Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Transition Metal-Free Base-Promoted Arylation of Sulfenate Anions with Diaryliodonium Salts

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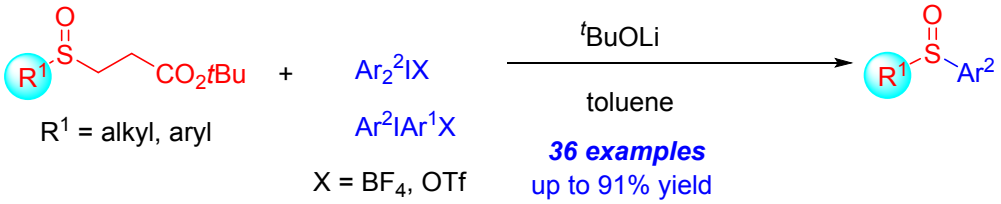
1. General Information:

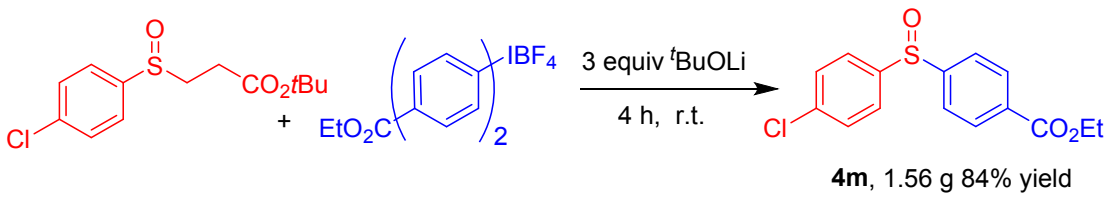
Unless otherwise noted, all reactions were carried out under a air atmosphere; materials obtained from commercial suppliers were used directly without further purification. ^{1}H NMR spectra, ^{13}C NMR spectra, and ^{19}F NMR spectra were recorded on a Bruker 400 (or 300, 500) MHz spectrometer in $CDCl_3$. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All the solvents were used directly without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate.

2. General procedure:



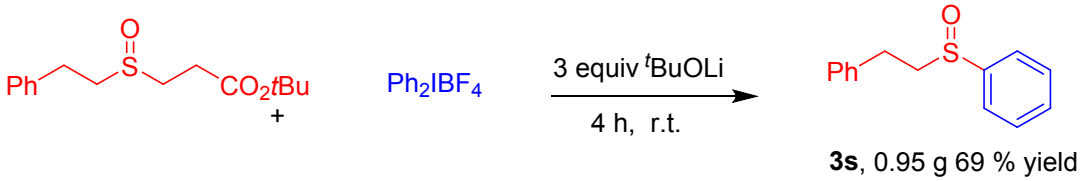
A Schlenk tube was charged with ^{t}BuOLi (48.15 mg, 0.6 mmol) in glove box, diaryliodonium salts (0.3 mmol), *β*-Sulfinylester (0.2 mmol) and 2.0 mL toluene were successively added. The reaction mixture was kept stirring at r.t. ^{o}C for 4 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

3. Gram-scale synthesis of 4m and 3s:



4m, 1.56 g 84% yield

A 100 mL Schlenk bottom flask was charged with ^{t}BuOLi (1.44 g, 18 mmol) in glove box , diaryliodonium salts (3.69 g, 7.2 mmol), *β*-Sulfinylester (1.733 g 6 mmol) and 40 mL toluene were successively added. The reaction mixture was kept stirring at r.t. ^{o}C for 4 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **4m** 1.56 g in 84% yield.



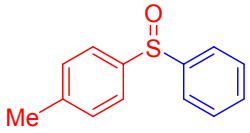
3s, 0.95 g 69 % yield

A 100 mL Schlenk bottom flask was charged with ^{t}BuOLi (1.44 g, 18 mmol) in glove box , diaryliodonium salts (2.65 g, 7.2 mmol), *β*-Sulfinylester (1.694 g 6 mmol) and 40 mL toluene were successively added. The reaction mixture was kept stirring at r.t. ^{o}C for 4 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography

on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **3s** 0.95 g in 69% yield.

4. Characterization data for the product

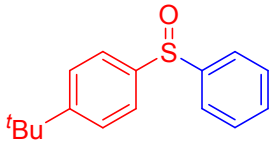
1-methyl-4-(phenylsulfinyl)benzene (3a)[1]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product (36.6 mg, 85% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.62 (m, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.47-7.40 (m, 3H), 7.25 (d, J = 8.4 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.7, 142.4, 141.6, 130.8, 129.9, 129.2, 124.9, 124.6, 21.3.

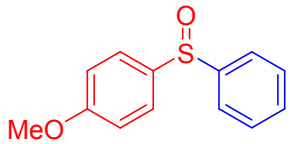
1-(tert-butyl)-4-(phenylsulfinyl)benzene (3b)[1]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product (42.3 mg, 82% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.47-7.41 (m, 5H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.6, 145.6, 142.2, 130.8, 129.1, 126.3, 124.7, 124.6, 34.8, 31.1.

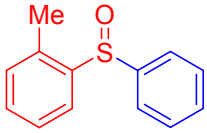
1-methoxy-4-(phenylsulfinyl)benzene (3c)[1]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product (36.2 mg, 78% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.59 (m, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.46-7.39 (m, 3H), 6.94 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.0, 145.8, 136.7, 130.7, 129.1, 127.1, 124.5, 114.8, 55.4.

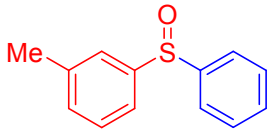
1-methyl-2-(phenylsulfinyl)benzene (3d)[1]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give the product (37.2 mg, 86% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 7.6 Hz 1H), 7.52-7.50 (m, 2H), 7.35-7.25 (m, 5H), 7.07 (d, J = 7.2 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.5, 142.8, 135.7, 131.0, 130.9, 130.9, 129.2 , 127.0, 125.8, 124.6, 18.5.

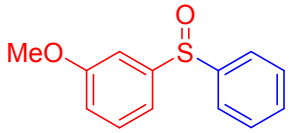
1-methyl-3-(phenylsulfinyl)benzene (3e)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give the product (37 mg, 85% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.62 (m, 2H), 7.47 (s, 1H), 7.46-7.39 (m, 4H), 7.31 (t, J = 7.6 Hz, 1H); 7.22 (d, J = 7.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.5, 145.3, 139.5, 131.8, 130.9, 129.2, 129.0, 124.9, 124.7, 121.9, 21.3.

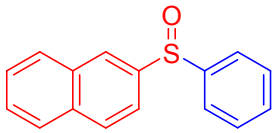
1-methoxy-3-(phenylsulfinyl)benzene (3f)[1]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give the product (37.8 mg, 81% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.63 (m, 2H), 7.47-7.40 (m, 3H), 7.33 (t, J = 7.6 Hz, 1H), 7.23 (s, 1H), 7.16 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.3, 146.9, 145.5, 131.0, 130.2, 129.2, 124.7, 117.3, 116.9, 109.0, 55.5.

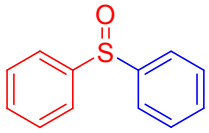
2-(phenylsulfinyl)naphthalene (3g)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product (43.7 mg, 87% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 (s, 1H), 7.94-7.92 (m, 1H), 7.86-7.81 (m, 2H), 7.70-7.68 (m, 2H), 7.56-7.54 (m, 2H), 7.50 (d, J = 8.8 Hz, 1H), 7.47-7.39 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.3, 142.4, 134.3, 132.7, 131.0, 129.6, 129.3, 128.5, 127.9, 127.8, 127.2, 125.2, 124.9, 120.5.

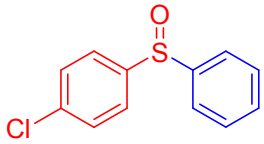
sulfinyldibenzene (3h)[1]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product (36.8 mg, 91% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.63 (m, 4H), 7.47-7.40 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.6, 131.0, 129.3, 124.8.

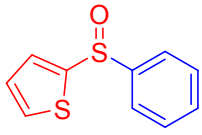
1-chloro-4-(phenylsulfinyl)benzene (3i)[1]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 39.4 mg, 83% yield) as a white.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.61 (m, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.48-7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.2, 144.1, 137.2, 131.3, 129.5, 129.4, 126.0, 124.6.

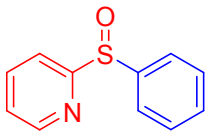
2-(phenylsulfinyl)thiophene (3j)[1]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product 32.4 mg, 78% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70-7.69 (m, 2H), 7.58-7.55 (m, 2H), 7.51-7.48 (m, 3H), 7.06-7.04 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.0, 145.1, 132.3, 131.3, 131.1, 129.2, 127.2, 124.3.

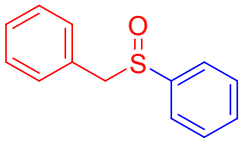
2-(phenylsulfinyl)pyridine (3k)[1]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product (34.2 mg, 84% yield) as a white solid.

^{1}H NMR ($CDCl_3$,400 MHz): δ 8.53 (d, J = 4.4 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.84 (t, J = 7.6 Hz, 1H) 7.79-7.77 (m, 2H), 7.46-7.40 (m, 3H), 7.29-7.26 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.8, 149.7, 144.1, 138.0, 131.0, 129.1, 124.9, 124.6, 118.4.

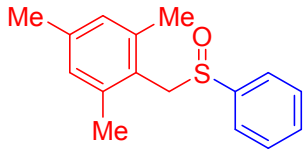
(benzylsulfinyl)benzene (3l)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product 32.6 mg, 75% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45-7.34 (m, 5H), 7.28-7.20 (m, 3H), 6.97 (d, J = 6.8 Hz, 2H), 4.07 (d, J = 12.4 Hz, 1H), 3.97 (d, J = 12.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.7, 131.1, 130.3, 129.1, 128.8, 128.4, 128.2, 124.4, 63.5.

1,3,5-trimethyl-2-((phenylsulfinyl)methyl)benzene (3m)

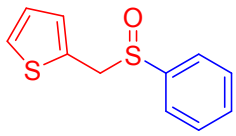


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product (38.2 mg, 74% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.38 (m, 5H), 6.82 (s, 2H), 4.38 (d, J = 12.8 Hz, 1H), 4.00 (d, J = 12.8 Hz, 1H), 2.26 (s, 3H), 2.08 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 138.2, 137.9, 131.0, 129.2, 128.8, 124.2, 123.8, 59.0, 20.9, 20.0.

HRMS (ESI): Calcd. for $C_{16}H_{18}NaOS$ $(M+Na)^+$ 281.0971, found 281.0976.

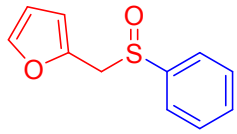
2-((phenylsulfinyl)methyl)thiophene (3n)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 32.5 mg, 73% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48-7.42 (m, 5H), 7.21 (d, J = 4.8 Hz, 1H), 6.92-6.90 (m, 1H), 6.72 (d, J = 3.2 Hz, 1H), 4.23 (q, J = 14.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.6, 131.2, 129.8, 129.0, 128.9, 127.2, 126.6, 124.3, 57.6.

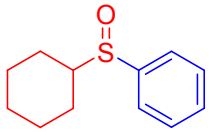
2-((phenylsulfinyl)methyl)furan (3o)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 28.8 mg, 70% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.45 (m, 5H), 7.31 (d, J = 2.0 Hz, 1H), 6.29 (d, J_1 = 2.0 Hz, J_2 = 3.0 Hz, 1H), 6.14 (d, J = 3.2 Hz, 1H), 4.16 (d, J = 13.6 Hz, 1H), 4.05 (d, J = 13.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.8, 143.3, 143.0, 131.3, 129.0, 124.2, 111.4, 110.9, 56.4.

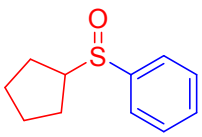
(cyclohexylsulfinyl)benzene (3p)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product 25.9 mg, 62% yield) as colourless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.55 (m, 2H), 7.52-7.41 (m, 3H), 2.59-2.51 (m, 1H), 1.84-1.81 (m, 4H), 1.65-1.63 (m, 1H), 1.48-1.34 (m, 2H), 1.28-1.16 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.8, 130.9, 128.9, 125.0, 63.1, 26.2, 25.6, 25.4, 25.3, 24.0.

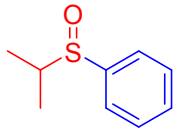
(cyclopentylsulfinyl)benzene (3q)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product 28.7 mg, 73% yield) as a colourless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.61 (m, 2H), 7.51-7.46 (m, 3H), 3.14-3.06 (m, 1H), 2.13-2.03 (m, 1H), 1.82-1.78 (m, 2H), 1.72-1.55 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 130.8, 129.0, 124.6, 64.3, 27.6, 26.1, 25.6, 24.8.

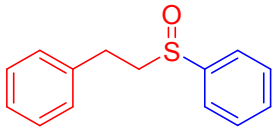
(isopropylsulfinyl)benzene (3r)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 21.8 mg, 65% yield as colourless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.55 (m, 2H), 7.53-7.48 (m, 3H), 2.87-2.77 (m, 1H), 1.22 (d, J = 7.2 Hz, 3H), 1.13 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.8, 131.0, 128.8, 125.0, 54.5, 15.8, 13.9.

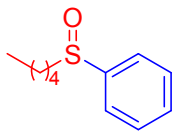
(phenethylsulfinyl)benzene (3s)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product 35 mg, 76% yield as acolourless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.63 (m, 2H), 7.55-7.49 (m, 3H), 7.31-7.27 (m, 2H), 7.23-7.17 (m, 3H), 3.14-3.01 (m, 3H), 2.92-2.86 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 138.7, 131.0, 129.2, 128.7, 128.5, 126.6, 124.0, 58.3, 28.1.

(pentylsulfinyl)benzene (3t)[3]

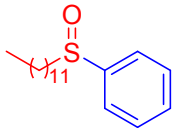


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 27.5 mg, 70% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.59 (m, 2H), 7.52-7.45 (m, 3H), 2.78-2.75 (m, 2H), 1.75-1.68 (m, 1H), 1.66-1.59 (m, 1H), 1.42-1.27 (m, 4H), 0.85 (t, J = 6.81, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.0, 130.8, 129.1, 123.9, 57.3, 30.7, 22.2, 21.8, 13.7.

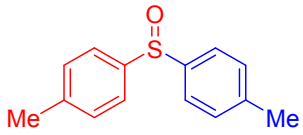
(dodecylsulfinyl)benzene (3u)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 39.5 mg, 67% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.59 (m, 2H), 7.52-7.47 (m, 3H), 2.82-2.71 (m, 2H), 1.78-1.67 (m, 1H), 1.65-1.54 (m, 1H), 1.45-1.33 (m, 2H), 1.30-1.23 (m, 16H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.1, 130.8, 129.1, 124.0, 57.3, 31.8, 29.5, 29.4, 29.4, 29.2, 29.2, 29.1, 28.6, 22.6, 22.1, 14.0.

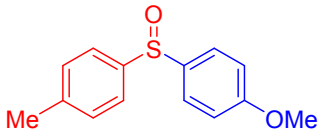
4,4'-sulfinylbis(methylbenzene) (4a)[2]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 39.9 mg, 87% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, J = 8.0 Hz, 4H), 7.24 (d, J = 8.0 Hz, 4H), 2.35 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.6, 141.3, 129.9, 124.8, 21.3.

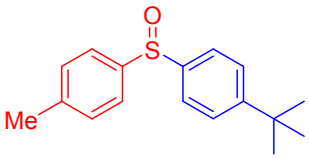
1-methoxy-4-(p-tolylsulfinyl)benzene (4b)[2]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 37.9 mg, 77% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.9, 142.6, 141.2, 137.0, 129.9, 127.0, 124.7, 114.7, 55.4, 21.3.

1-(tert-butyl)-4-(p-tolylsulfinyl)benzene (4c)

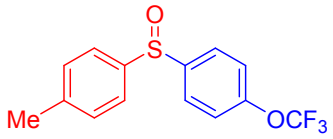


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 47.6 mg, 87% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.52 (m, 4H), 7.45 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H), 1.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.4, 142.5, 141.3, 129.9, 126.3, 124.9, 124.7, 124.6, 34.9, 31.1, 21.3.

HRMS (ESI): Calcd. for $C_{17}H_{20}NaOS$ $(M+Na)^+$ 295.1127, found 295.1133.

1-methyl-4-((4-(trifluoromethoxy)phenyl)sulfinyl)benzene (4d)

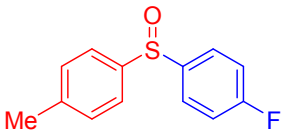


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 45.1 mg, 75% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.30-7.27 (m, 4H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.9 (q, J = 1.81 Hz), 144.3, 142.1, 142.0.0, 130.2, 126.4, 125.0, 121.5, 120.4 (q, J = 257 Hz), 21.3; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -57.81.

HRMS (ESI): Calcd. for $C_{14}H_{11}F_3NaO_2S$ $(M+Na)^+$ 323.0324, found 323.0325.

1-fluoro-4-(p-tolylsulfinyl)benzene (4e)[5]

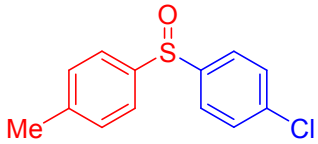


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 41.5 mg, 89% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.59 (m, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 8.8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.1 (d, J = 250 Hz), 142.2, 141.8, 141.4, (d, J = 3.1 Hz), 130.0, 127.0 (d, J = 8.8

Hz), 124.8, 116.5 (d, J = 22.2 Hz), 21.3; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -108.65.

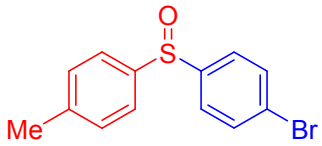
1-chloro-4-(p-tolylsulfinyl)benzene (4f)[4]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 44.1 mg, 88% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.4, 142.1, 142.0, 137.0, 130.1, 129.5, 126.0, 124.9, 21.4.

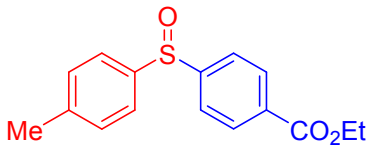
1-bromo-4-(p-tolylsulfinyl)benzene (4g)[2]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 44.2 mg, 75% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, J = 8.8 Hz, 2H), 7.50 (t, J = 8.4 Hz, 4H), 7.26 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.0, 142.0, 132.4, 130.1, 126.1, 125.3, 124.9, 21.4.

ethyl 4-(p-tolylsulfinyl)benzoate (4h)

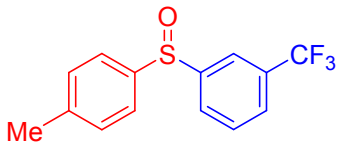


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 48.3 mg, 84% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.6 Hz, 2H), 4.37 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H)，1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.5, 150.7, 142.1, 142.0, 132.6, 130.3, 130.2, 125.1, 124.3, 61.3, 21.6, 14.2.

HRMS (ESI): Calcd. for $C_{16}H_{16}ClNaO_3S$ $(M+Na)^+$ 311.0712, found 311.0713.

1-(p-tolylsulfinyl)-3-(trifluoromethyl)benzene (4i)

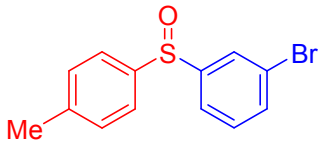


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 37.5 mg, 66% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.4, 142.4, 141.7, 131.8 (q, J = 32.8 Hz), 130.3, 129.8, 127.7, 127.5 (q, J = 3.6 Hz), 125.0, 123.4 (q, J = 271.3 Hz), 121.4 (q, J = 3.7 Hz), 21.4; ^{19}F NMR ($CDCl_3$, 282 MHz): δ -62.75.

HRMS (ESI): Calcd. for $C_{14}H_{11}F_3NaOS$ $(M+Na)^+$ 307.0375, found 307.0377.

1-bromo-3-(p-tolylsulfinyl)benzene (4j)

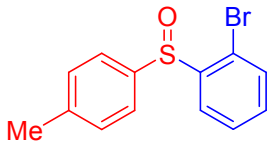


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 38.6 mg, 65% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (s, 1H), 7.54-7.512 (m, 4H), 7.33-7.27 (m, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.1, 142.1, 141.9, 133.8, 130.7, 130.2, 127.2, 125.0, 123.4, 123.0, 21.4.

HRMS (ESI): Calcd. for $C_{13}H_{11}BrNaOS$ $(M+Na)^+$ 316.9606, found 316.9613.

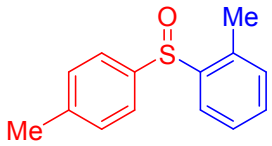
1-bromo-2-(p-tolylsulfinyl)benzene (4k)[5]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 52.2 mg, 88% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.0, 142.1, 141.2, 133.1, 132.1, 129.9, 128.4, 126.3, 126.2, 119.9, 21.4.

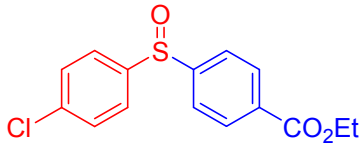
1-methyl-2-(p-tolylsulfinyl)benzene **(4l)**[4]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 40.9 mg, 89% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.22 (t, J = 8.0 Hz, 2H), 7.14 (d, J = 7.2 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.9, 141.6, 141.3, 135.5, 130.8, 130.7, 129.9, 127.0, 126.0, 124.4, 21.3, 18.5.

ethyl 4-((4-chlorophenyl)sulfinyl)benzoate (4m)

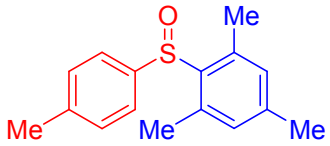


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product 1.56 g, 84% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.3, 150.0, 143.6, 137.7, 133.0, 130.5, 129.8, 126.1, 124.2, 61.4, 14.2.

HRMS (ESI): Calcd. for $C_{15}H_{13}ClNaO_3S$ $(M+Na)^+$ 331.0166, found 331.0163.

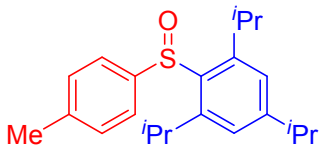
1,3,5-trimethyl-2-(p-tolylsulfinyl)benzene (4n)[9]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 7) give the product as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.86 (s, 2H), 2.42 (s, 6H), 2.36 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.9, 141.1, 139.8, 139.6, 136.6, 130.7, 129.5, 124.5, 21.2, , 21.1, 19.3.

