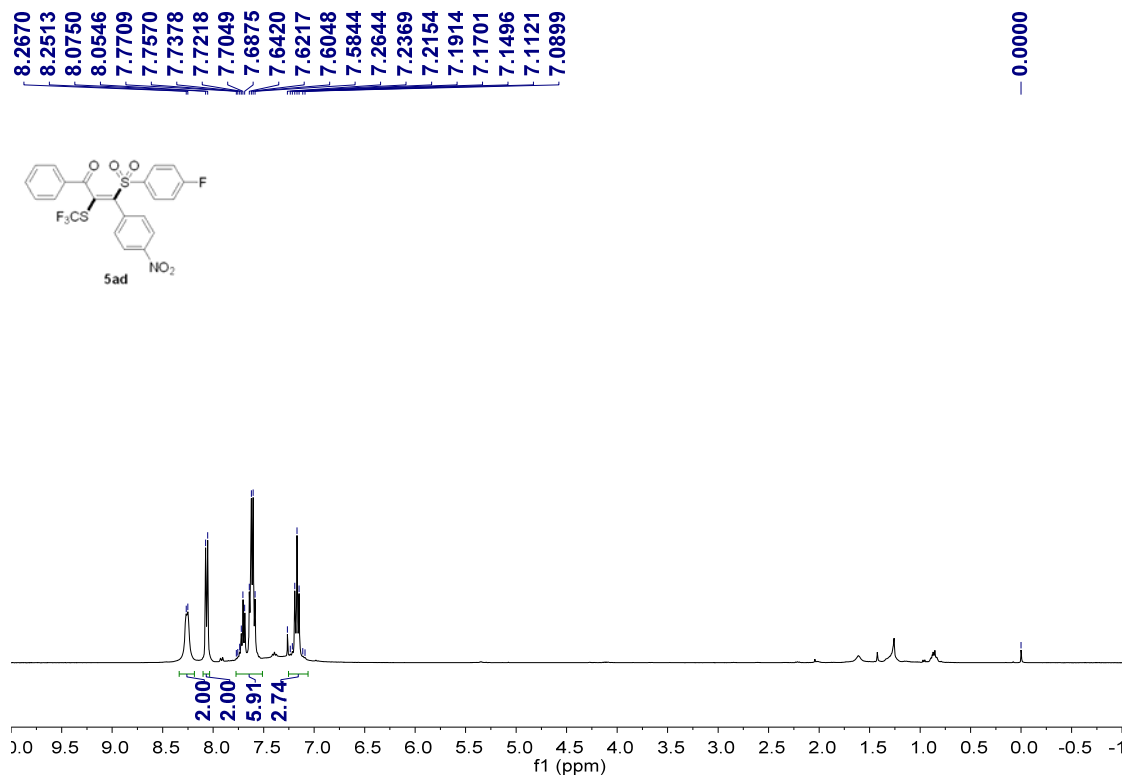
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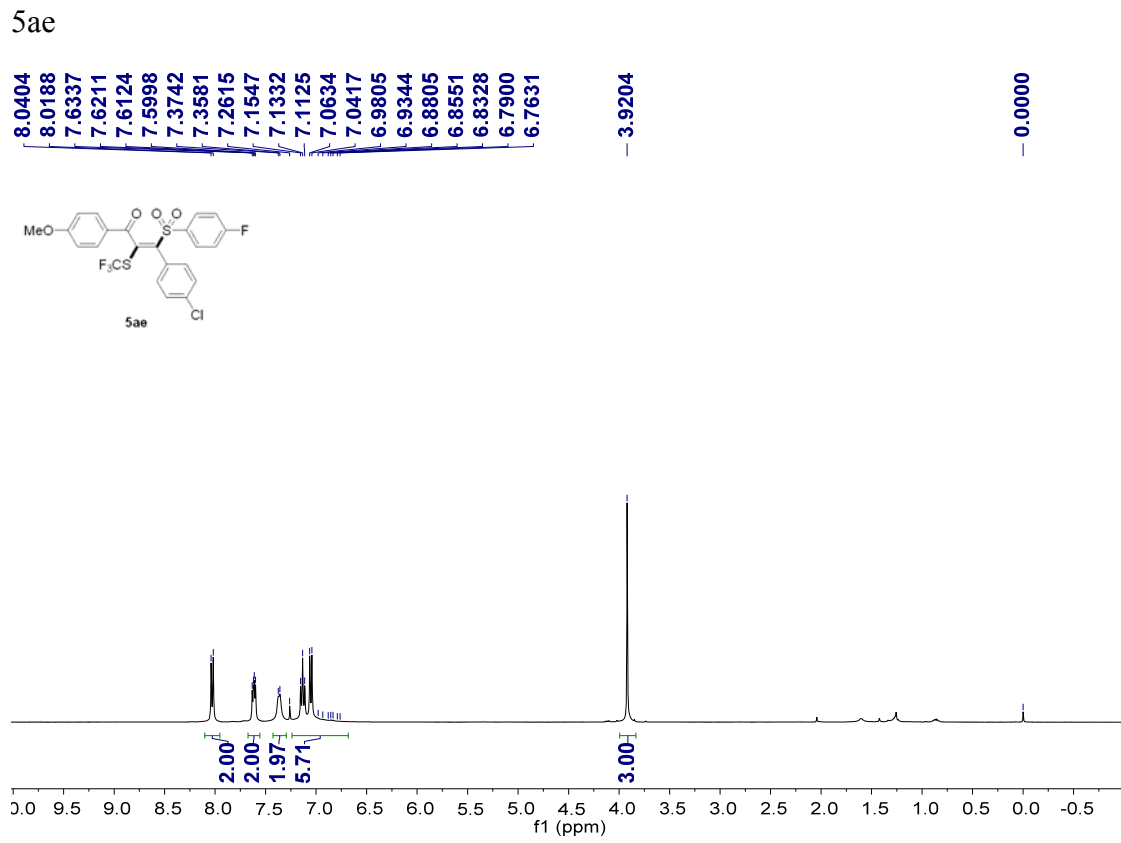
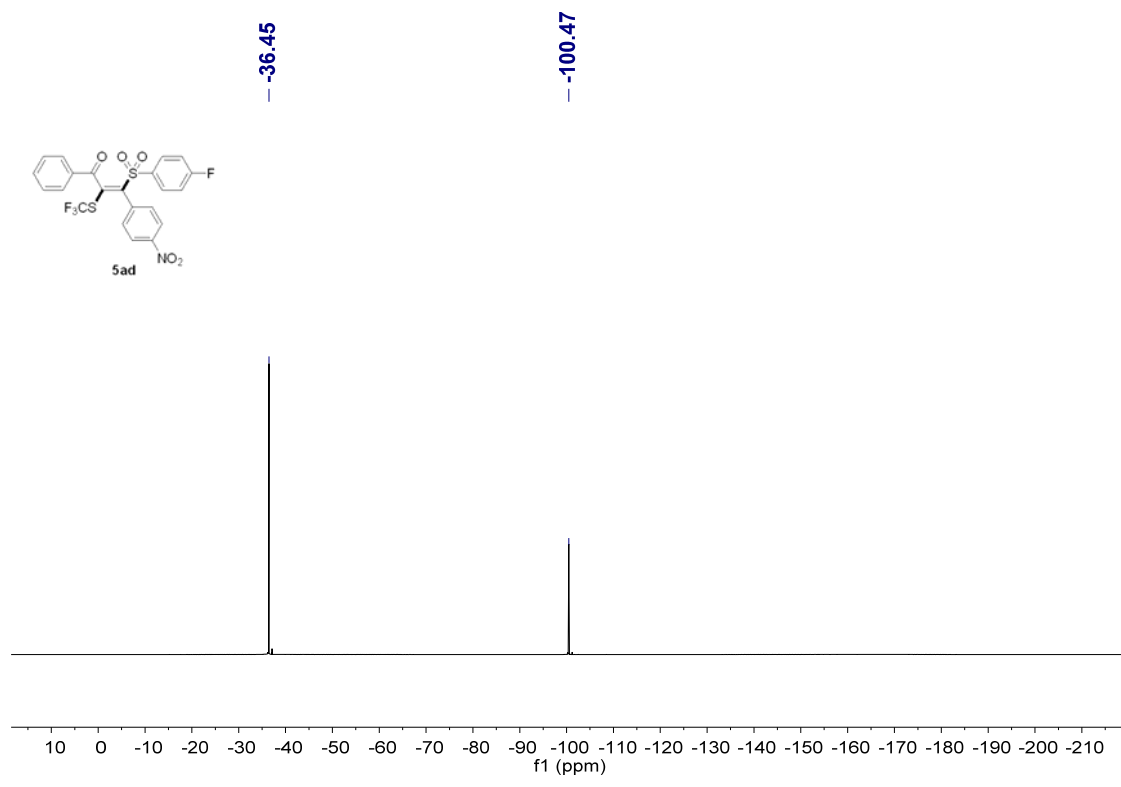


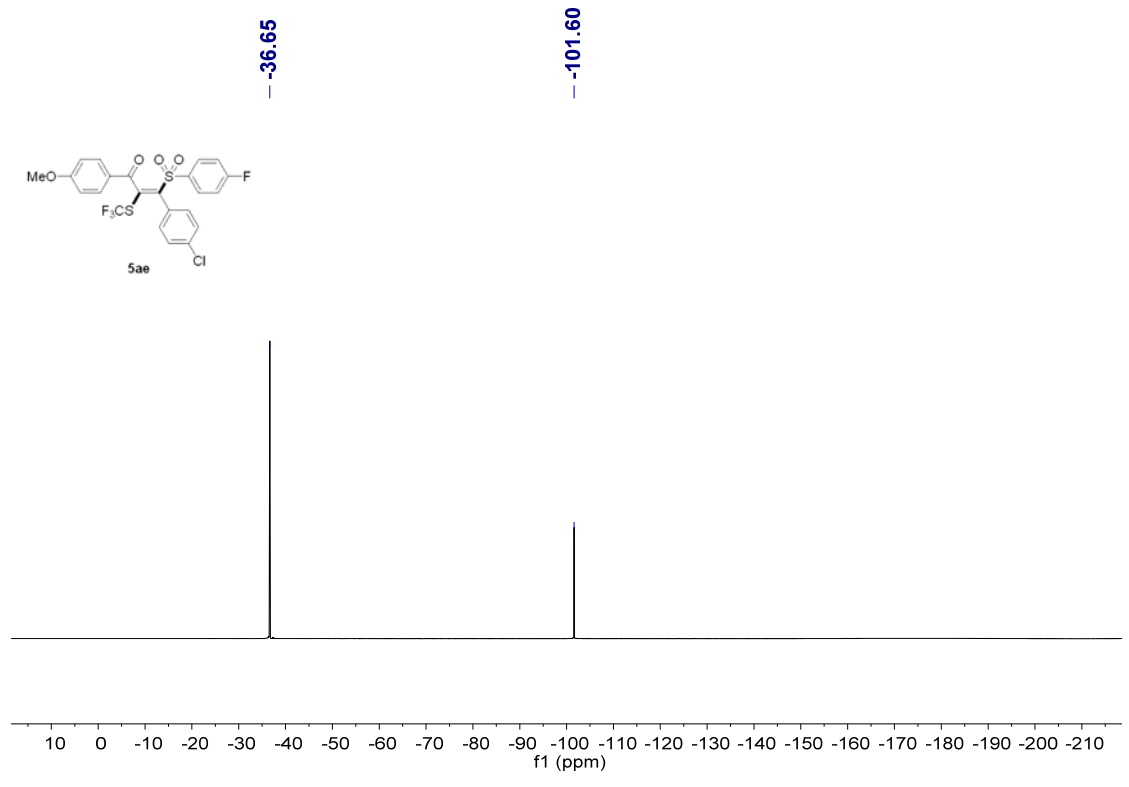
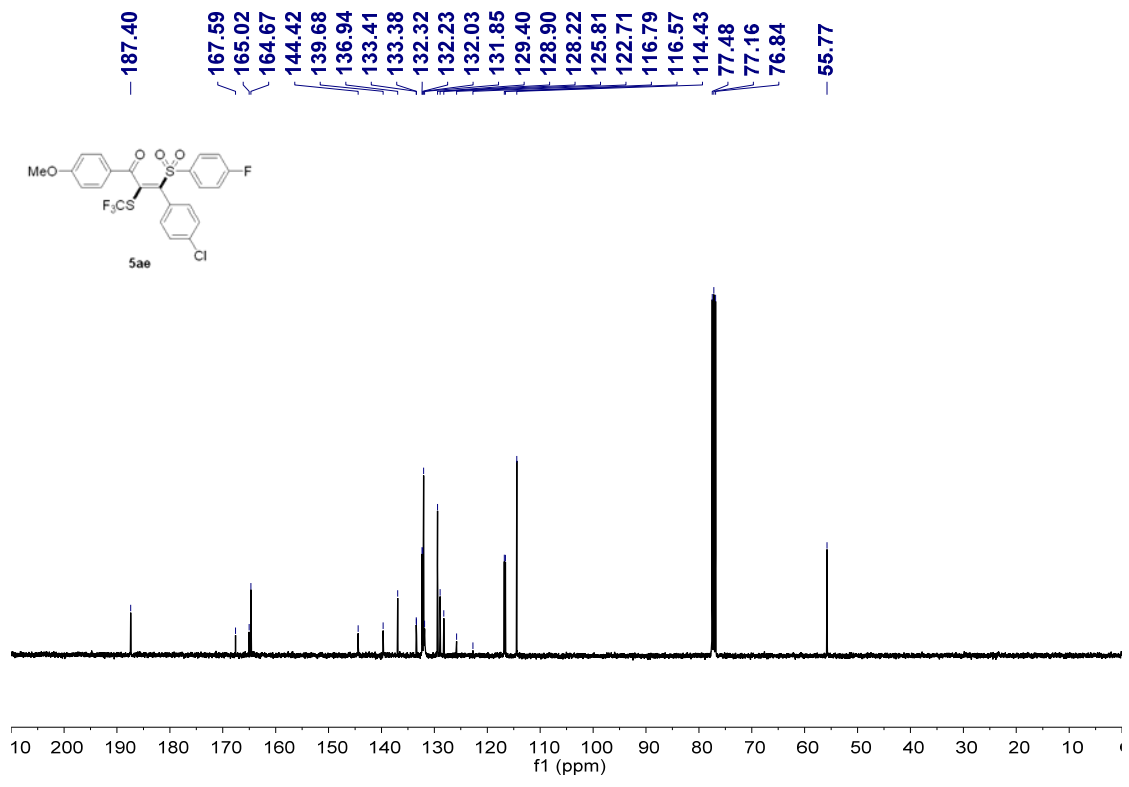




