

Supplementary Information

Direct difunctionalization of alkynes with sulfinic acids and molecular iodine: a simple and convenient approach to (*E*)- β - iodovinyl sulfones

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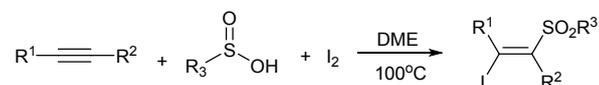
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1. General information

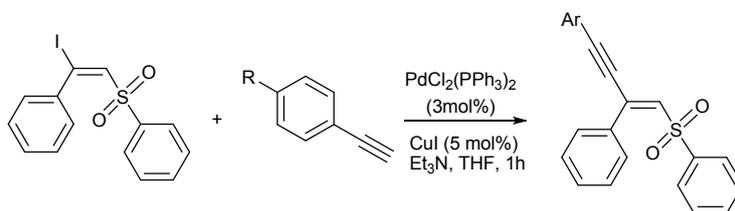
All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. ^1H NMR and ^{13}C NMR were recorded in CDCl_3 on a Bruker Avance III 400 spectrometer with TMS as internal standard (400 MHz ^1H , 100 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh).

2. General procedure for direct synthesis of (*E*)- β -iodovinyl sulfones via difunctionalization of alkynes with sulfinic acids and molecular iodine.



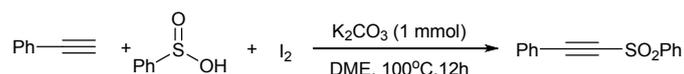
In a sealed tube, alkynes (0.5 mmol), sulfinic acids (1.0 mmol), molecular iodine (0.5 mmol), and DME (2 mL) were added. The mixture was allowed to stir at 100°C for 12-24h. After the reaction, the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product.

3. The procedure (A) for the reaction of (*E*)- β -iodovinyl sulfone with alkynes leading to alkynylation products.



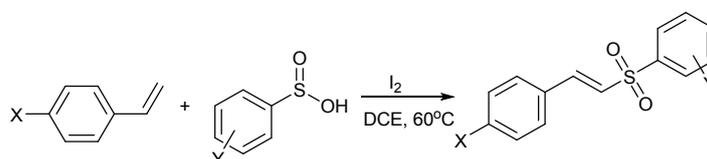
To a mixture of (*E*)- β -iodovinyl sulfone **3aa** (0.25 mmol), PdCl₂(PPh₃)₂ (3 mol%) CuI (5 mol%), Et₃N (0.25 mmol), and alkyne (0.75 mmol) in a 25 mL round-bottomed flask at room temperature, was added the THF (2 mL). The reaction vessel was allowed to stir at room temperature for 1 h. After the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products.

4. The procedure (B) for the synthesis of acetylenic sulfone (5aa).



In a sealed tube, phenylacetylene **1a** (0.5 mmol), benzenesulfinic acid **2a** (1.0 mmol), molecular iodine (0.5 mmol), K₂CO₃ (1 mmol), and DME (2 mL) were added. The mixture was allowed to stir at 100°C for 12h. After the reaction, the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **5aa** (78%).

5. The procedure (C) for the synthesis of (*E*)-vinyl sulfones.

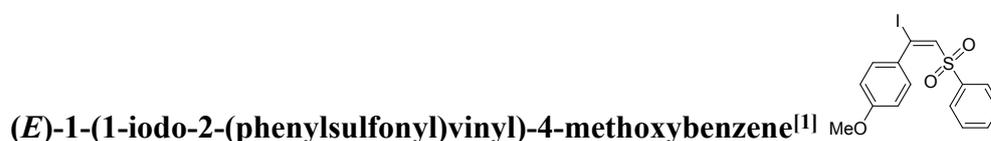


In a sealed tube, alkenes (0.5 mmol), sulfinic acids (1.0 mmol), molecular iodine (0.5 mmol), and DCE (2 mL) were added. The mixture was allowed to stir at 60°C for 12h. After the reaction, the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired (*E*)-vinyl sulfones.

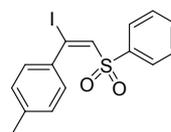
6. Characterization data of products **3aa-6af**



Compound **3aa** was obtained in 88% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.61-7.55 (m, 3H), 7.41 (s, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.34-7.28 (m, 3H), 7.25-7.23 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 141.1, 140.3, 139.6, 133.5, 129.8, 129.0, 128.0, 127.8, 127.7, 114.7; HRMS calc. for C₁₄H₁₁IO₂SNa (M+Na)⁺, 392.9422; found, 392.9424.

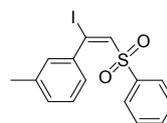


Compound **3ba** was obtained in 88% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.63 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.33 (s, 1H), 7.27 (t, *J* = 6.6 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 160.9, 140.5, 140.2, 133.5, 131.8, 130.0, 129.0, 127.8, 115.5, 113.3, 55.4; HRMS calc. for C₁₅H₁₃IO₃SNa (M+Na)⁺, 422.9528; found, 422.9529.



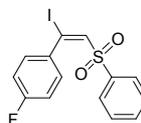
(E)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-4-methylbenzene^[1]

Compound **3ca** was obtained in 75% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.64-7.62 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 2H), 7.37 (s, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 140.6, 140.4, 140.3, 136.8, 133.5, 129.0, 128.6, 127.8, 115.4, 21.5; HRMS calc. for C₁₅H₁₃IO₂SNa (M+Na)⁺, 406.9579; found, 406.9577.



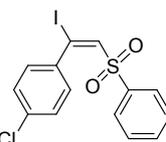
(E)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-3-methylbenzene

Compound **3da** was obtained in 90% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.59-7.53 (m, 3H), 7.41 (s, 1H), 7.39 (t, *J* = 8.3 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.93 (s, 1H), 2.28 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 141.1, 140.3, 139.5, 137.7, 133.4, 130.7, 128.9, 128.0, 127.9, 127.9, 124.8, 115.2, 21.3; HRMS calc. for C₁₅H₁₄IO₂S (M+H)⁺, 384.9759; found, 384.9759.



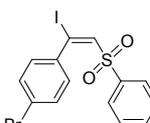
(E)-1-fluoro-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene^[1]

Compound **3ea** was obtained in 71% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.64-7.58 (m, 3H), 7.45 (t, *J* = 8.1 Hz, 2H), 7.40 (s, 1H), 7.28-7.25 (m, 2H), 6.99 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 163.2 (d, *J* = 250.1 Hz), 141.5, 140.2, 135.6 (d, *J* = 14.1 Hz), 133.7, 130.0 (d, *J* = 34.6 Hz), 129.1, 127.8, 115.1 (d, *J* = 22.0 Hz), 113.1; HRMS calc. for C₁₄H₁₀FIO₂SNa (M+Na)⁺, 410.9328; found, 410.9324.



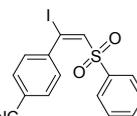
(E)-1-chloro-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene^[1]

Compound **3fa** was obtained in 73% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.65-7.59 (m, 3H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.39 (s, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 141.6, 140.1, 138.0, 136.0, 133.7, 129.2, 129.1, 128.3, 127.8, 112.7; HRMS calc. for C₁₄H₁₀ClIO₂SNa (M+Na)⁺, 426.9032; found, 426.9033.



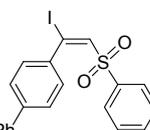
(E)-1-bromo-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene^[1]

Compound **3ga** was obtained in 83% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.65-7.60 (m, 3H), 7.48-7.43 (m, 4H), 7.40 (s, 1H), 7.12 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 141.6, 140.1, 138.5, 133.7, 131.2, 129.3, 129.2, 127.8, 124.3, 112.6; HRMS calc. for C₁₄H₁₀BrIO₂SNa (M+Na)⁺, 470.8527; found, 470.8529.



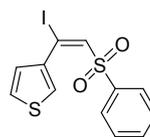
(E)-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzonitrile^[1]

Compound **3ha** was obtained in 78% yield according to the general procedure (16h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.67-7.62 (m, 5H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.41 (s, 1H), 7.36 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 144.1, 142.1, 139.9, 134.1, 131.8, 129.4, 128.2, 127.8, 118.0, 113.4, 110.4; HRMS calc. for C₁₅H₁₀INO₂SNa (M+Na)⁺, 417.9375; found, 417.9370.



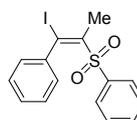
(E)-4-(1-iodo-2-(phenylsulfonyl)vinyl)biphenyl^[1]

Compound **3ia** was obtained in 90% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.65-7.59 (m, 4H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.52-7.48 (m, 4H), 7.45 (s, 1H), 7.44-7.38 (m, 3H), 7.32 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 142.7, 141.3, 140.3, 140.0, 138.4, 133.5, 129.0, 128.9, 128.4, 128.0, 127.9, 127.1, 126.6, 114.4; HRMS calc. for C₂₀H₁₅IO₂SNa (M+Na)⁺, 468.9735; found, 468.9729.



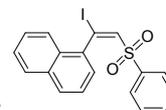
(E)-3-(1-iodo-2-(phenylsulfonyl)vinyl)thiophene

Compound **3ja** was obtained in 62% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.66-7.63 (m, 2H), 7.60 (dd, *J*₁ = 1.3 Hz, *J*₂ = 3.0 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 8.1 Hz, 2H), 7.39 (s, 1H), 7.21 (dd, *J*₁ = 3.0 Hz, *J*₂ = 5.0 Hz, 1H), 6.95 (dd, *J*₁ = 1.3 Hz, *J*₂ = 5.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 141.3, 140.2, 138.8, 133.5, 129.0, 128.4, 127.6, 125.5, 108.0; HRMS calc. for C₁₂H₉IO₂S₂Na (M+Na)⁺, 398.8986; found, 398.8983.



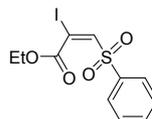
(E)-1-(1-iodo-1-phenylprop-1-en-2-ylsulfonyl)benzene

Compound **3ka** was obtained in 70% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.53-7.50 (m, 3H), 7.37 (t, *J* = 6.5 Hz, 2H), 7.25-7.22 (m, 3H), 7.12-7.10 (m, 2H), 2.56 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 144.0, 142.8, 140.4, 133.1, 128.9, 128.7, 127.7, 127.7, 127.6, 116.1, 27.0; HRMS calc. for C₁₅H₁₄IO₂S (M+H)⁺, 384.9759; found, 384.9757.



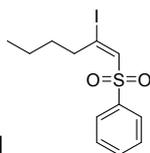
(E)-1-(1-iodo-2-(phenylsulfonyl)prop-1-enyl)naphthalene

Compound **3la** was obtained in 82% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.86-7.80 (m, 2H), 7.71 (s, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.47-7.38 (m, 4H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 143.7, 139.2, 136.1, 133.4, 133.1, 130.2, 128.5, 128.3, 127.8, 126.6, 126.3, 125.2, 125.0, 124.9, 112.4; HRMS calc. for C₁₈H₁₃IO₂SNa (M+Na)⁺, 442.9579; found, 442.9578.



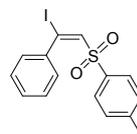
(E)-ethyl 2-iodo-3-(phenylsulfonyl)acrylate

Compound **3ma** was obtained in 36% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.00-7.98 (m, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 2H), 6.98 (s, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 164.6, 139.7, 139.0, 134.3, 129.6, 128.2, 100.4, 63.4, 13.8; HRMS calc. for C₁₁H₁₁IO₄SNa (M+Na)⁺, 388.9320; found, 388.9319.



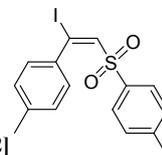
(E)-2-iodohex-1-enylsulfonylbenzene^[1]

Compound **3na** was obtained in 12% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.95-7.92 (m, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 2H), 7.04 (s, 1H), 3.06 (t, *J* = 7.4 Hz, 2H), 1.56-1.51 (m, 2H), 1.42-1.37 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 141.0, 138.6, 133.7, 129.5, 127.5, 126.2, 39.9, 32.0, 21.7, 13.8; HRMS calc. for C₁₂H₁₅IO₂SNa (M+Na)⁺, 372.9735; found, 372.9733.



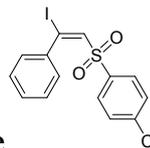
(E)-1-(2-iodo-2-phenylvinylsulfonyl)-4-methylbenzene^[1]

Compound **3ab** was obtained in 88% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.38 (s, 1H), 7.34-7.28 (m, 3H), 7.26-7.24 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 144.6, 141.3, 139.7, 137.4, 129.8, 129.7, 127.9, 127.9, 127.7, 114.2, 21.6; HRMS calc. for C₁₅H₁₃IO₂SNa (M+Na)⁺, 406.9579; found, 406.9577.



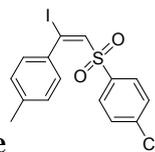
(E)-1-(2-iodo-2-p-tolylvinylsulfonyl)-4-methylbenzene^[2]

Compound **3bb** was obtained in 74% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.33 (s, 1H), 7.24-7.18 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 144.5, 140.7, 140.2, 137.5, 136.9, 129.7, 128.6, 127.9, 127.8, 114.8, 21.6, 21.5; HRMS calc. for C₁₆H₁₅IO₂SNa (M+Na)⁺, 420.9735; found, 420.9736.



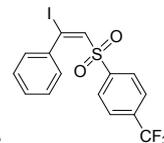
(E)-1-chloro-4-(2-iodo-2-phenylvinylsulfonyl)benzene

Compound **3ac** was obtained in 81% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.41 (s, 1H), 7.37-7.28 (m, 5H), 7.22-7.20 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 141.0, 140.2, 139.5, 138.7, 130.0, 129.3, 129.3, 128.1, 127.7, 115.3; HRMS calc. for C₁₄H₁₀ClIO₂SNa (M+Na)⁺, 426.9032; found, 426.9037.



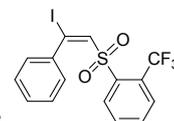
(E)-1-chloro-4-(2-iodo-2-p-tolylvinylsulfonyl)benzene

Compound **3bc** was obtained in 70% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.51 (d, *J* = 8.3Hz, 2H), 7.37 (s, 1H), 7.29-7.24 (m, 4H), 7.00 (t, *J* = 8.6 Hz, 2H), 2.43 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 164.5, 162.0, 144.8, 141.7, 137.3, 135.7, 130.1, 130.0, 129.8, 127.8, 115.2, 115.0, 112.6, 21.6; HRMS calc. for C₁₅H₁₂ClIO₂SNa (M+Na)⁺, 440.9189; found, 440.9187.



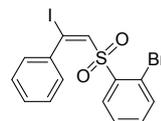
(E)-1-(2-iodo-2-phenylvinylsulfonyl)-4-(trifluoromethyl)benzene

Compound **3ad** was obtained in 77% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.69-7.62 (m, 4H), 7.45 (s, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.30-7.26 (m, 2H), 7.18 (d, *J* = 7.1 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 143.7, 140.7, 139.4, 135.0 (d, *J* = 32.9 Hz), 130.1, 128.4, 128.1, 127.6, 126.0 (q, *J* = 3.6 Hz), 123.0 (q, *J* = 256.1 Hz), 116.0; HRMS calc. for C₁₅H₁₀F₃IO₂SNa (M+Na)⁺, 460.9296; found, 460.9299.



(E)-1-(2-iodo-2-phenylvinylsulfonyl)-2-(trifluoromethyl)benzene

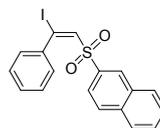
Compound **3ae** was obtained in 86% yield according to the general procedure (16h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 1.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.16-7.14 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 141.7 (q, *J* = 22.4 Hz), 139.5, 138.7, 133.5, 132.0, 132.0, 129.8, 128.5 (d, *J* = 33.3 Hz), 128.2 (q, *J* = 6.0 Hz), 128.0, 127.5, 122.6 (q, *J* = 272.7 Hz), 114.5; HRMS calc. for C₁₅H₁₀F₃IO₂SNa (M+Na)⁺, 460.9296; found, 460.9297.



(E)-1-bromo-2-(2-iodo-2-phenylvinylsulfonyl)benzene

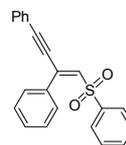
Compound **3af** was obtained in 87% yield according to the general procedure (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.65 (dd, *J*₁ = 1.1 Hz, *J*₂ = 8.0 Hz, 1H), 7.62 (s, 1H), 7.48 (dd, *J*₁ = 1.6 Hz, *J*₂ = 7.9 Hz, 1H), 7.32-7.28 (m, 1H), 7.20-7.17 (m, 1H),

7.15-7.10 (m, 5H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 140.4, 139.8, 139.3, 134.9, 134.2, 131.2, 129.8, 127.8, 127.4, 127.4, 120.6, 114.7; ^1H HRMS calc. for $\text{C}_{14}\text{H}_{10}\text{BrIO}_2\text{SNa}$ ($\text{M}+\text{Na}$) $^+$, 470.8527; found, 470.8529.



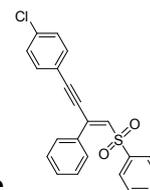
(E)-2-(2-iodo-2-phenylvinylsulfonyl)naphthalene

Compound **3ag** was obtained in 74% yield according to the general procedure (12h). ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.03 (d, $J = 1.5$ Hz, 1H), 7.89 (t, $J = 8.8$ Hz, 2H), 7.81 (t, $J = 8.1$ Hz, 1H), 7.69-7.58 (m, 3H), 7.49 (s, 1H), 7.26-7.23 (m, 1H), 7.21 (d, $J = 4.3$ Hz, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 141.3, 139.5, 136.9, 135.1, 132.0, 130.0, 129.9, 129.4, 129.3, 127.9, 127.7, 127.6, 122.4, 114.8; HRMS calc. for $\text{C}_{18}\text{H}_{13}\text{IO}_2\text{SNa}$ ($\text{M}+\text{Na}$) $^+$, 442.9579; found, 442.9578.



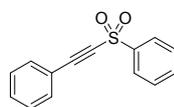
(E)-4-(phenylsulfonyl)but-3-en-1-yne-1,3-diyl)dibenzene

Compound **4aa** was obtained in 92% yield according to the procedure A (1h). ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.70-7.67 (m, 2H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.49-7.43 (m, 5H), 7.42-7.34 (m, 7H), 7.00 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 141.0, 137.4, 135.3, 134.2, 133.3, 132.0, 129.7, 129.6, 129.1, 128.9, 128.5, 128.0, 127.8, 121.6, 97.7, 88.3; HRMS calc. for $\text{C}_{22}\text{H}_{17}\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$, 345.0949; found, 345.0943.