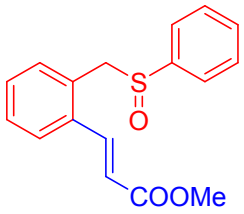
1,3,5-triisopropyl-2-(p-tolylsulfinyl)benzene (4o)[10]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 7) give the product as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.08 (s, 2H), 3.80-3.73 (m, 2H), 2.95-2.84 (m, 1H), 2.36 (s, 3H),1.26-1.24 (m, 12H), 1.03-0.82 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.2, 151.1, 143.1, 139.3, 135.6, 129.4, 124.6, 123.2, 34.3, 28.7, 24.6, 23.7, 21.2, 21.1.

methyl (E)-3-(2-((phenylsulfinyl)methyl)phenyl)acrylate (5)[7]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product (34 mg, 56% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59 (d, J = 16.0 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.43 (t, J = 7.0 Hz, 1H), 7.37-7.27 (m, 6H), 7.06 (d, J = 7.5 Hz, 1H), 6.12 (d, J = 15.5 Hz, 1H), 4.27 (d, J = 13.0 Hz, 1H), 4.17 (d, J = 12.5 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.7, 142.1, 140.4, 134.6, 132.4, 131.4, 129.8, 128.9, 128.8, 128.3, 126.7, 124.4, 120.0, 60.4, 51.7.

benzyl(imino)(phenyl)-λ^6-sulfanone (6)[8]

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product (57 mg, 82% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78 (d, J = 8.5 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.34 (d, J = 7.5 Hz, 1H), 7.30-7.27 (m, 2H), 7.12 (d, J = 8.5 Hz,

2H), 4.40 (d, J = 13.0 Hz, 1H), 4.32 (d, J = 13.5 Hz, 1H), 2.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.3, 133.0, 131.0, 128.8, 128.7, 128.5, 128.4, 64.6.

5. References:

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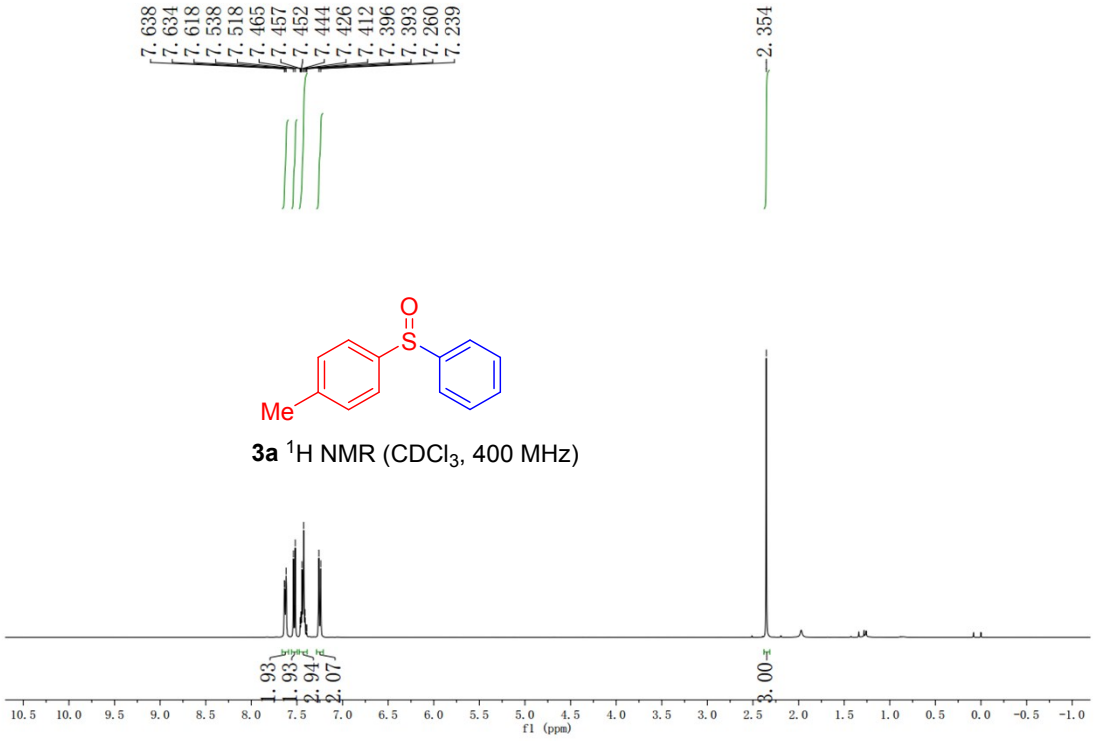
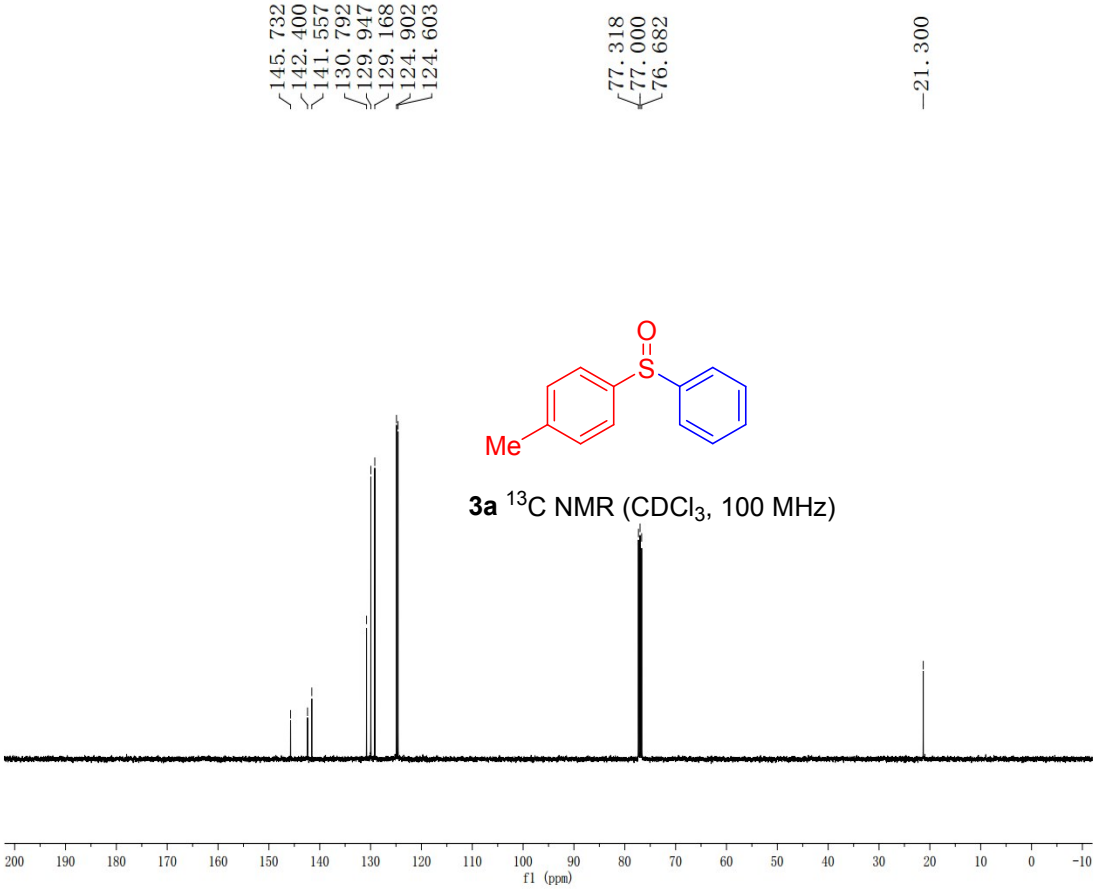
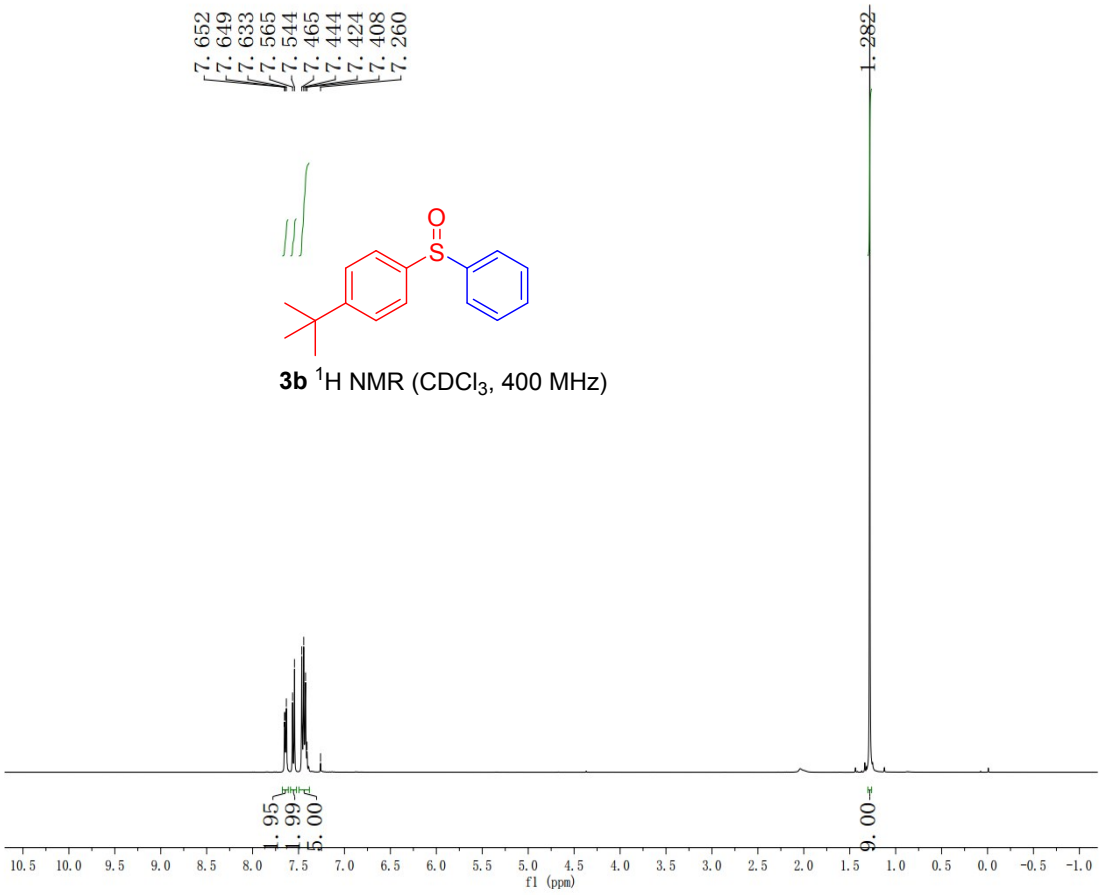
6. Copies of NMR spectra



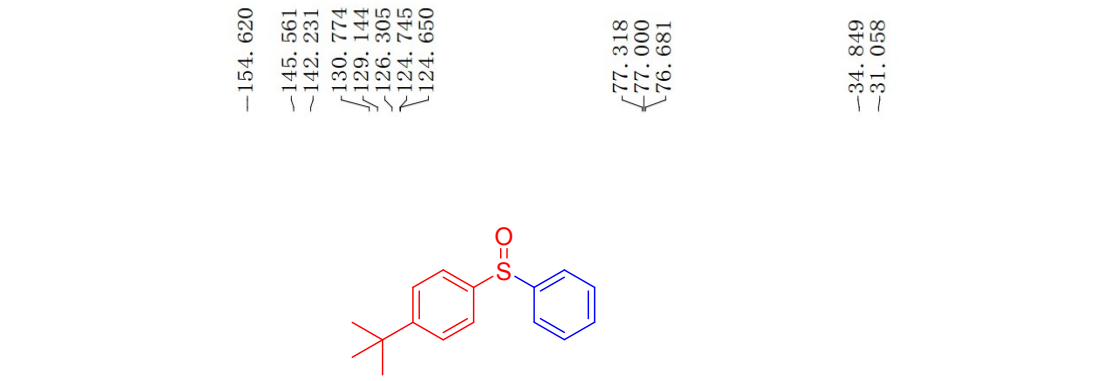
3a ^{1}H NMR ($CDCl_3$, 400 MHz)



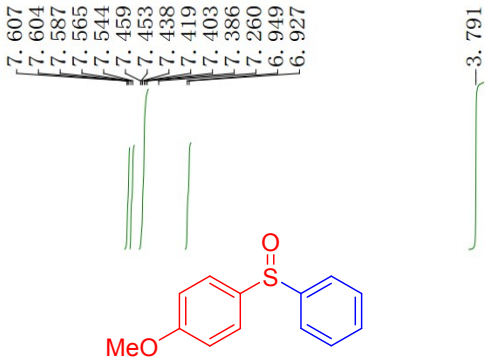
3a ^{13}C NMR ($CDCl_3$, 100 MHz)



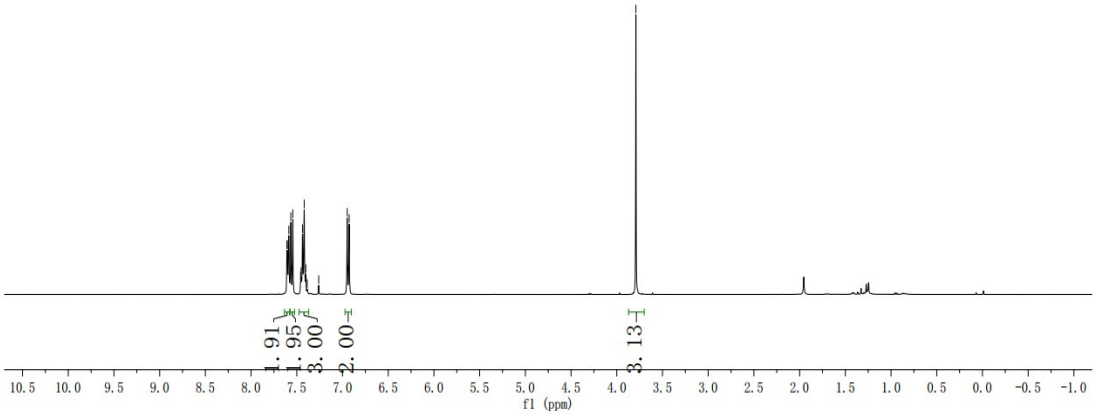
3b ^{1}H NMR ($CDCl_3$, 400 MHz)

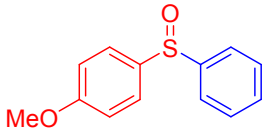


3b ^{13}C NMR ($CDCl_3$, 100 MHz)

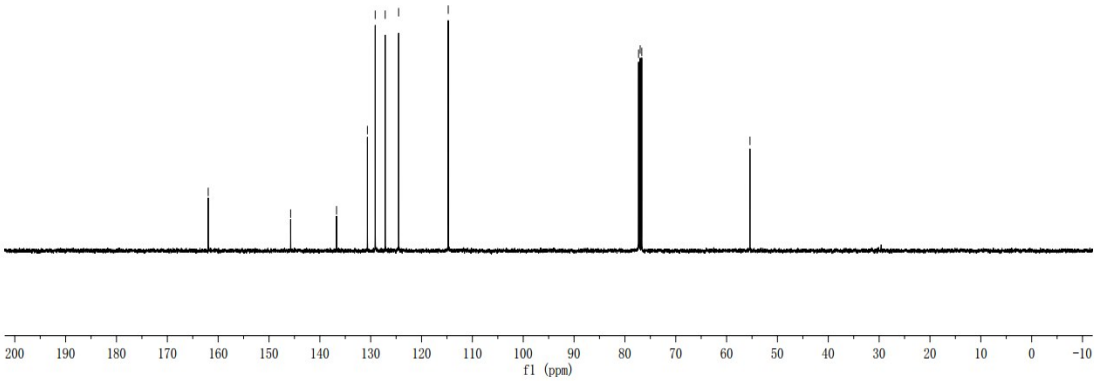


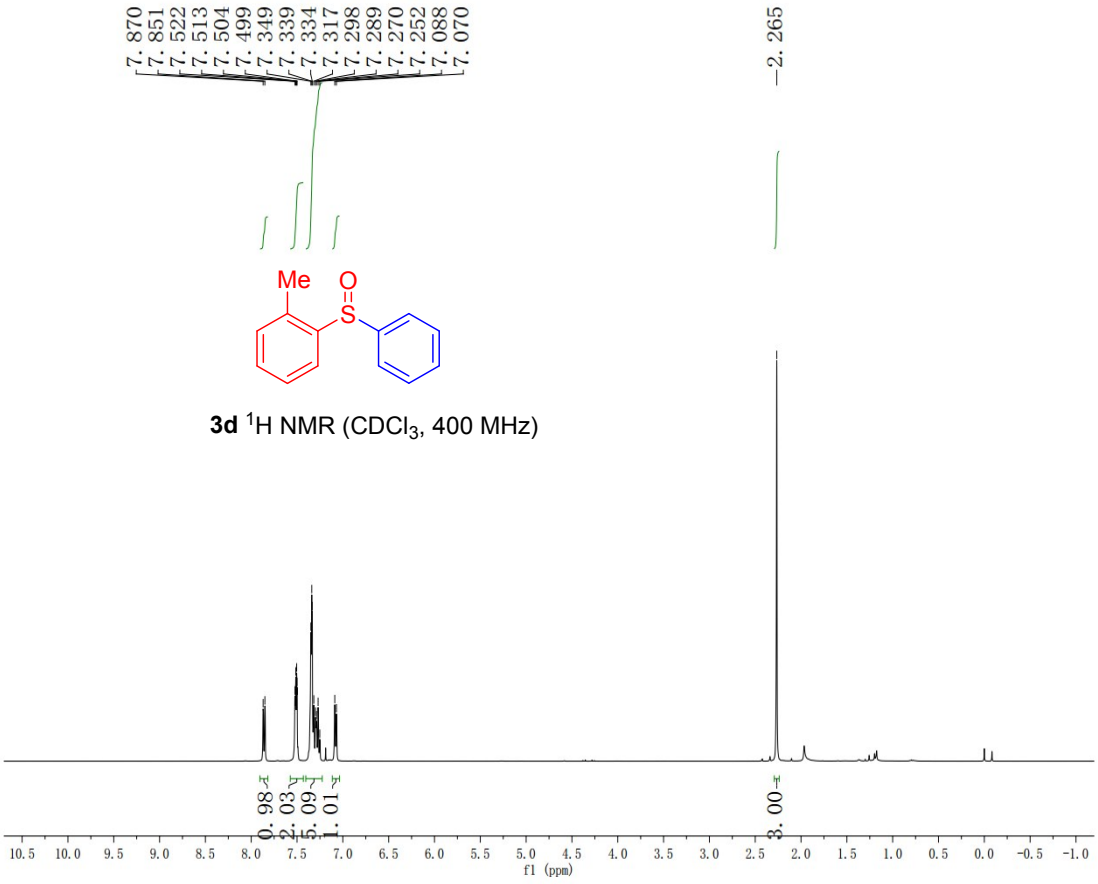
3c ^{1}H NMR ($CDCl_3$, 400 MHz)



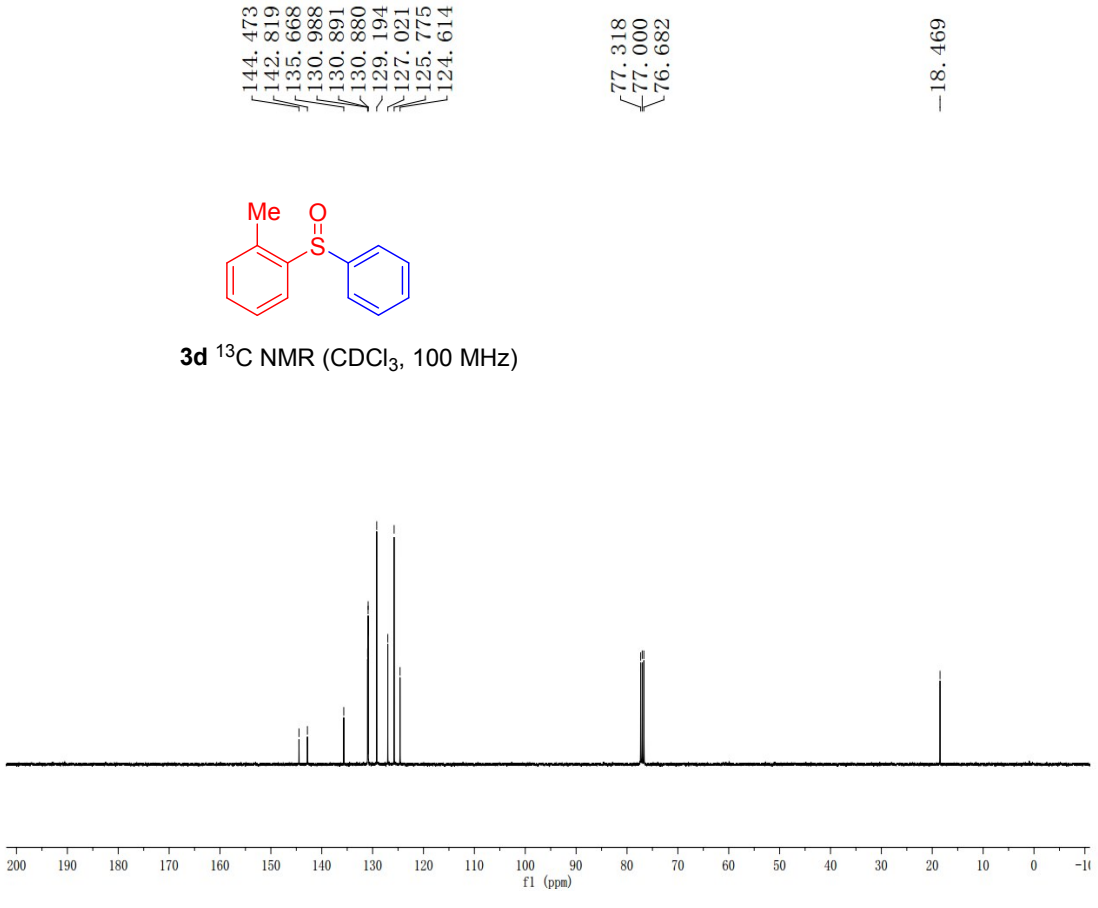


3c ^{13}C NMR ($CDCl_3$, 100 MHz)