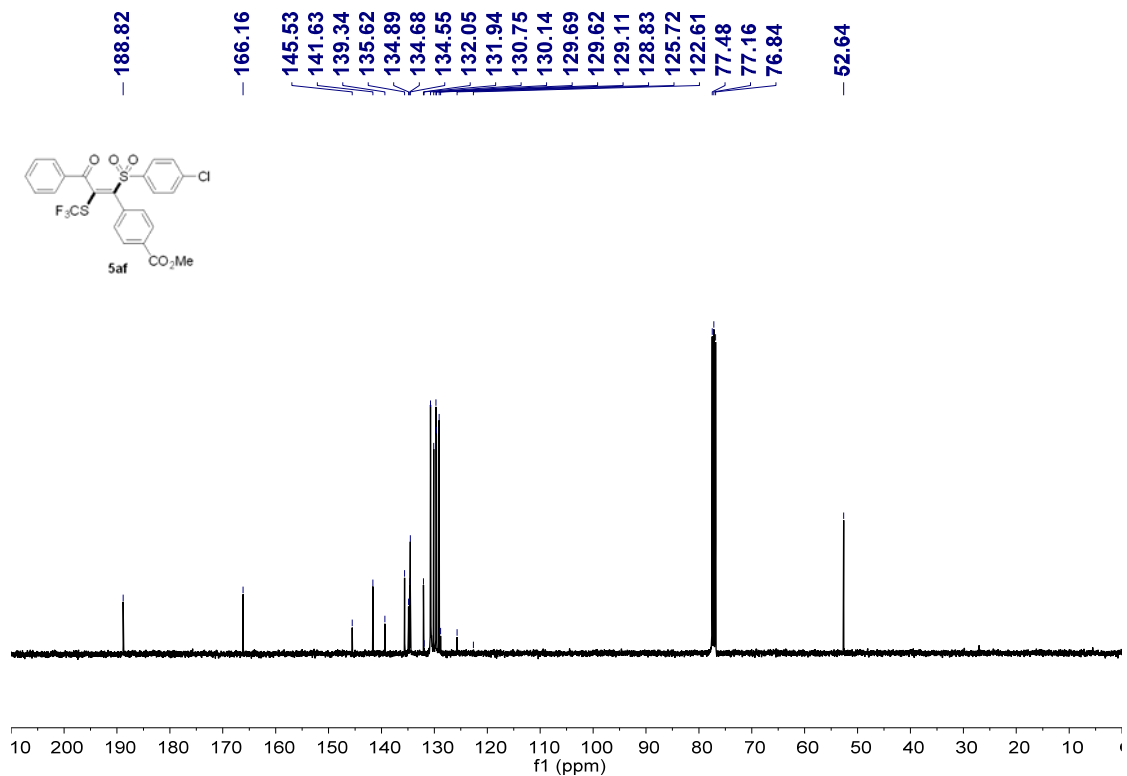
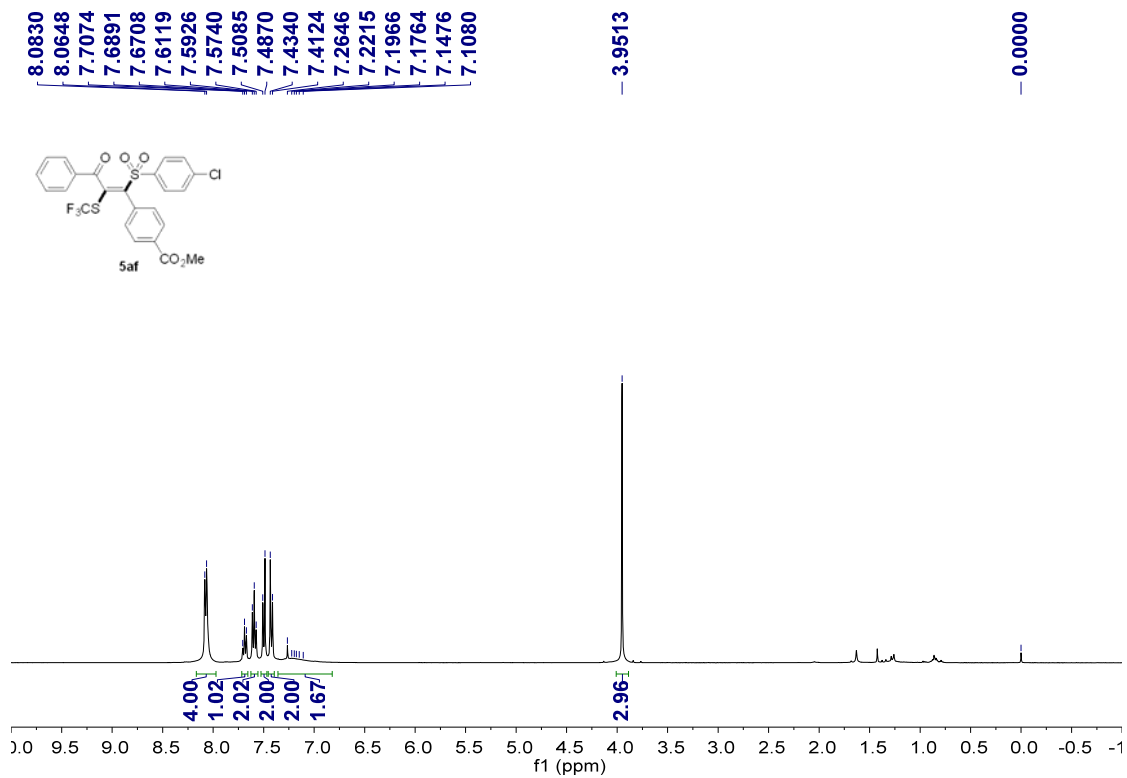
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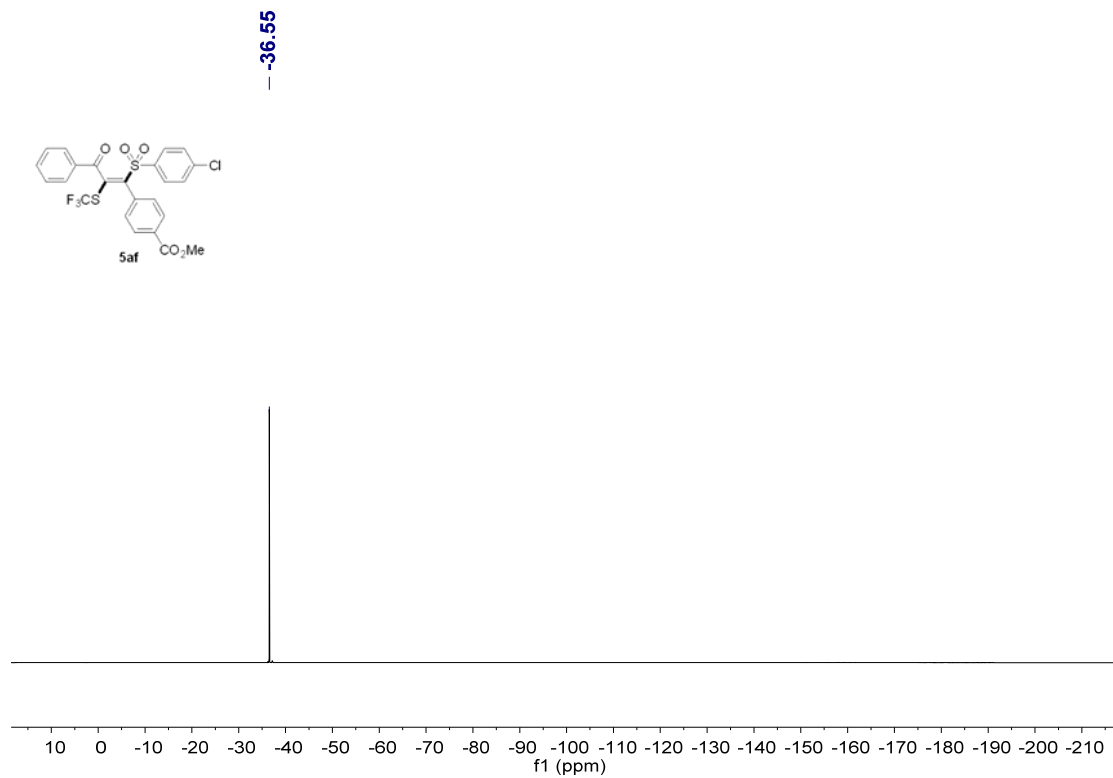




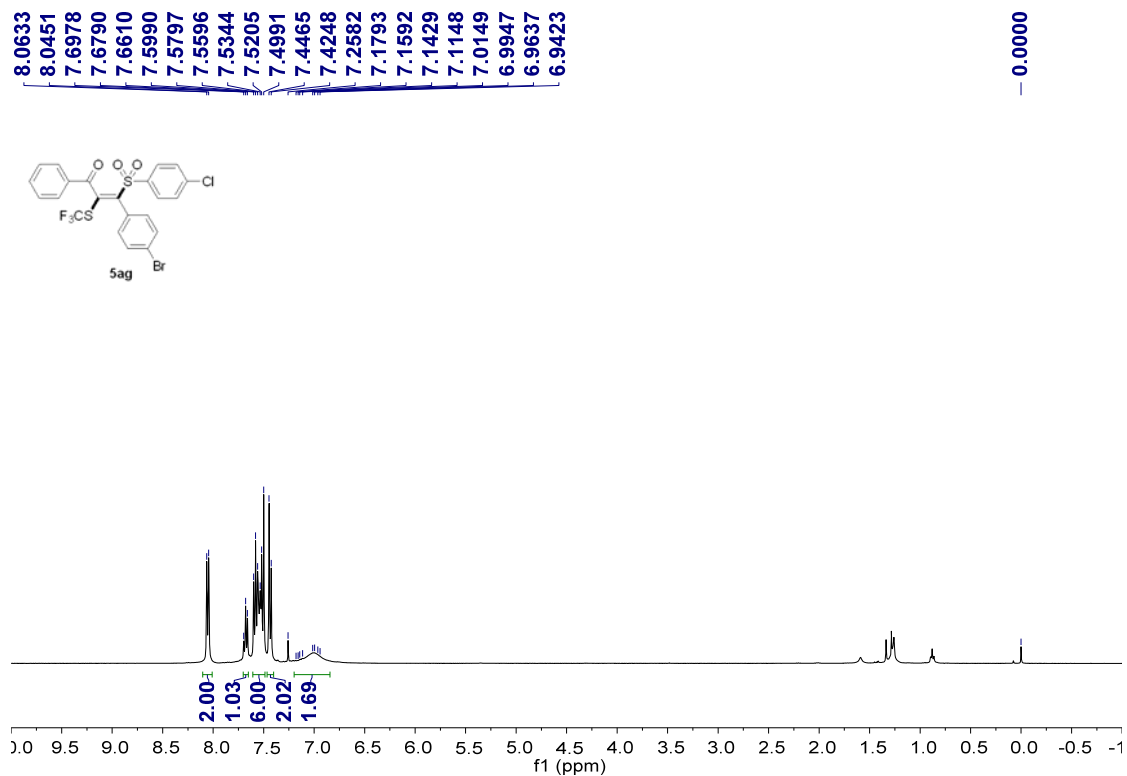


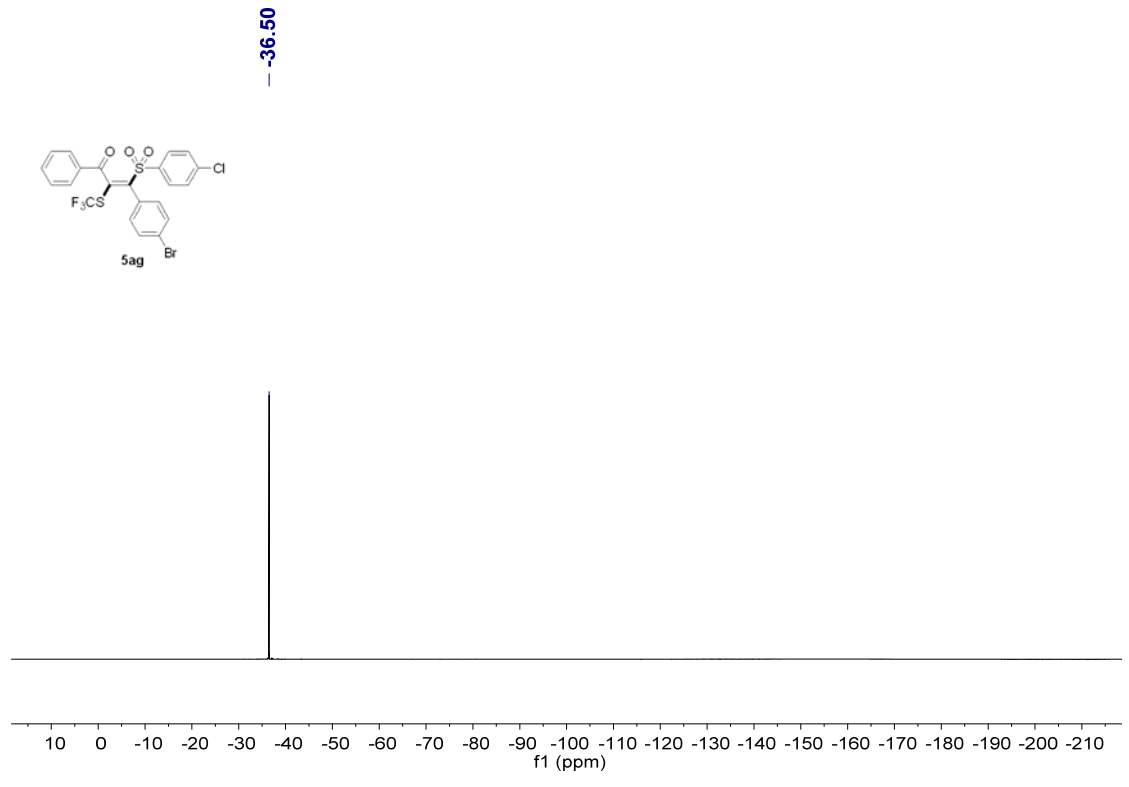