(E)-1-chloro-4-(3-phenyl-4-(phenylsulfonyl)but-3-en-1-ynyl)benzene

Compound **4af** was obtained in 84% yield according to the procedure A (1h). ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.69-7.67 (m, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.47-7.45 (m, 3H), 7.43-7.36 (m, 6H), 7.35-7.31 (m, 2H), 6.99 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 140.8, 137.0, 135.9, 135.7, 134.0, 133.3, 133.2, 129.7, 129.0, 128.9, 128.9, 128.1, 127.8, 120.0, 96.3, 89.1; HRMS calc. for $\text{C}_{22}\text{H}_{15}\text{ClO}_2\text{SNa}$ ($\text{M}+\text{Na}$) $^+$, 401.0379; found, 401.0383.



(phenylethynylsulfonyl)benzene 5aa^[3]

Compound **5aa** was obtained in 78% yield according to the procedure B (12h). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.12-8.10 (m, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.65-7.61 (t, *J* = 7.9 Hz, 2H), 7.56-7.54 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 141.8, 134.2, 132.8, 131.6, 129.4, 128.7, 127.4, 117.9, 93.5, 85.4; HRMS calc. for C₁₄H₁₀O₂SNa (M+Na)⁺, 265.0299; found, 265.0293.



Compound **6ea** was obtained in 73% yield according to the procedure C. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.69-7.63 (m, 2H), 7.57 (t, *J* = 7.9 Hz, 2H), 7.52-7.49 (m, 2H), 7.10 (t, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 15.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 165.6 (d, *J* = 251.5 Hz), 141.2, 140.7, 133.5, 130.6 (d, *J* = 8.7 Hz), 129.4, 128.7, 127.7, 127.1 (d, *J* = 2.4 Hz), 116.3 (d, *J* = 22.0 Hz); HRMS calc. for C₁₄H₁₁FO₂SNa (M+Na)⁺, 285.0361; found, 285.0366.



Compound **6fa** was obtained in 74% yield according to the procedure C. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.68-7.63 (m, 2H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.45-7.37 (m, 4H), 6.87 (d, *J* = 15.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 141.0, 140.5, 137.3, 133.5, 130.9, 129.8, 129.4, 129.4, 128.0, 127.7; HRMS calc. for C₁₄H₁₁ClO₂SNa (M+Na)⁺, 301.0066; found, 301.0065.

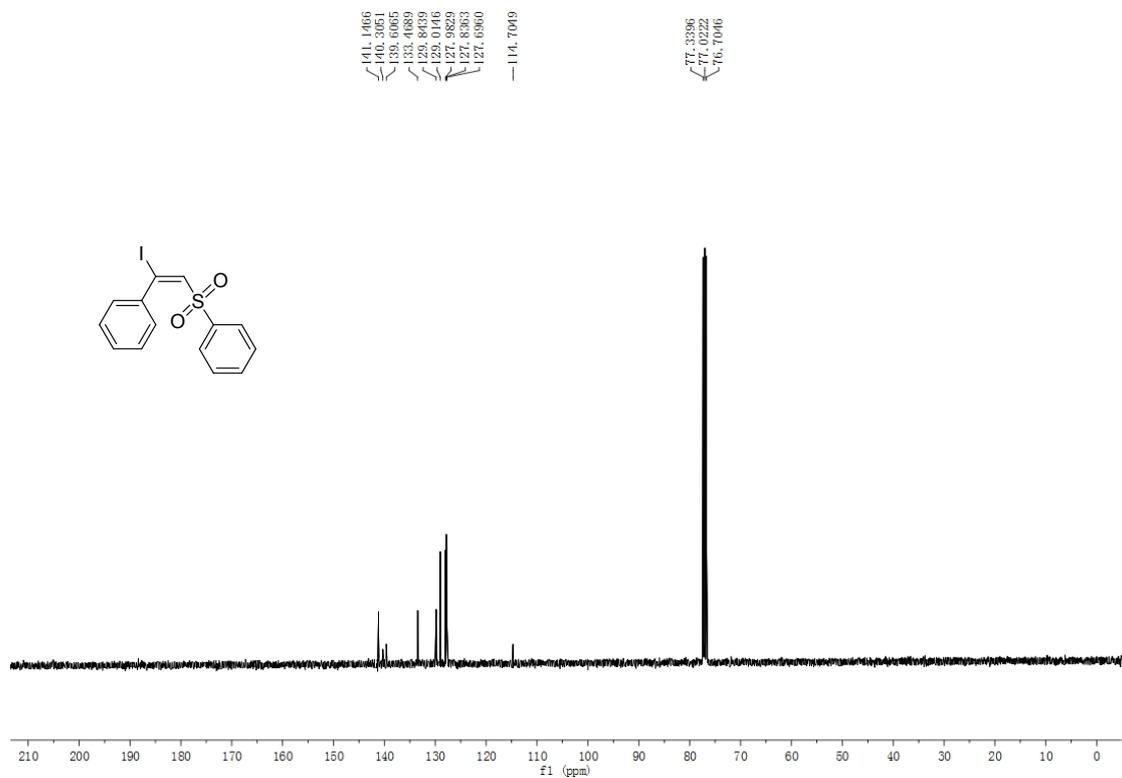
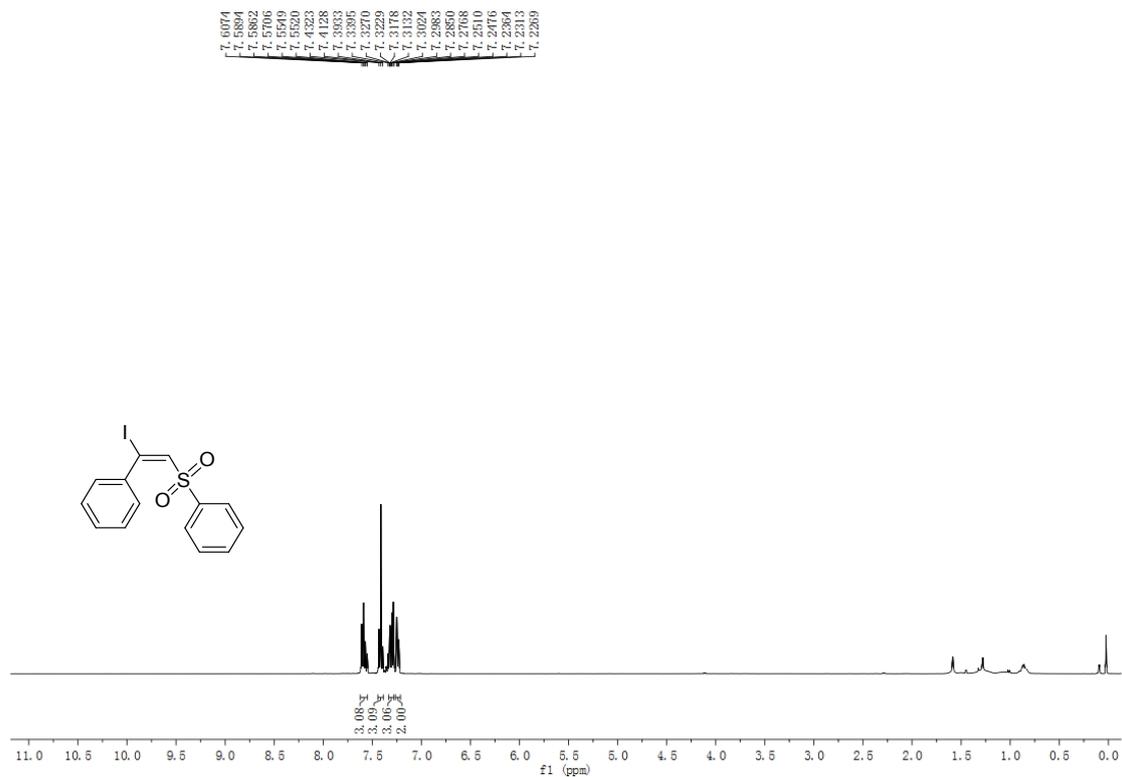


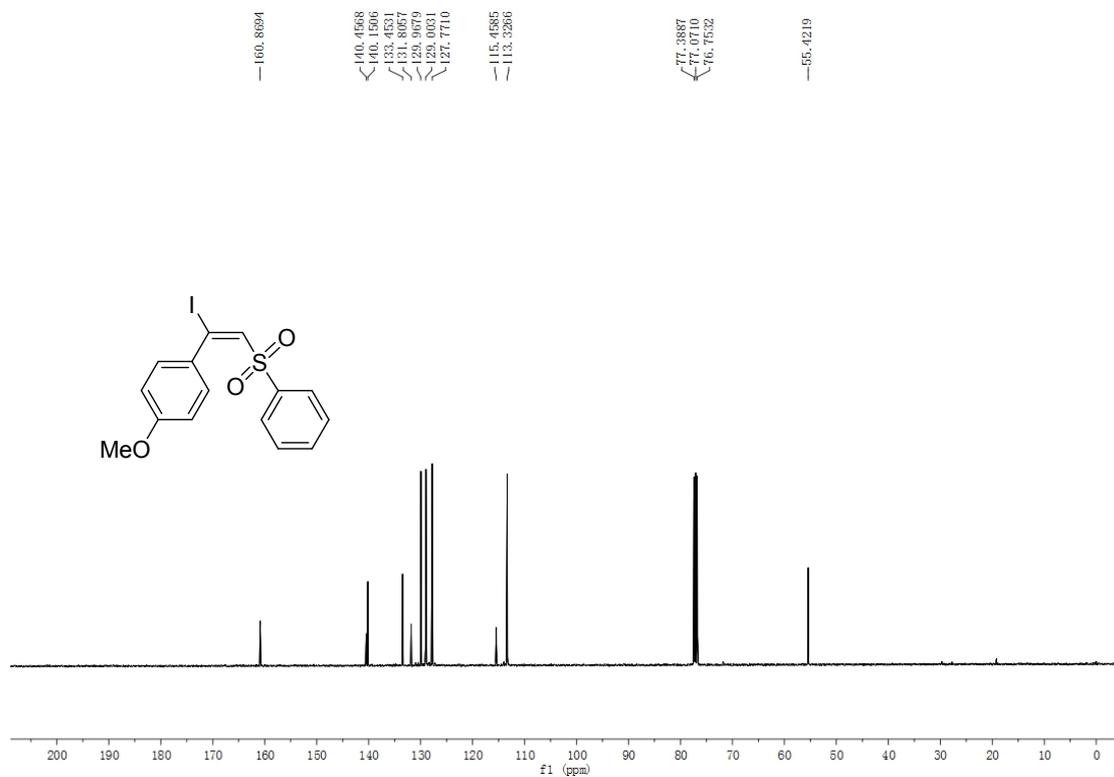
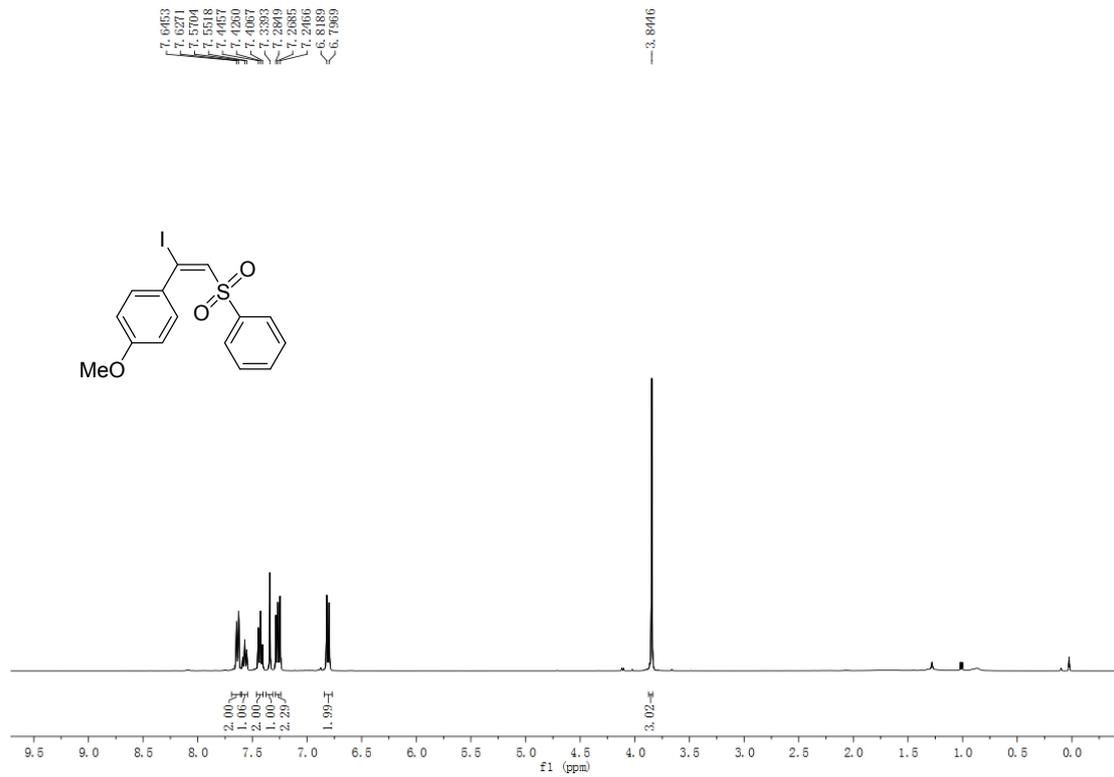
Compound **6af** was obtained in 77% yield according to the procedure C. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.28 (dd, *J*₁ = 1.7 Hz, *J*₂ = 7.9 Hz, 1H), 7.81 (d, *J* = 15.4 Hz, 1H), 7.71 (d, *J*₁ = 1.1 Hz, *J*₂ = 7.9 Hz, 1H), 7.55-7.53 (m, 3H), 7.49-7.43 (m, 4H), 7.14 (d, *J* = 15.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 145.5, 139.9, 135.5, 134.5, 132.4, 131.5, 131.1, 129.2, 128.7, 128.1, 125.0, 121.0; HRMS calc. for C₁₄H₁₁O₂BrSNa (M+Na)⁺, 344.9561; found, 344.9563.

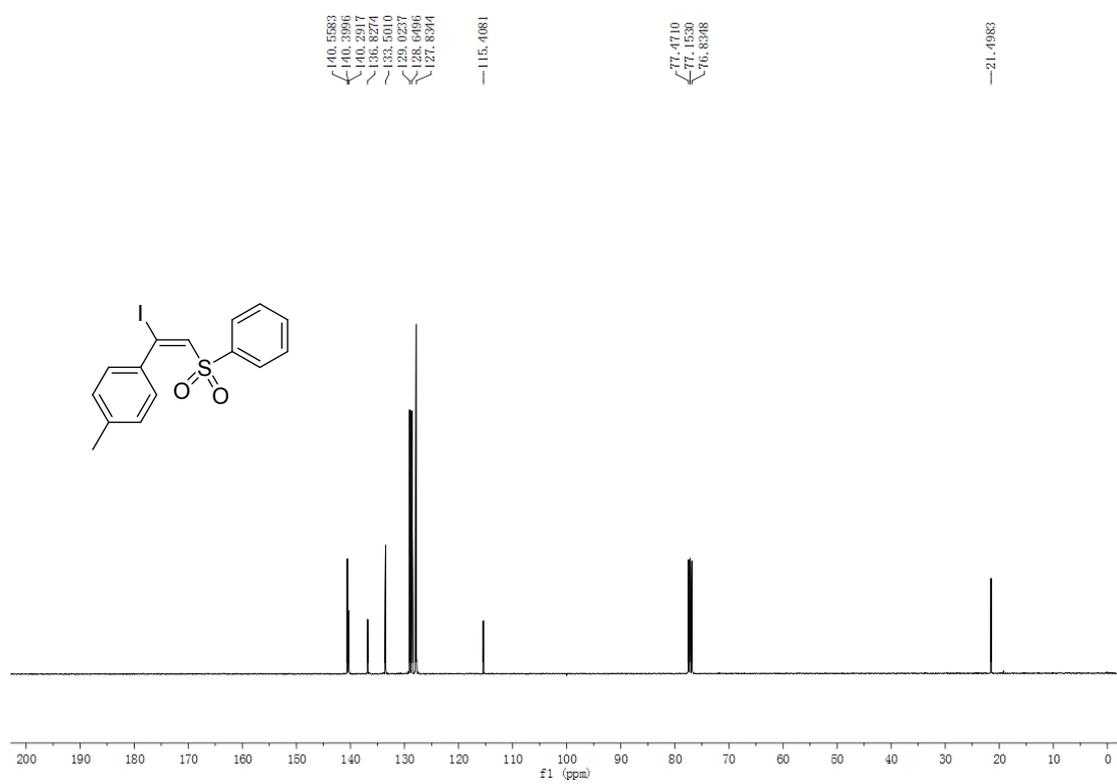
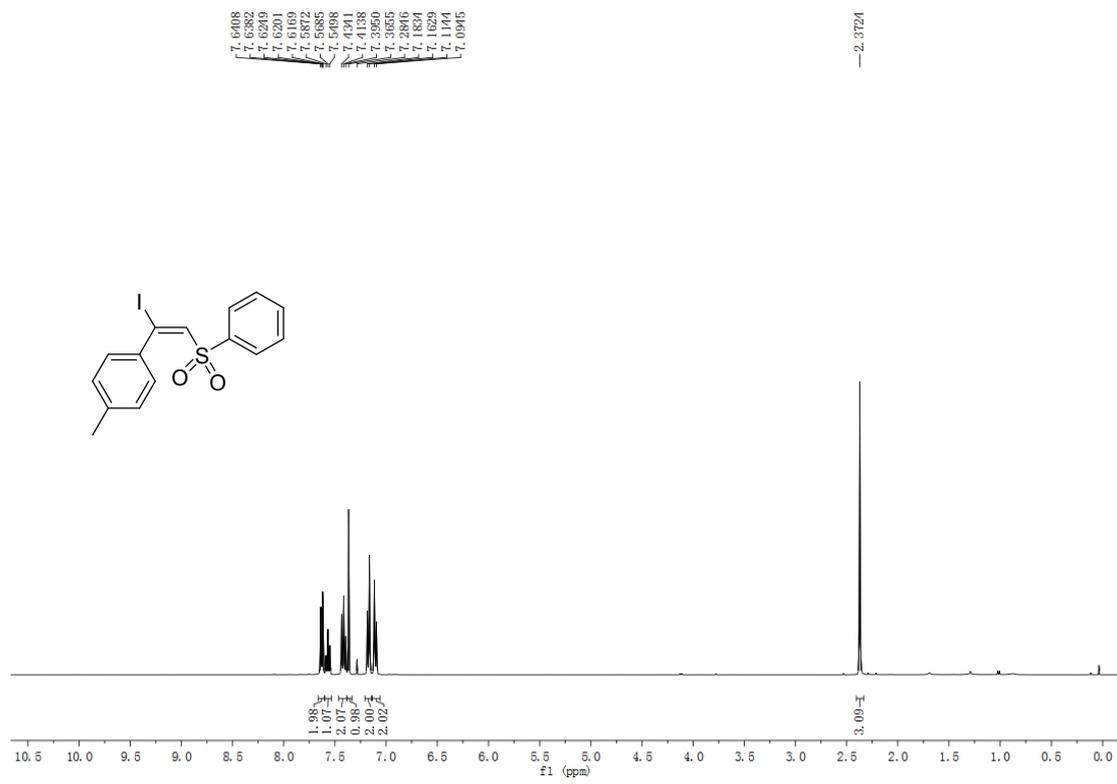
7. Reference