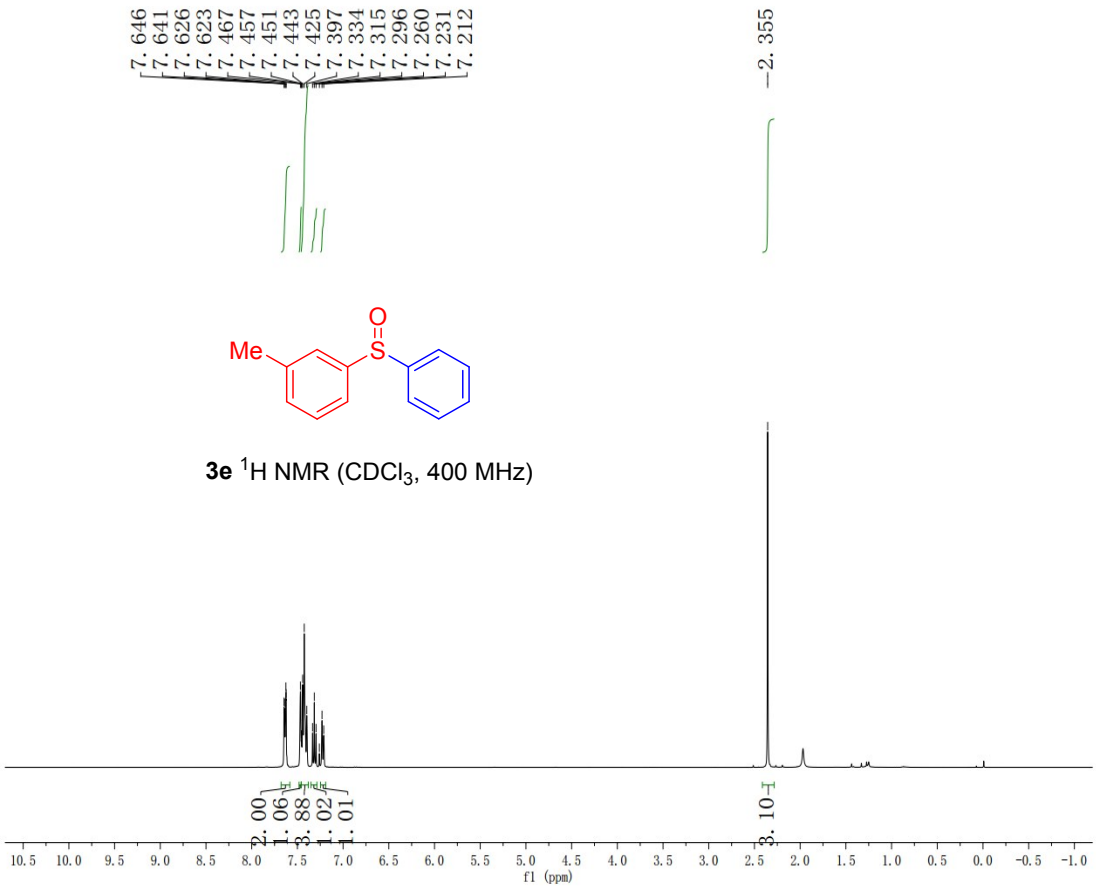




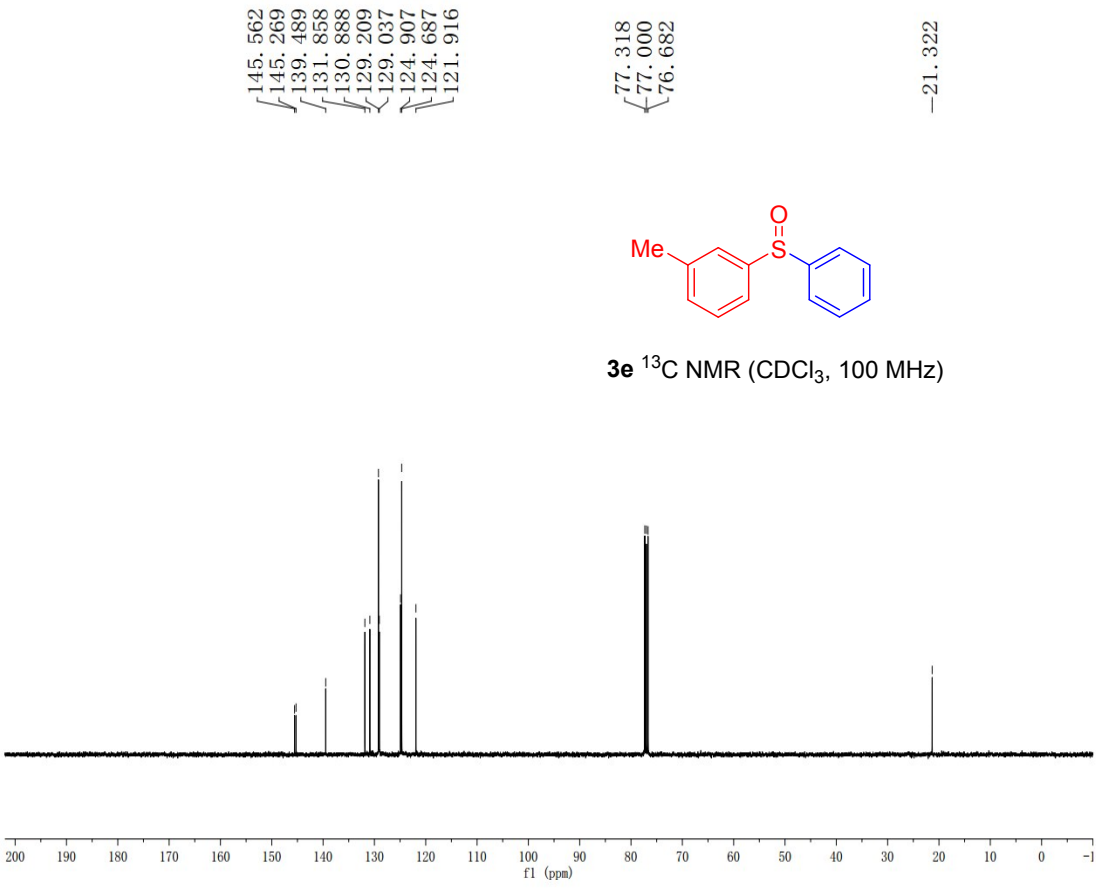
3d ^{1}H NMR ($CDCl_3$, 400 MHz)



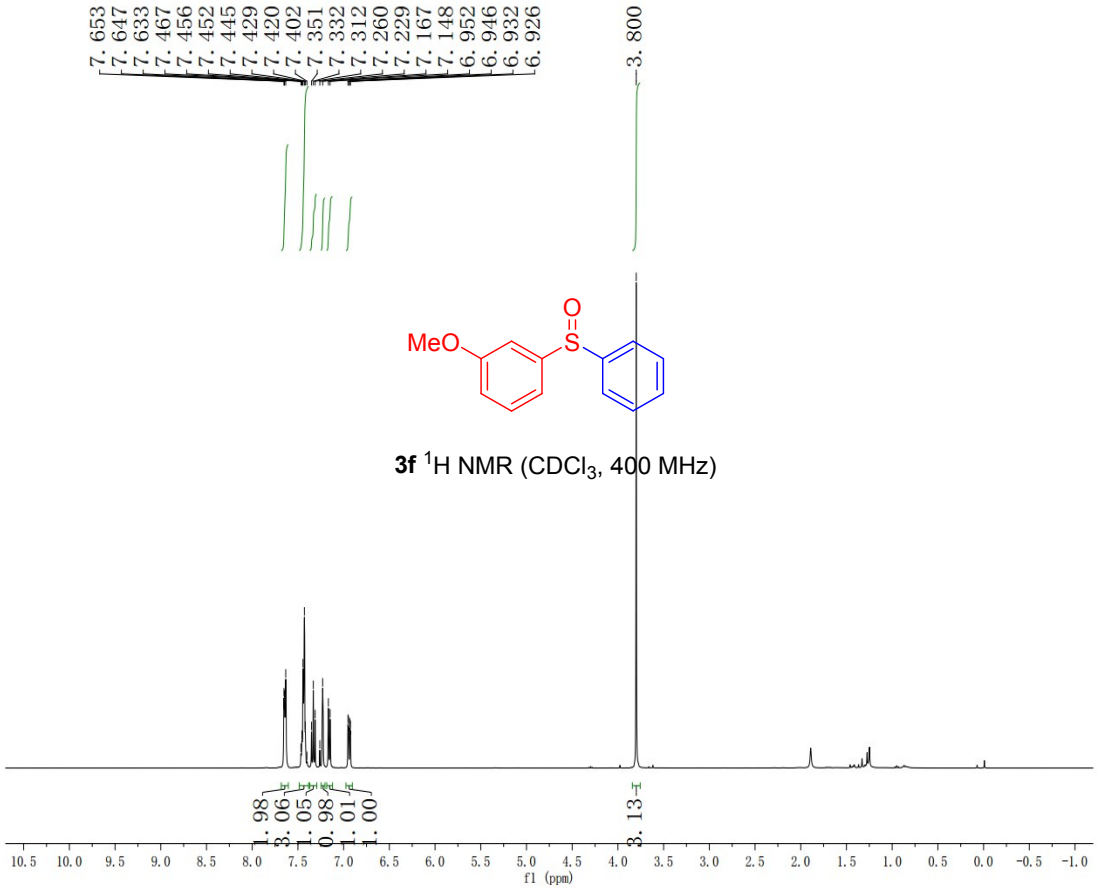
3d ^{13}C NMR ($CDCl_3$, 100 MHz)



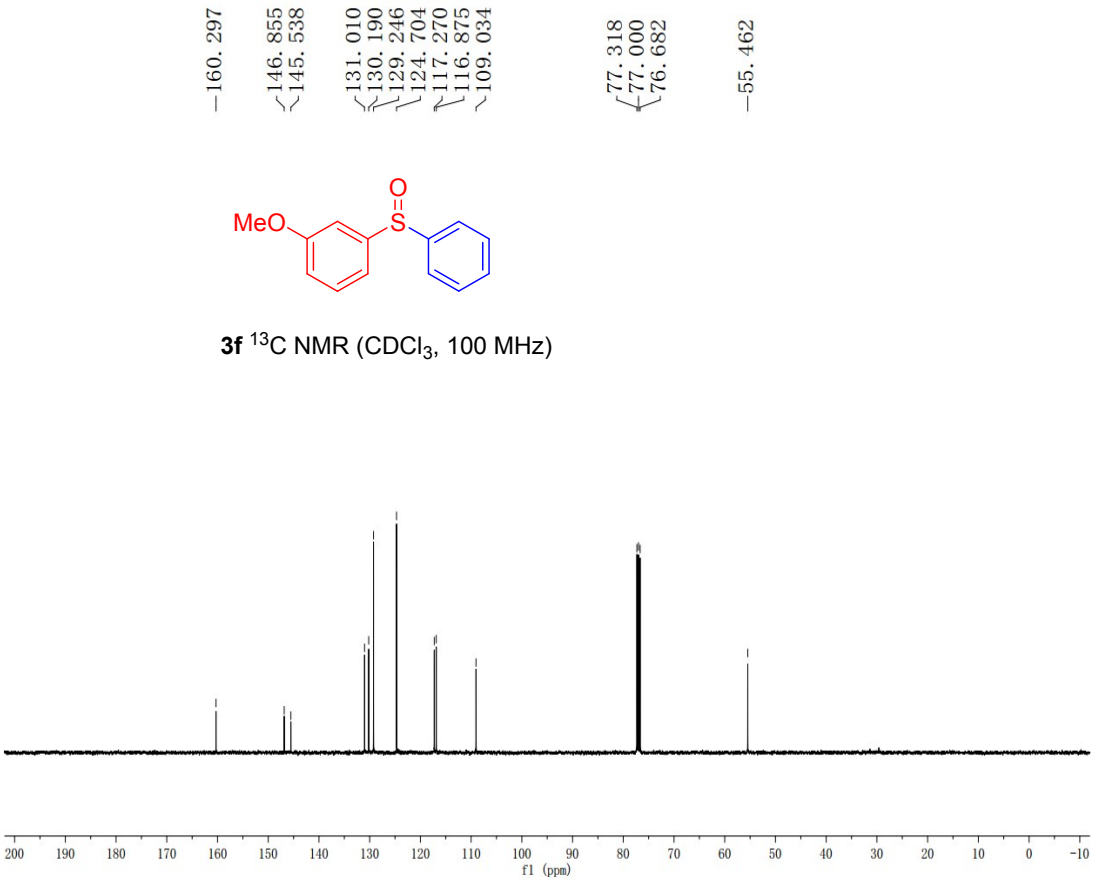
3e ^{1}H NMR ($CDCl_3$, 400 MHz)



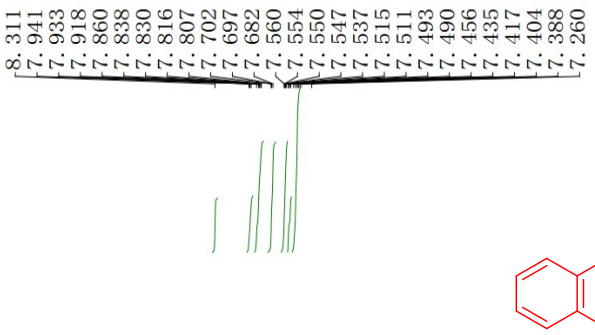
3e ^{13}C NMR ($CDCl_3$, 100 MHz)



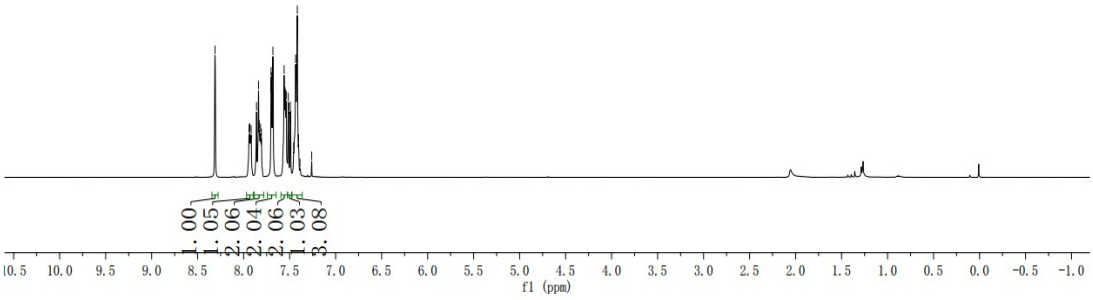
3f ^{1}H NMR ($CDCl_3$, 400 MHz)

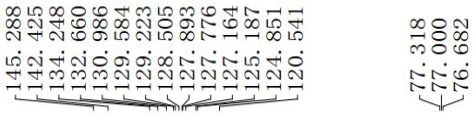


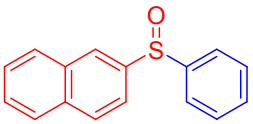
3f ^{13}C NMR ($CDCl_3$, 100 MHz)



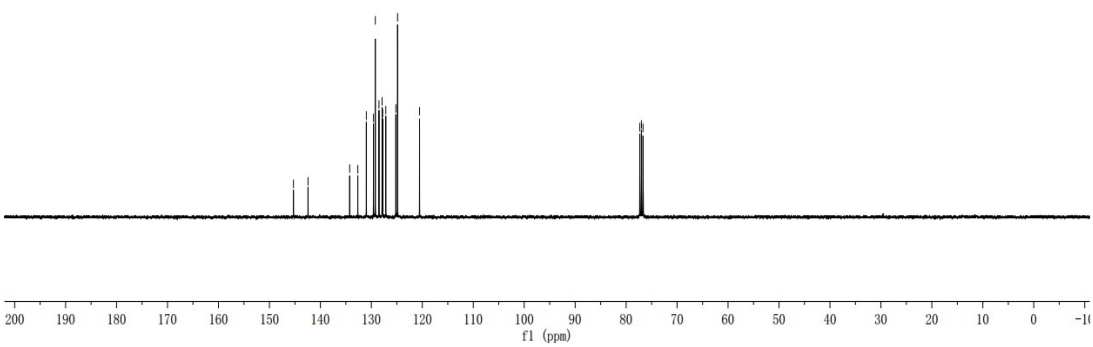
3g ^{1}H NMR ($CDCl_3$, 400 MHz)

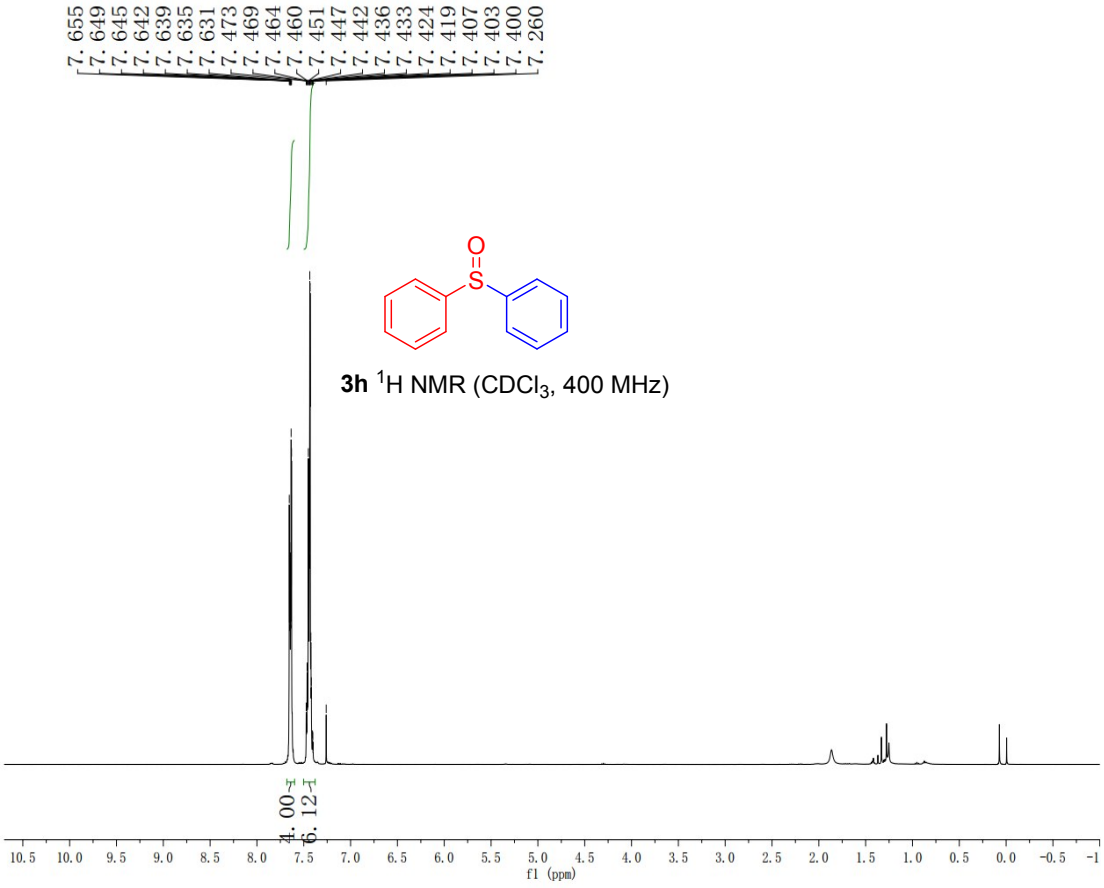




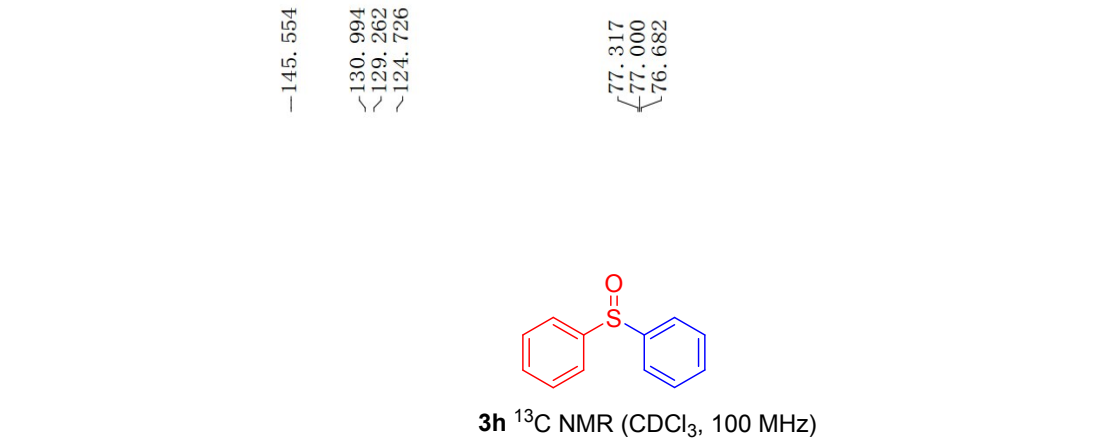


3g ^{13}C NMR ($CDCl_3$, 100 MHz)

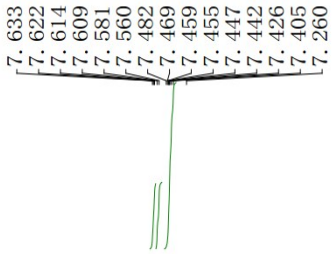


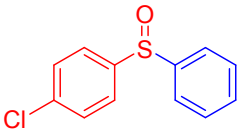


3h ^{1}H NMR ($CDCl_3$, 400 MHz)

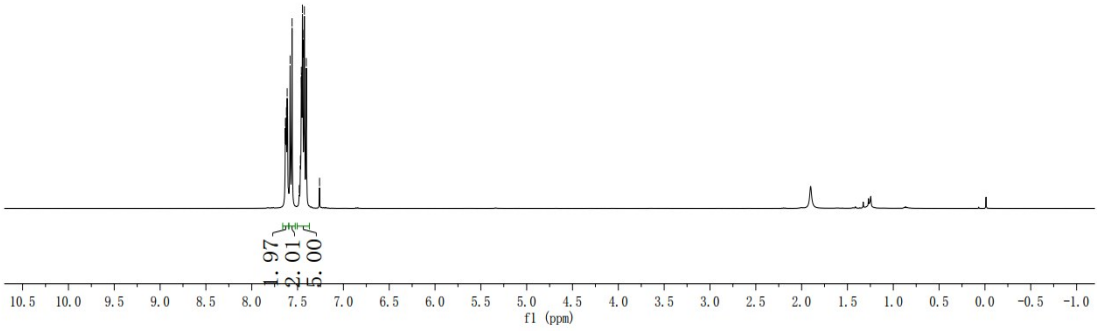


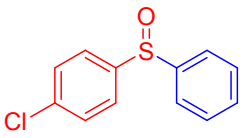
3h ^{13}C NMR ($CDCl_3$, 100 MHz)



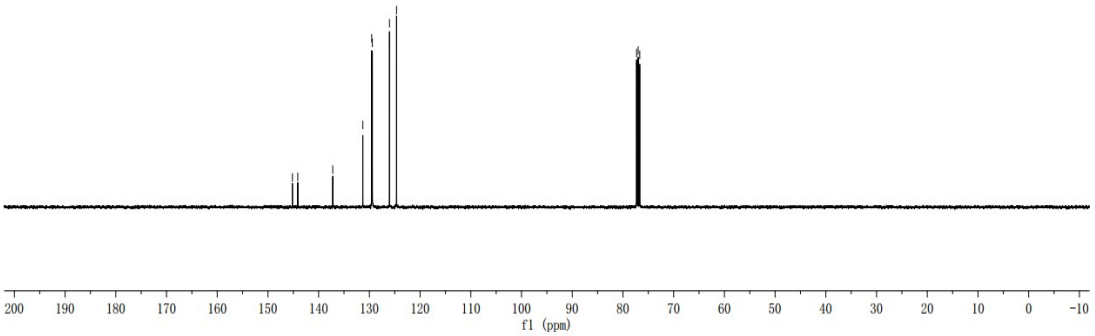


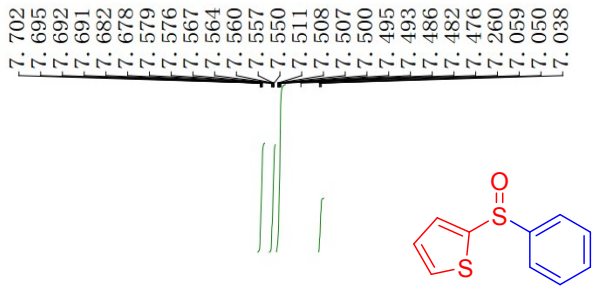
3i ^{1}H NMR ($CDCl_3$, 400 MHz)