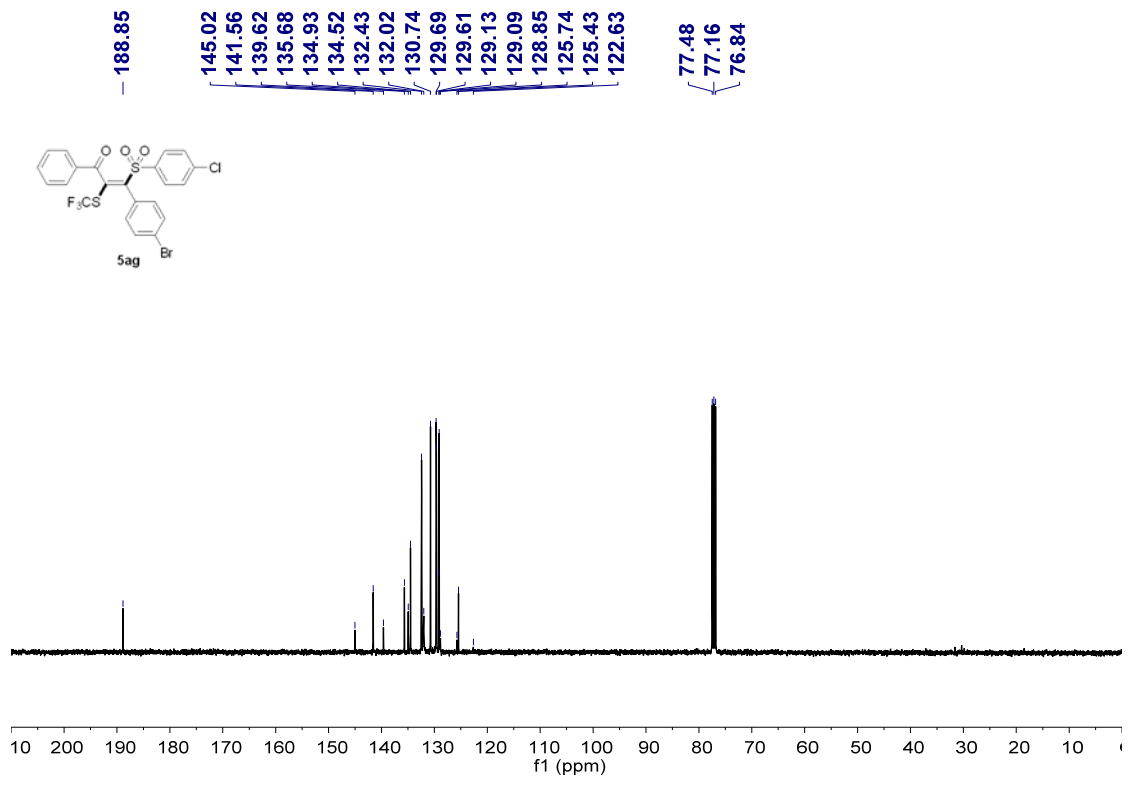
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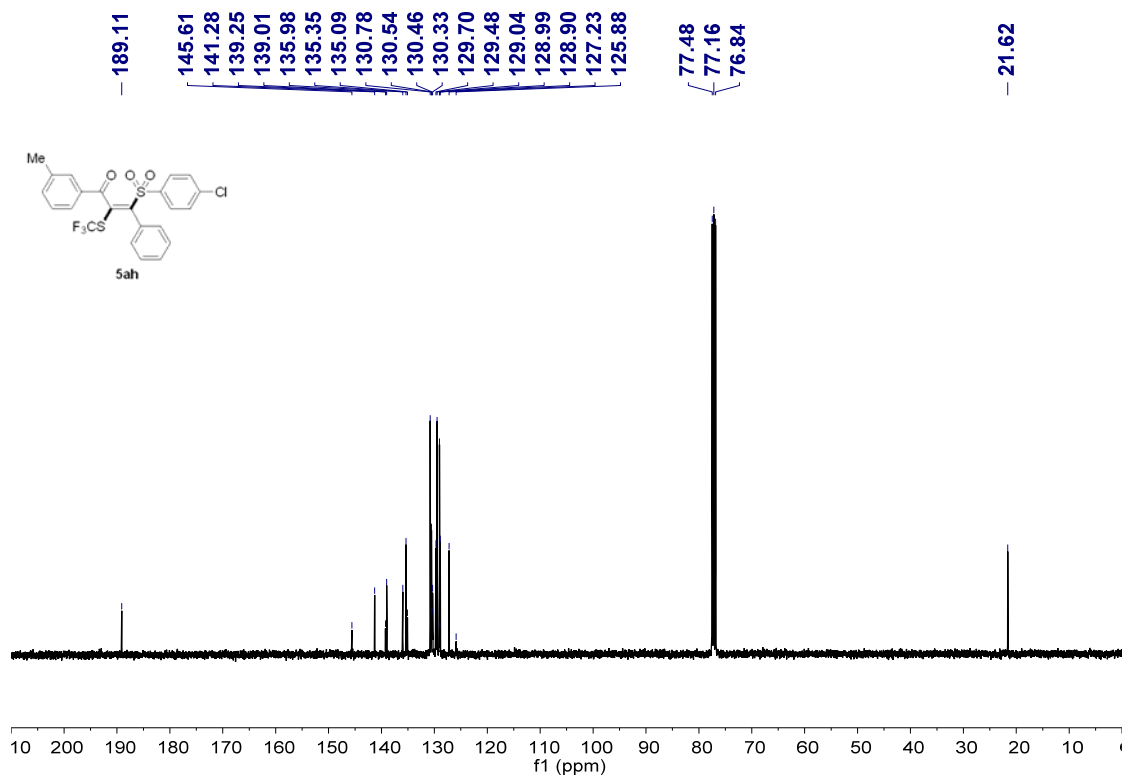
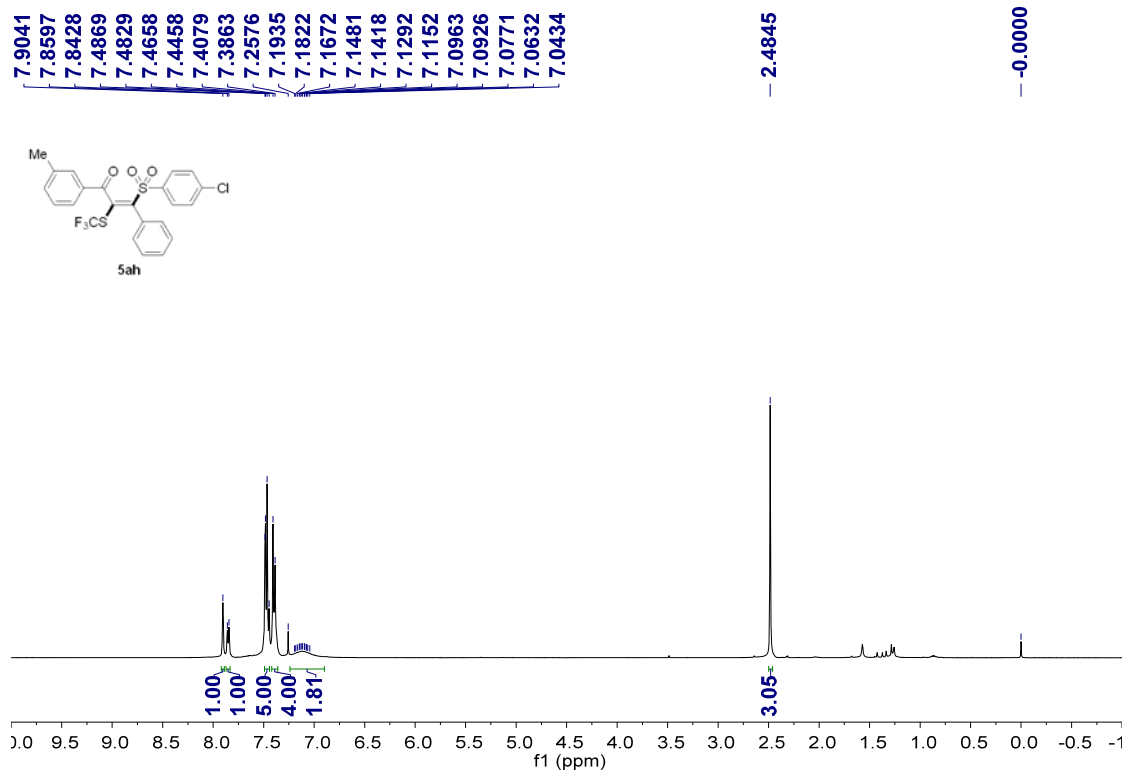


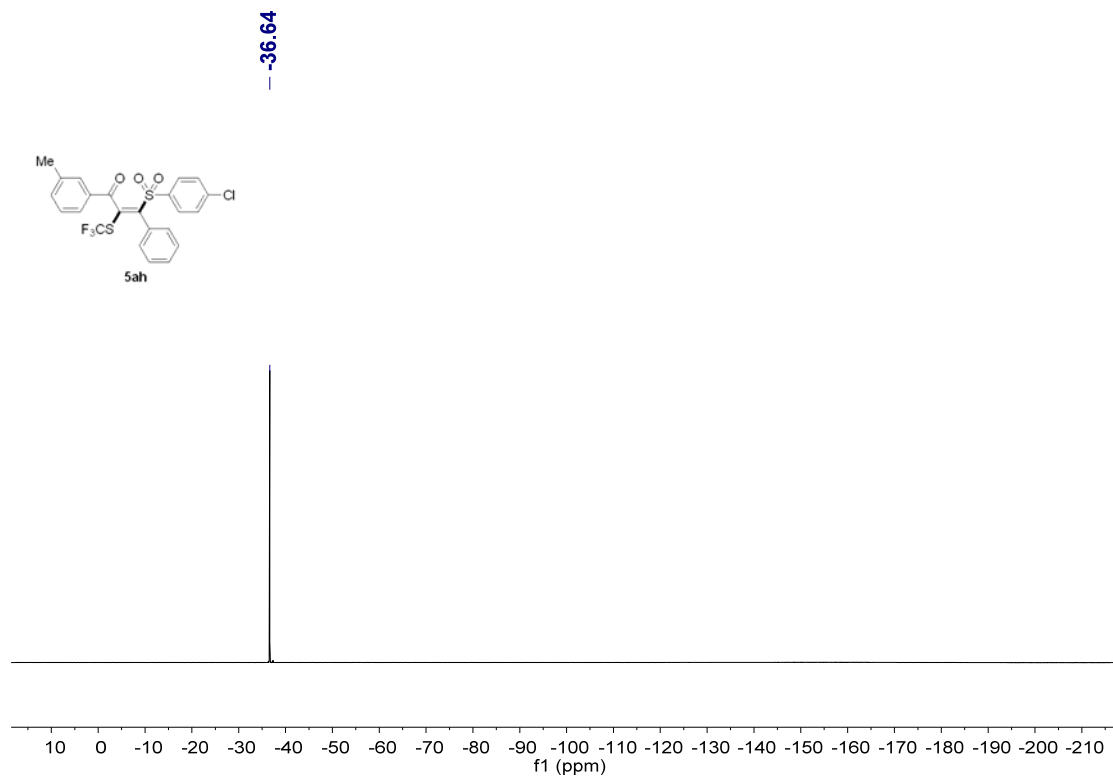
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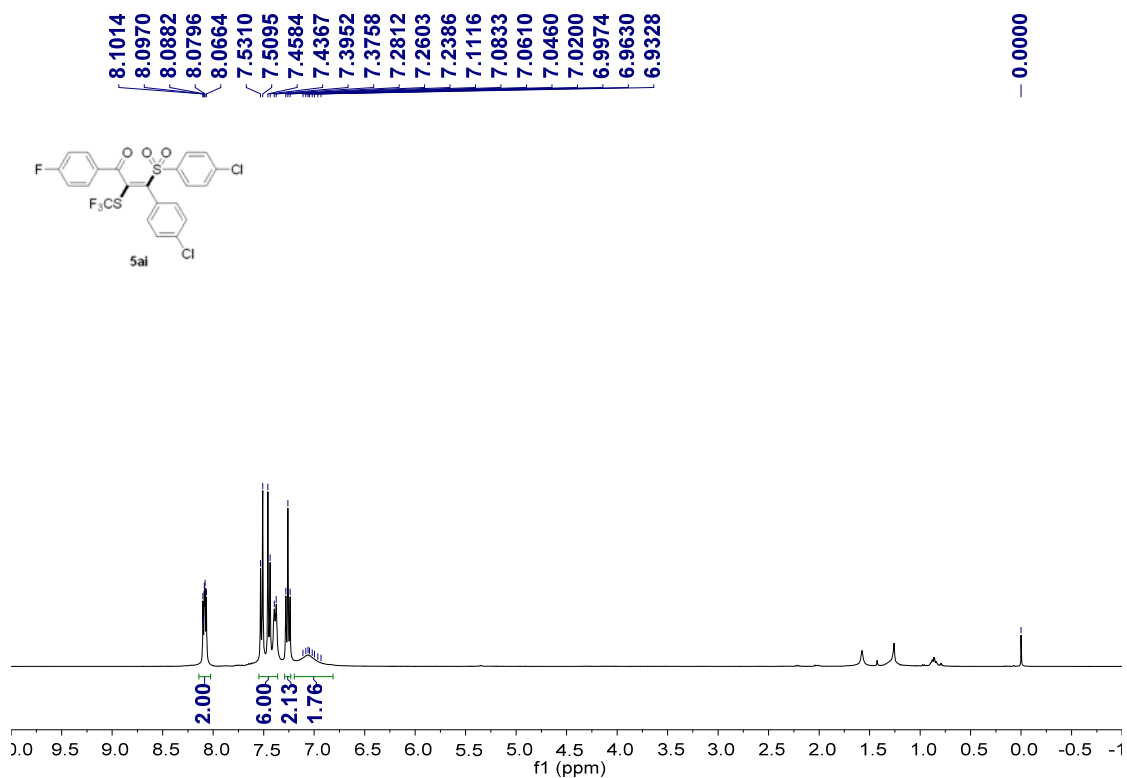