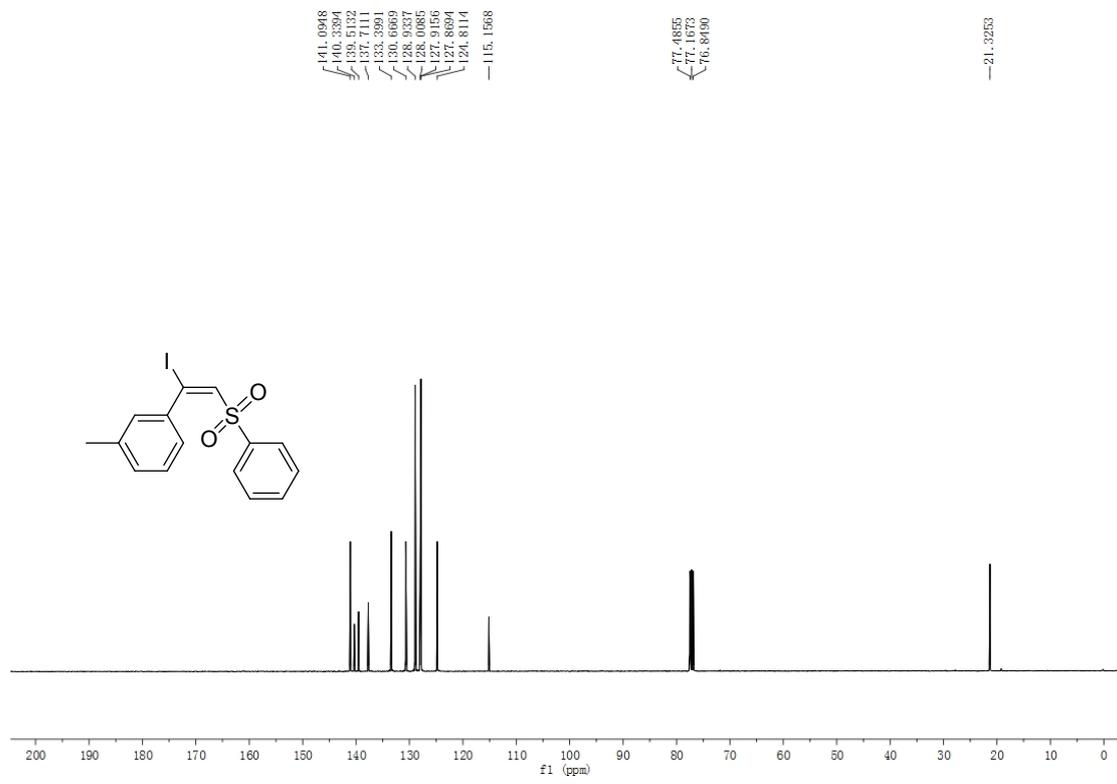
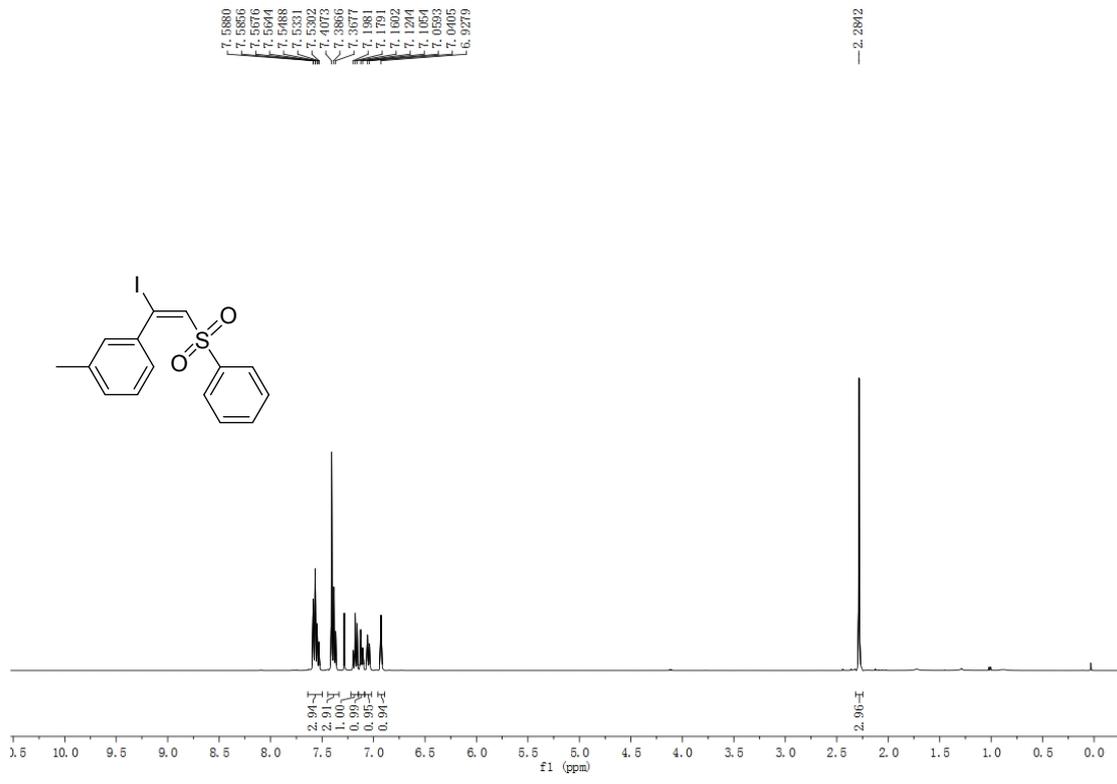
- [1] X. Q. Li, X. S. Xu and X. H. Shi, *Tetrahedron Lett*; 2013, **54**, 3071.
- [2] V. Nair, A. Augustine and T. D. Suja, *Synthesis*, 2002, 2259.
- [3] H. Qian and X. Huang, *Tetrahedron Lett* 2002, **43**, 1059.
- [4] (a) M. Bian, F. Xu and C. Ma, *Synthesis*, 2007, 2951. (b) A. Battace, T. Zair, H. Doucet and M. Santelli, *Synthesis*, 2006, 3495.

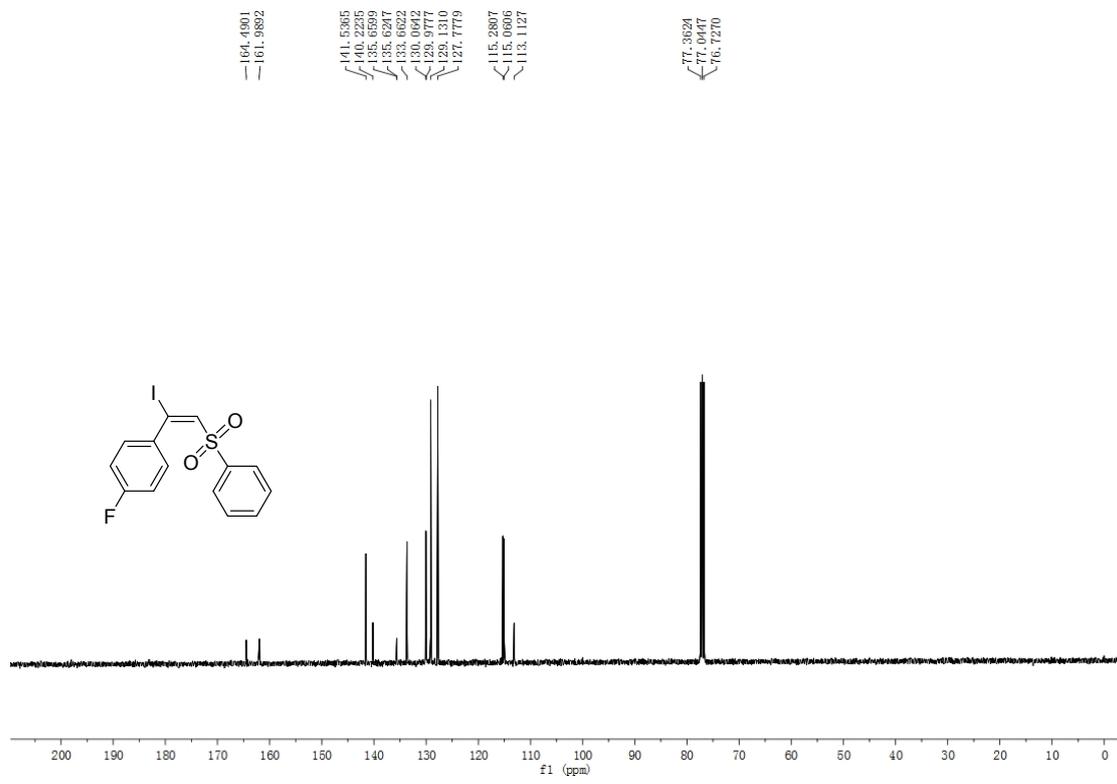
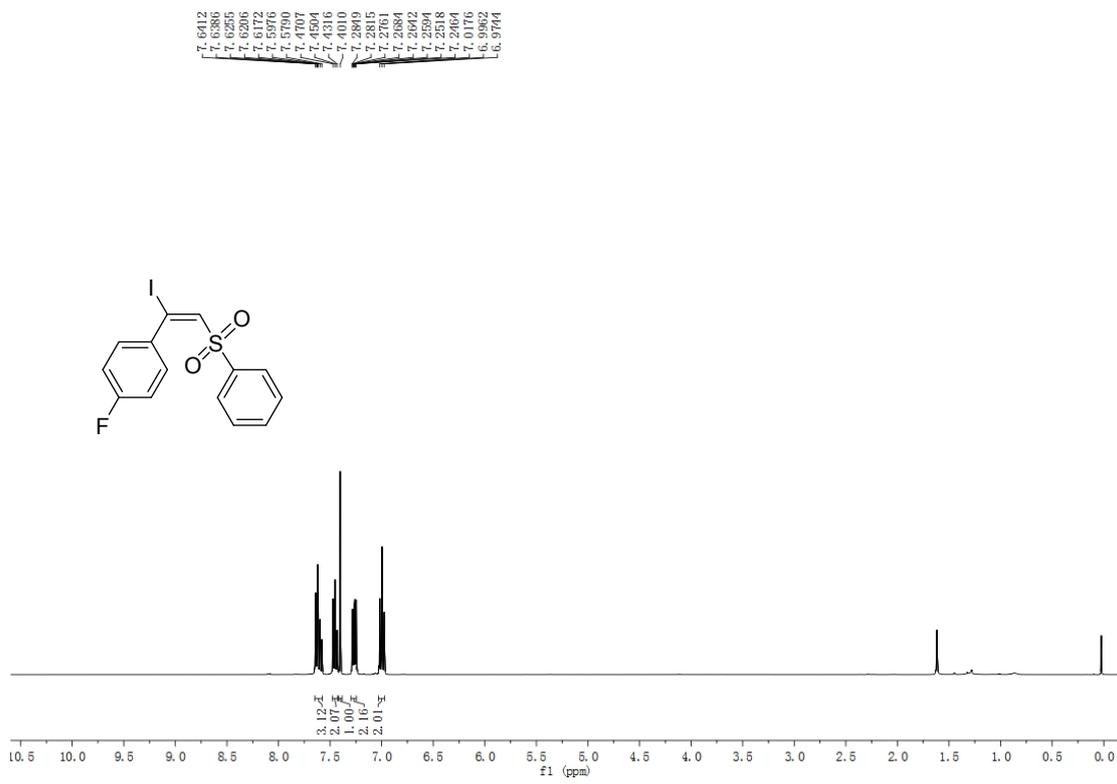
8. Copies of NMR Spectra for 3aa-6af.

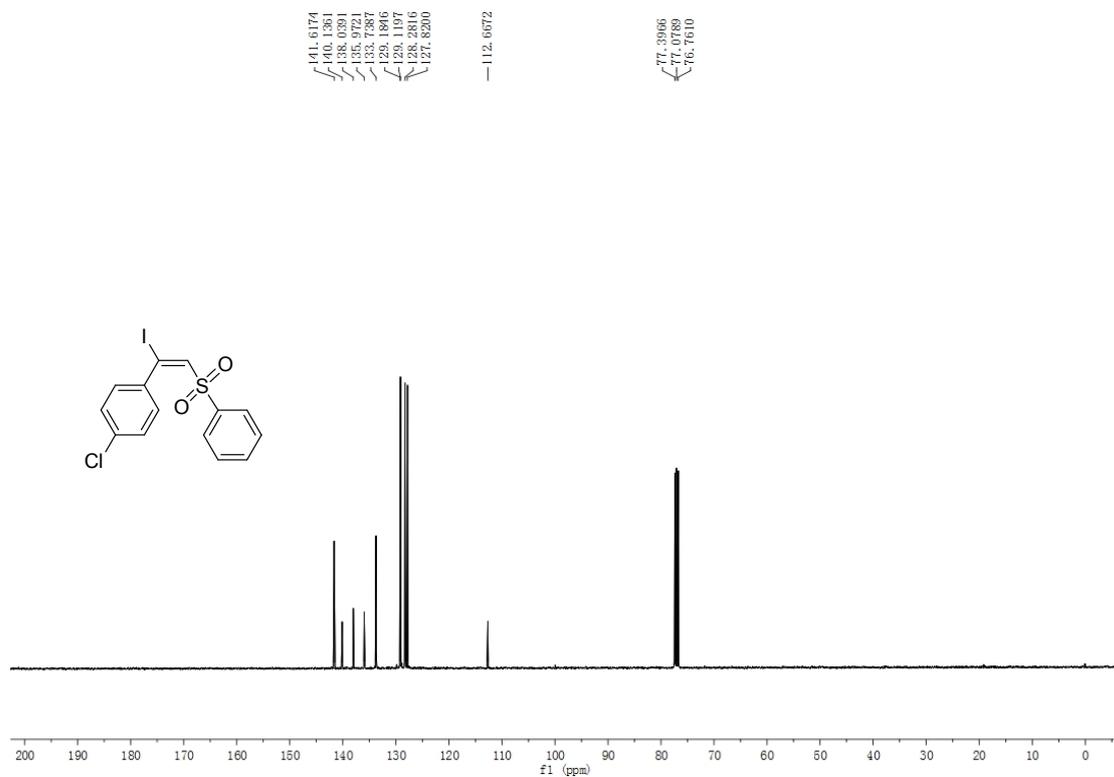
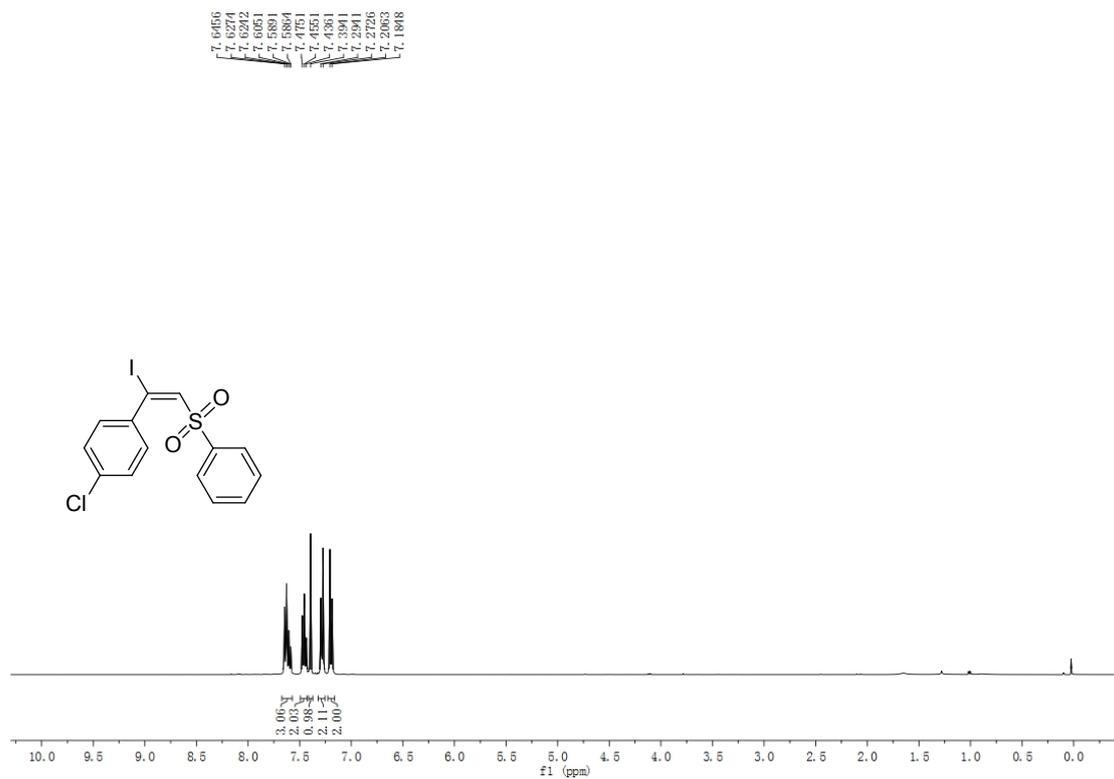




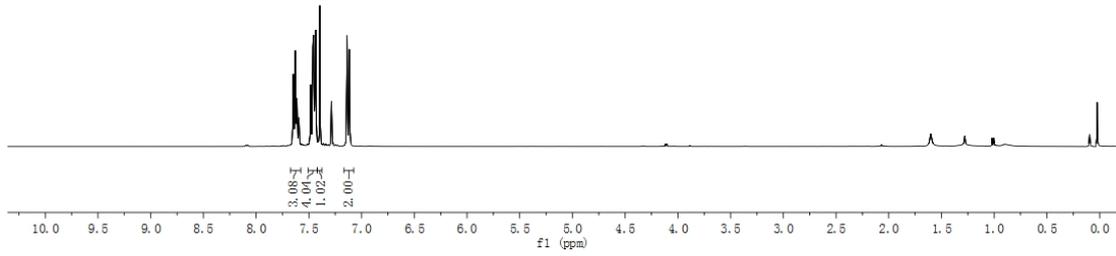
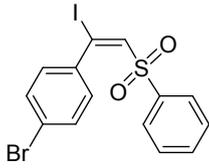