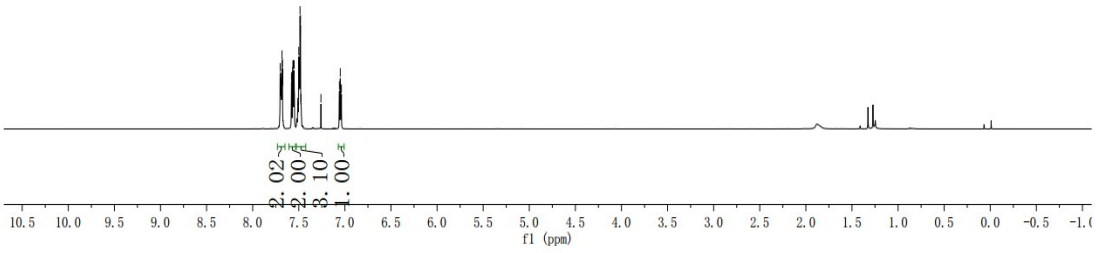


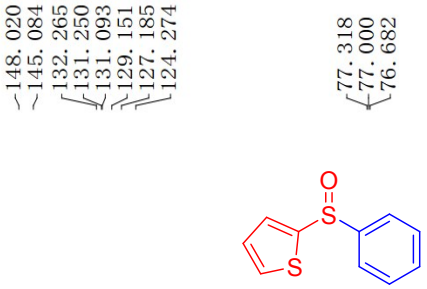
3i ^{13}C NMR ($CDCl_3$, 100 MHz)



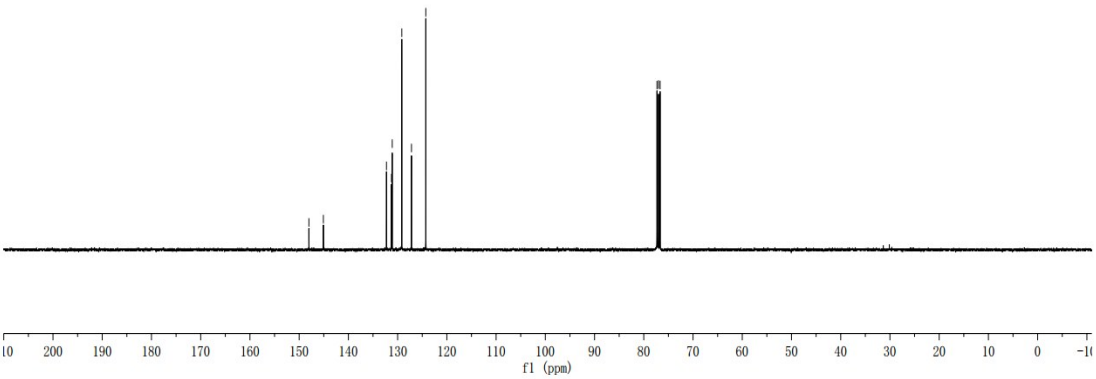


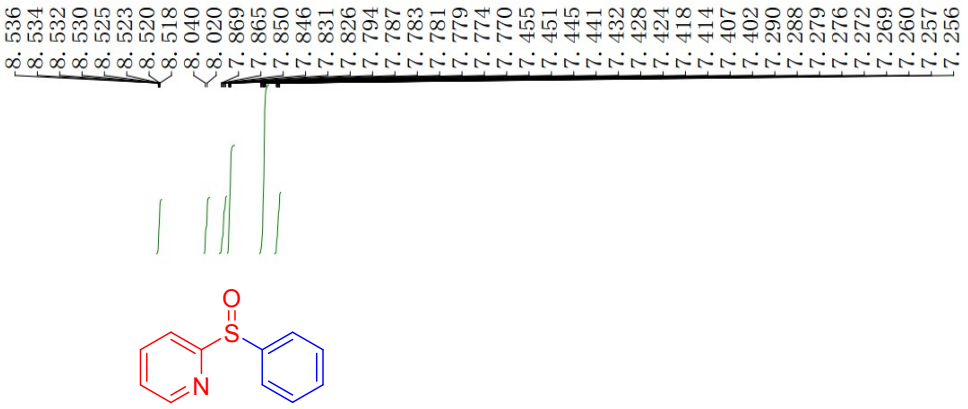
3j ^{1}H NMR ($CDCl_3$, 400 MHz)



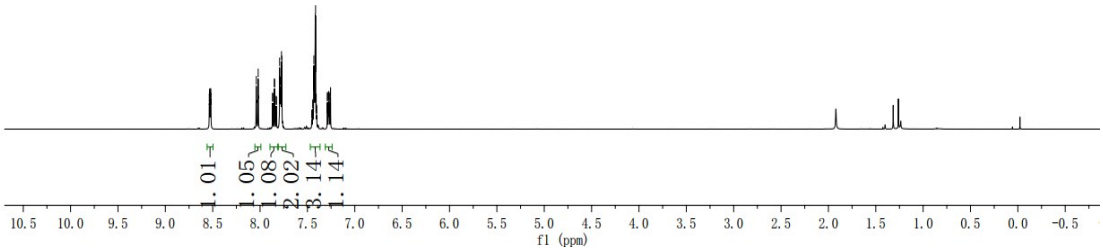


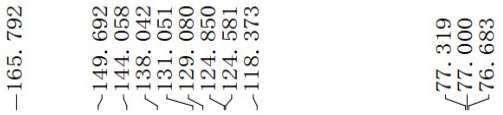
3j ^{13}C NMR ($CDCl_3$,100 MHz)

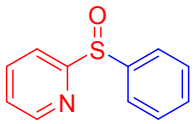




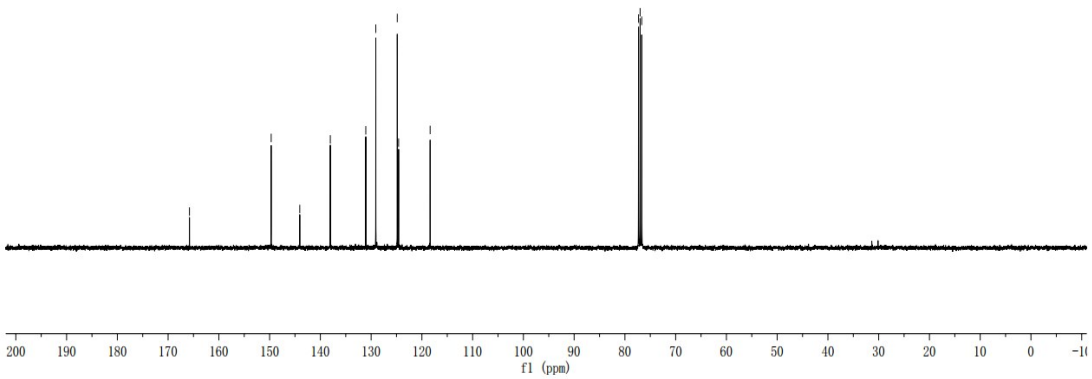
3k ^{1}H NMR ($CDCl_3$, 400 MHz)

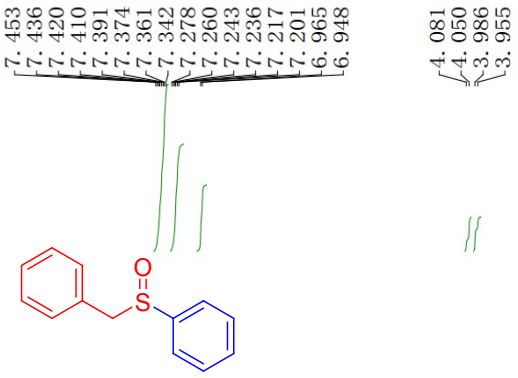




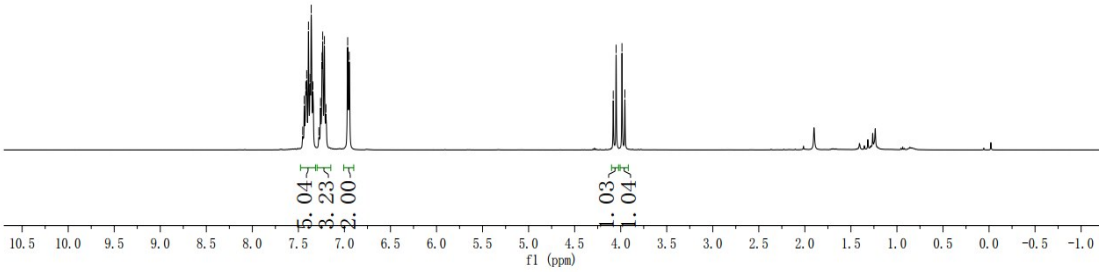


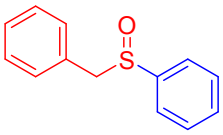
3k ^{13}C NMR ($CDCl_3$, 100 MHz)



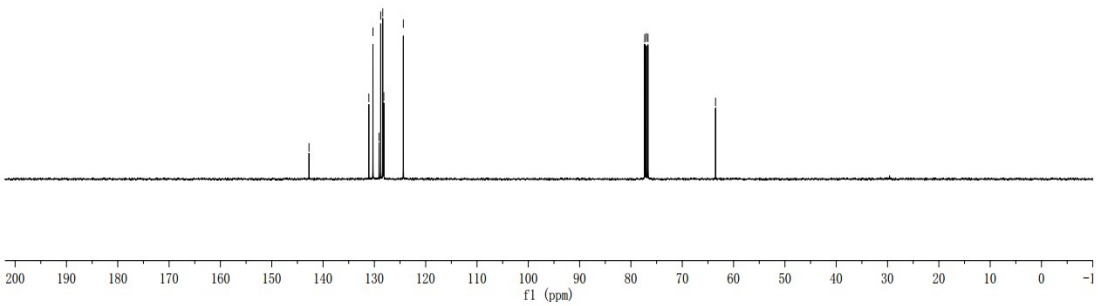


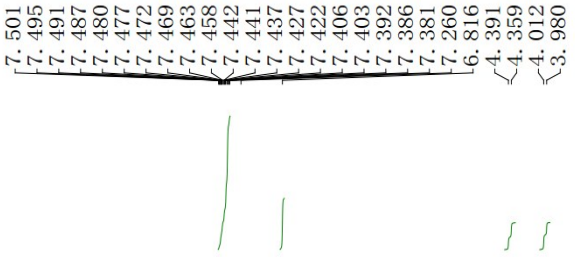
3l ^{1}H NMR ($CDCl_3$, 400 MHz)

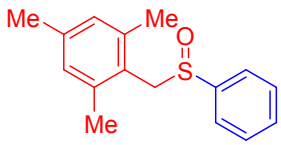




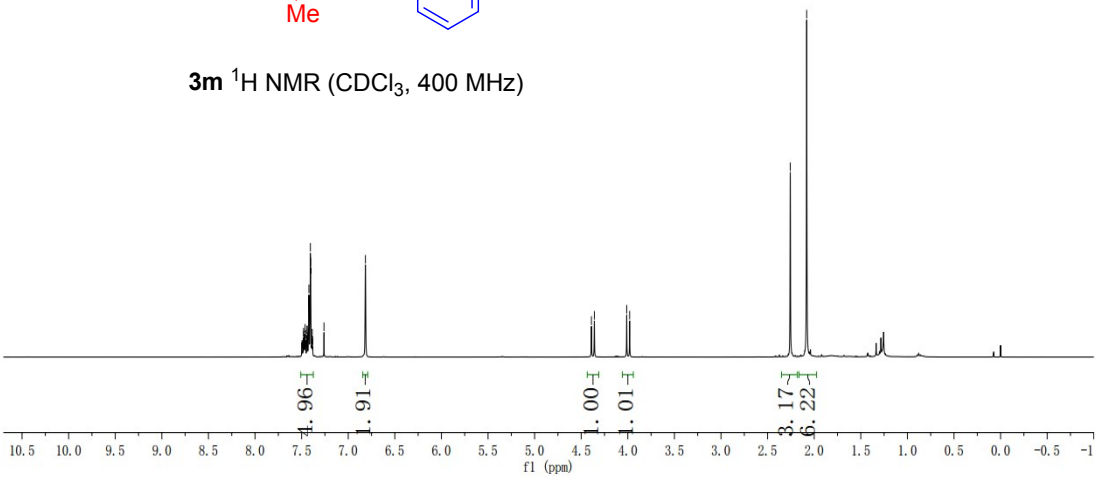
3l ^{13}C NMR ($CDCl_3$, 100 MHz)

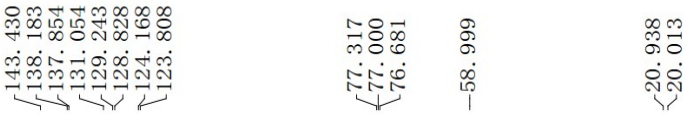


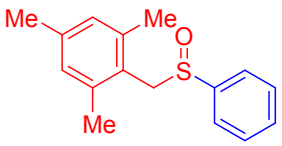




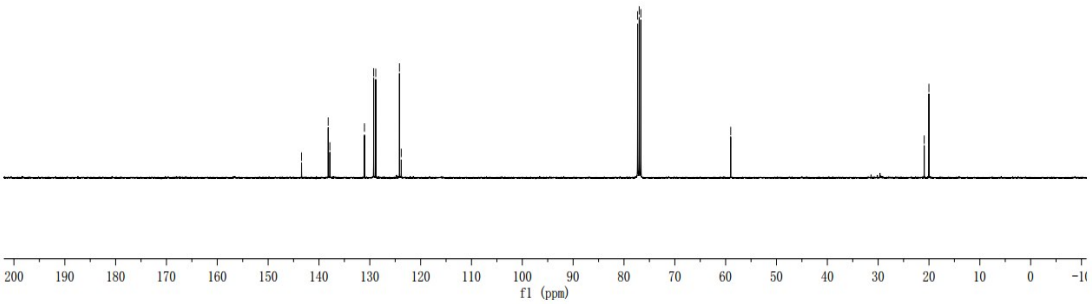
3m ^{1}H NMR ($CDCl_3$, 400 MHz)

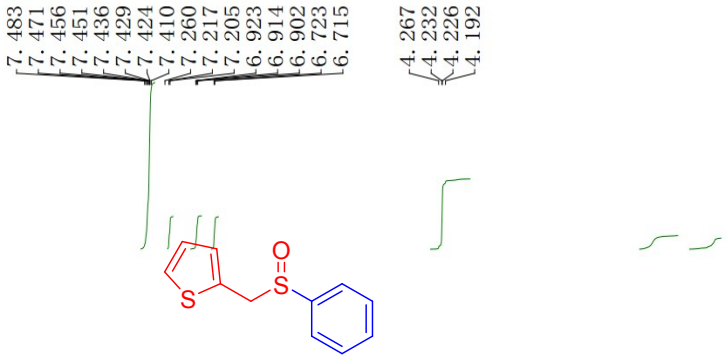




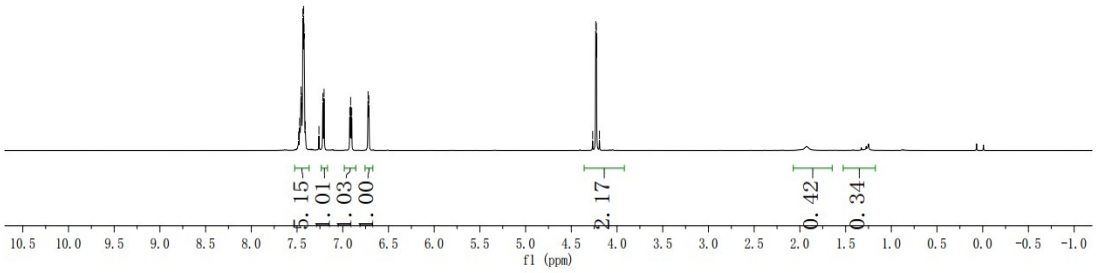


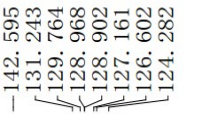
3m ^{13}C NMR ($CDCl_3$, 100 MHz)

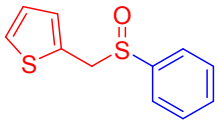




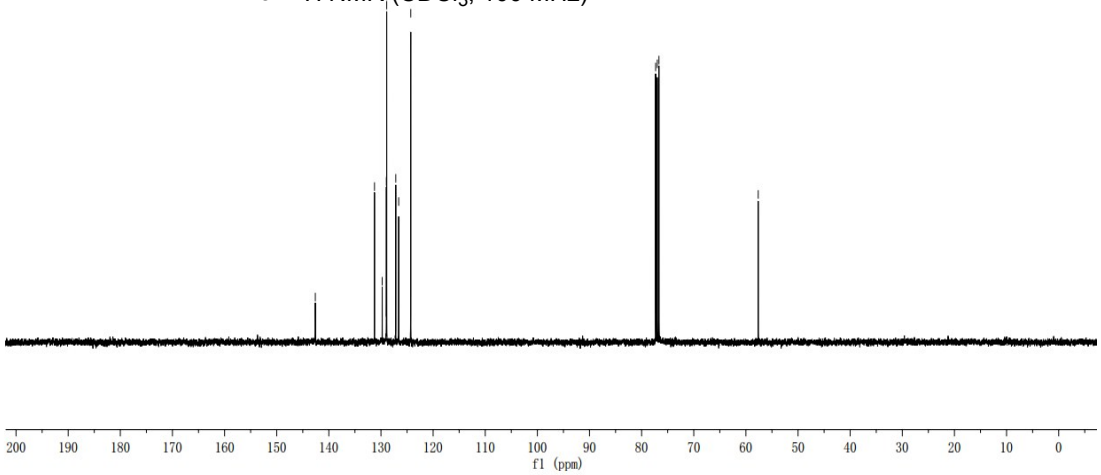
3n ^{1}H NMR ($CDCl_3$, 400 MHz)

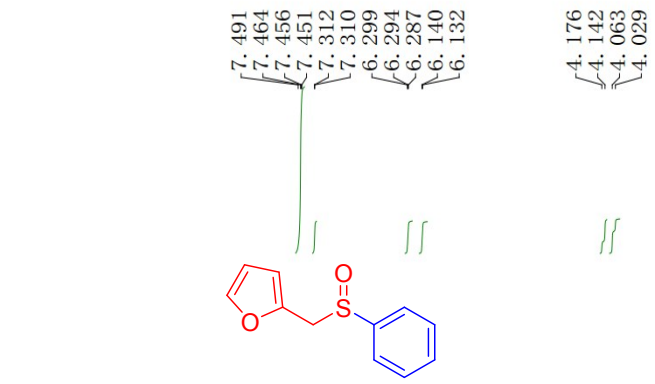




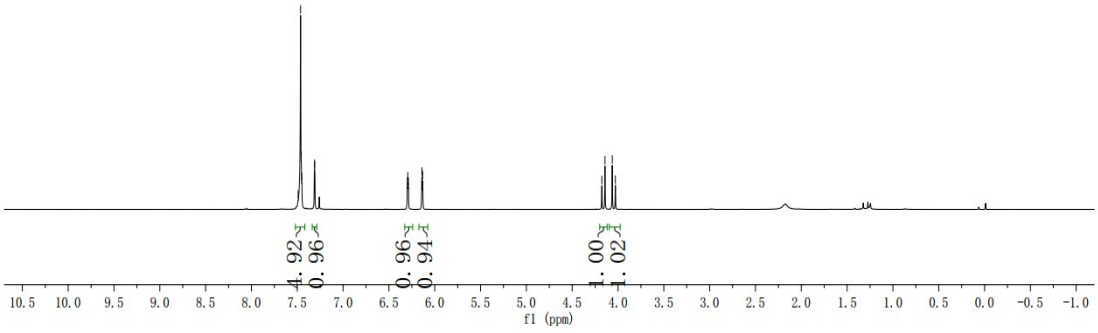


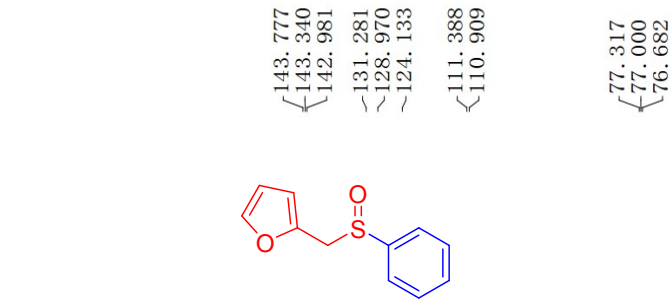
3n ^{1}H NMR ($CDCl_3$, 100 MHz)



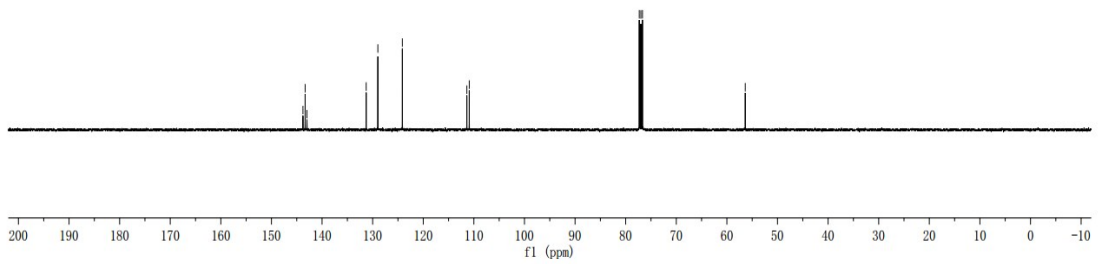


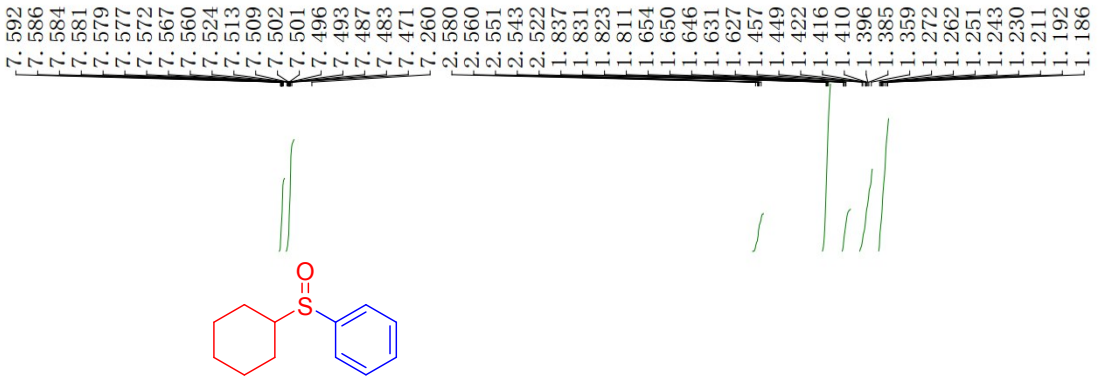
3o ^{1}H NMR ($CDCl_3$, 400 MHz)