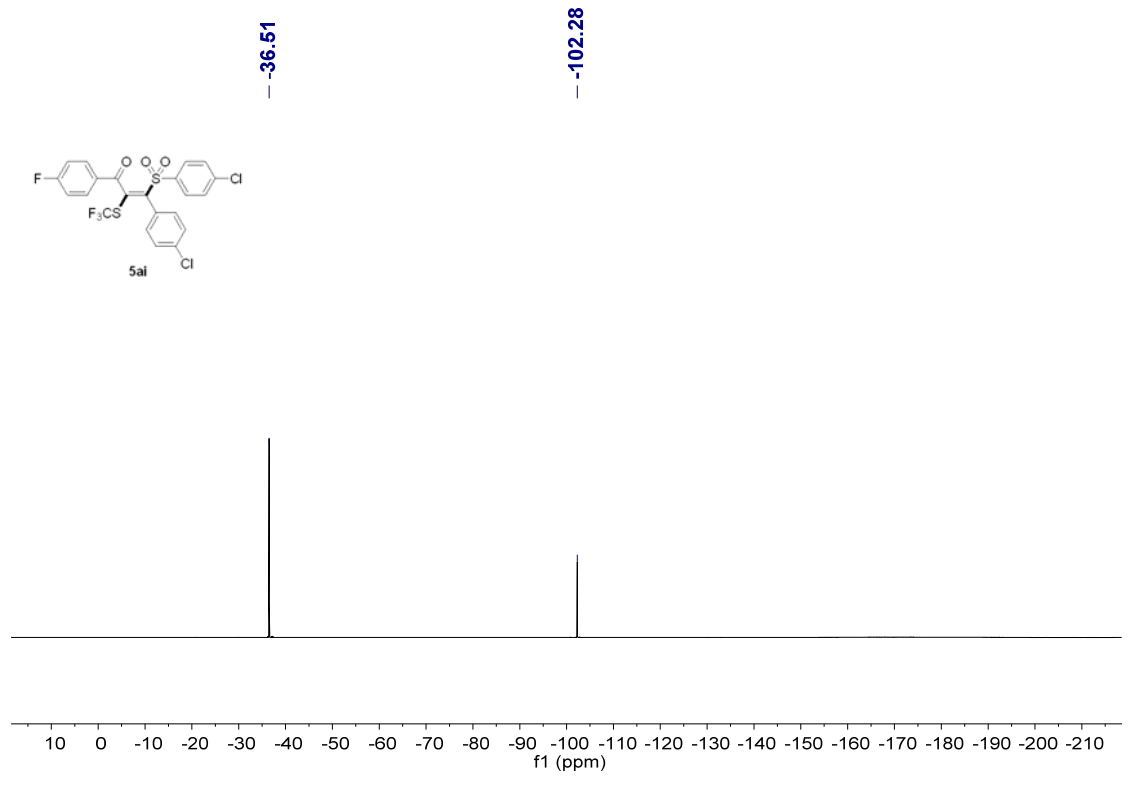
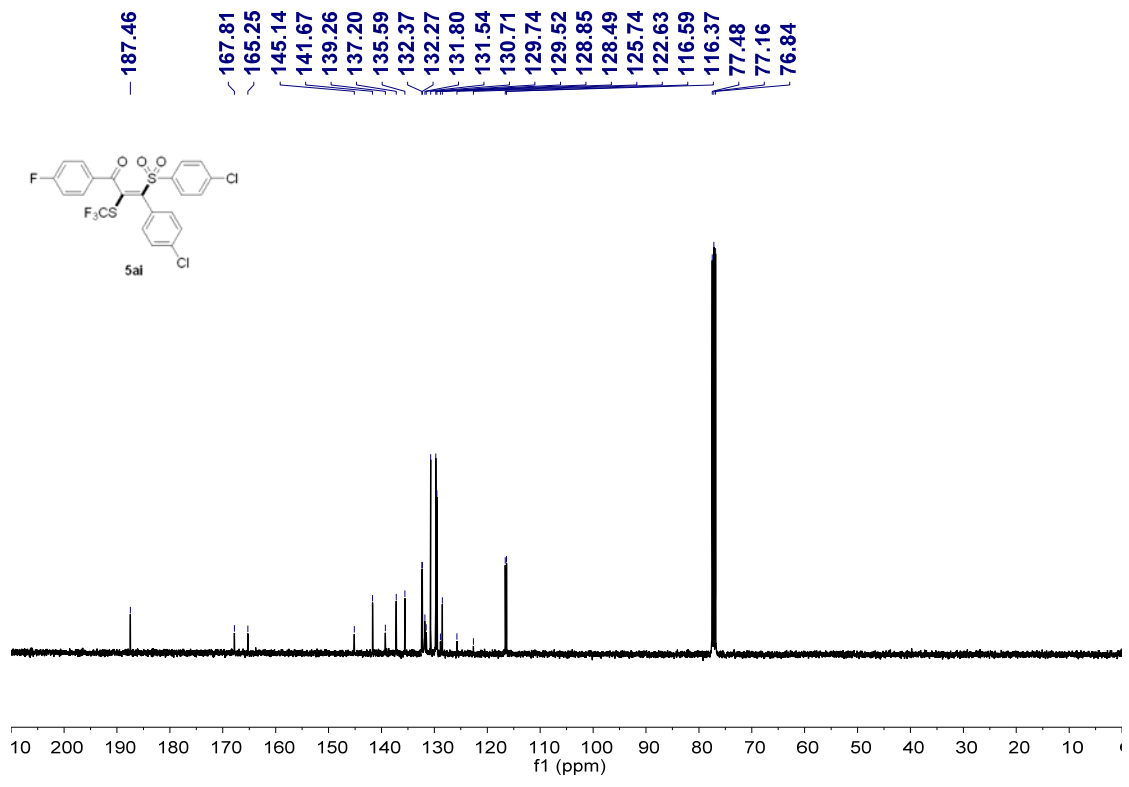
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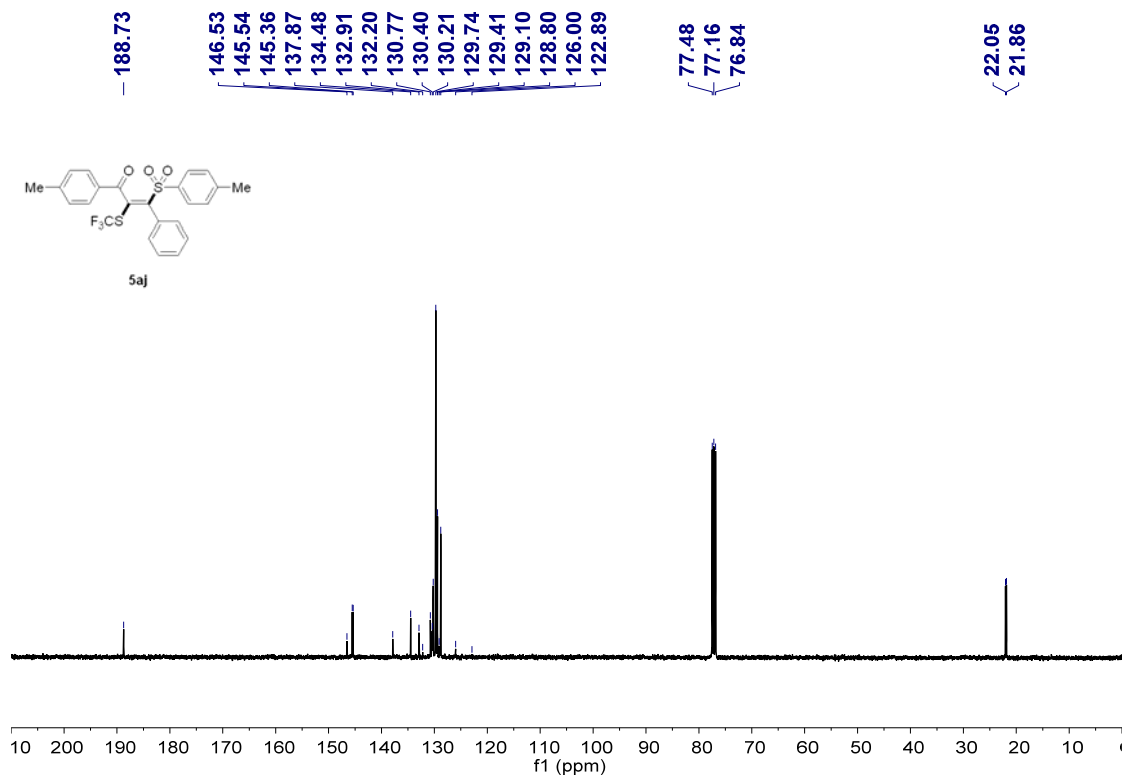
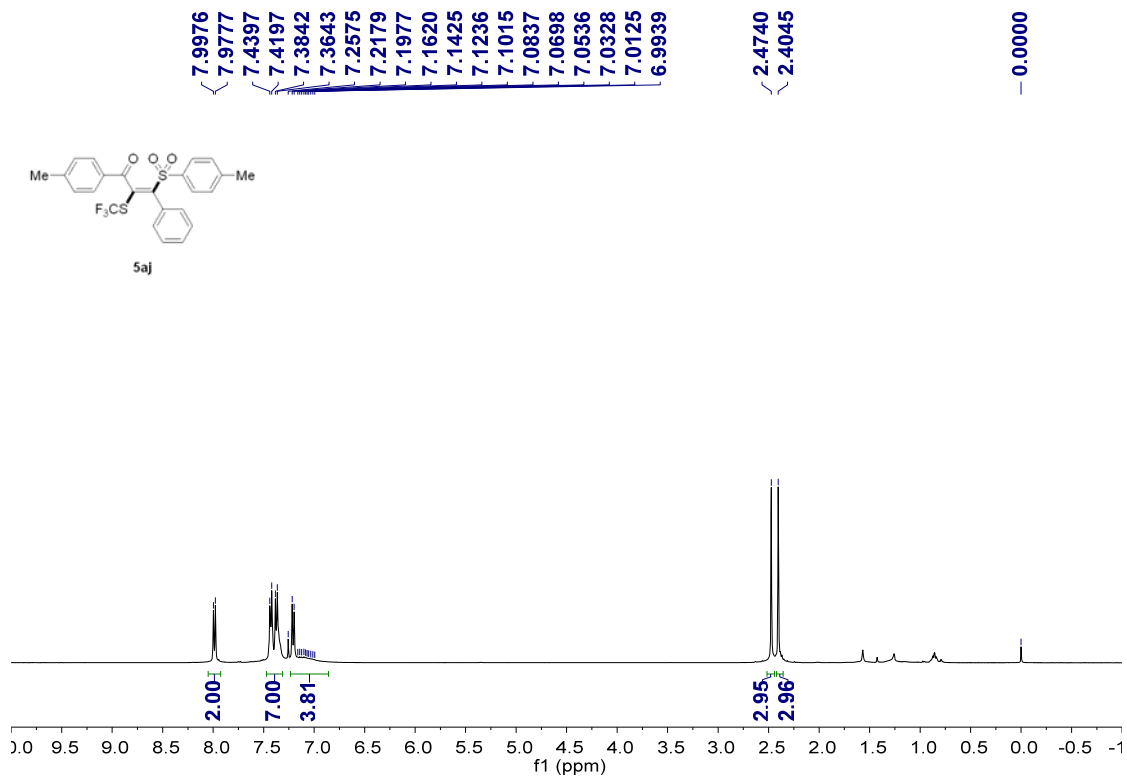


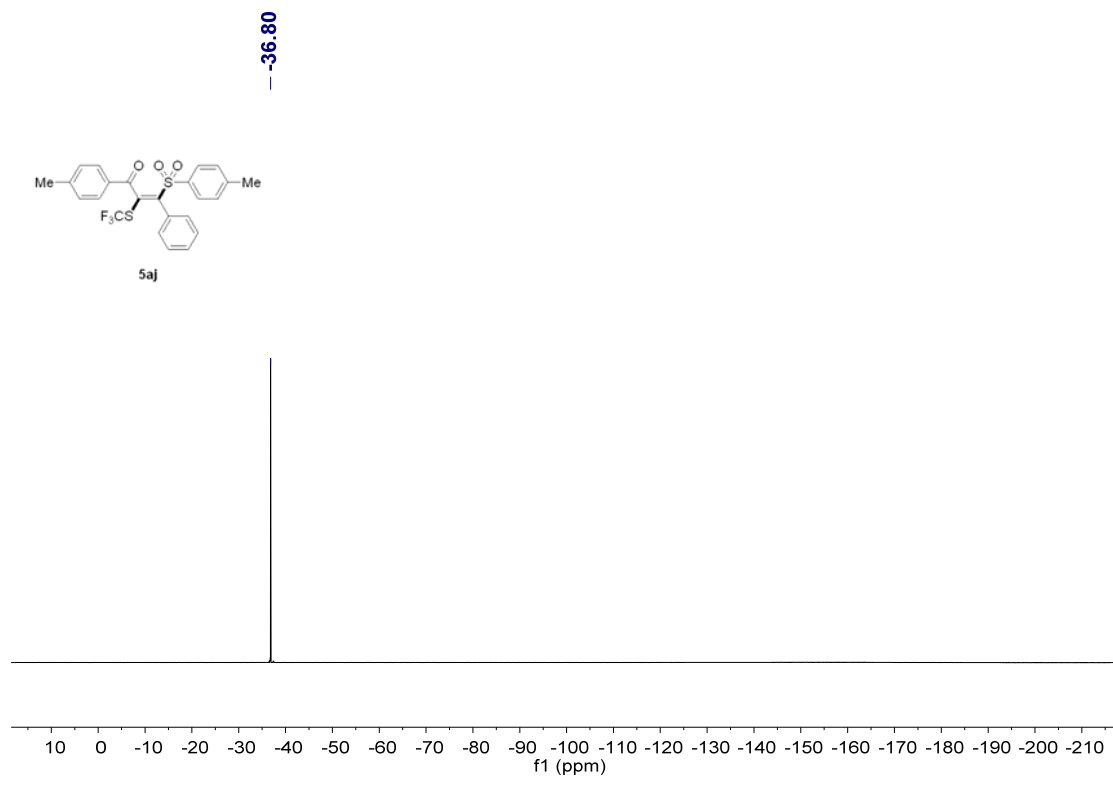