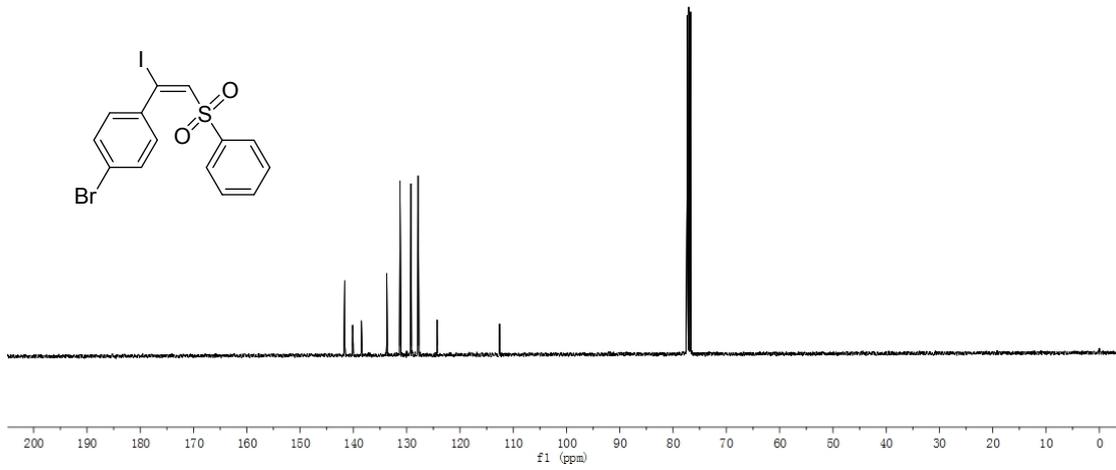
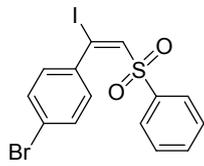




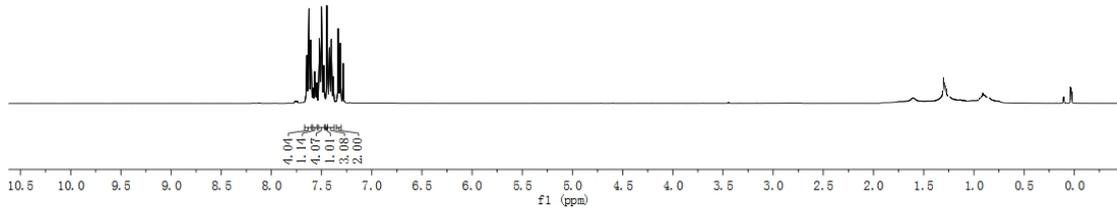
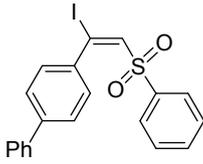
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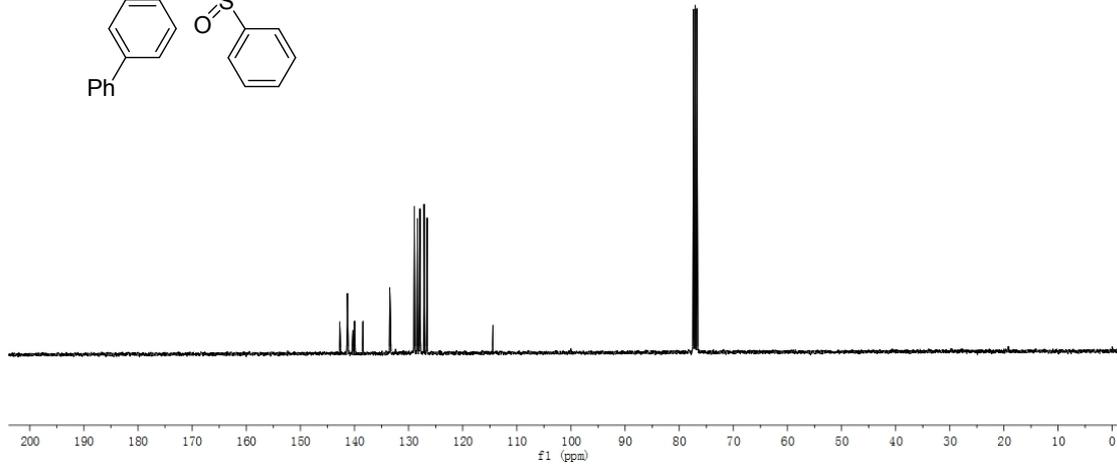
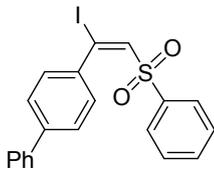


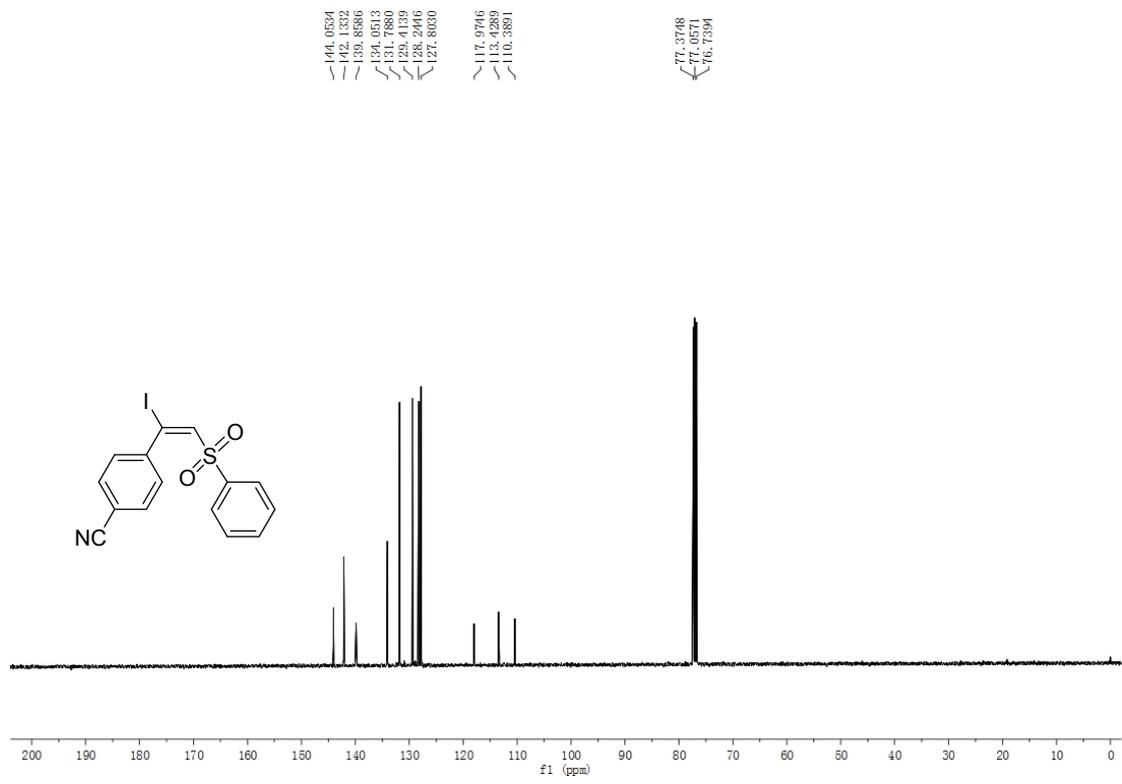
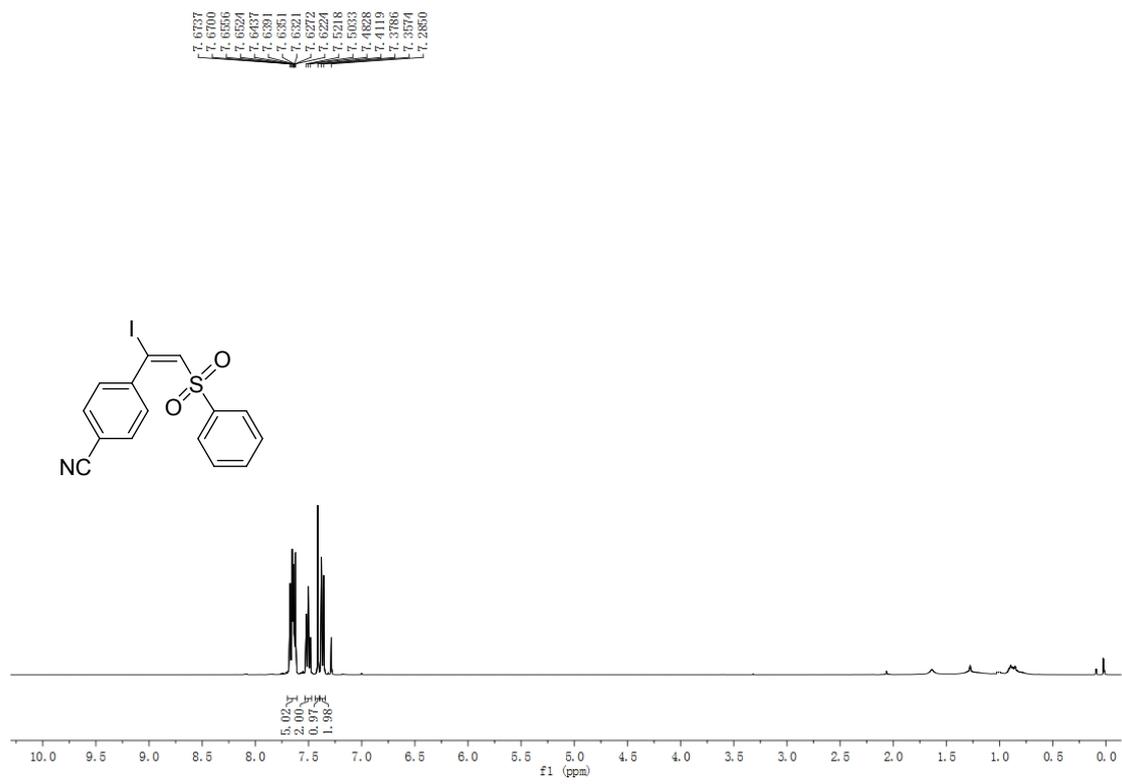
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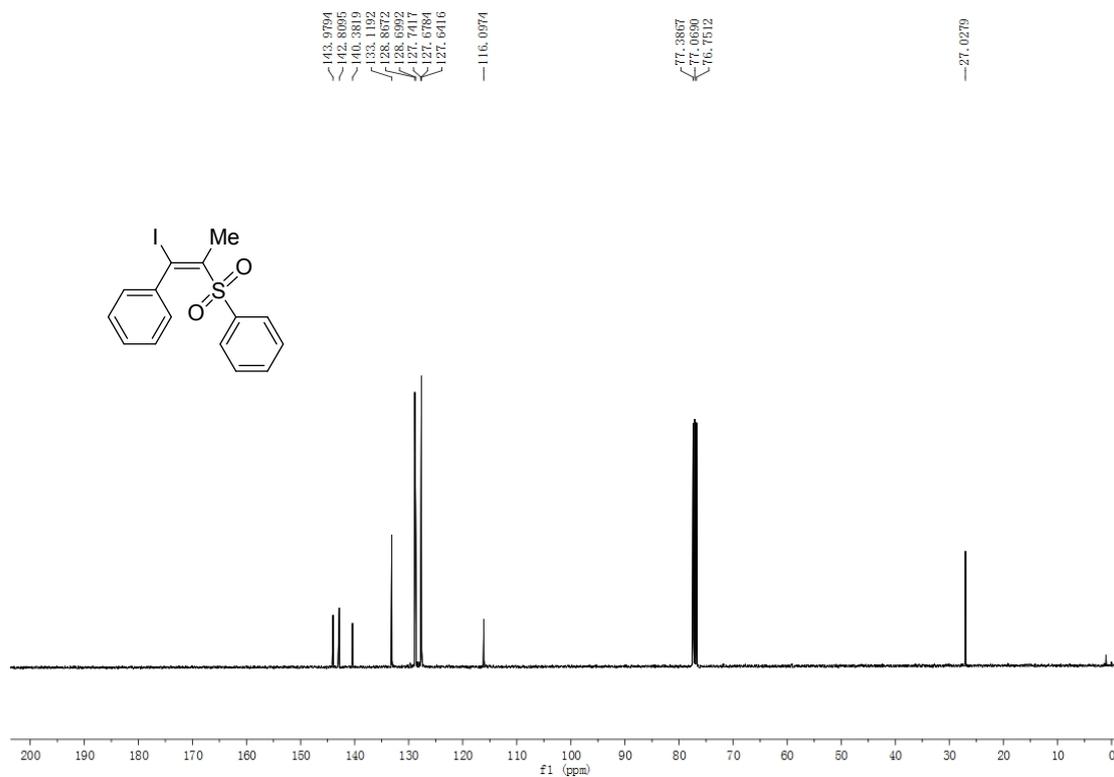
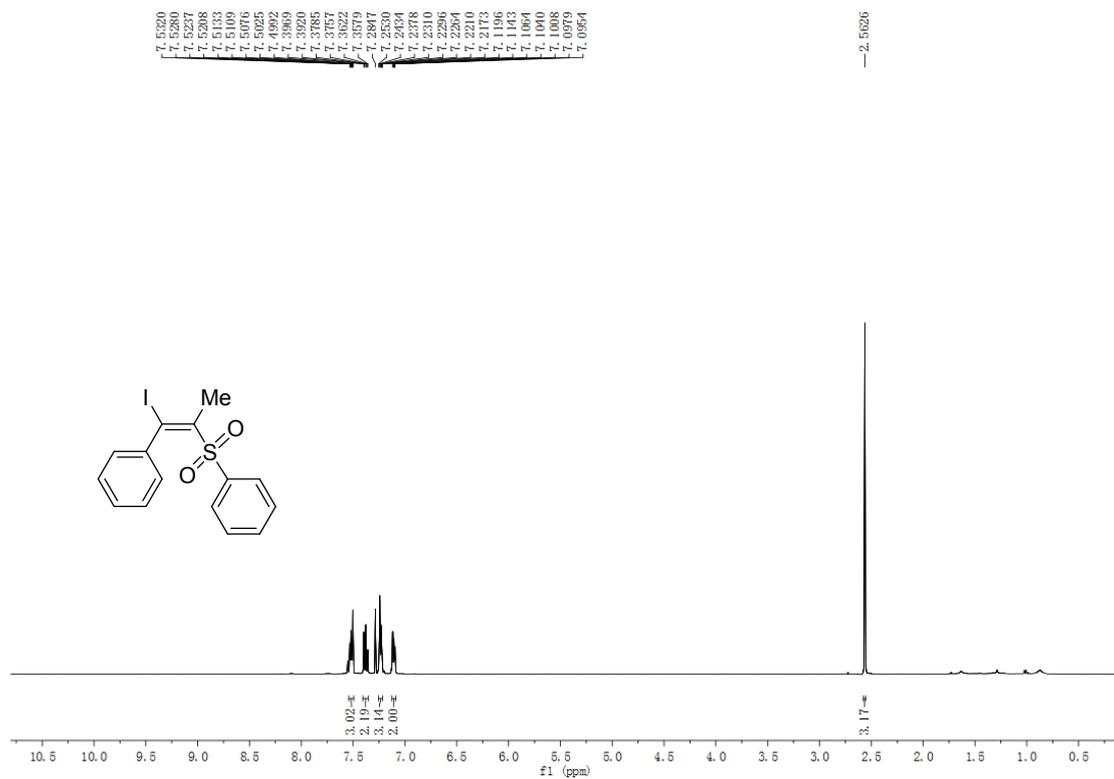