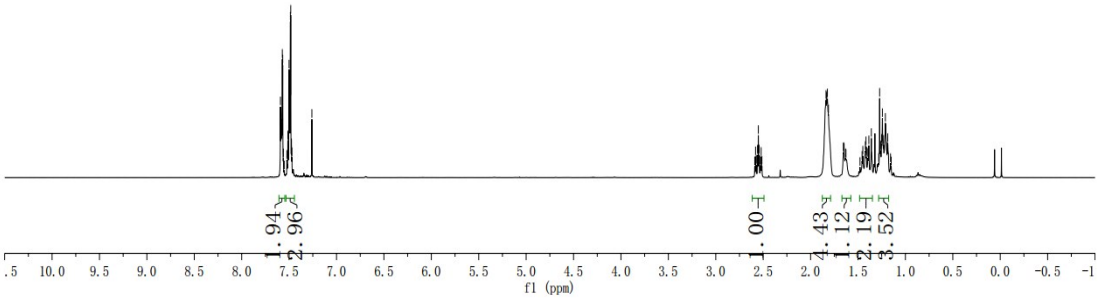


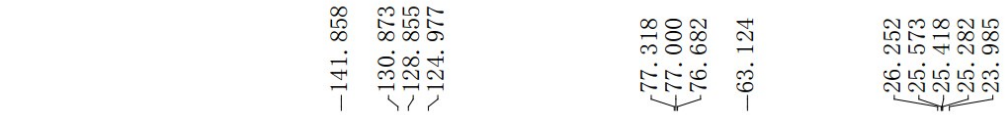
3o ^{13}C NMR ($CDCl_3$, 100 MHz)

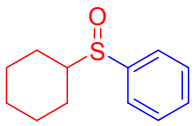




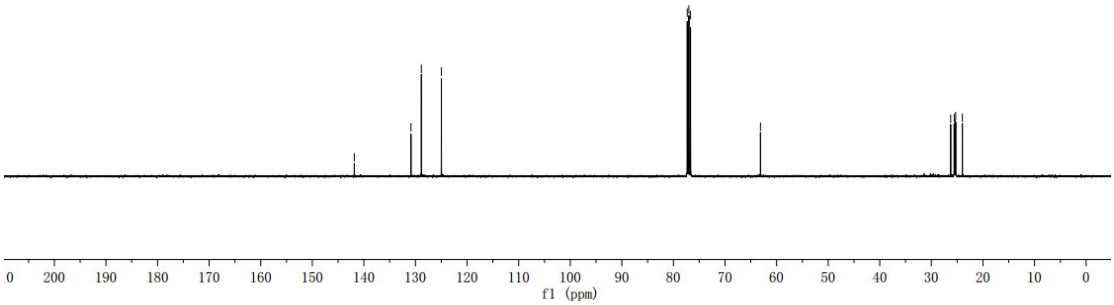
3p ^{1}H NMR ($CDCl_3$, 400 MHz)

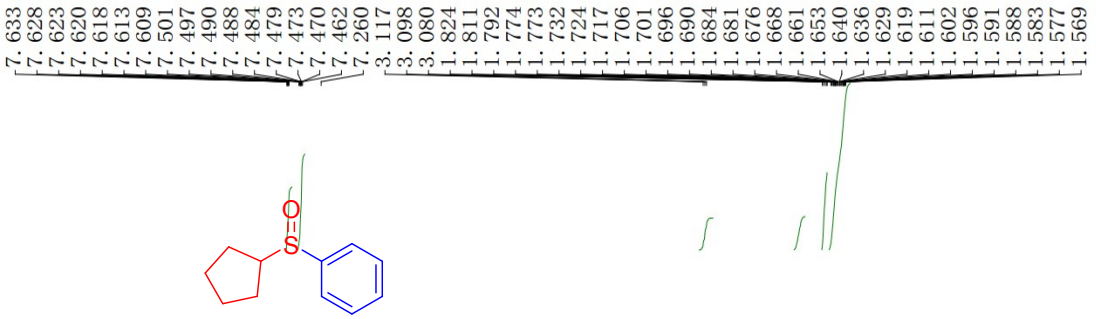




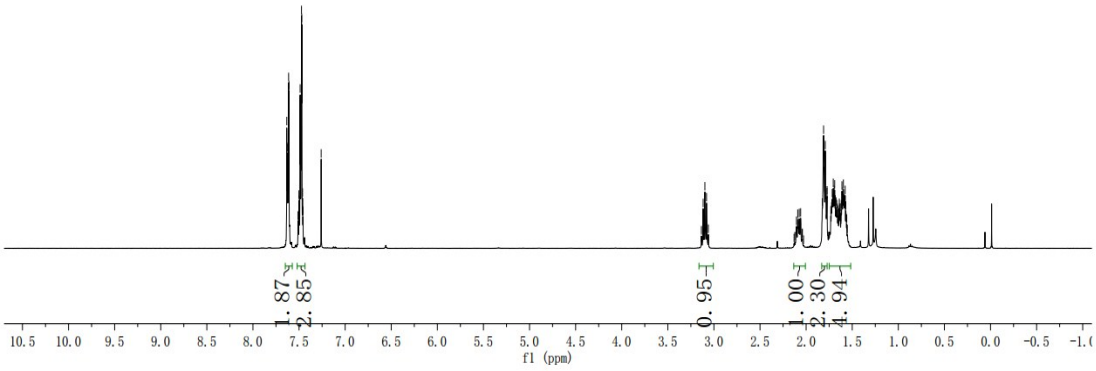


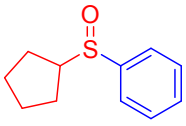
3p ^{13}C NMR ($CDCl_3$, 100 MHz)



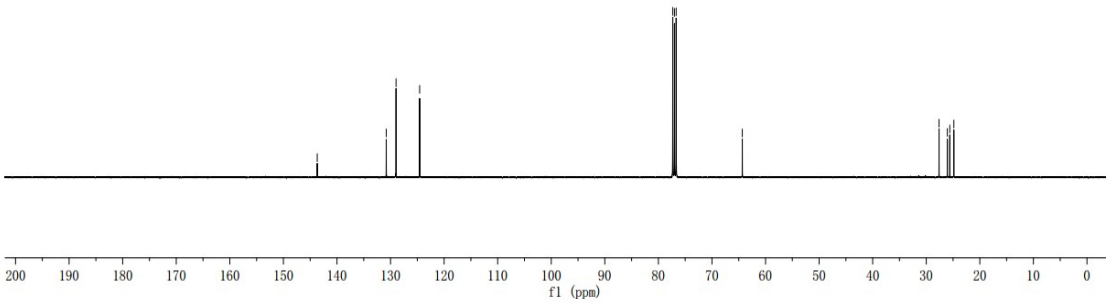


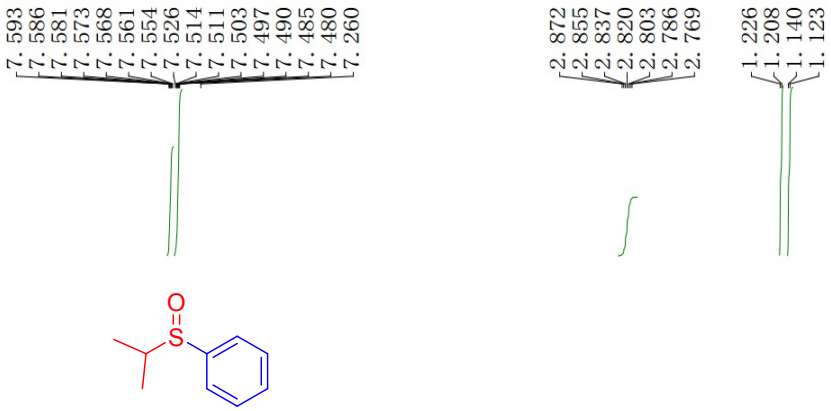
3q ^{1}H NMR ($CDCl_3$, 400 MHz)



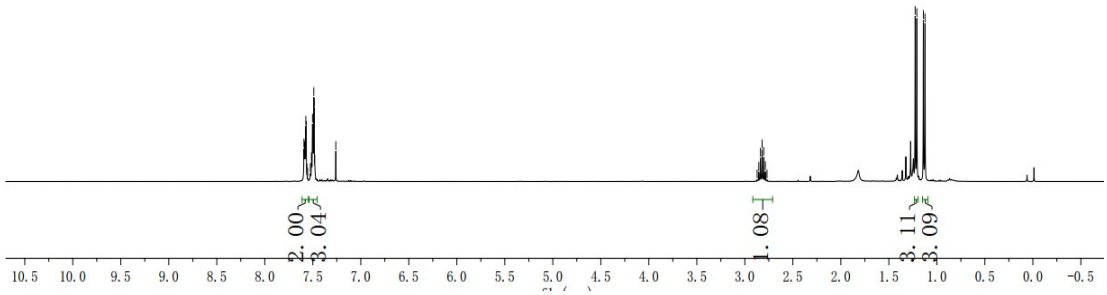


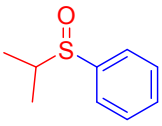
3q ^{13}C NMR ($CDCl_3$, 100 MHz)



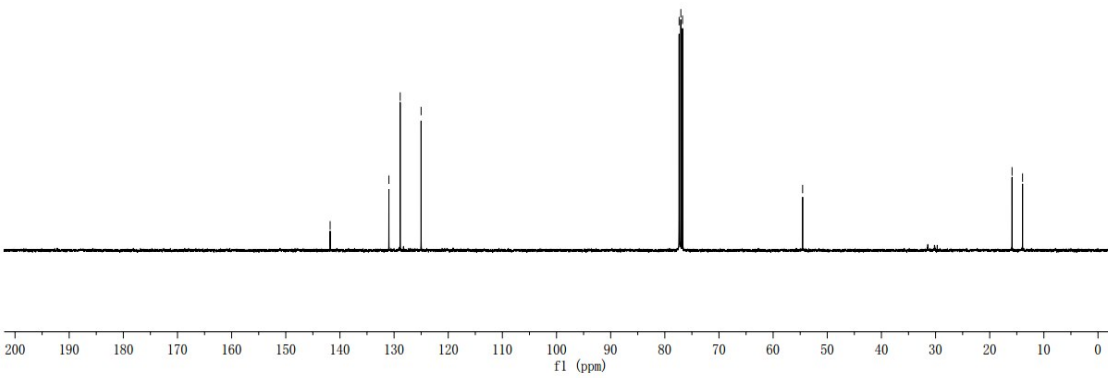


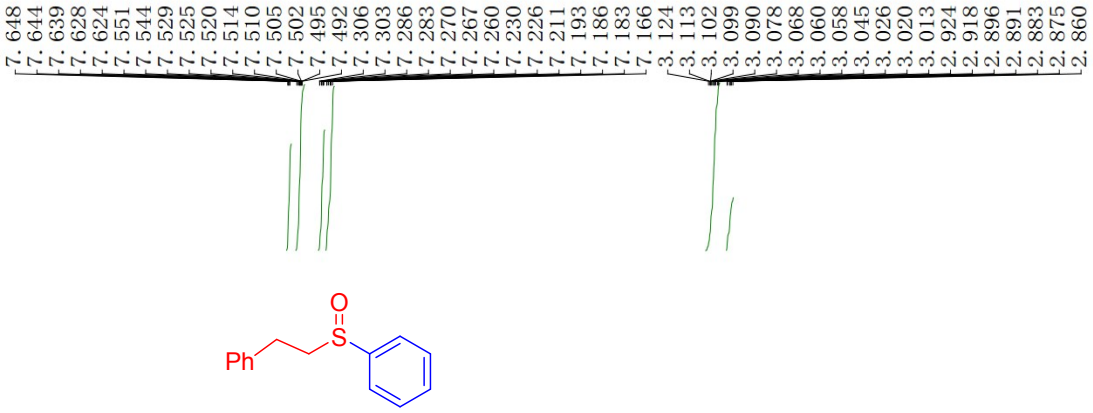
3r ^{1}H NMR ($CDCl_3$, 400 MHz)



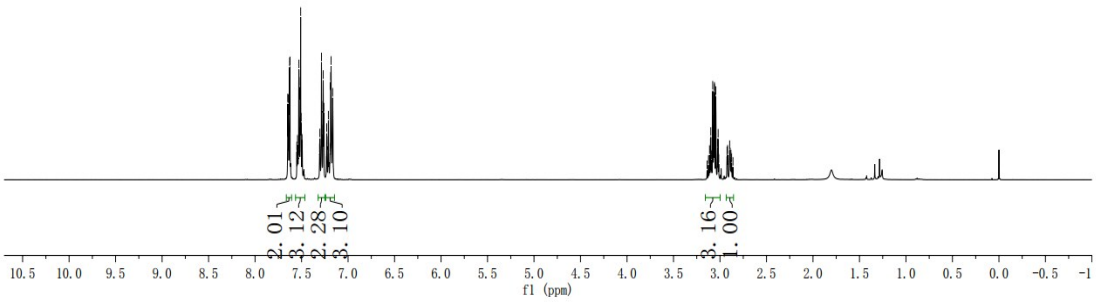


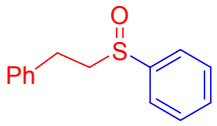
3r ^{1}H NMR ($CDCl_3$, 100 MHz)



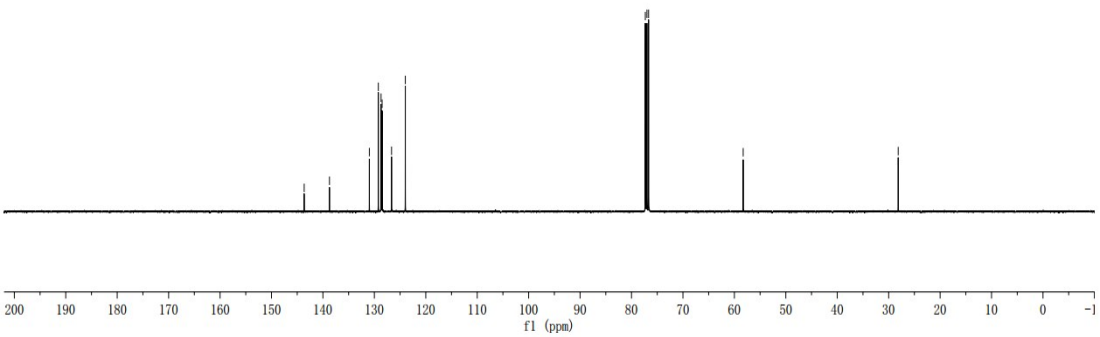


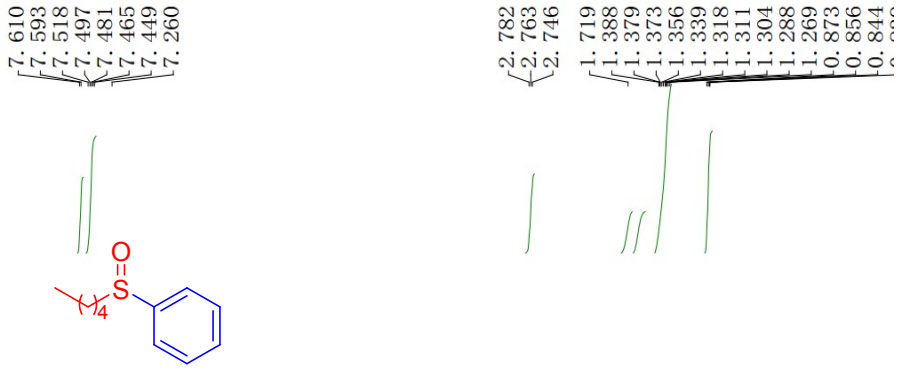
3s ^{1}H NMR ($CDCl_3$, 400 MHz)



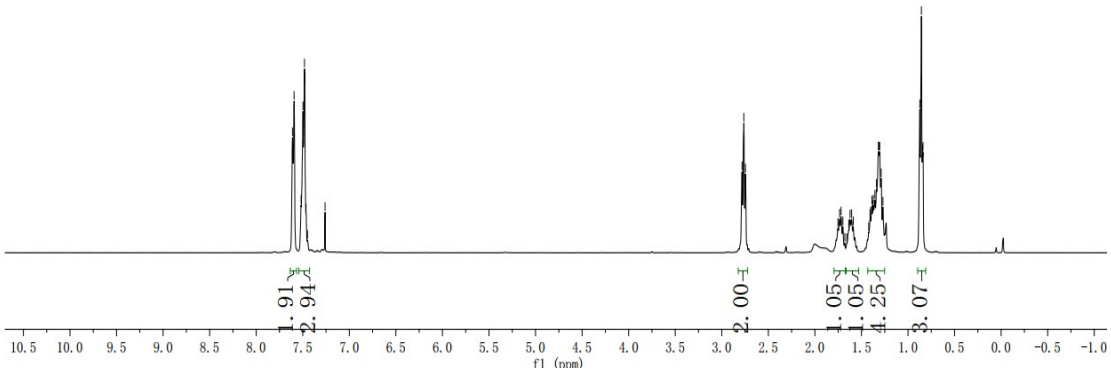


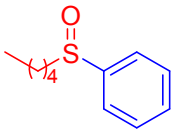
3s ^{13}C NMR ($CDCl_3$, 100 MHz)



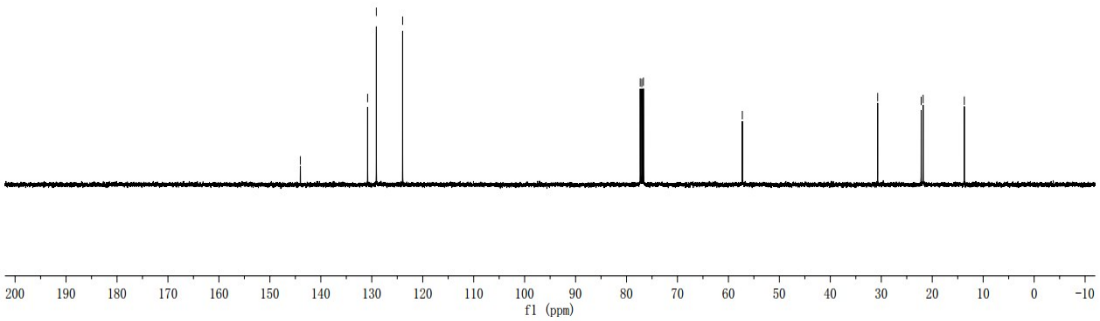


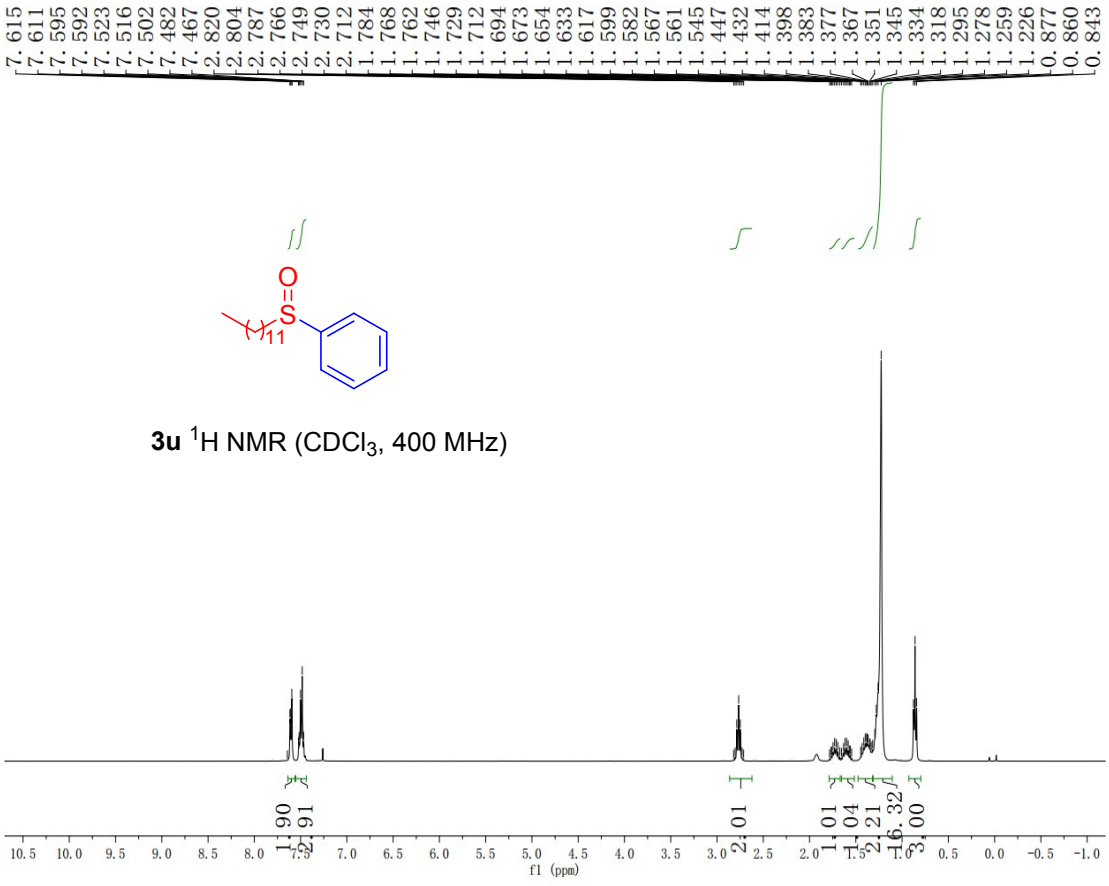
3t ^{1}H NMR ($CDCl_3$, 400 MHz)