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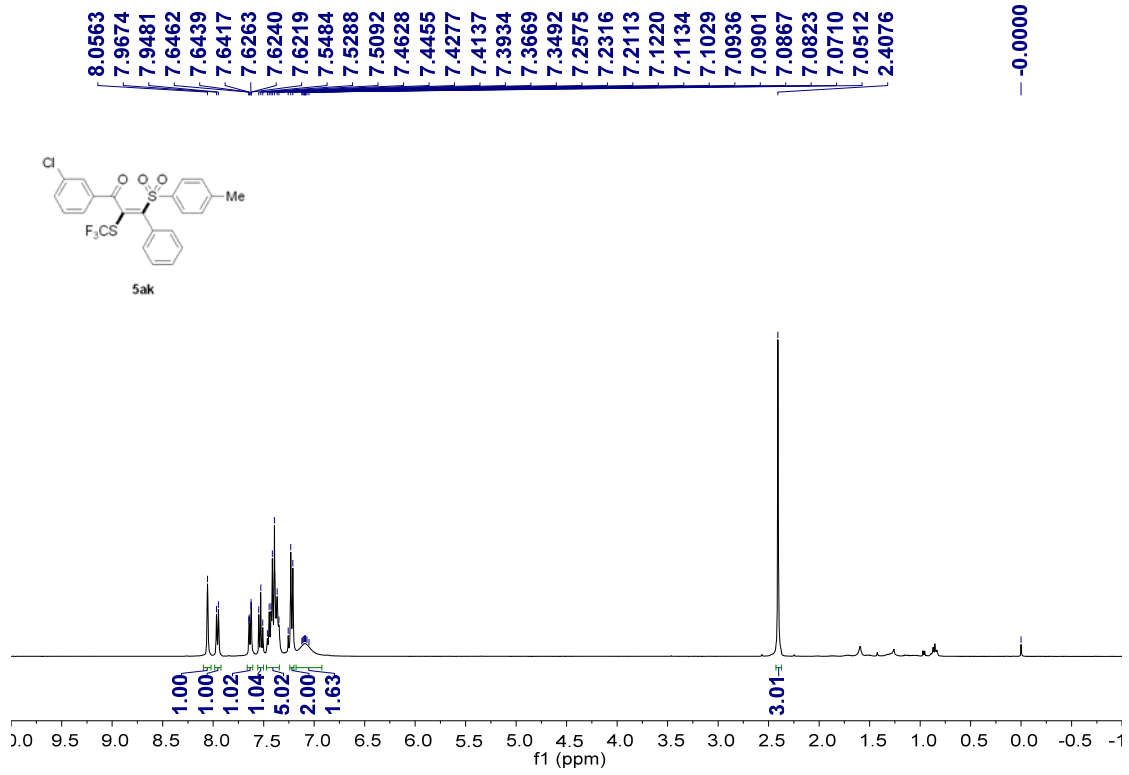


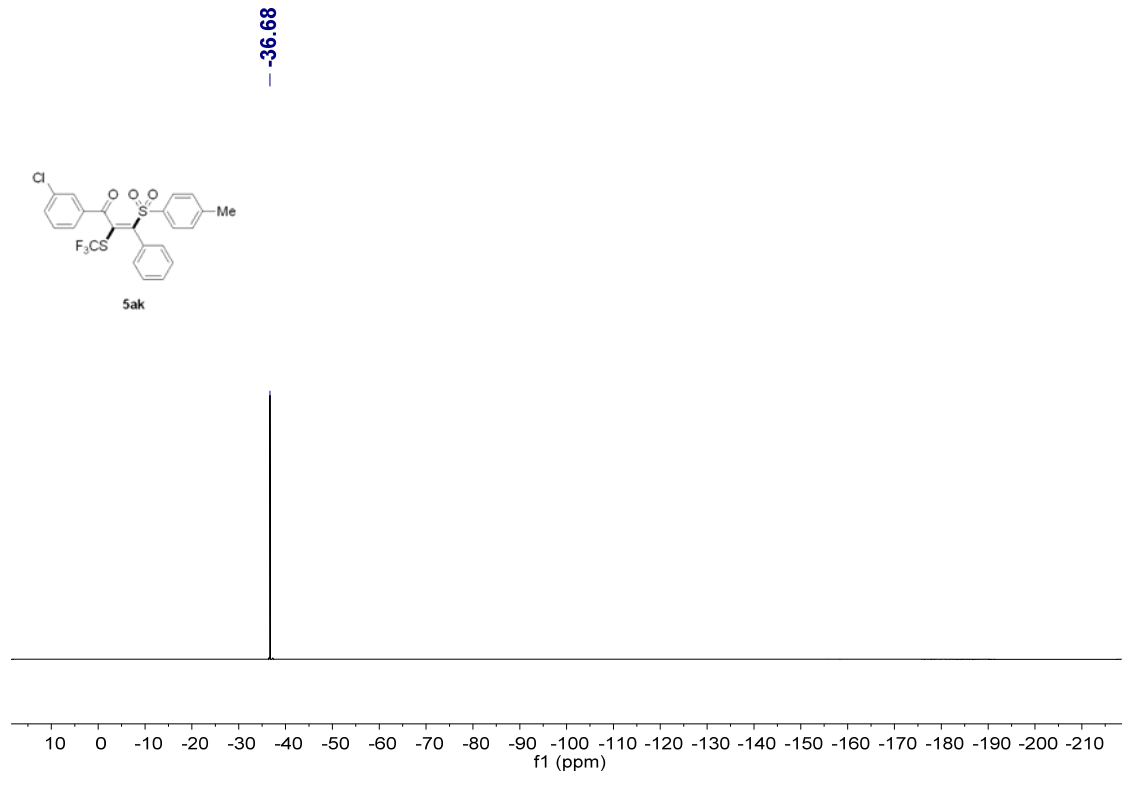
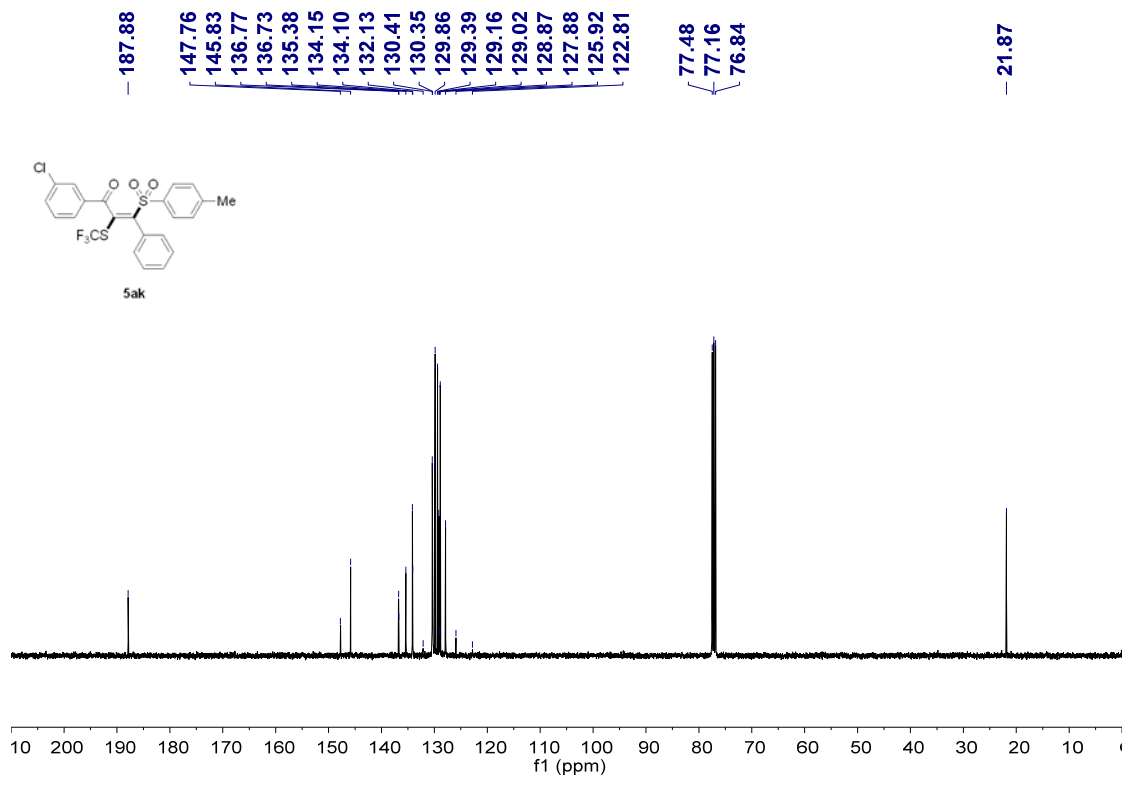
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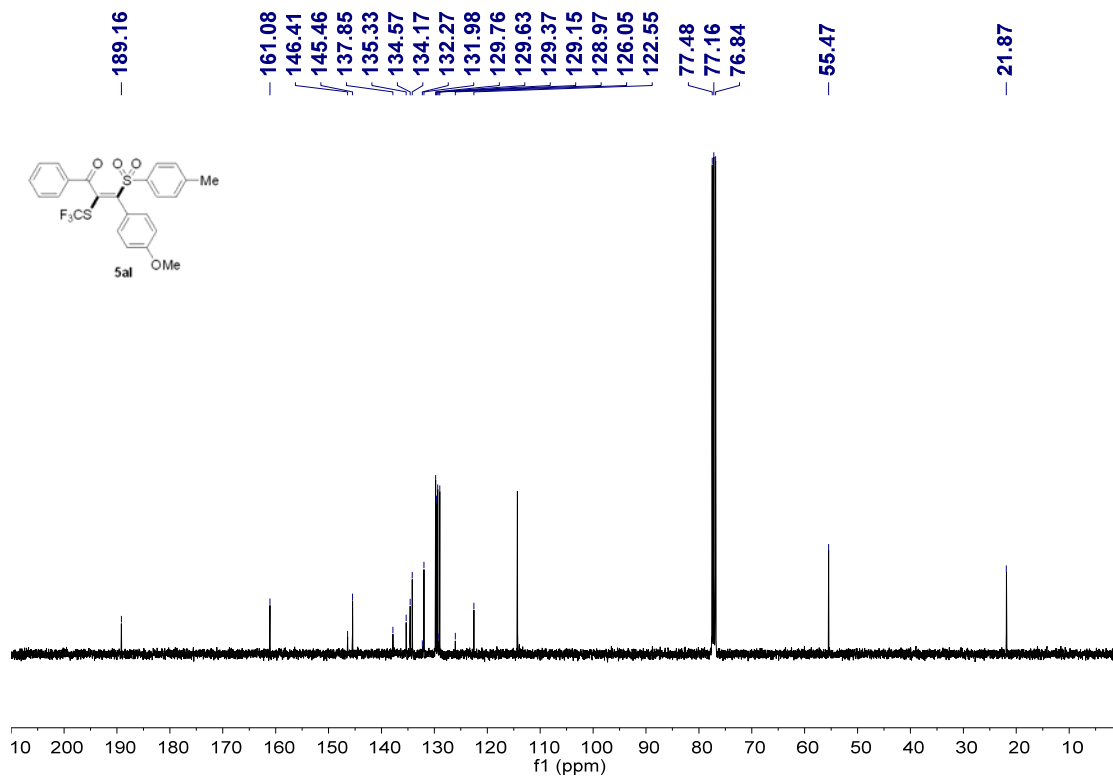