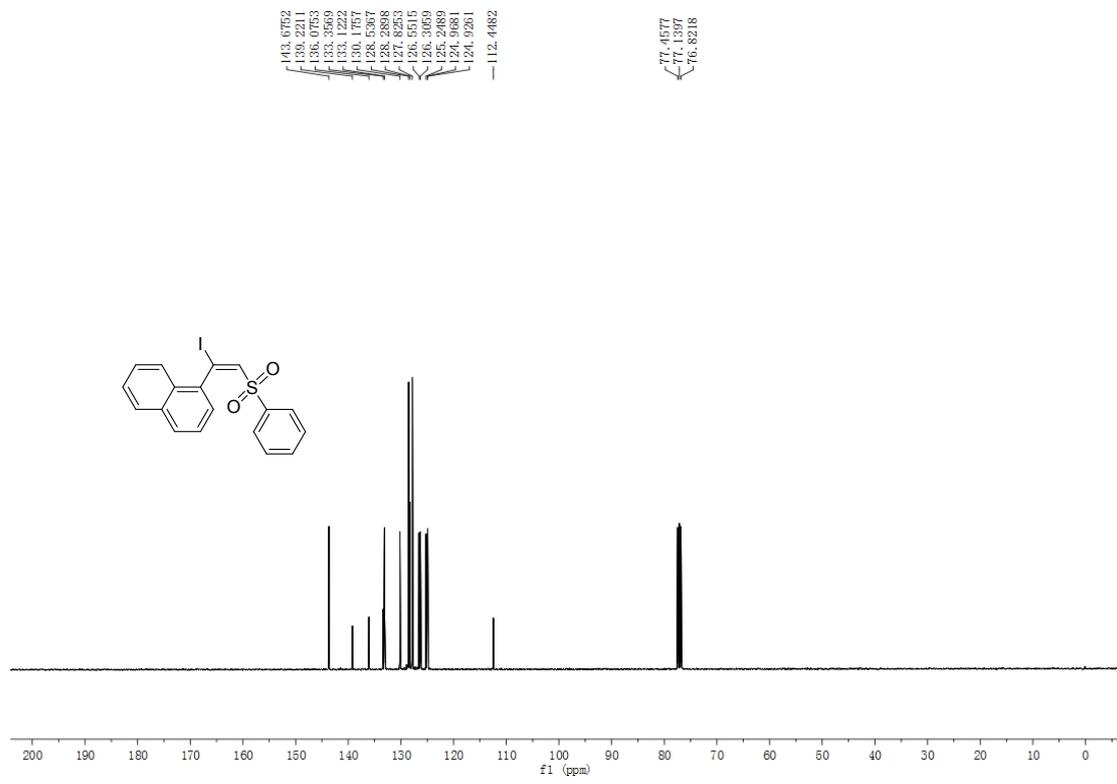
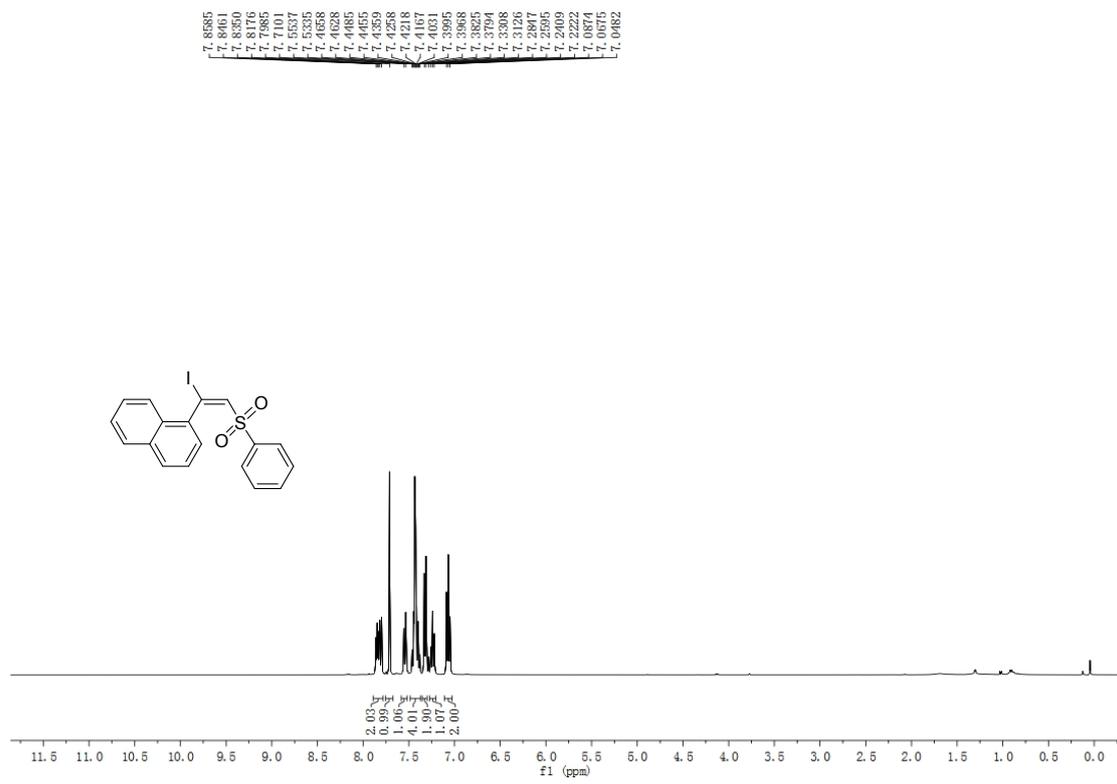
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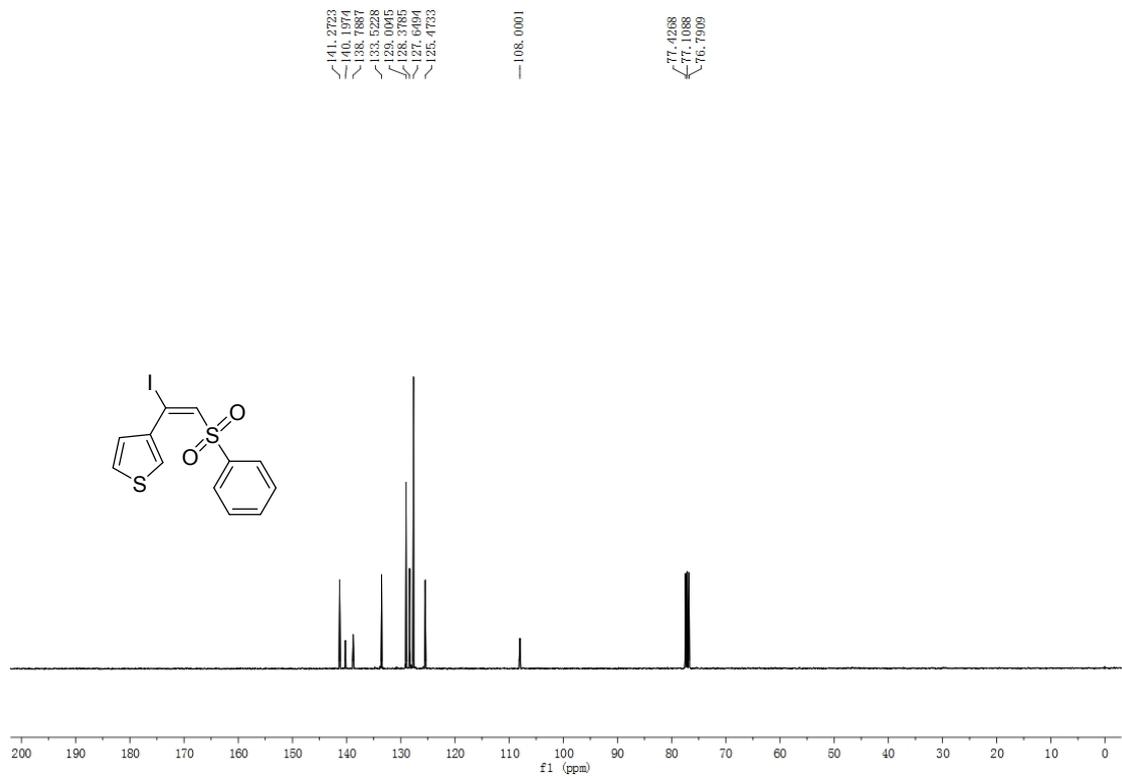
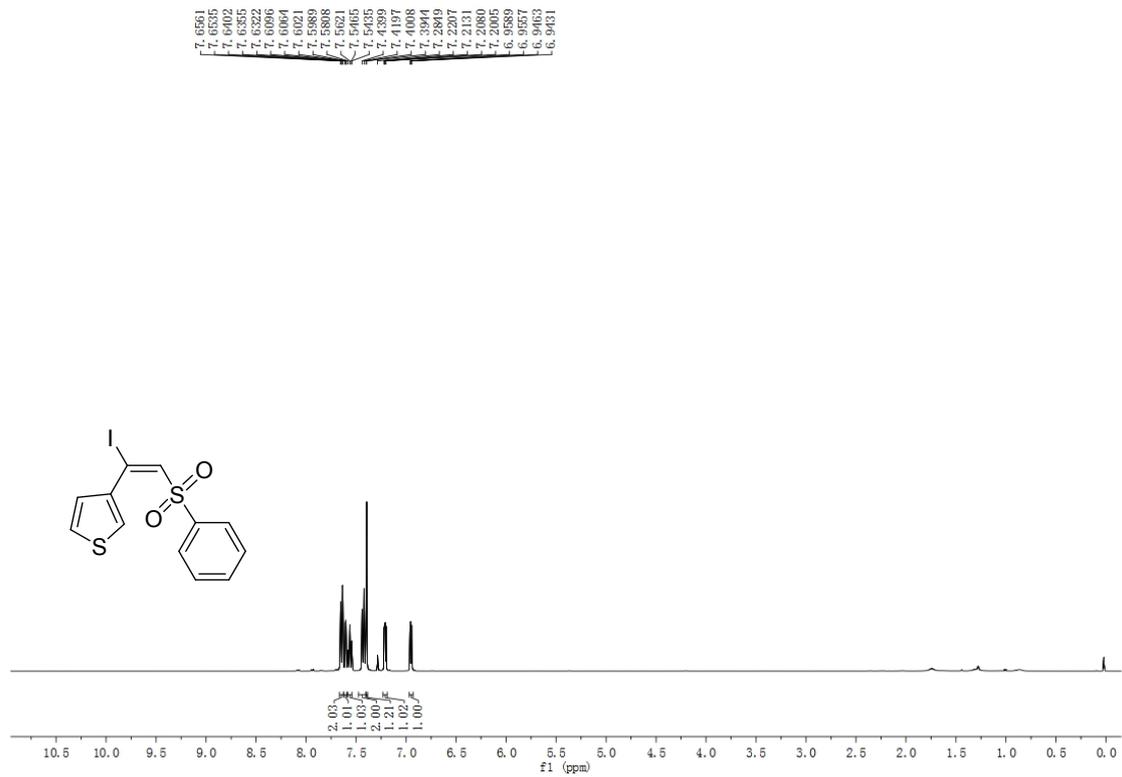
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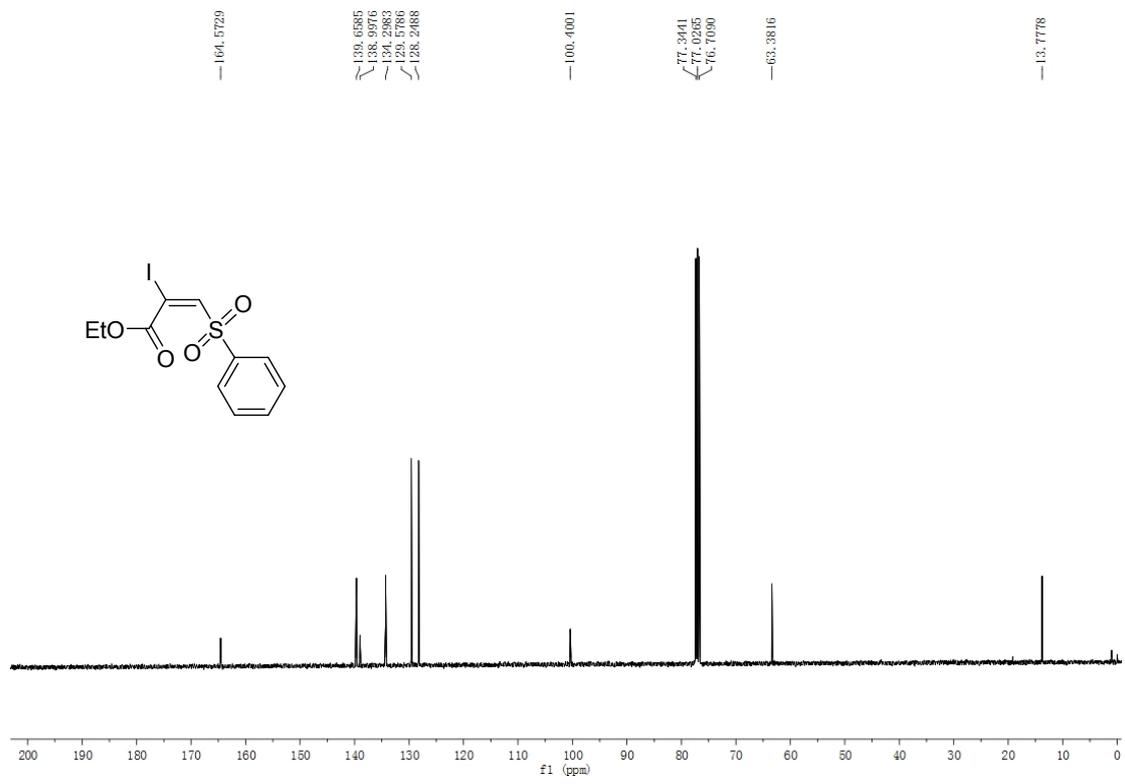
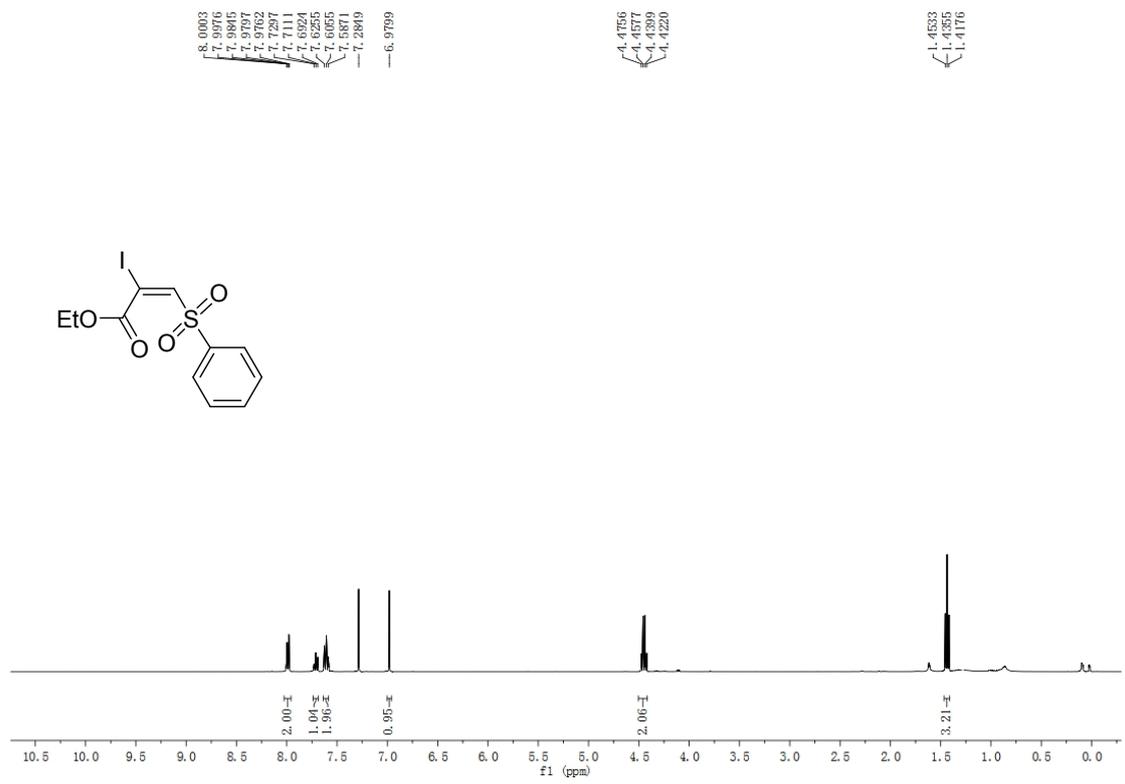
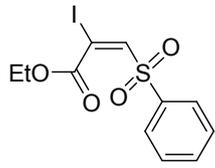


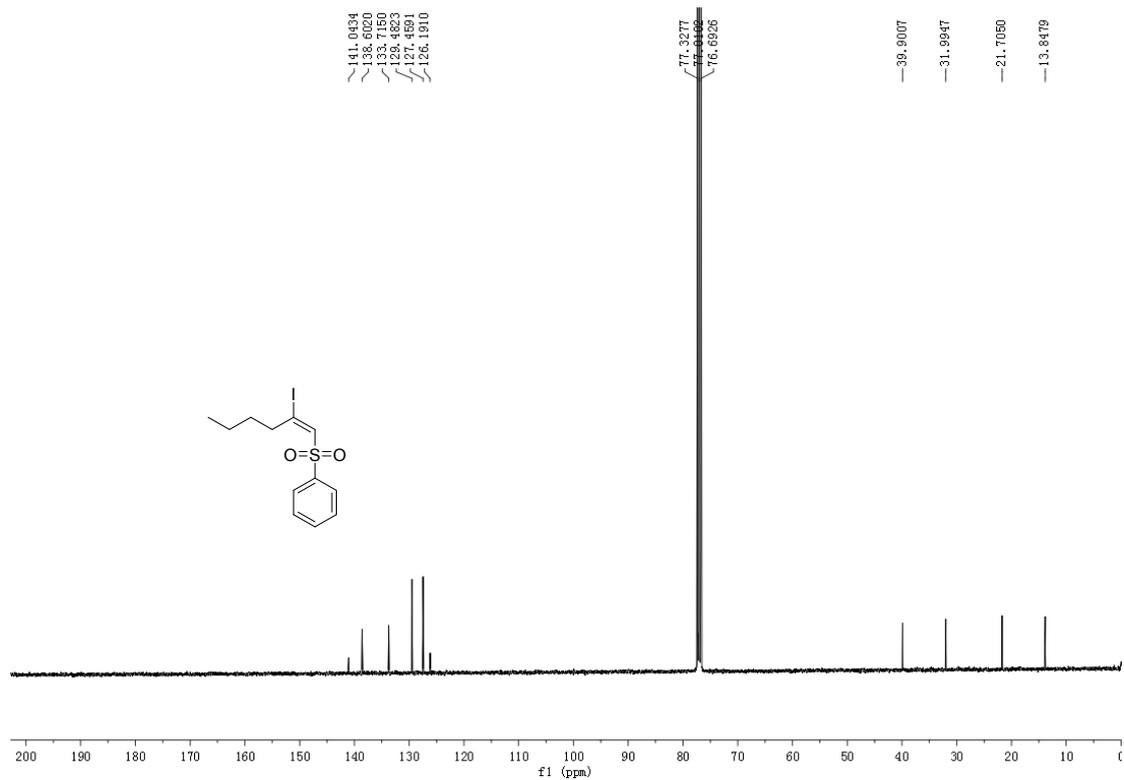
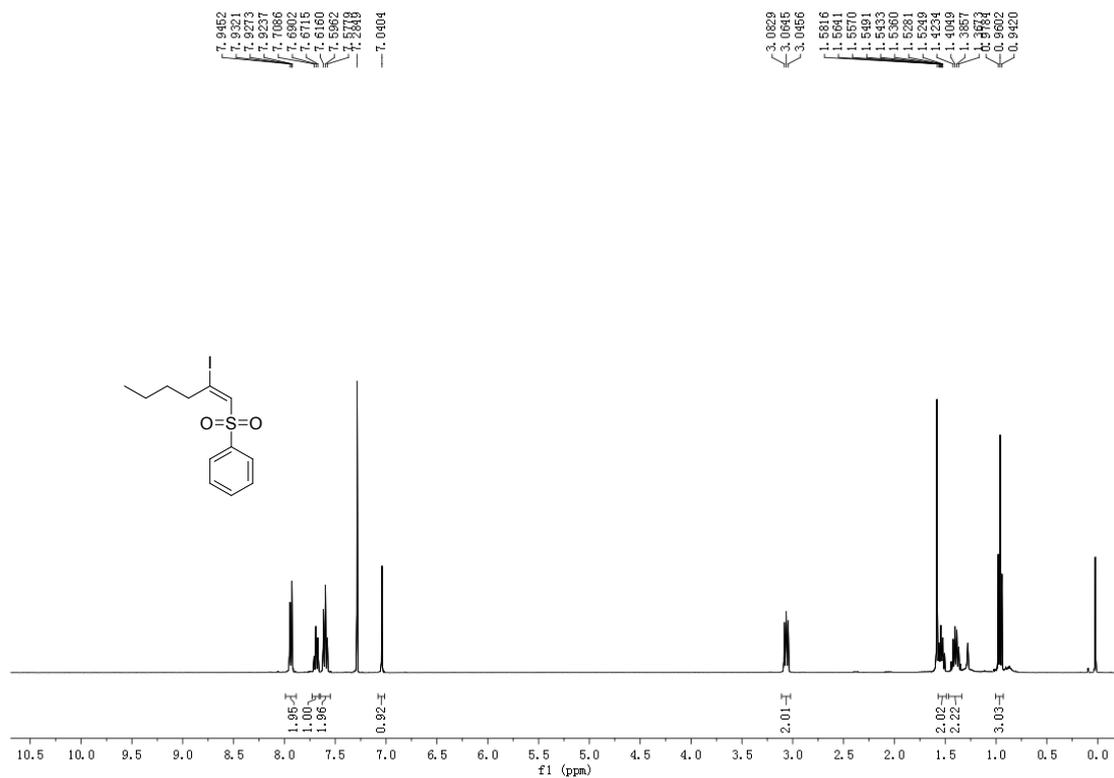