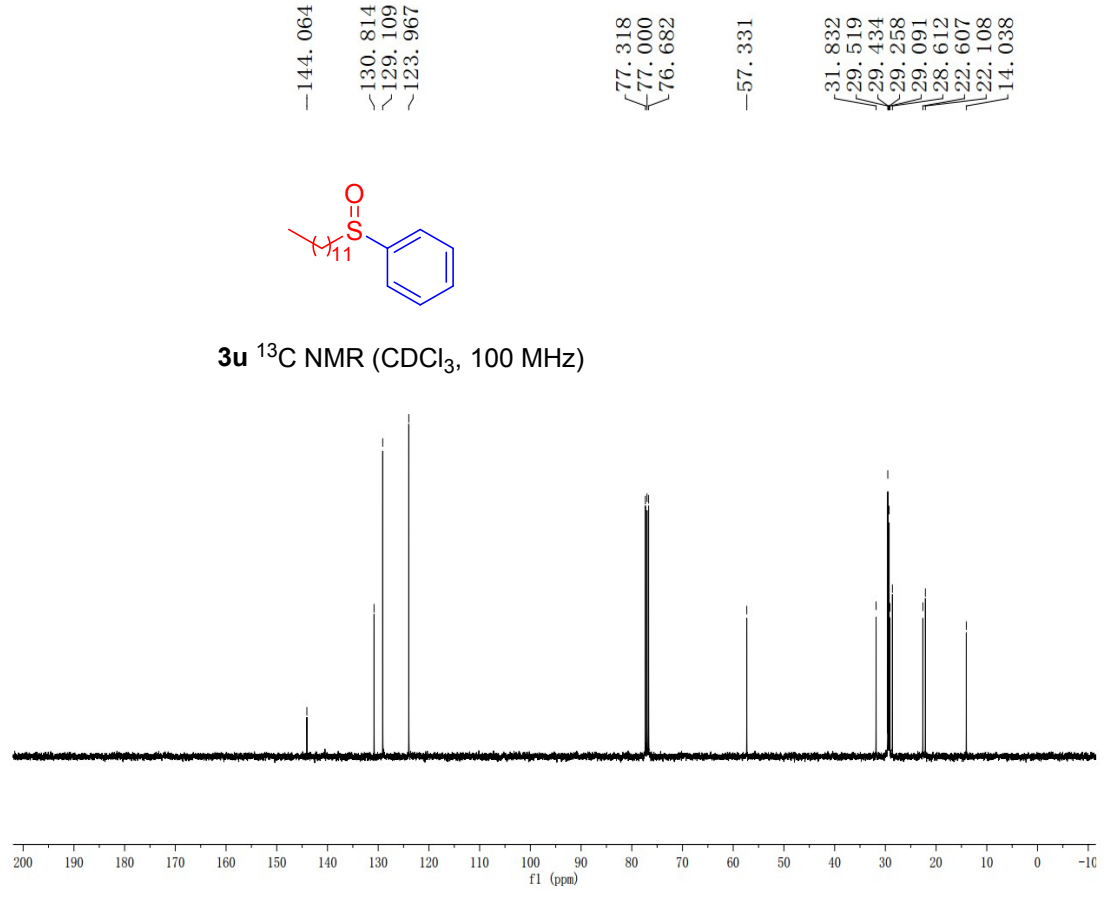


3t ^{13}C NMR ($CDCl_3$, 100 MHz)

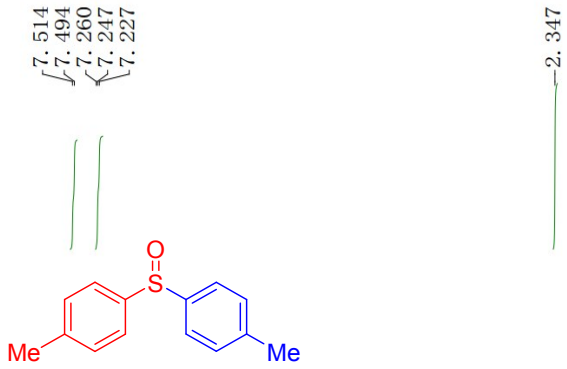




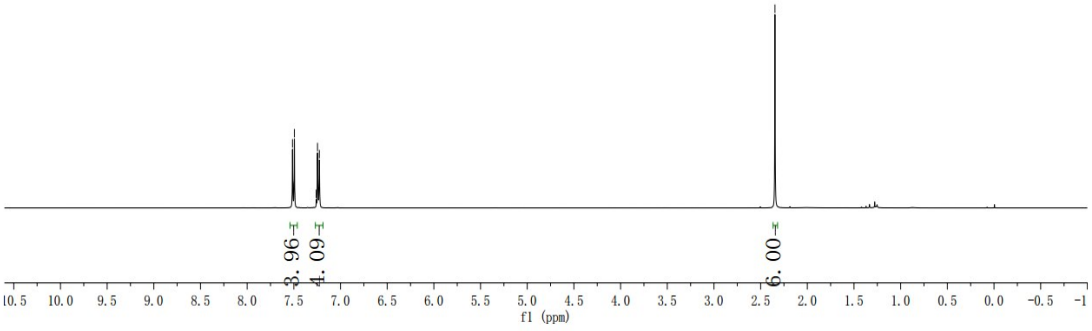
3u ^{1}H NMR ($CDCl_3$, 400 MHz)

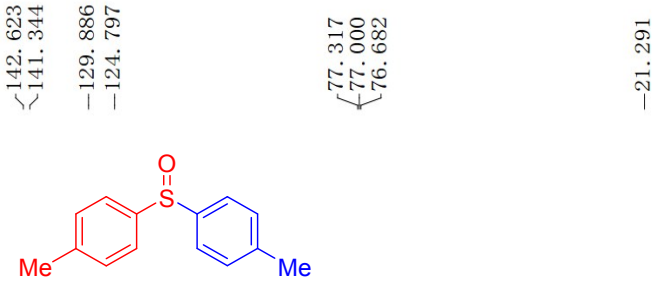


3u ^{13}C NMR ($CDCl_3$, 100 MHz)

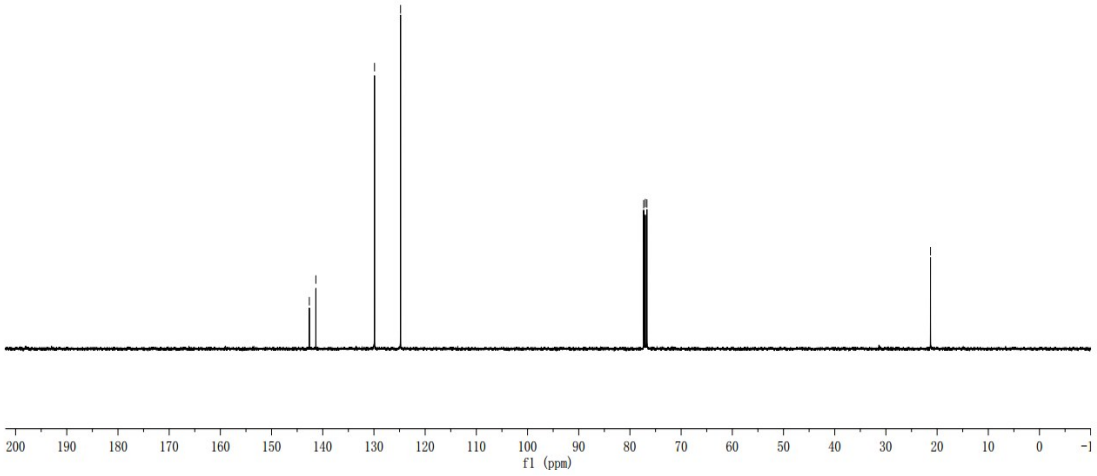


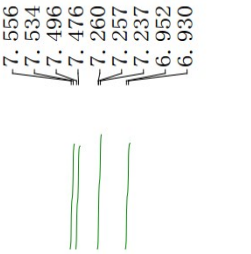
4a ^{1}H NMR ($CDCl_3$, 400 MHz)

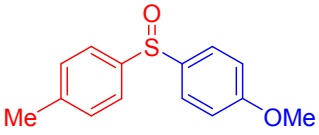




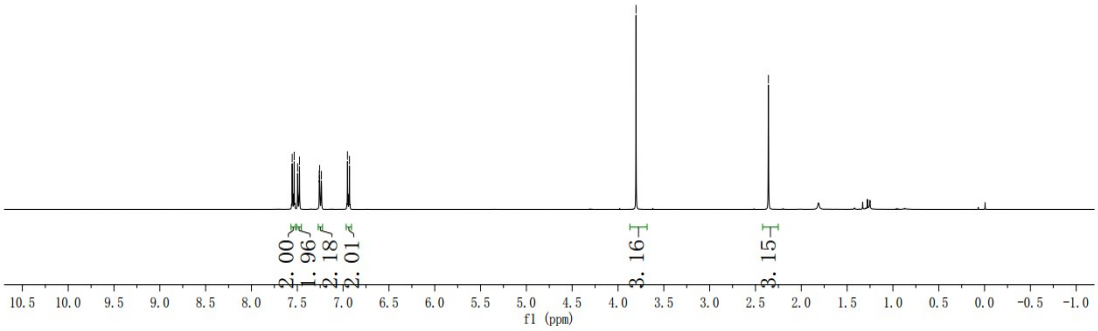
4a ^{13}C NMR ($CDCl_3$, 100 MHz)

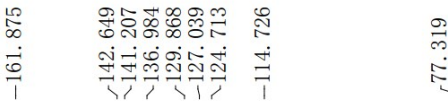


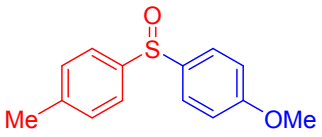




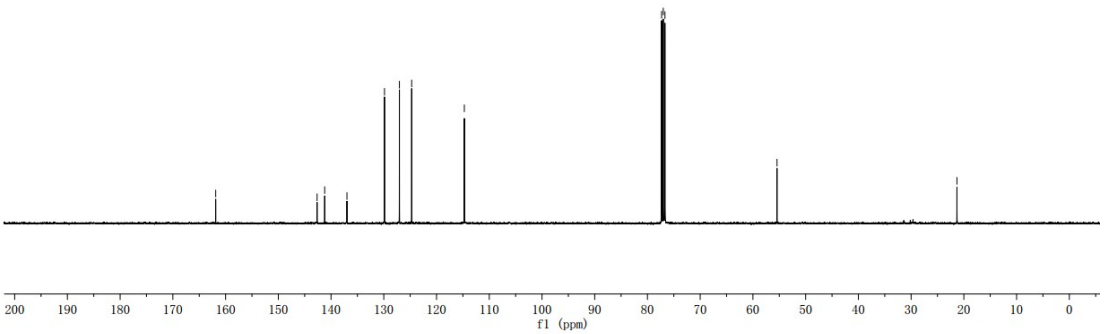
4b ^{1}H NMR ($CDCl_3$, 400 MHz)

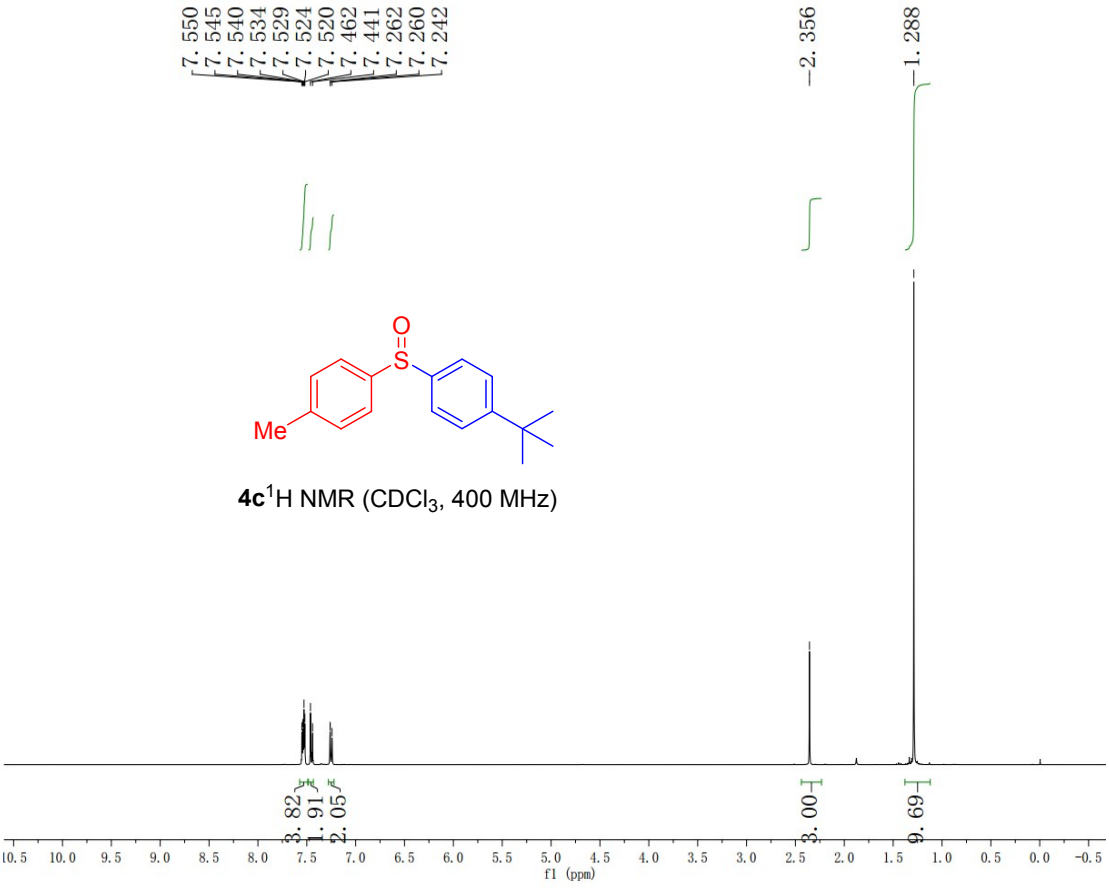




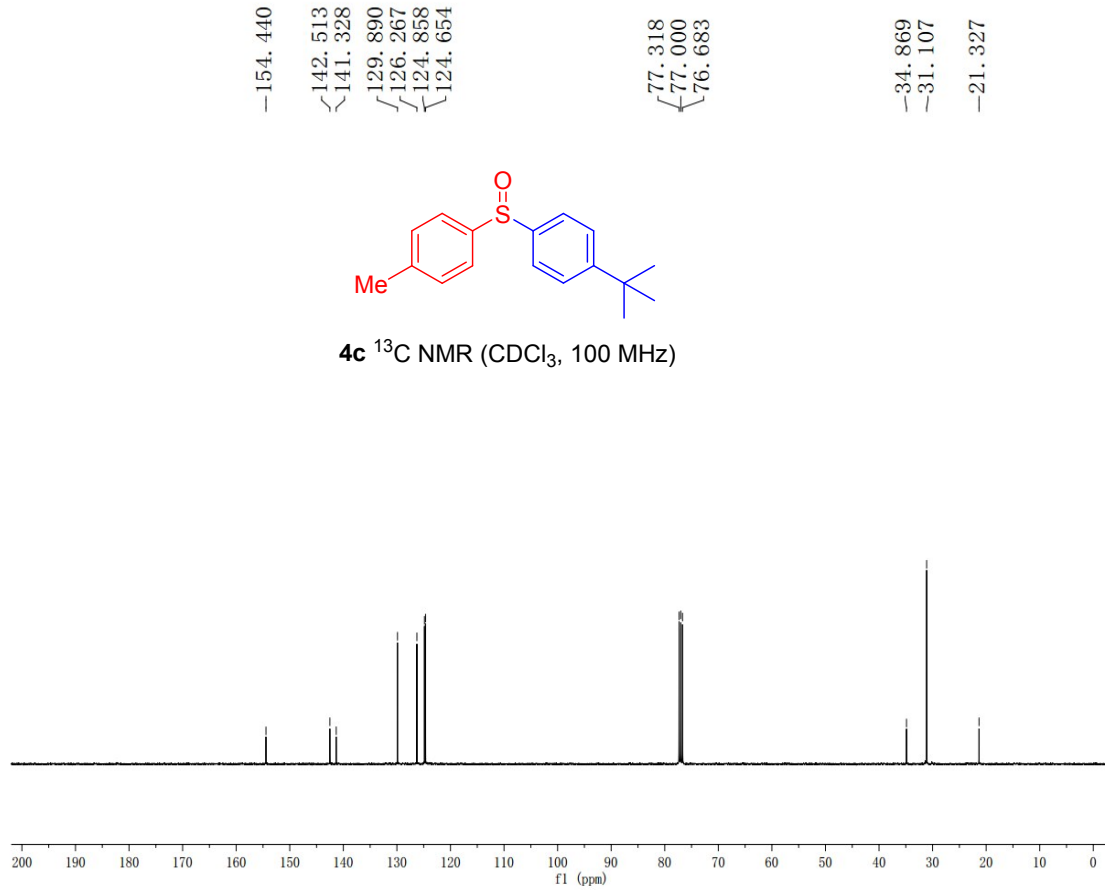


4b ^{13}C NMR ($CDCl_3$, 100 MHz)

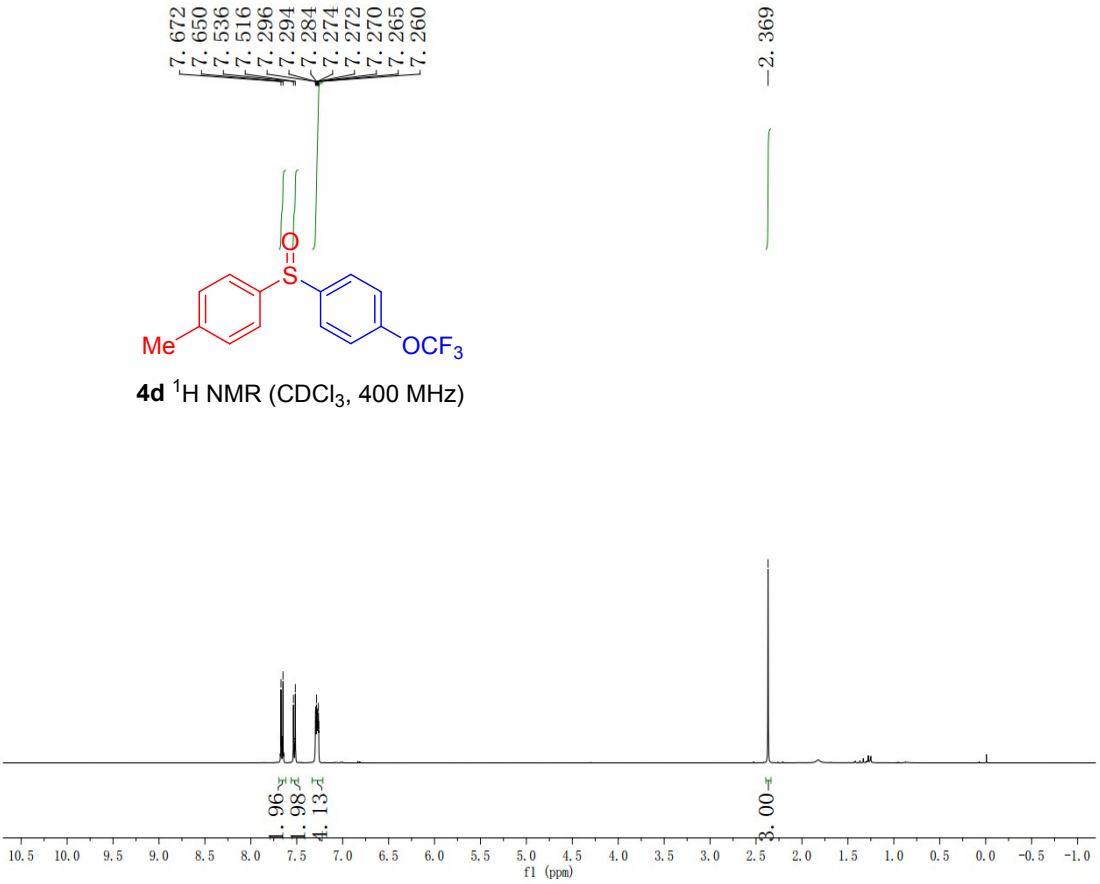




4c ^{1}H NMR ($CDCl_3$, 400 MHz)

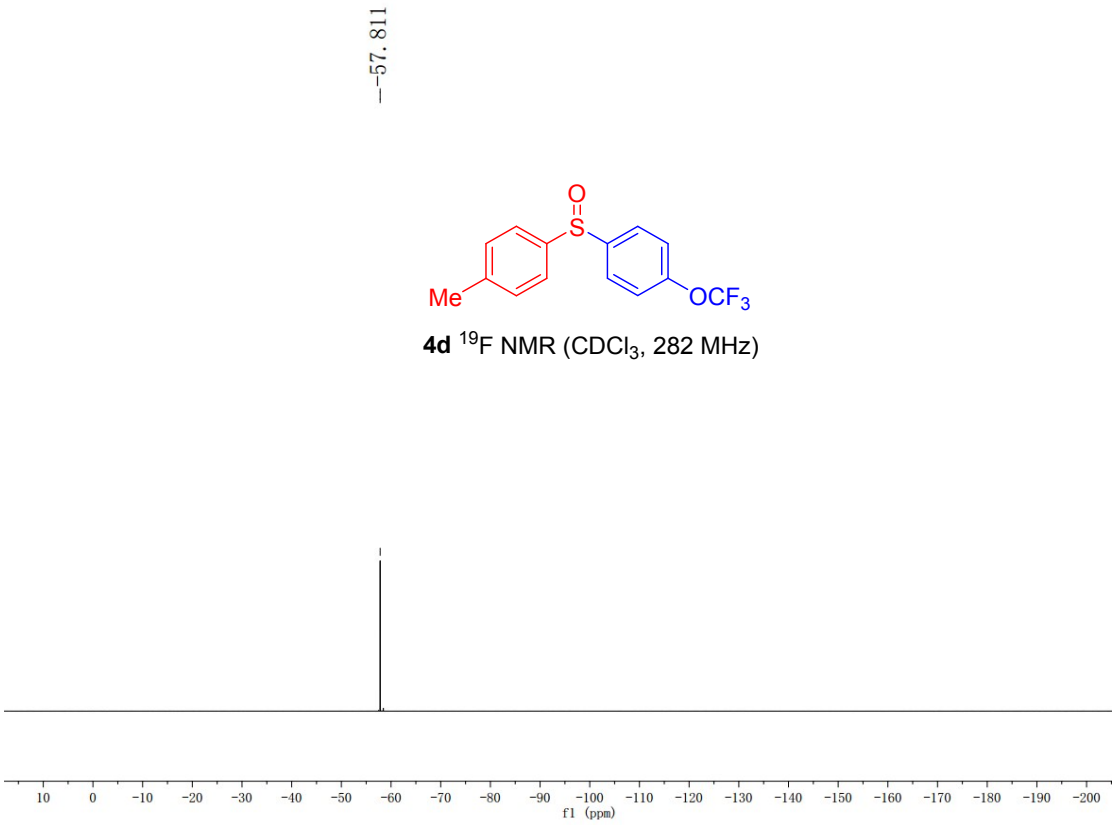


4c ^{13}C NMR ($CDCl_3$, 100 MHz)