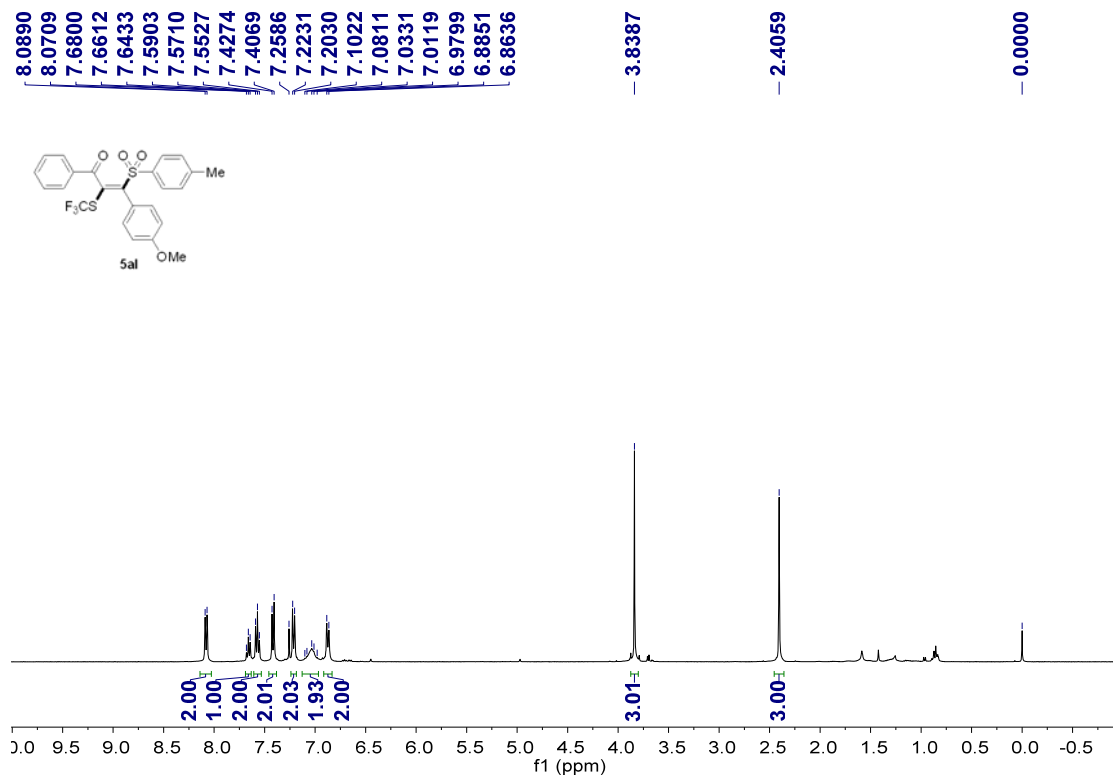


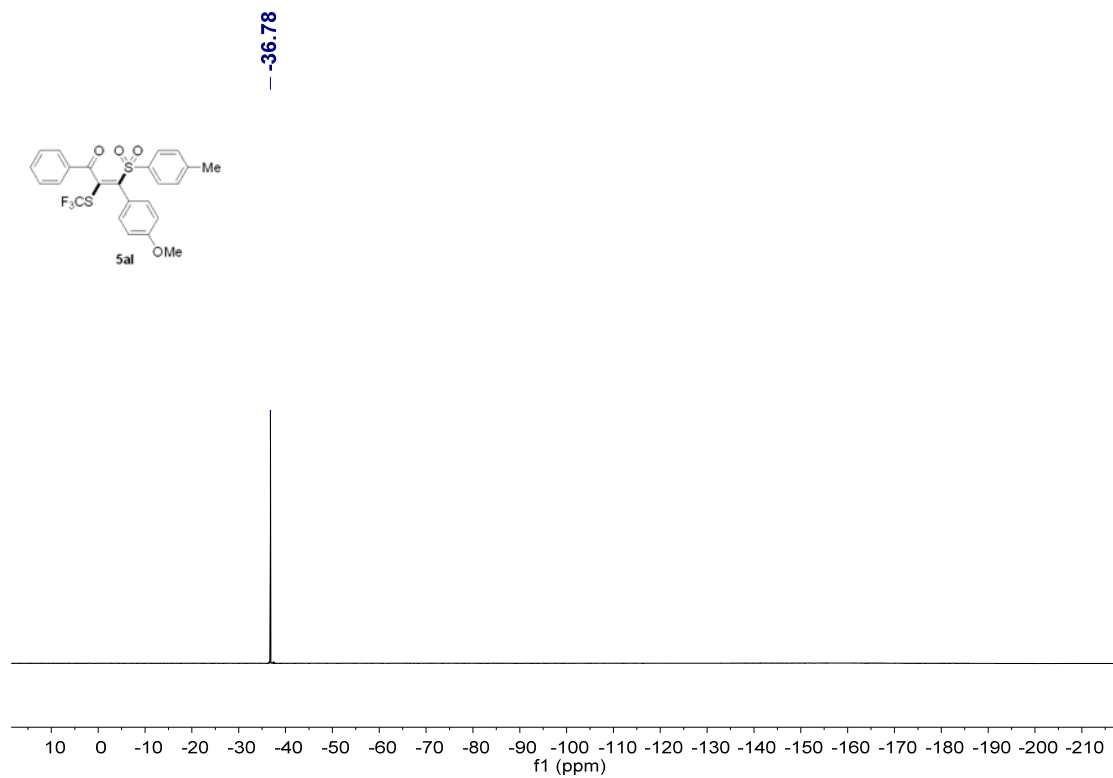
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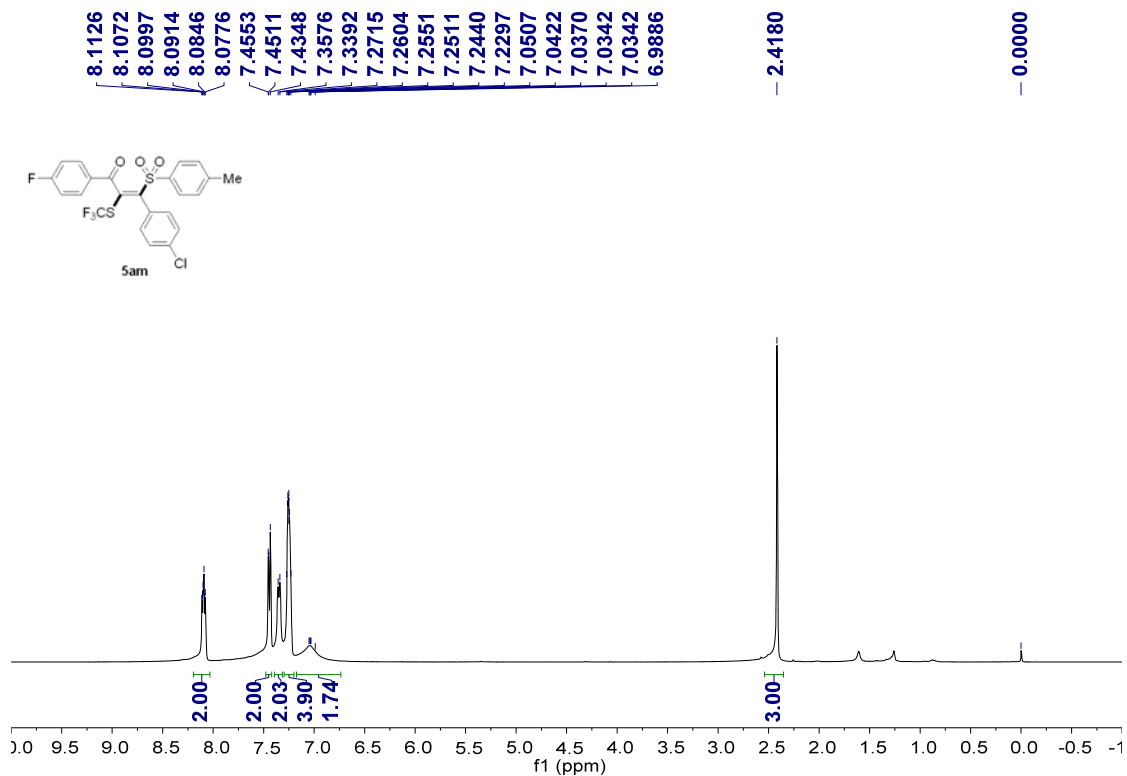


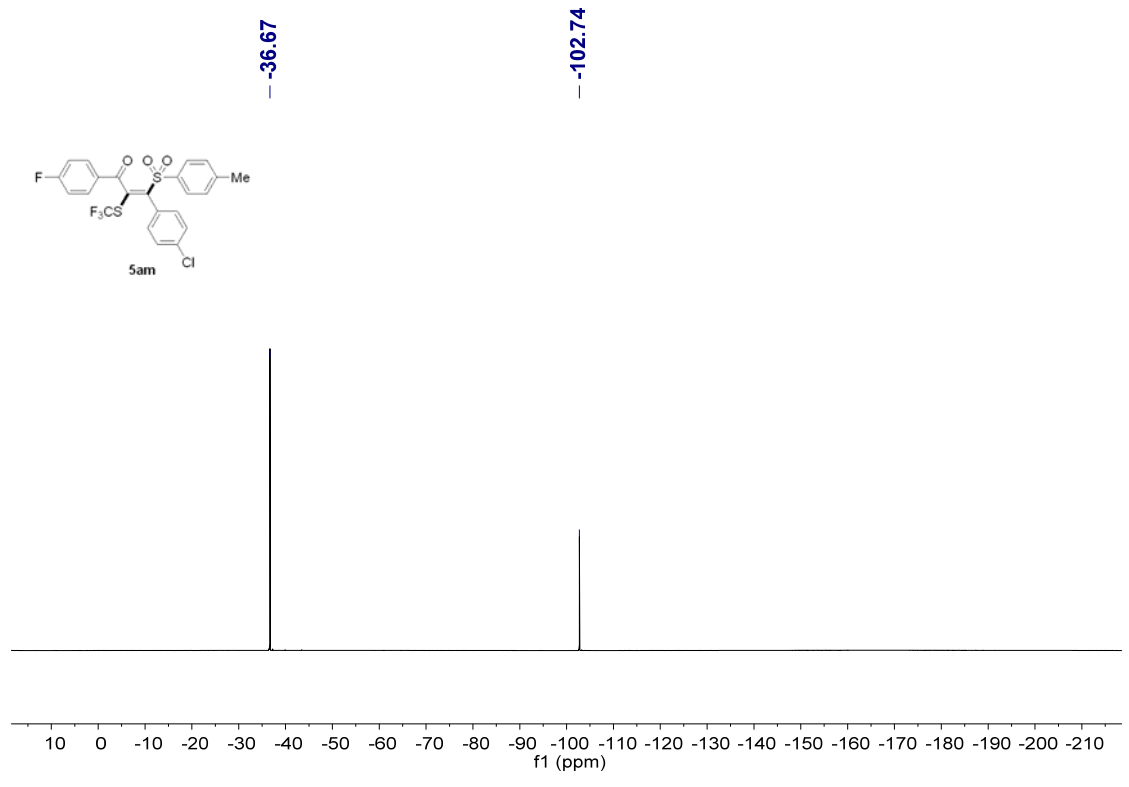
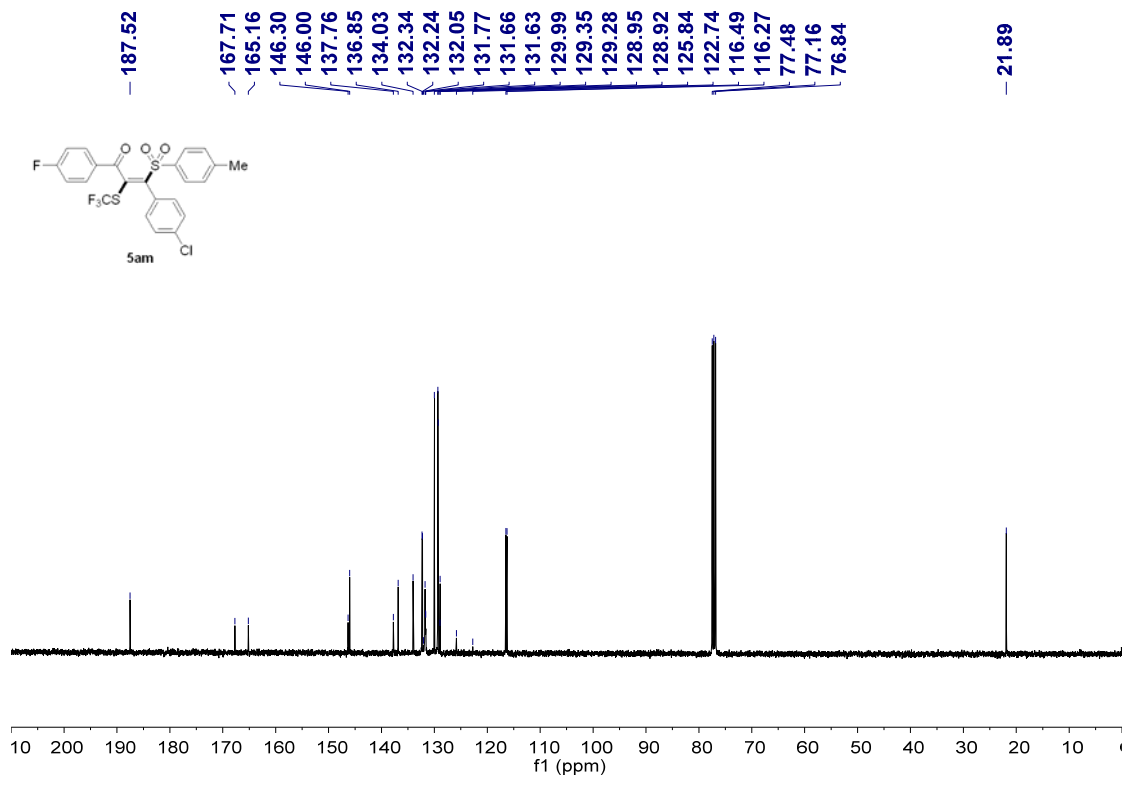