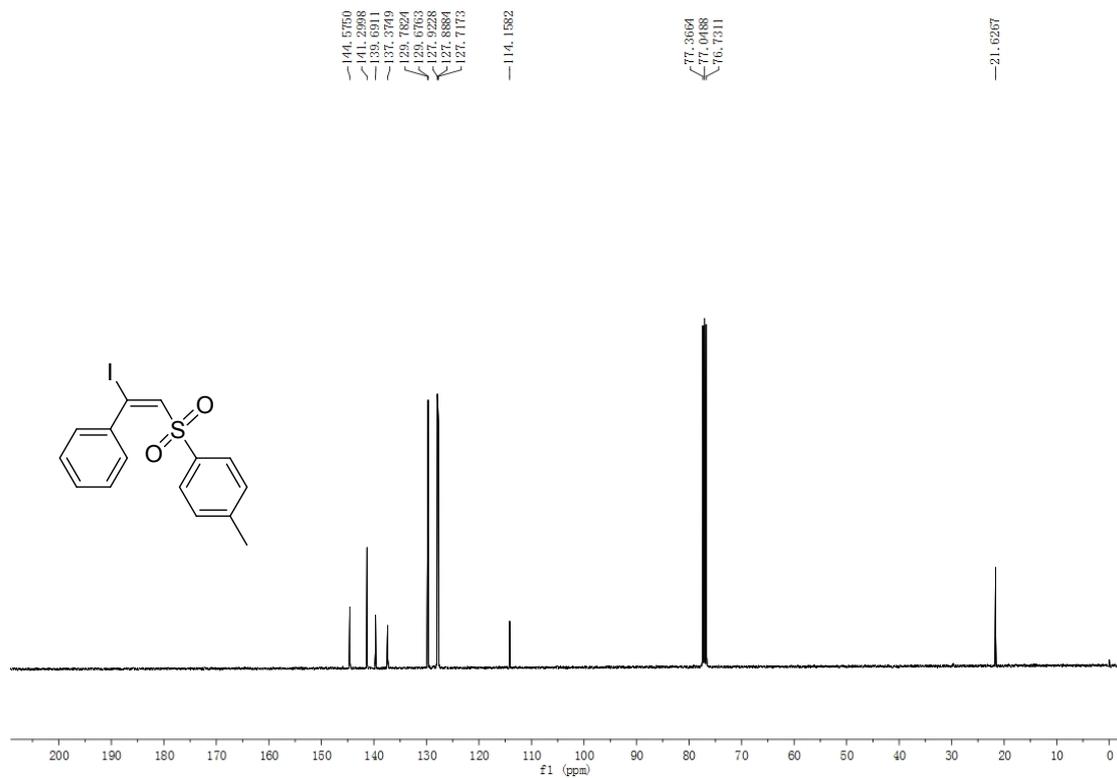
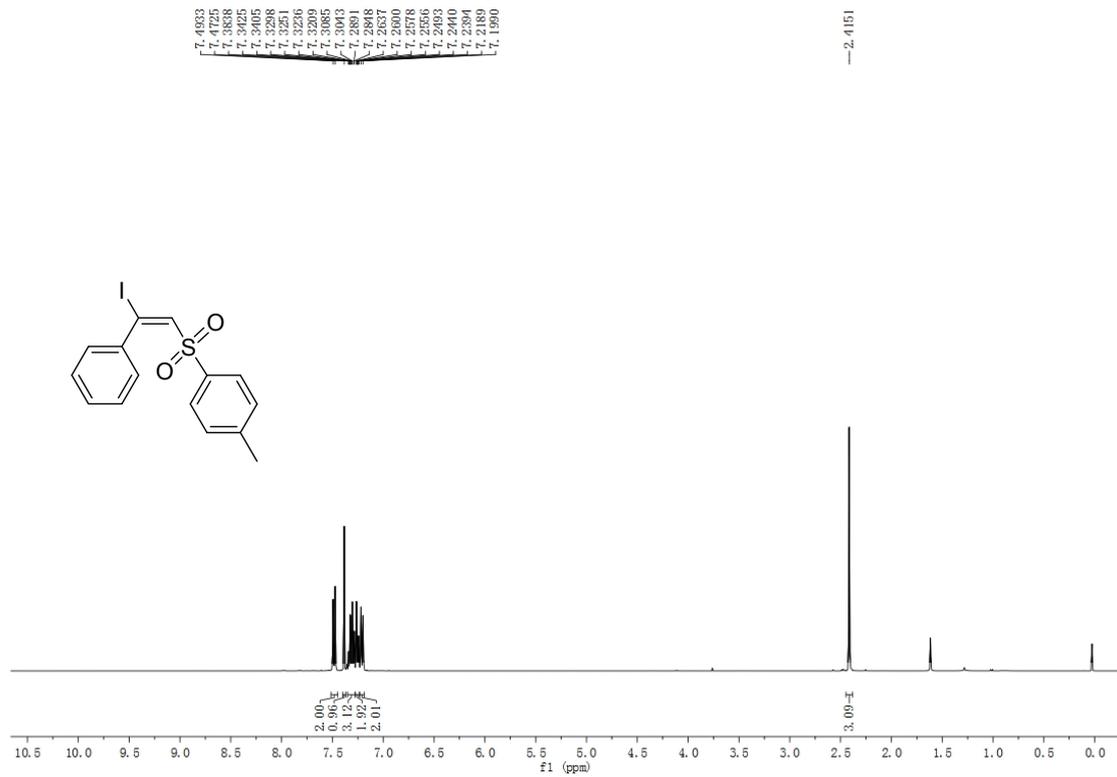


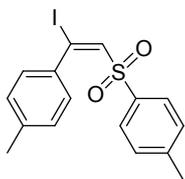
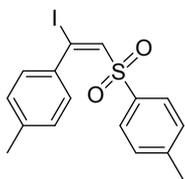




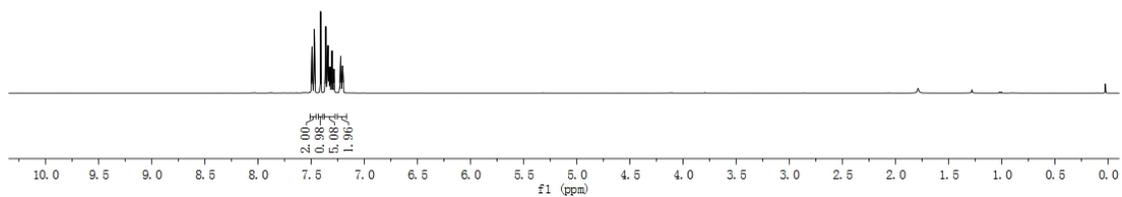
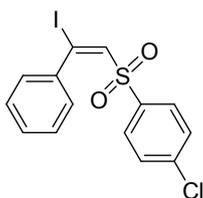






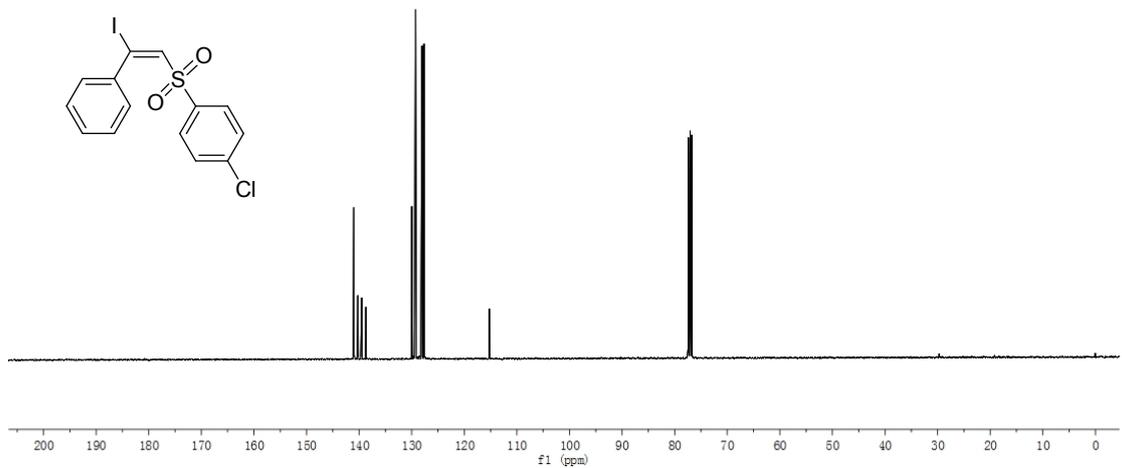
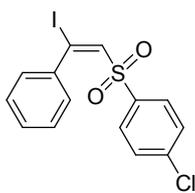


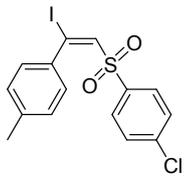
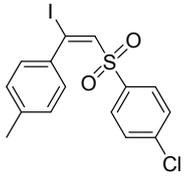
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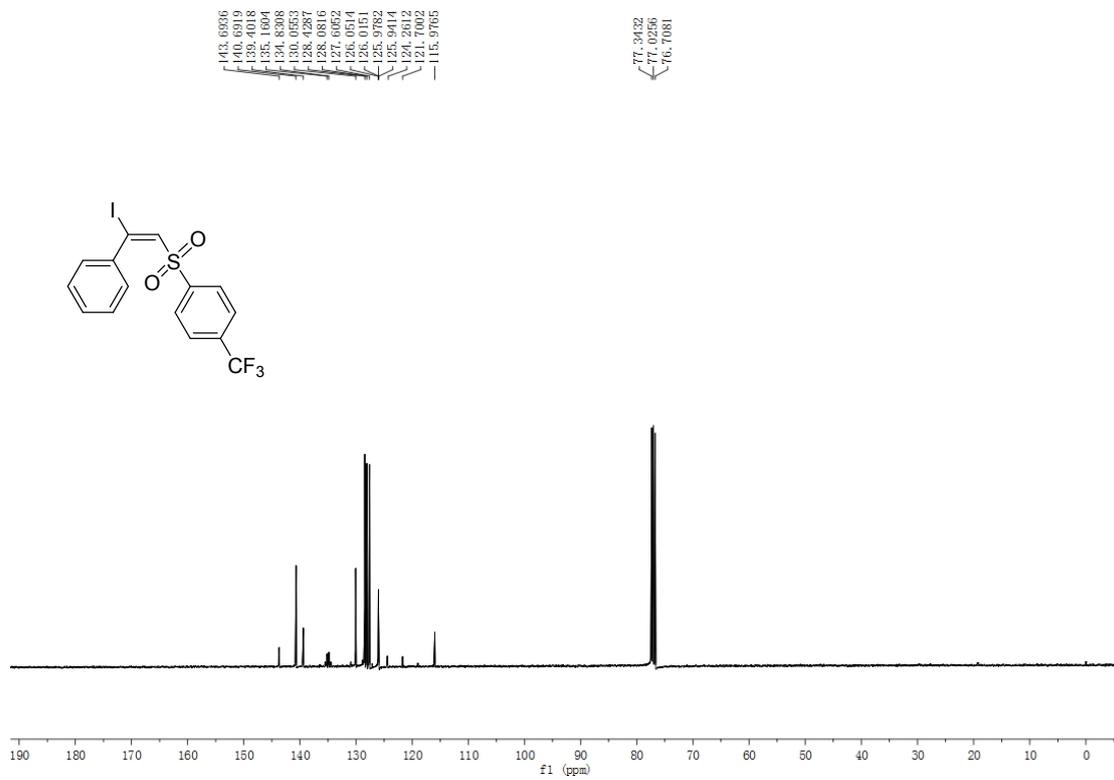
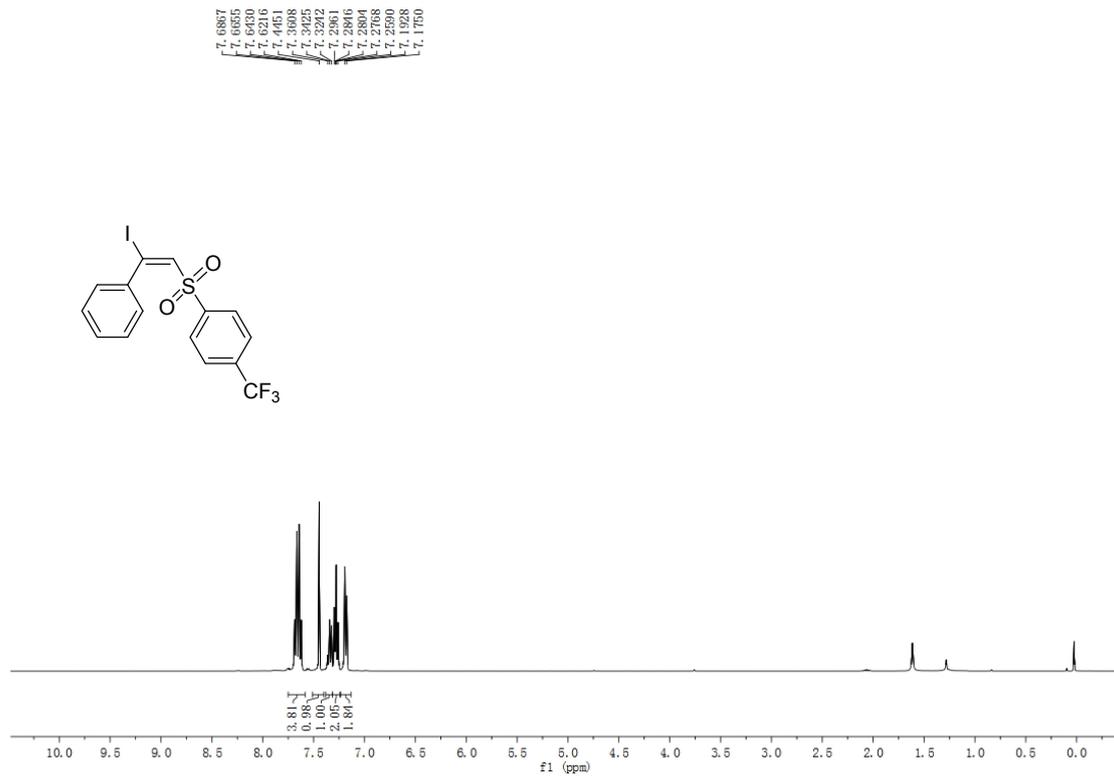