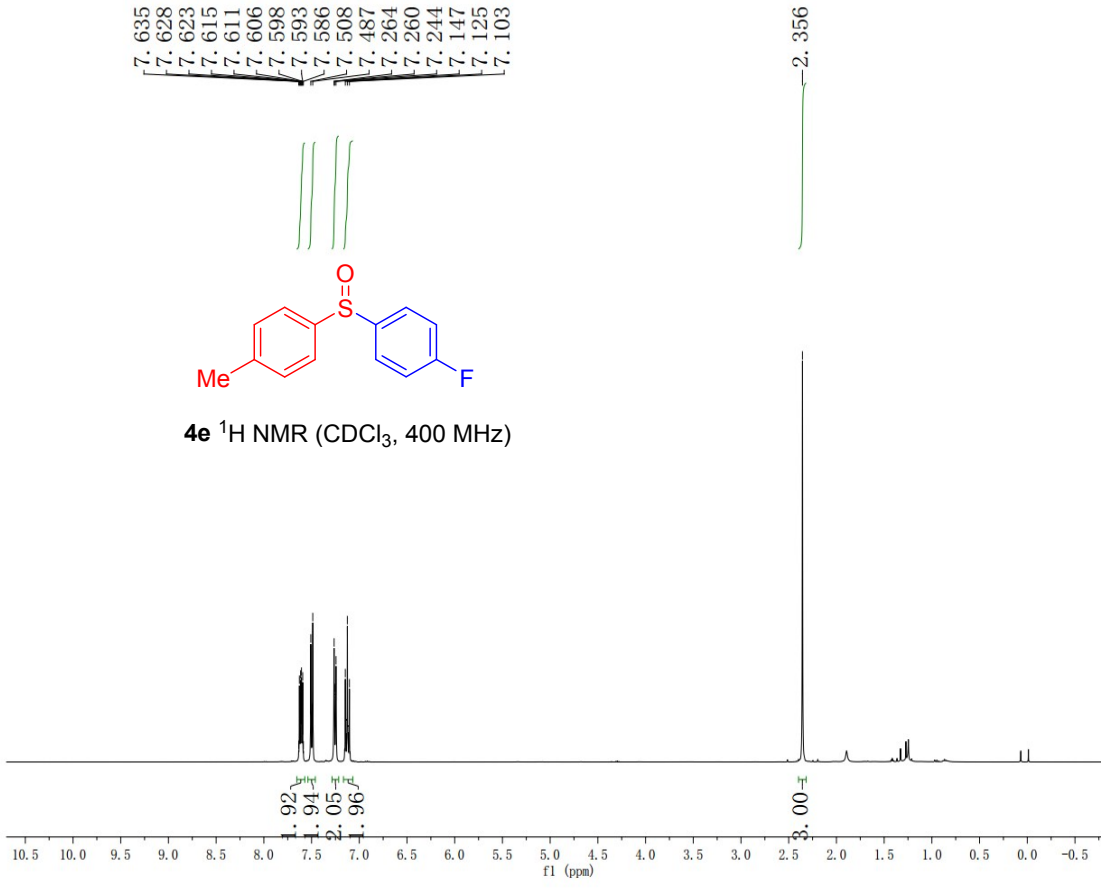


4d ^{1}H NMR ($CDCl_3$, 400 MHz)

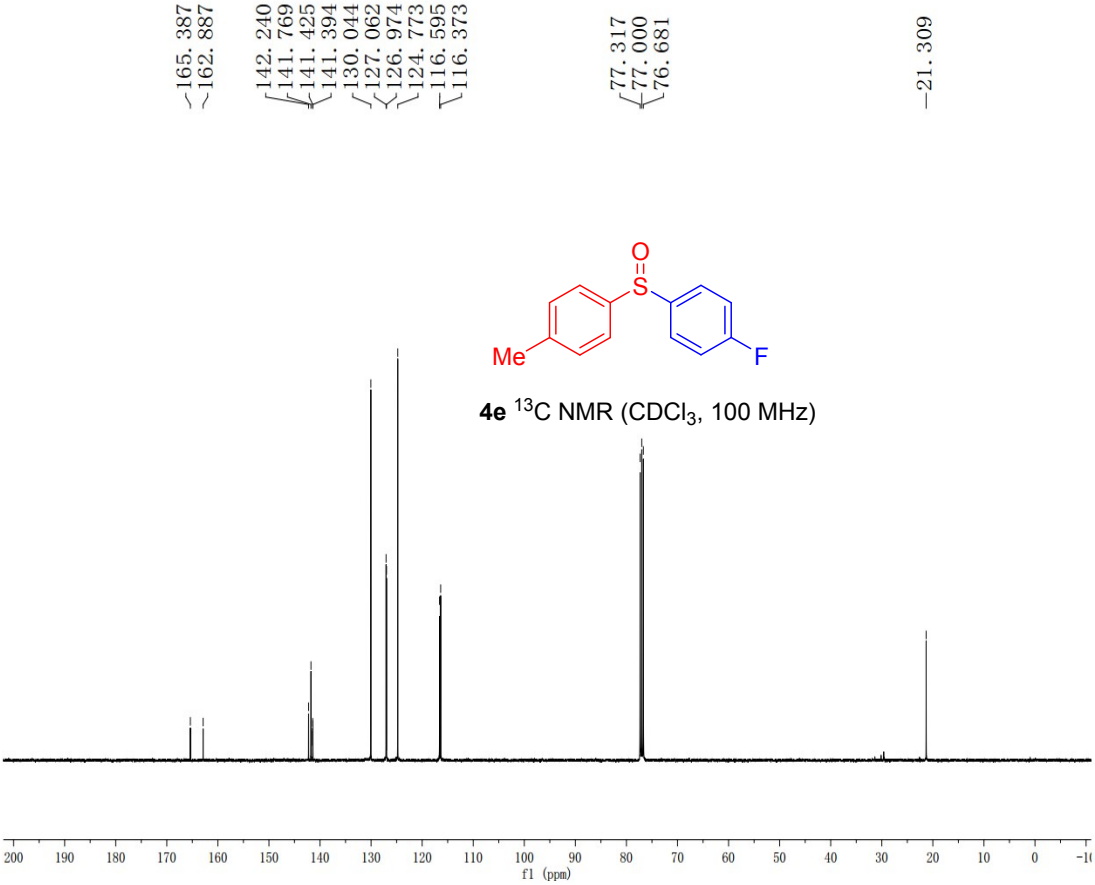
4d ^{13}C NMR ($CDCl_3$, 100 MHz)



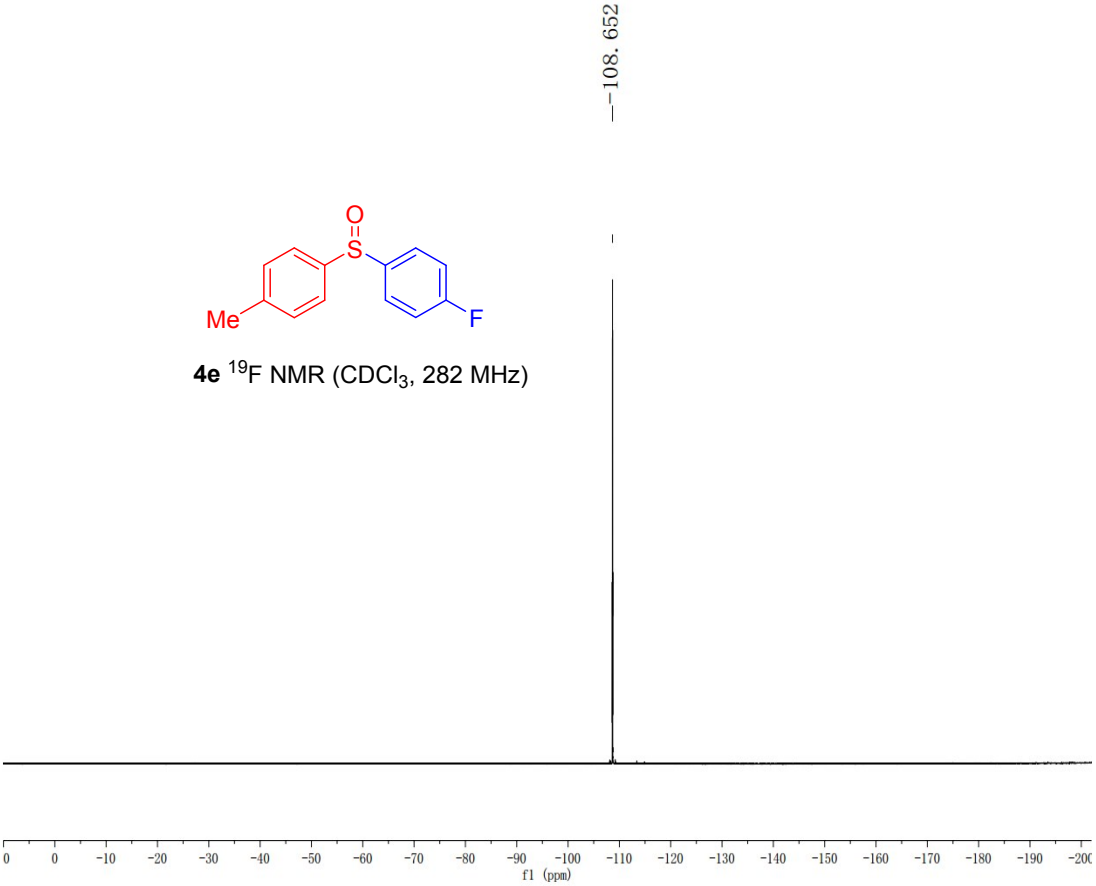
4d ^{19}F NMR ($CDCl_3$, 282 MHz)



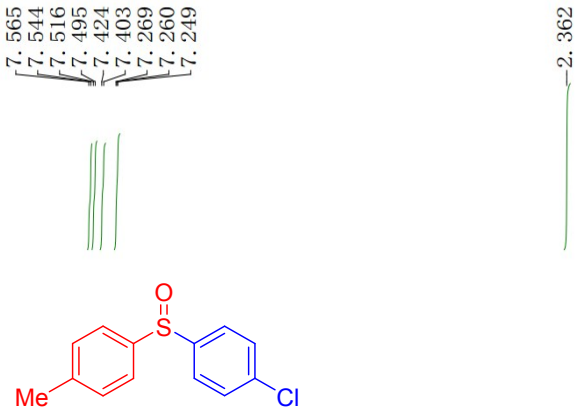
4e ^{1}H NMR ($CDCl_3$, 400 MHz)



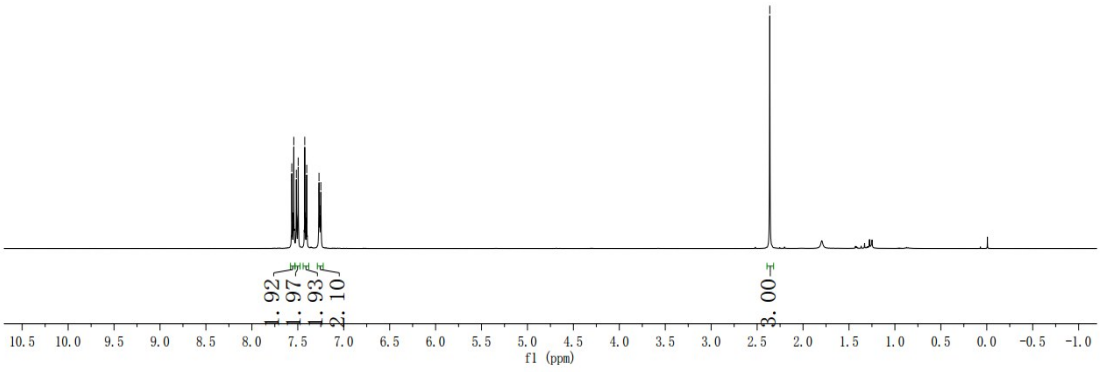
4e ^{13}C NMR ($CDCl_3$, 100 MHz)

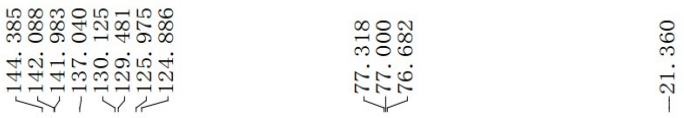


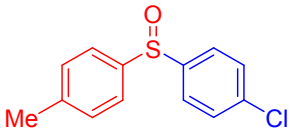
4e ^{19}F NMR ($CDCl_3$, 282 MHz)



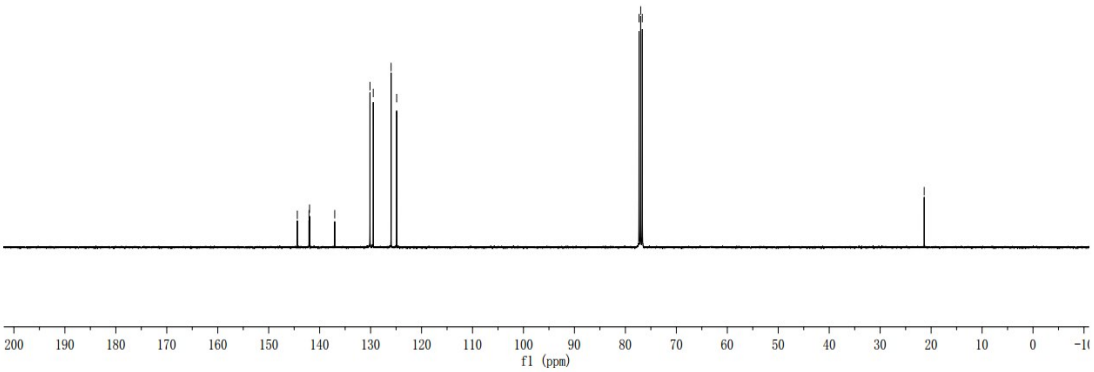
4f ^{1}H NMR ($CDCl_3$, 400 MHz)

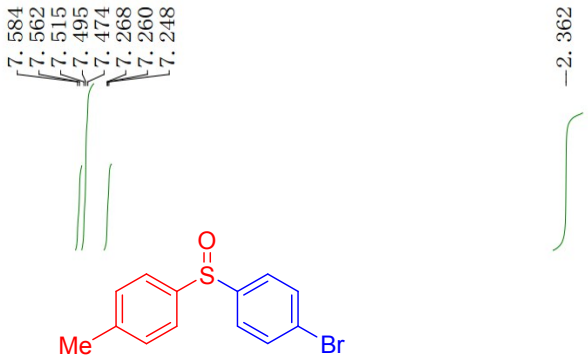




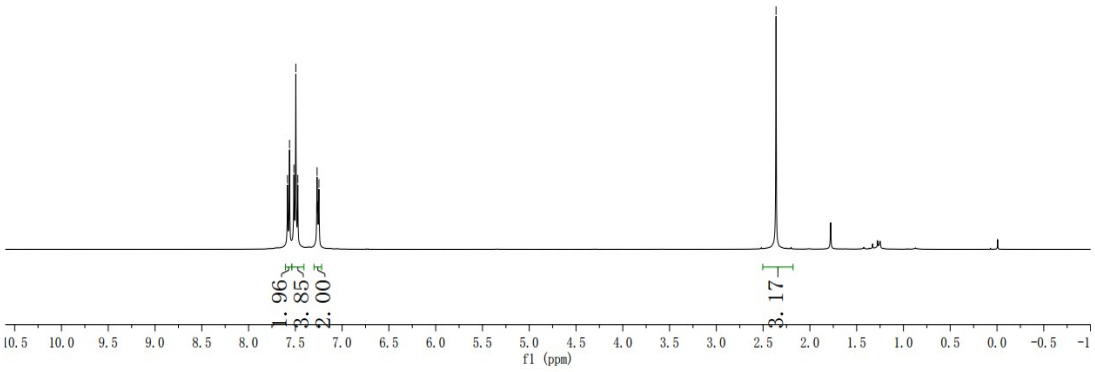


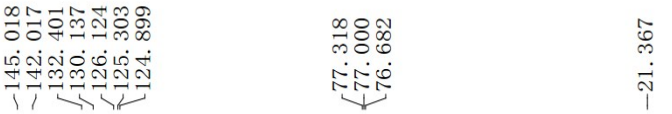
4f ^{13}C NMR ($CDCl_3$, 100 MHz)

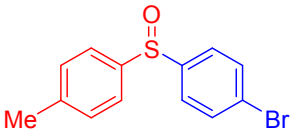




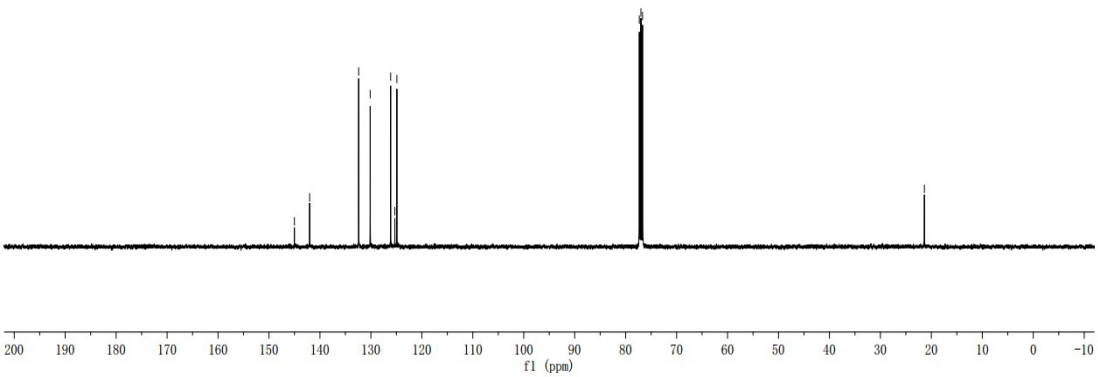
4g ^{1}H NMR ($CDCl_3$, 400 MHz)

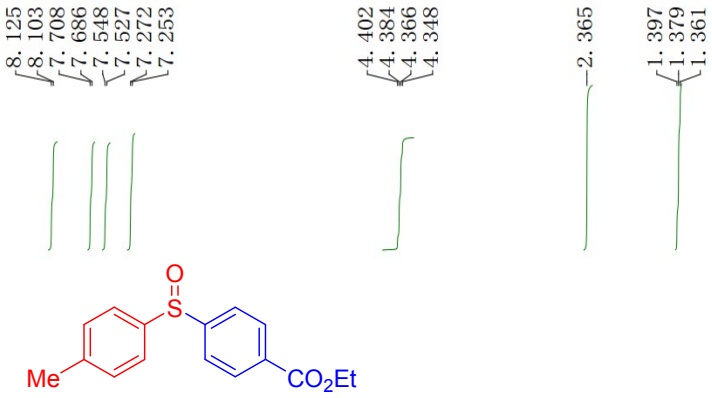




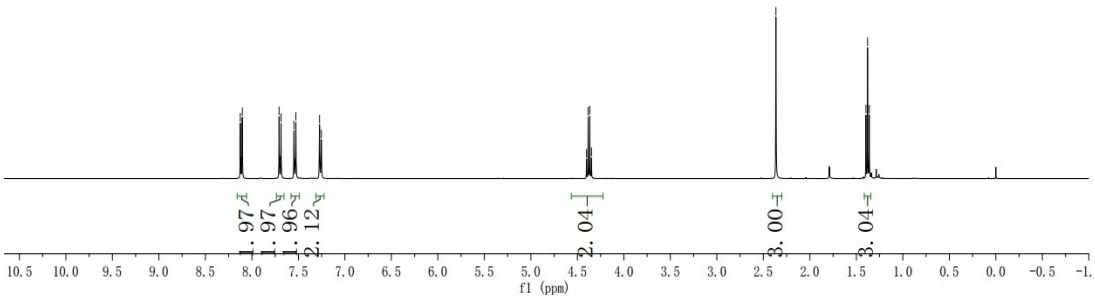


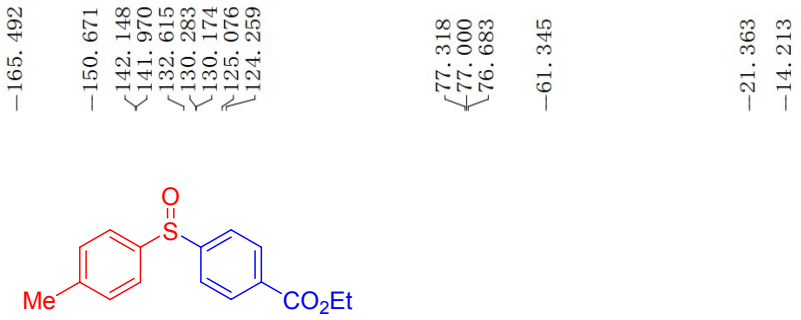
4g ^{13}C NMR ($CDCl_3$, 100 MHz)



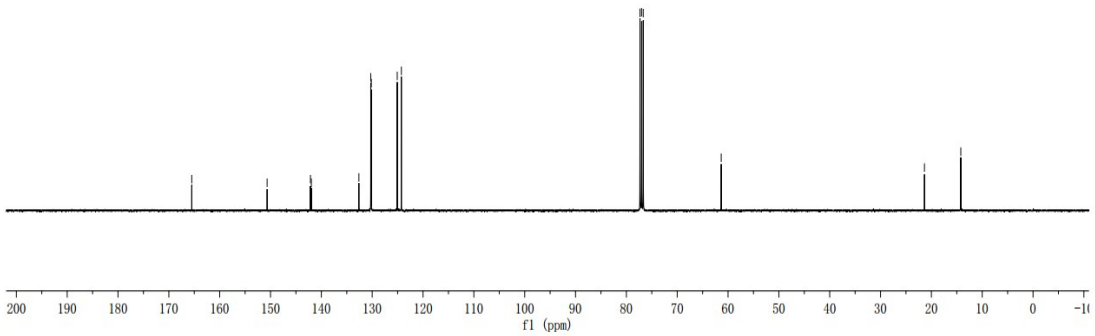


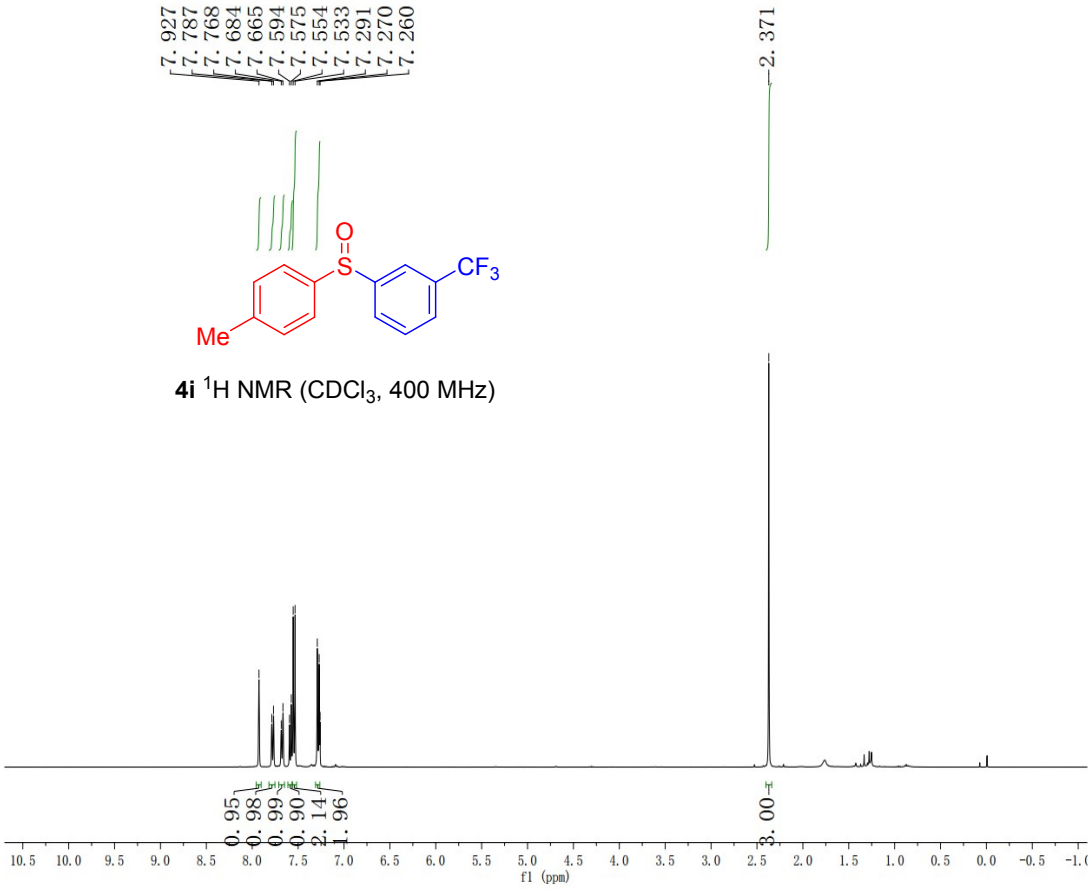
4h ^{1}H NMR ($CDCl_3$, 400 MHz)