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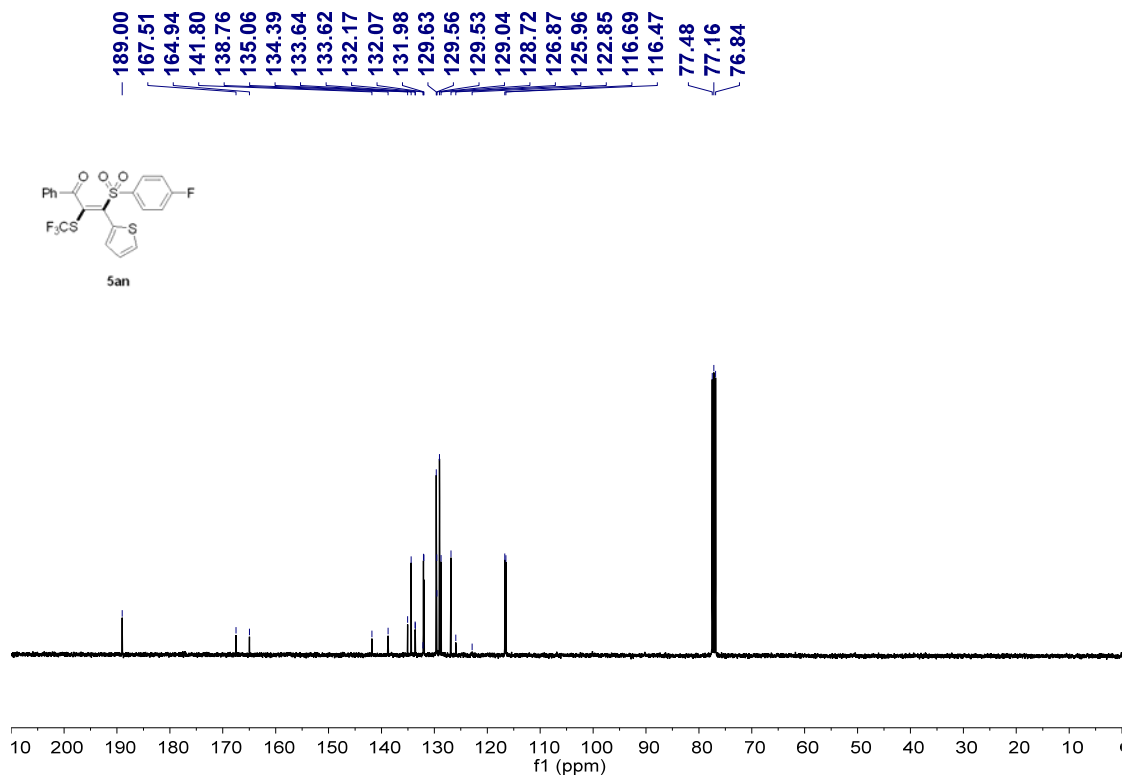
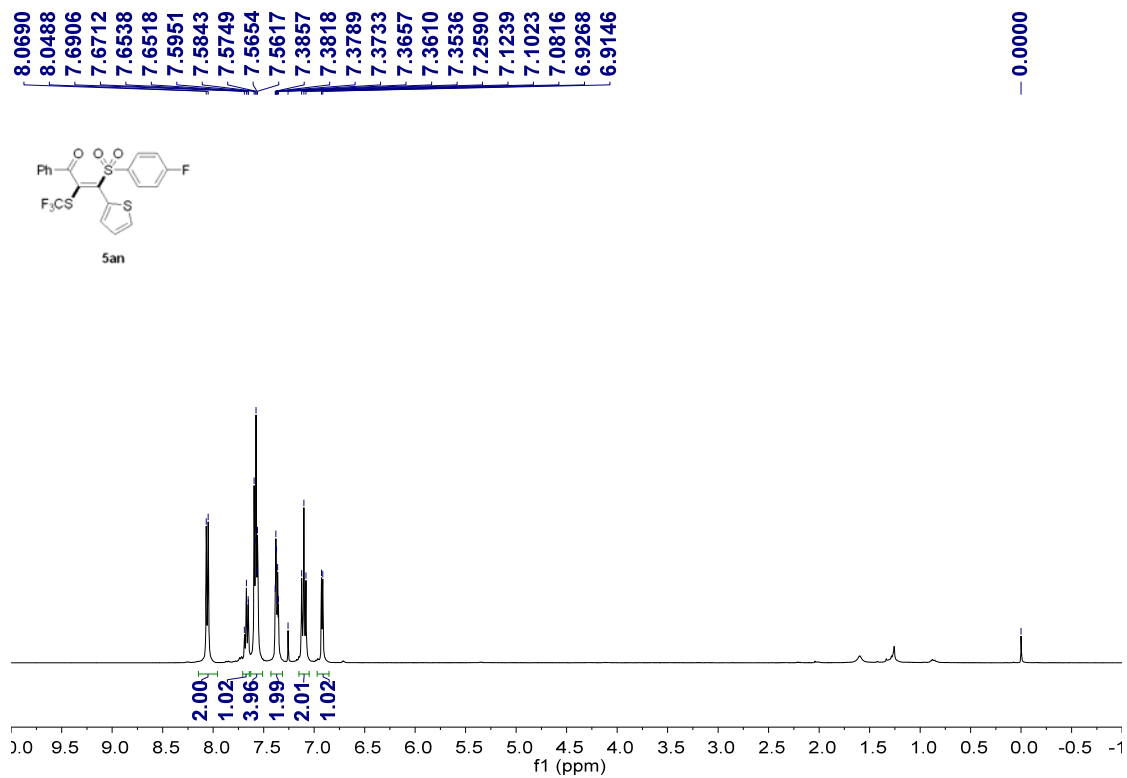


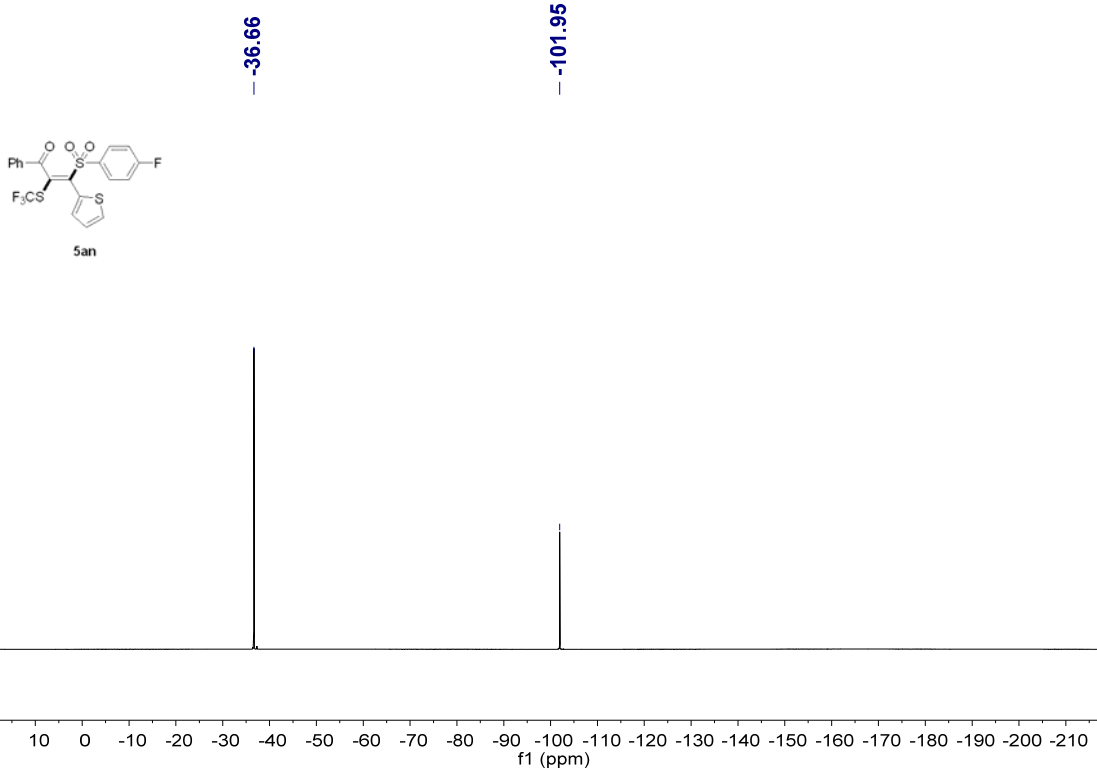
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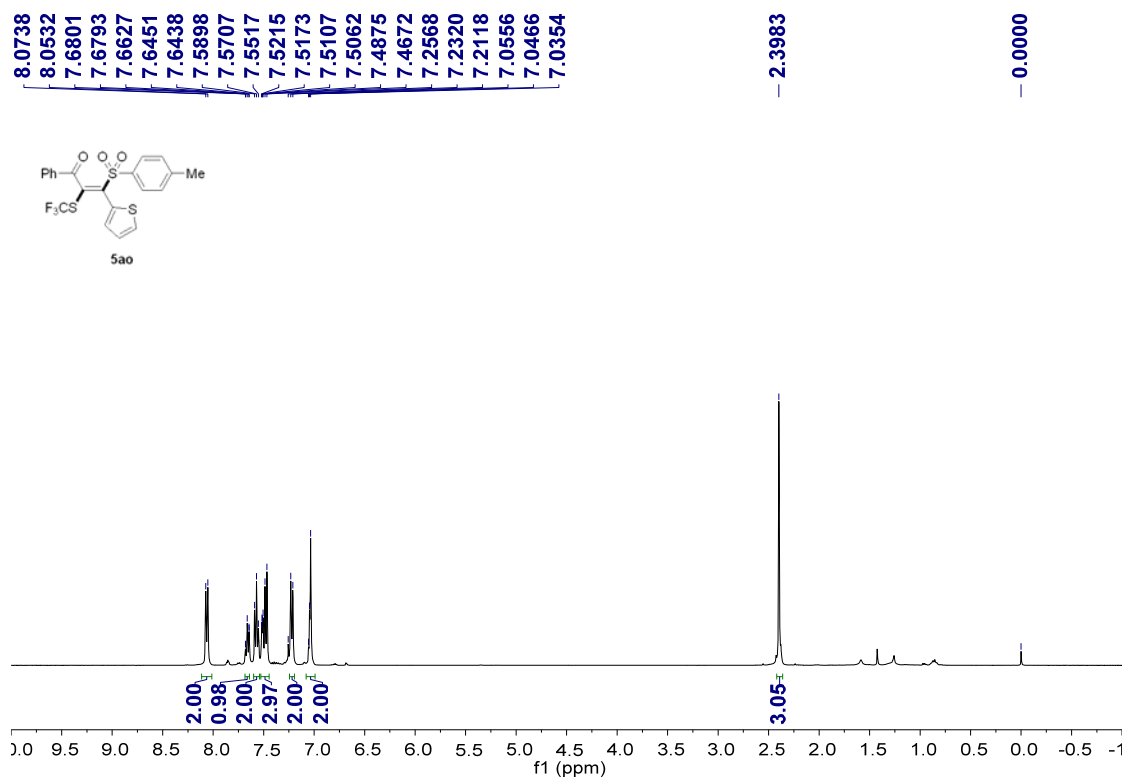