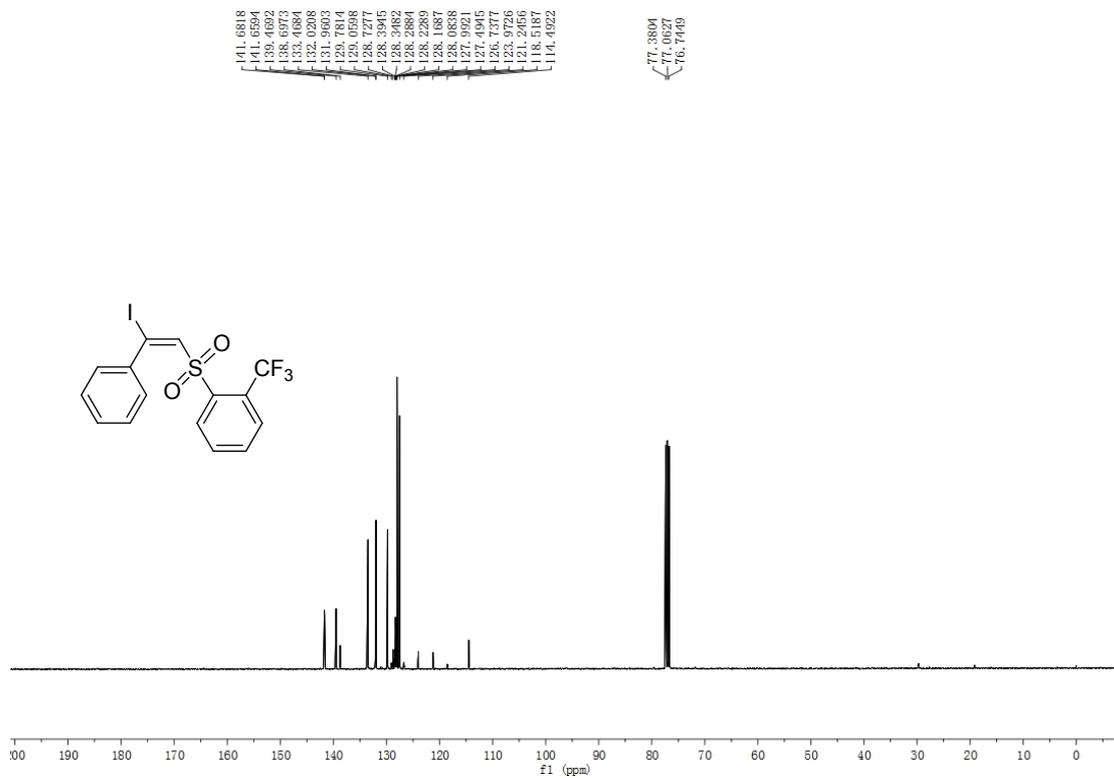
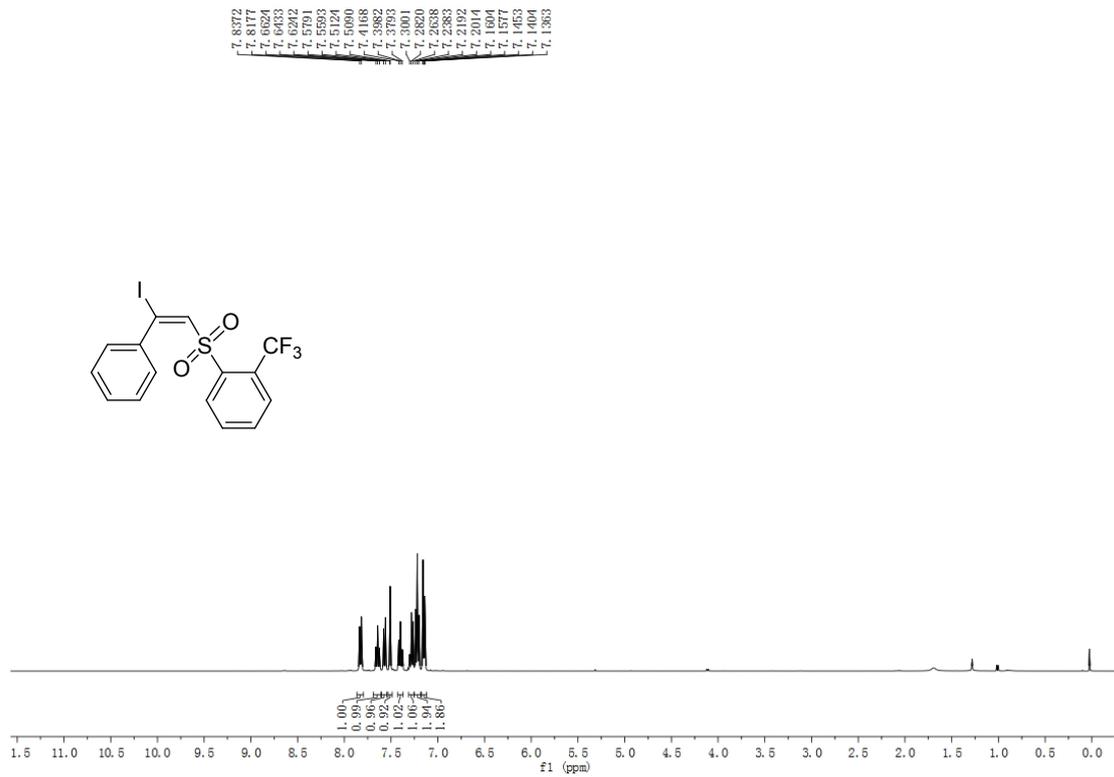
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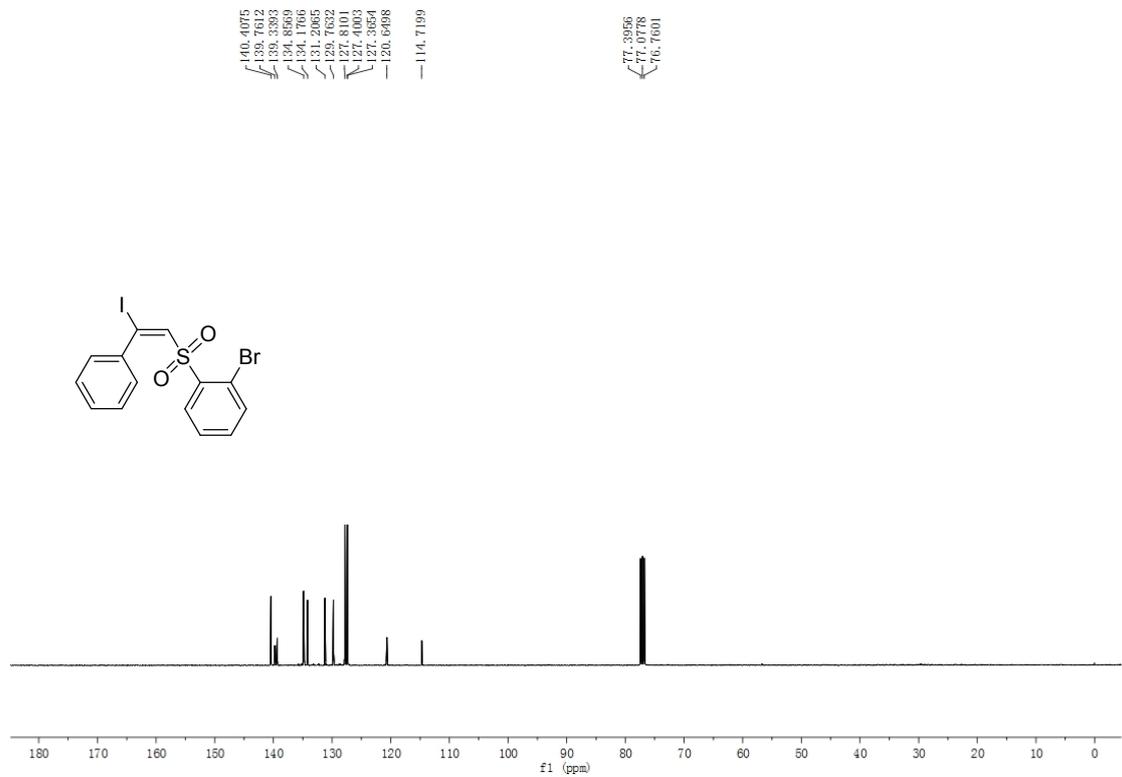
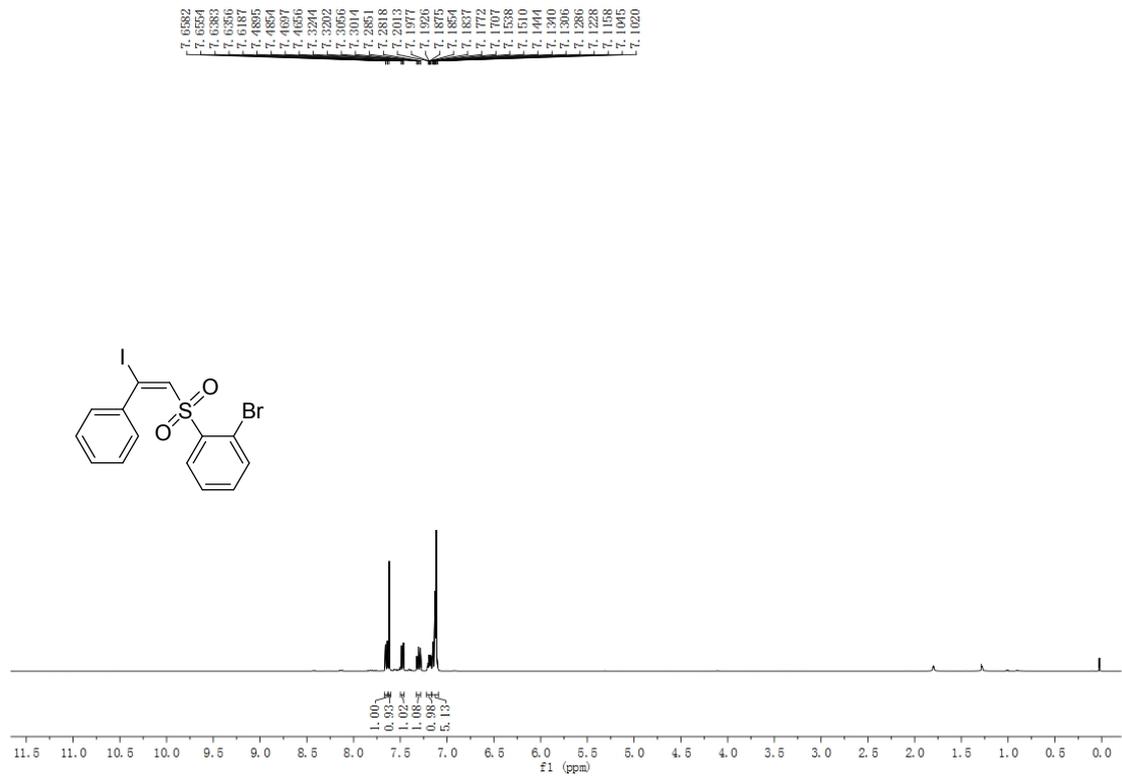
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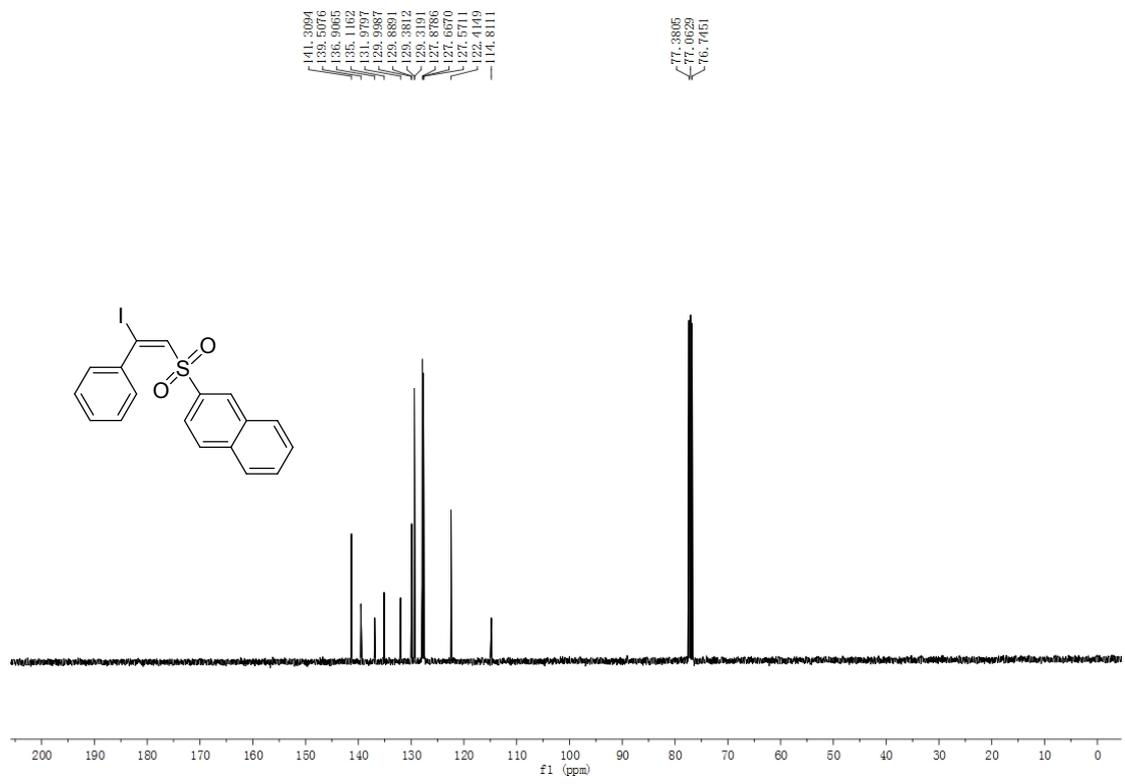
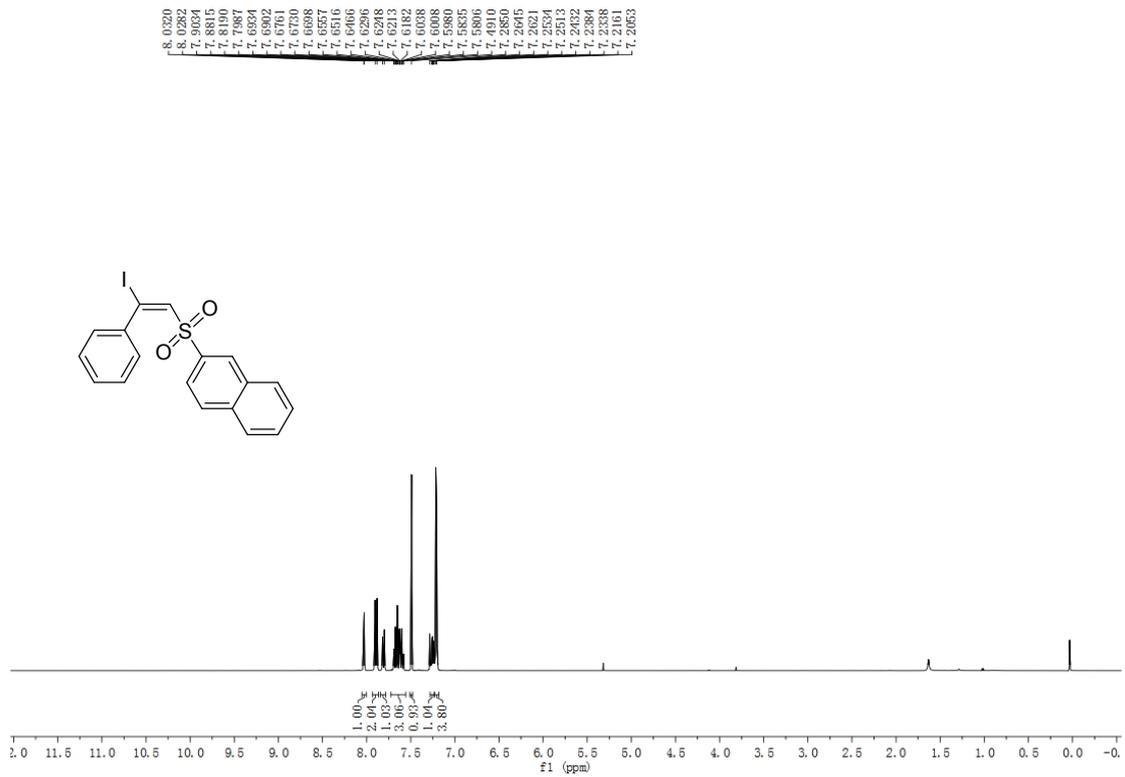




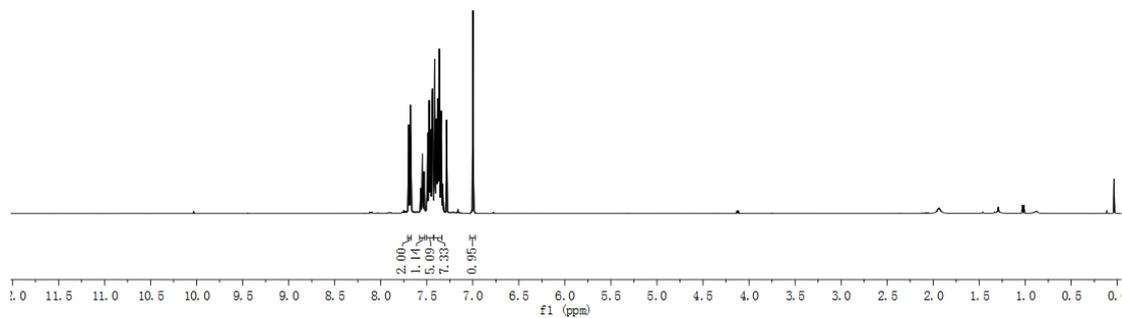
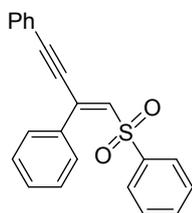




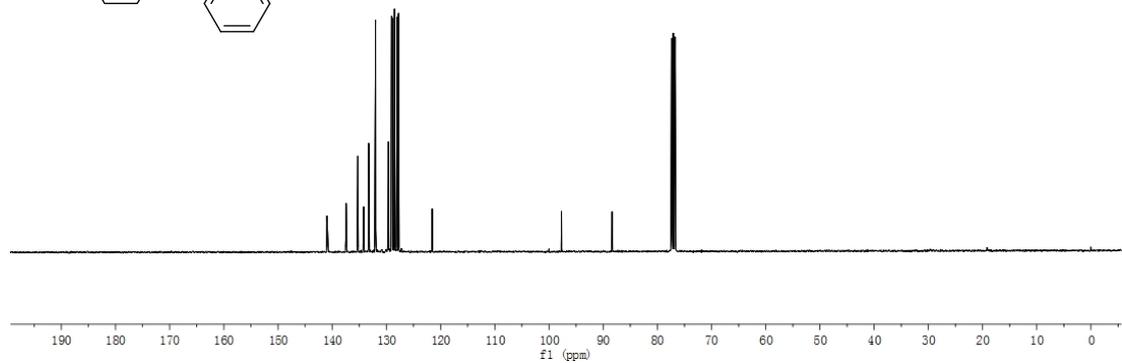
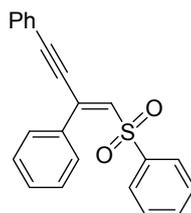


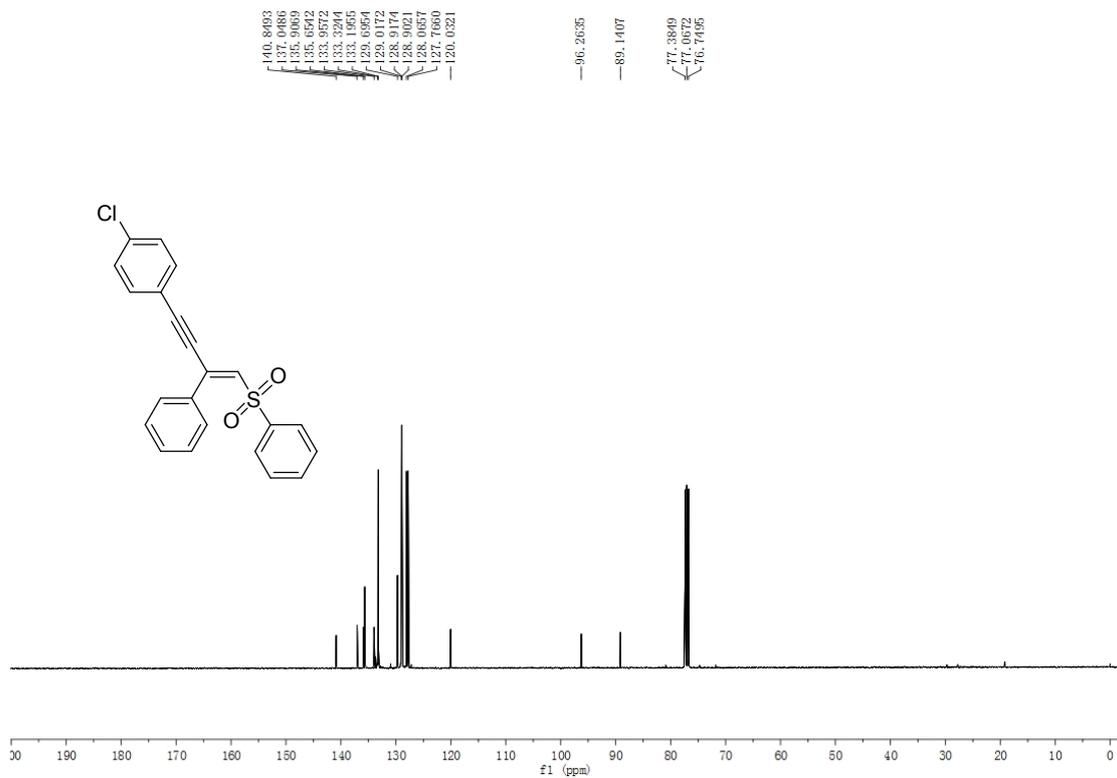
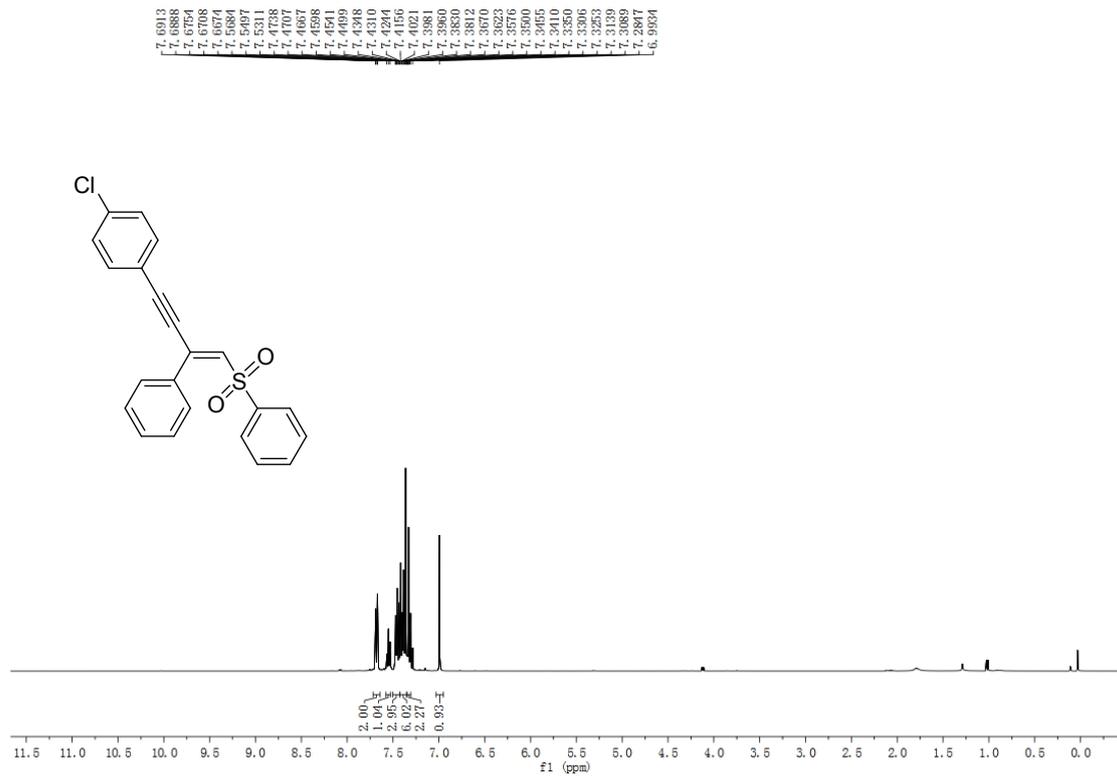