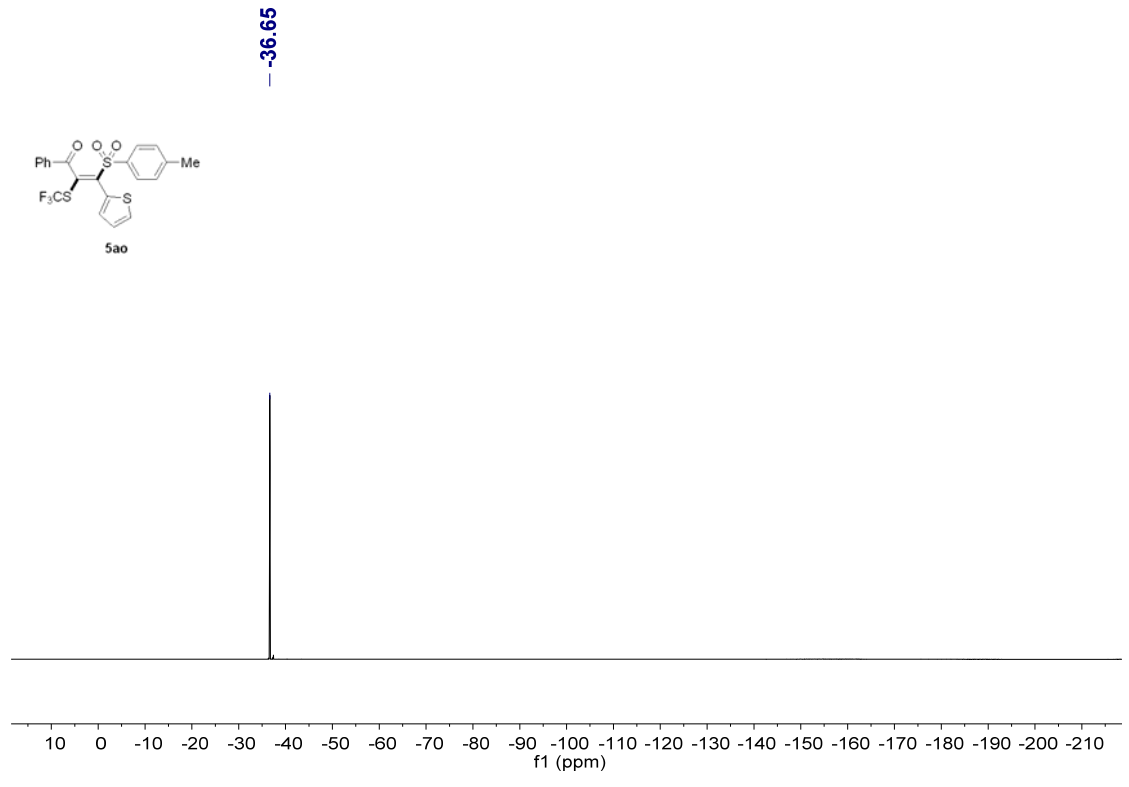
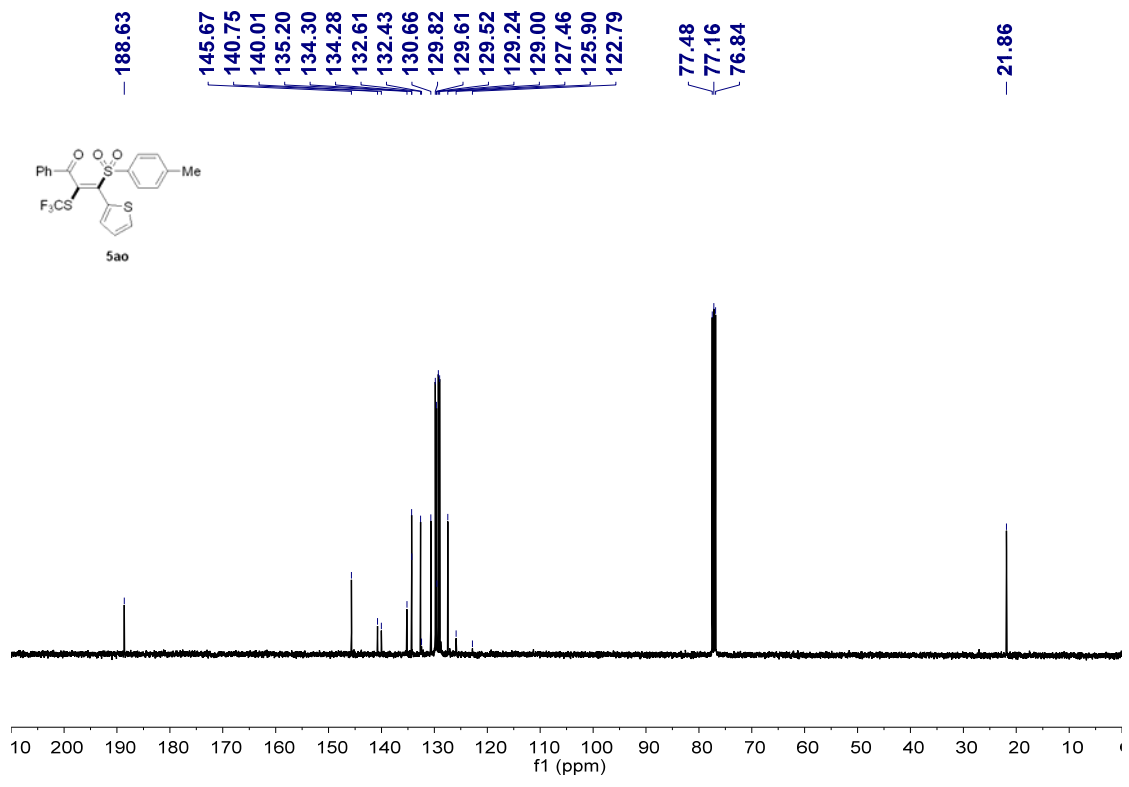
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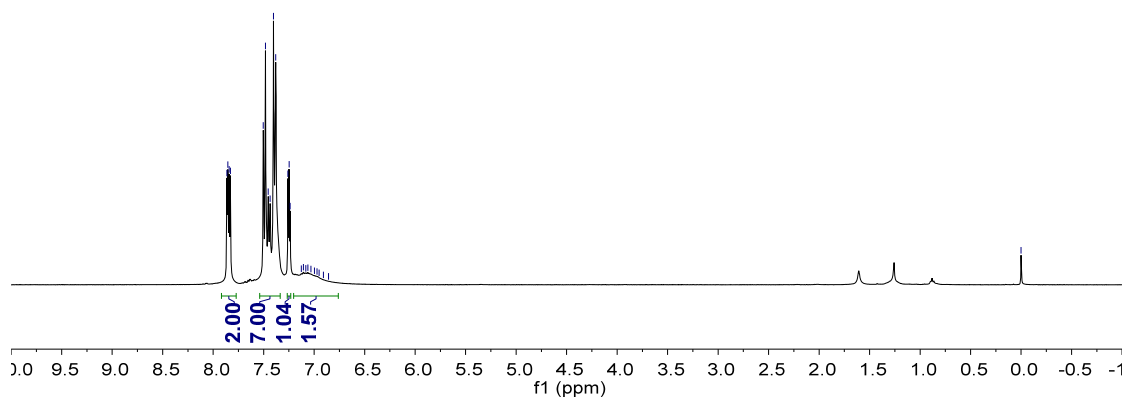
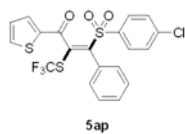




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