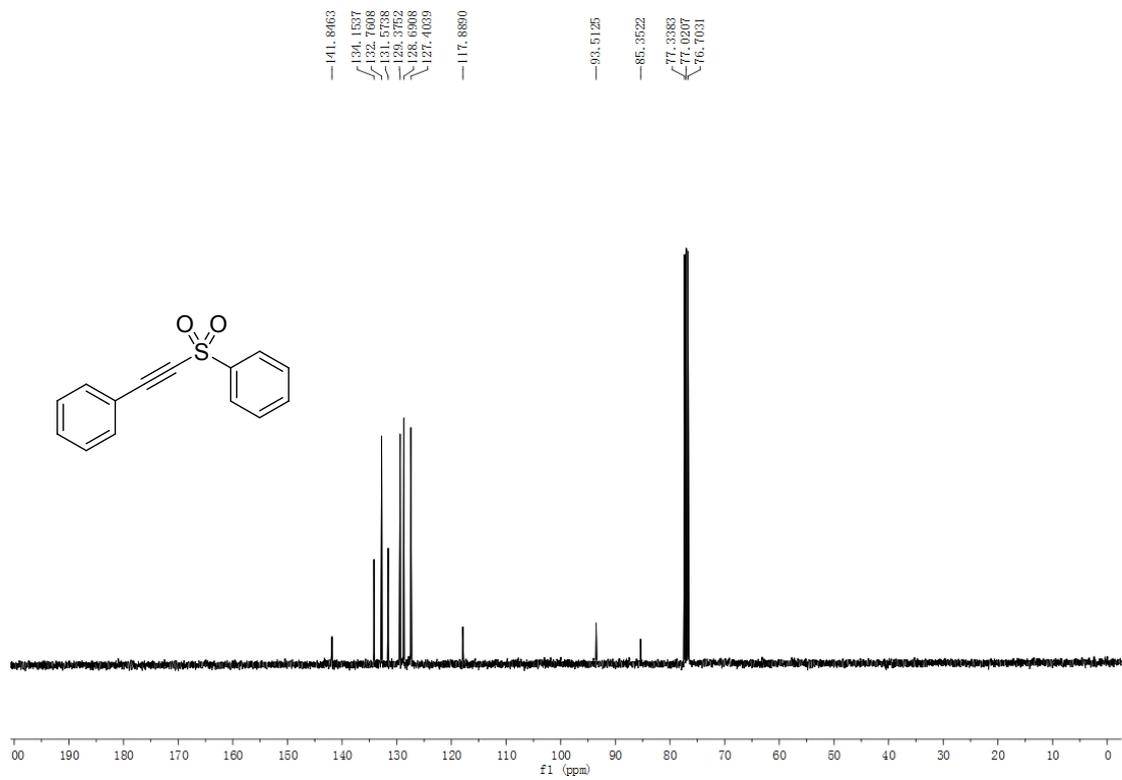
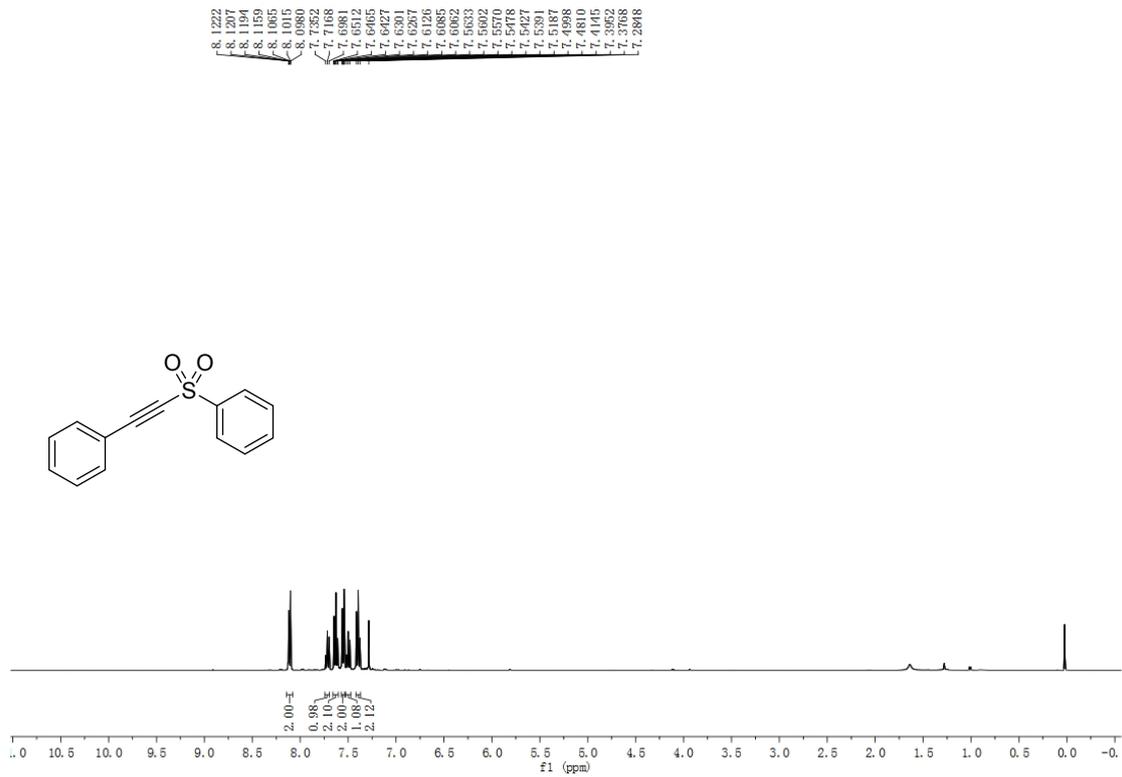
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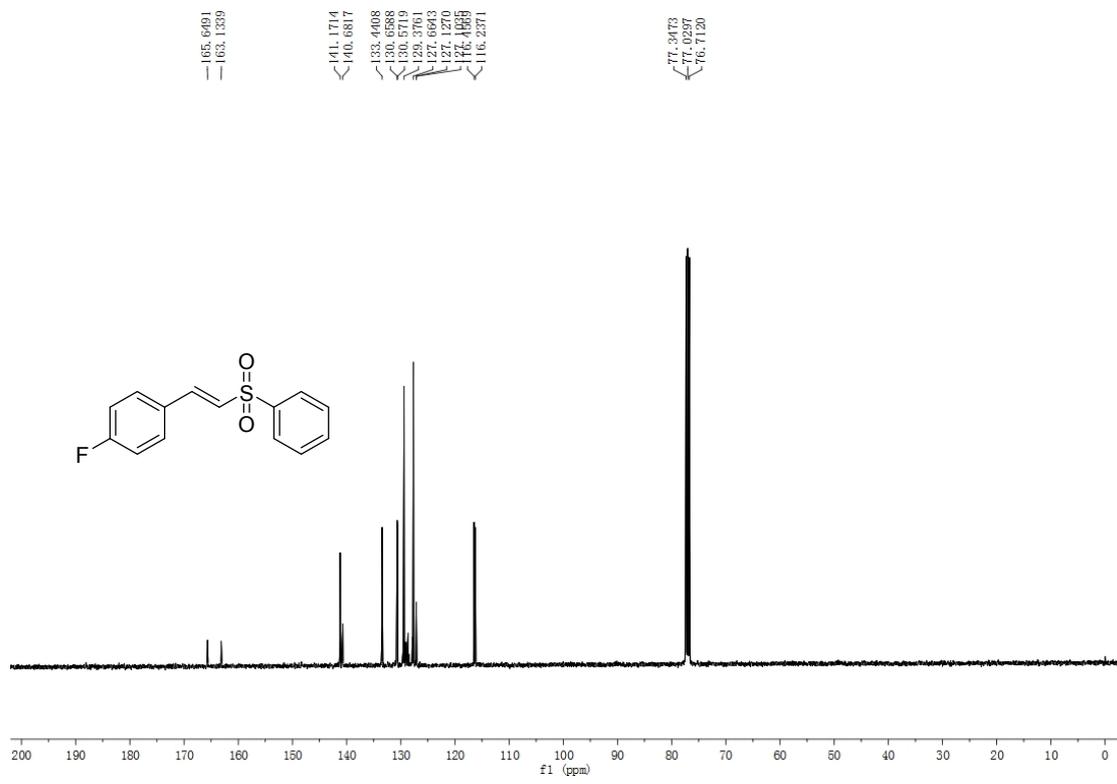
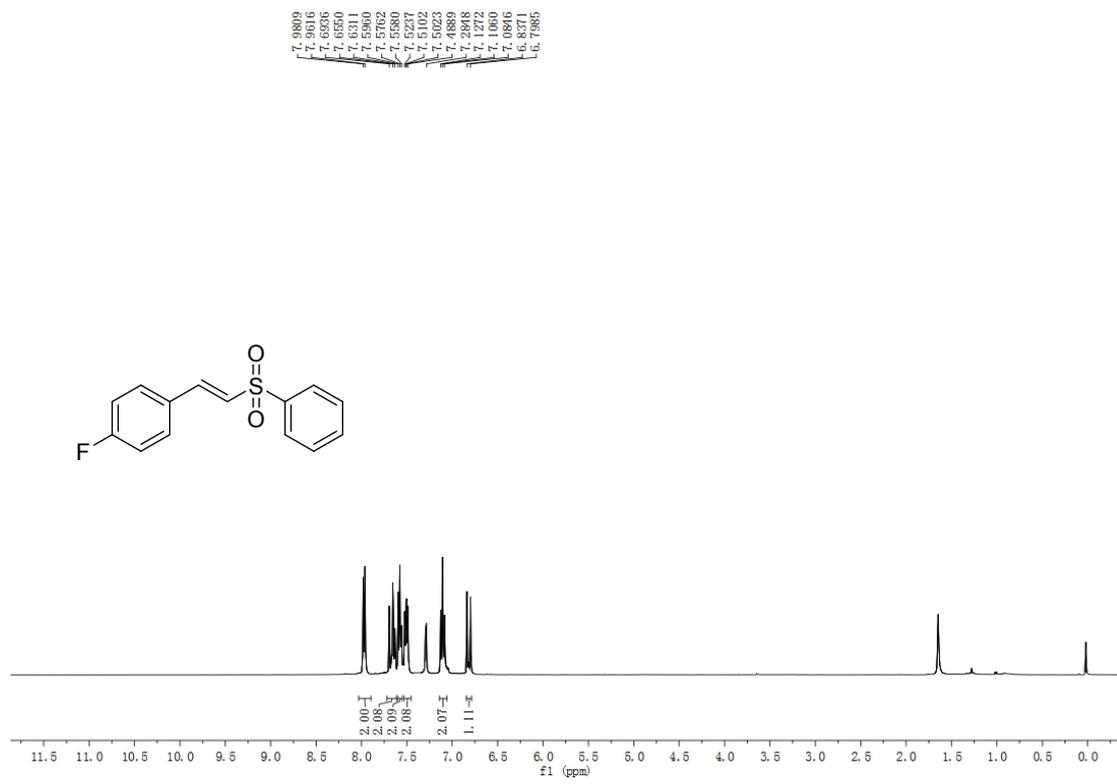


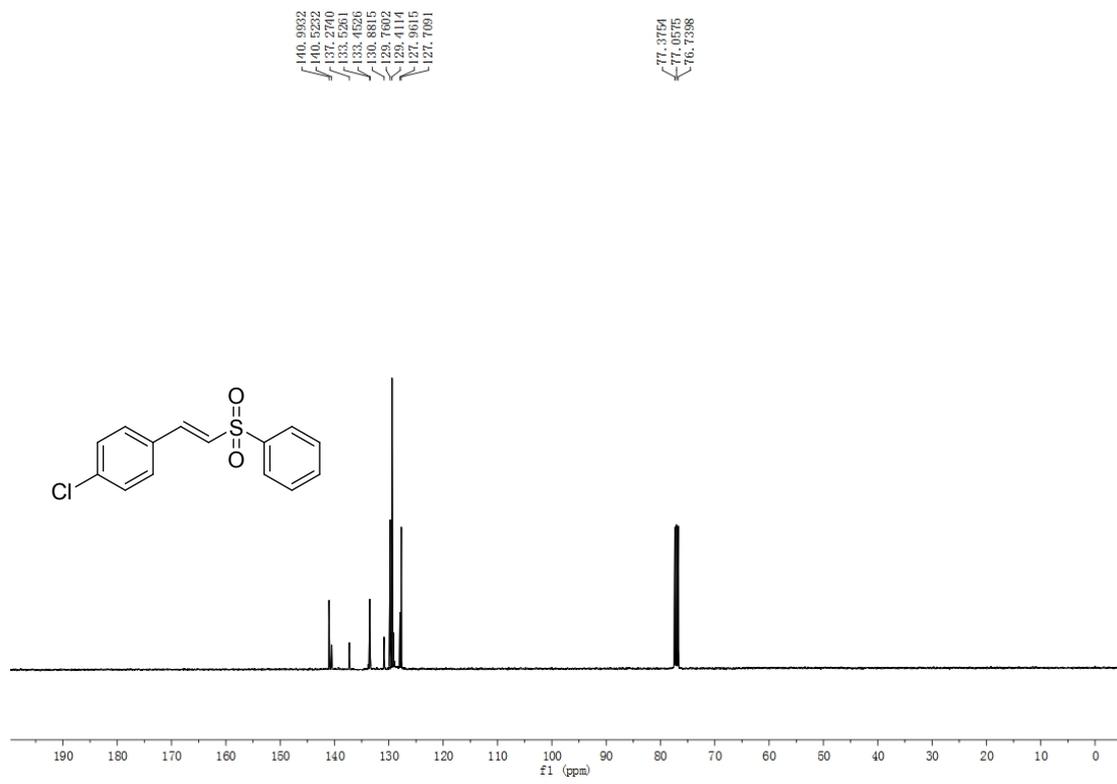
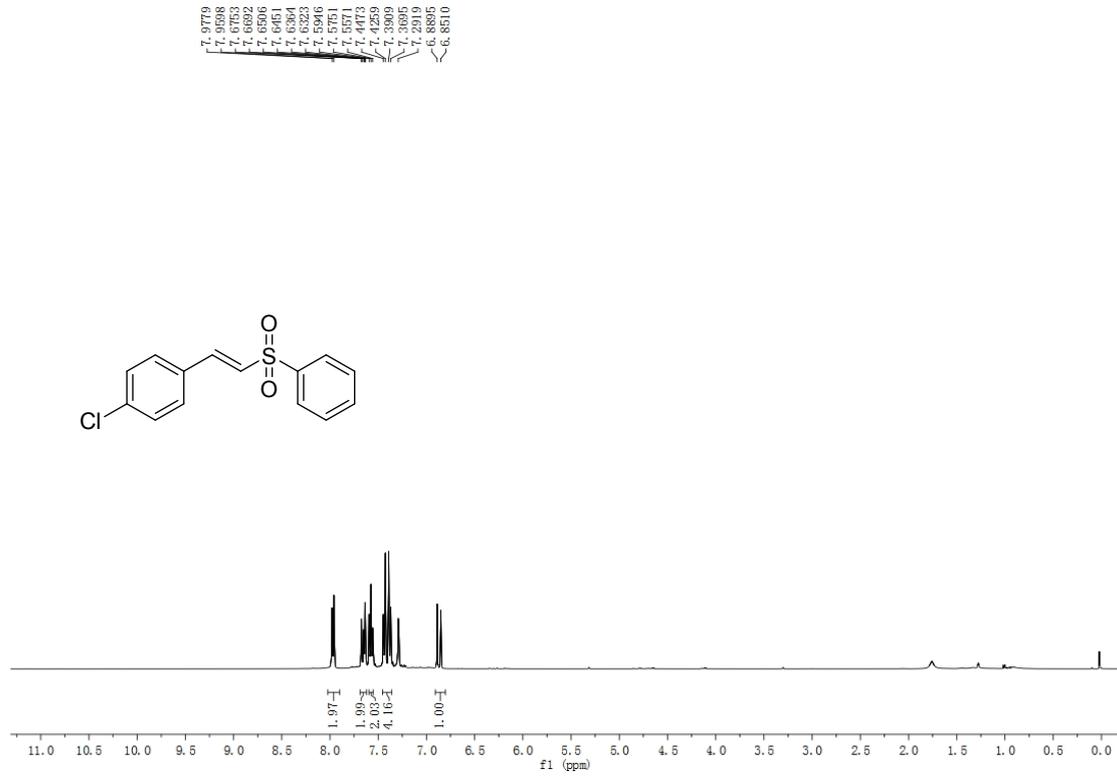
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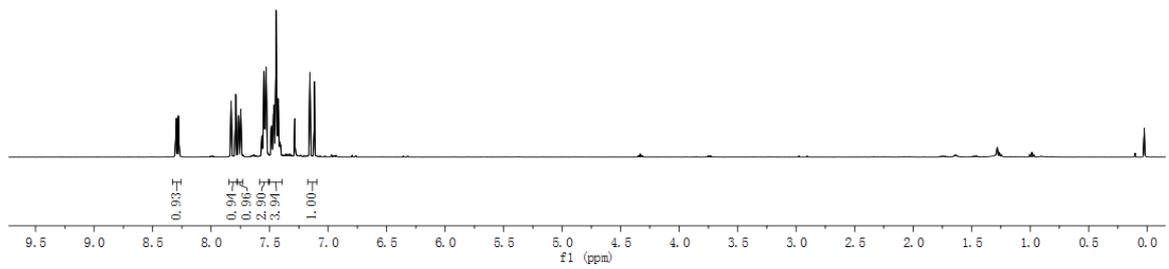
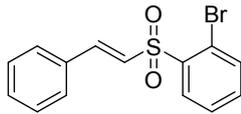








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