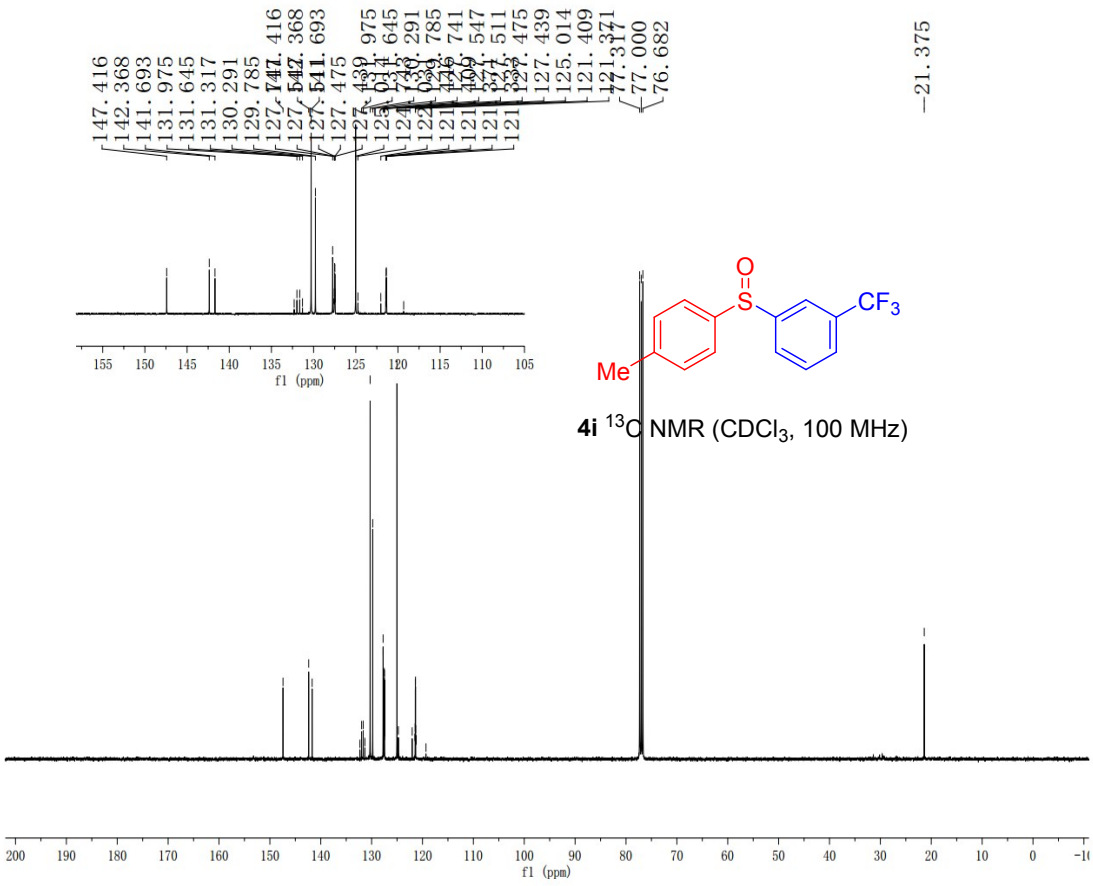


4h ^{13}C NMR ($CDCl_3$, 100 MHz)

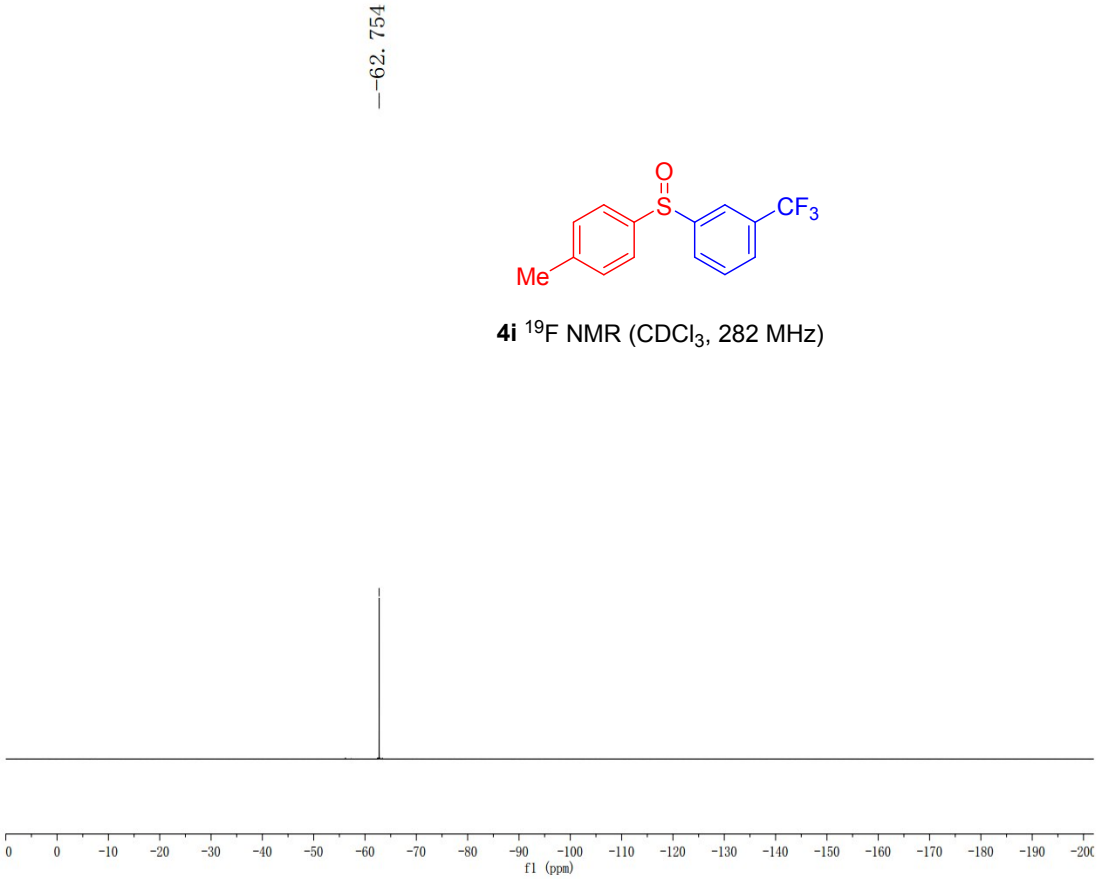




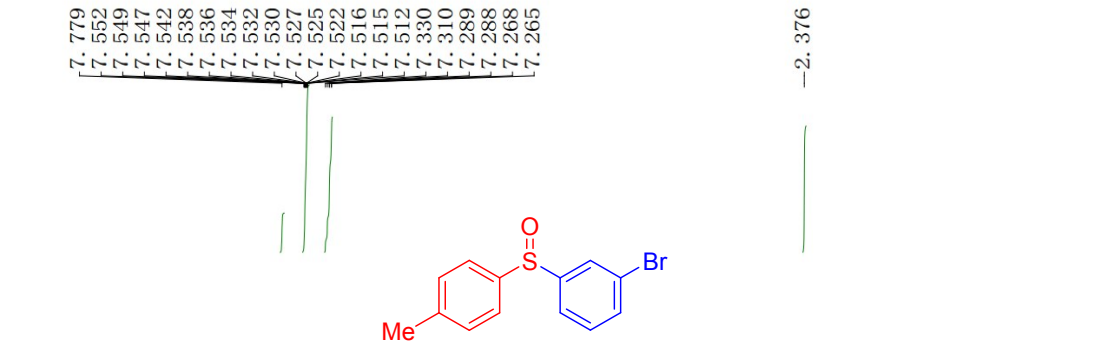
4i ^{1}H NMR ($CDCl_3$, 400 MHz)



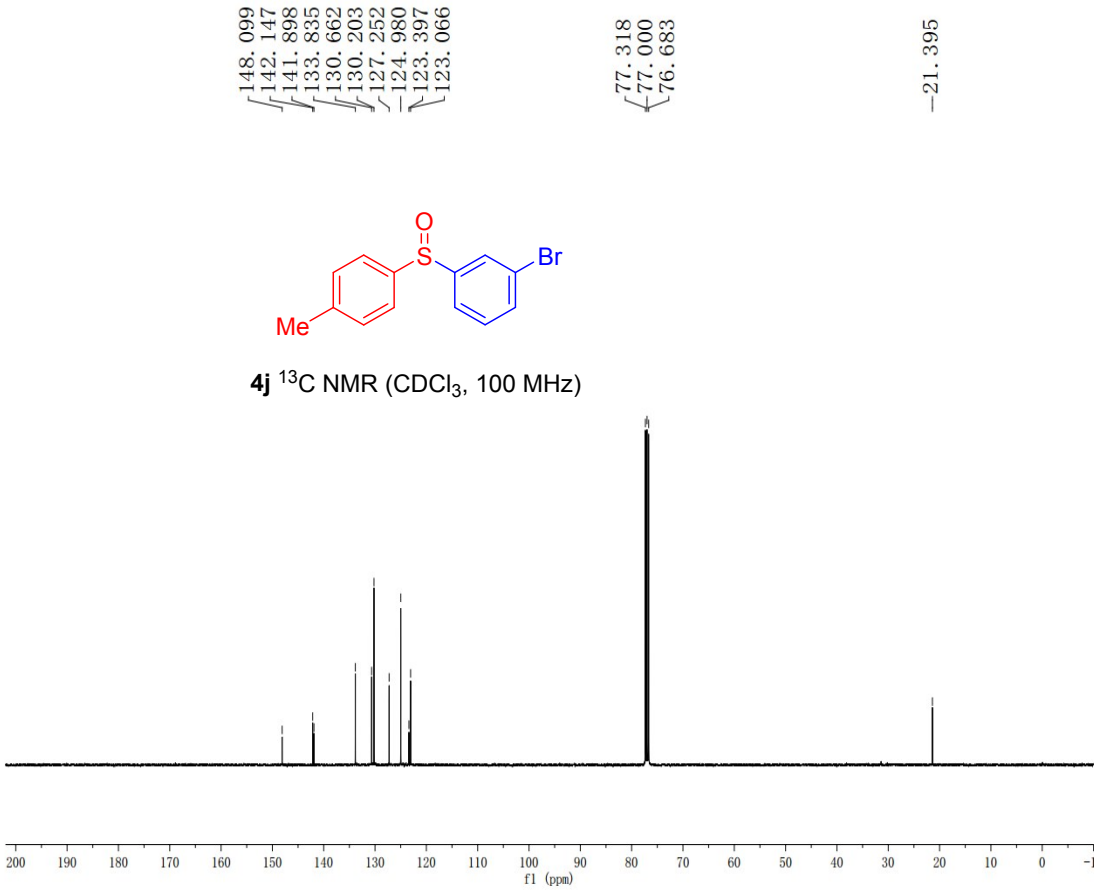
4i ^{13}C NMR ($CDCl_3$, 100 MHz)



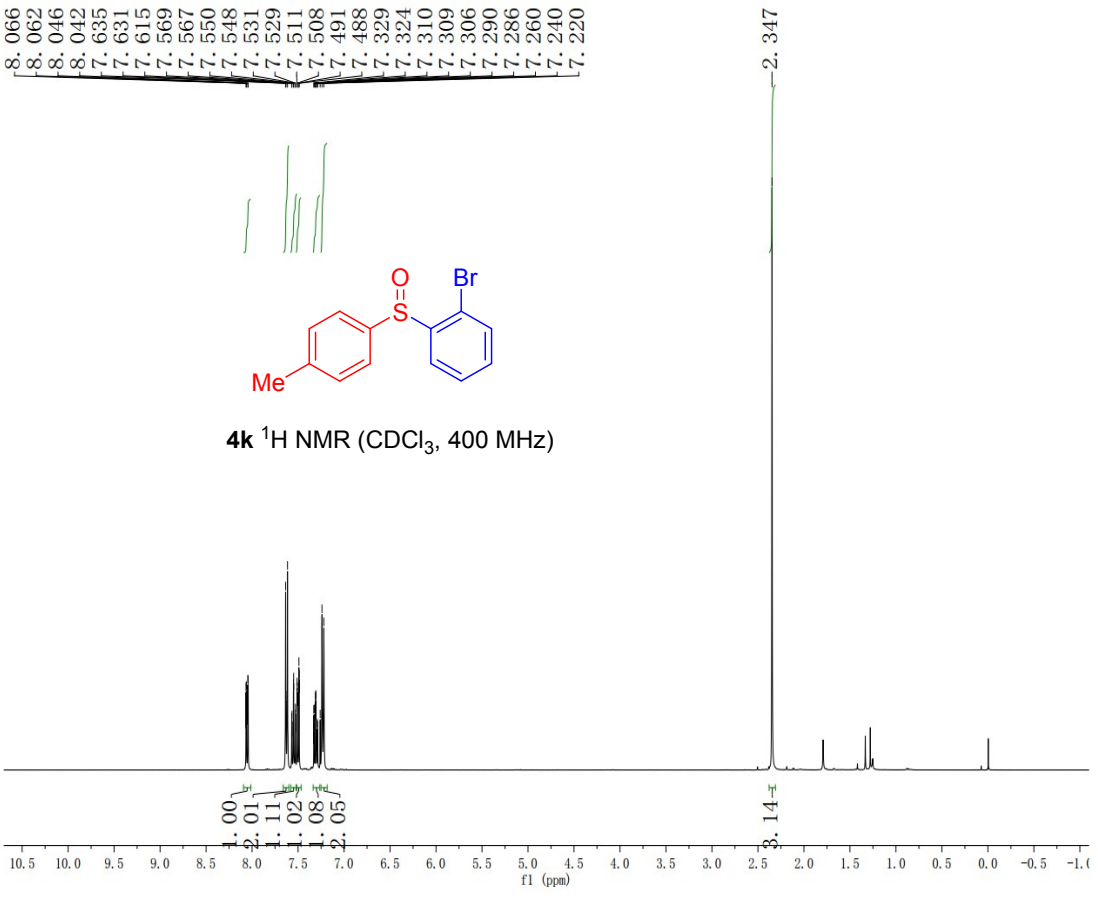
4i ^{19}F NMR ($CDCl_3$, 282 MHz)



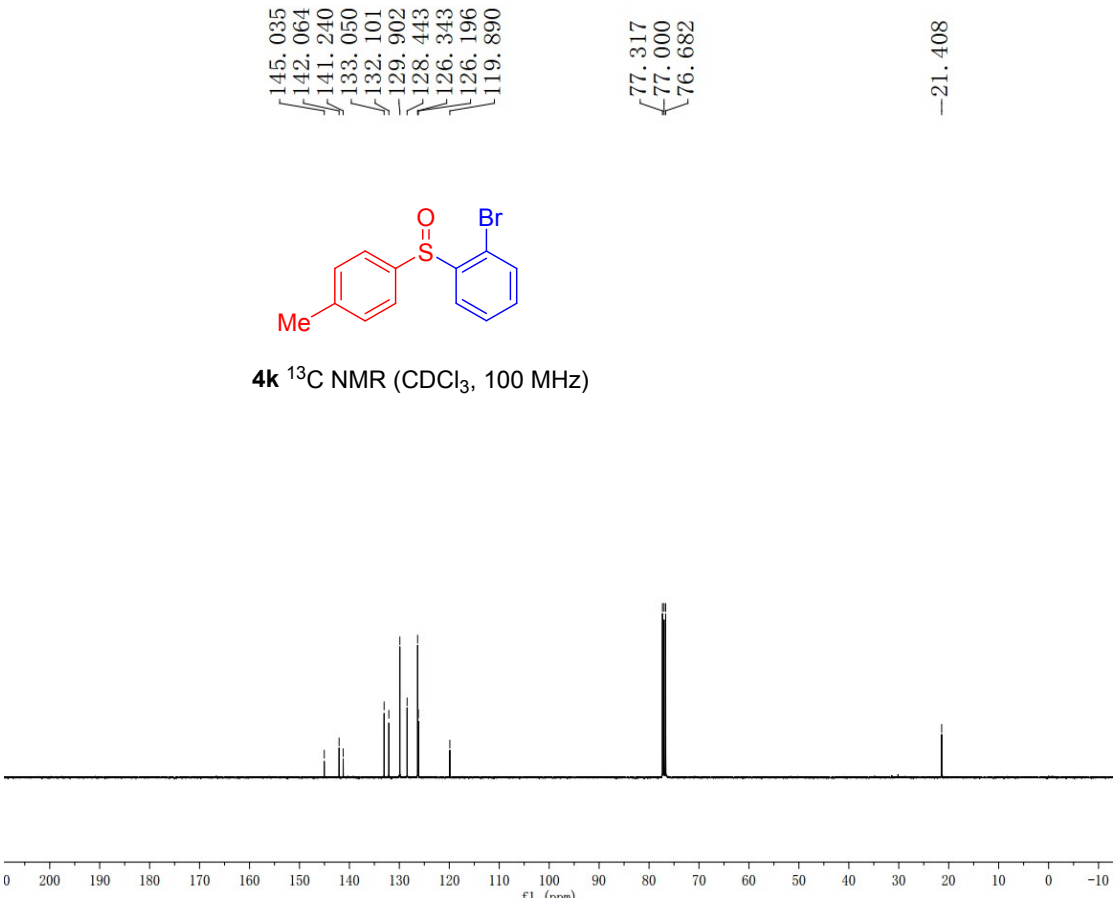
4j ^{1}H NMR ($CDCl_3$, 400 MHz)



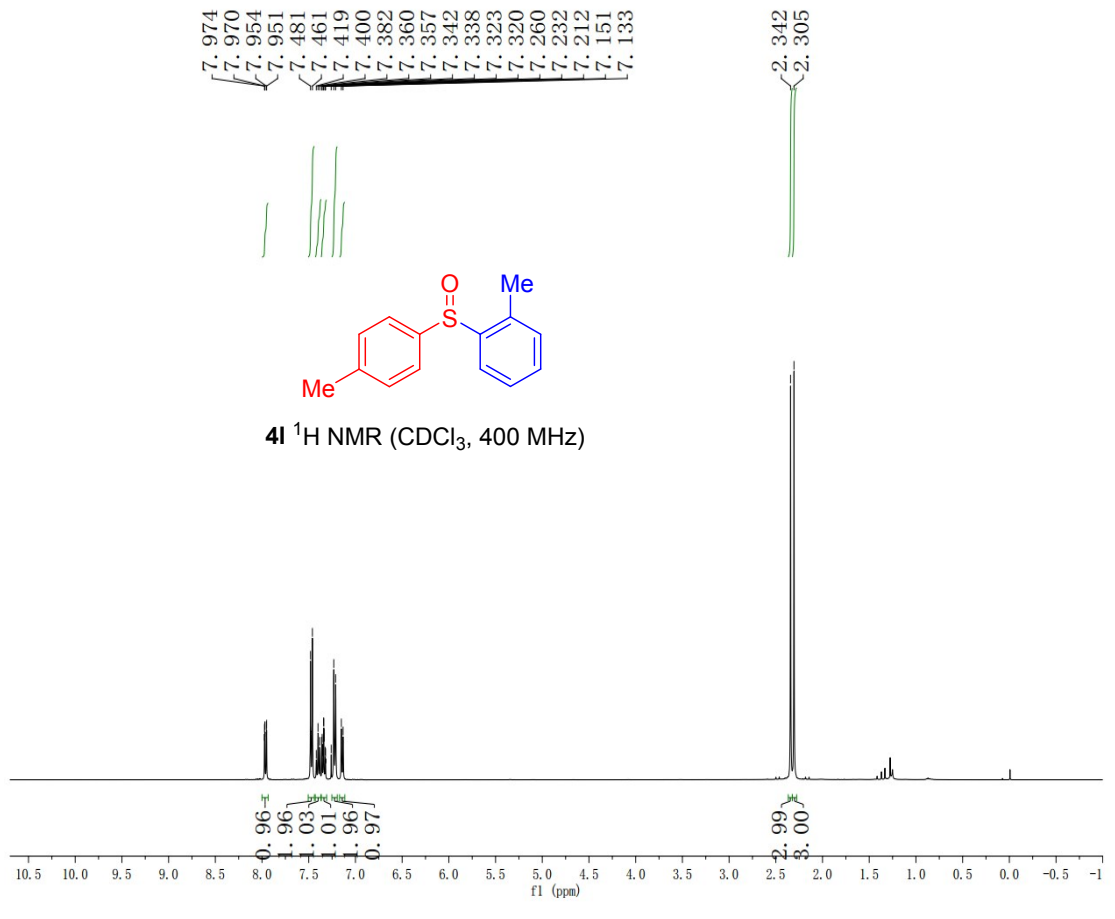
4j ^{13}C NMR ($CDCl_3$, 100 MHz)



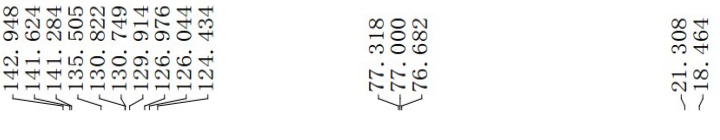
4k ^{1}H NMR ($CDCl_3$, 400 MHz)

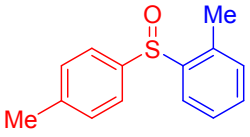


4k ^{13}C NMR ($CDCl_3$, 100 MHz)

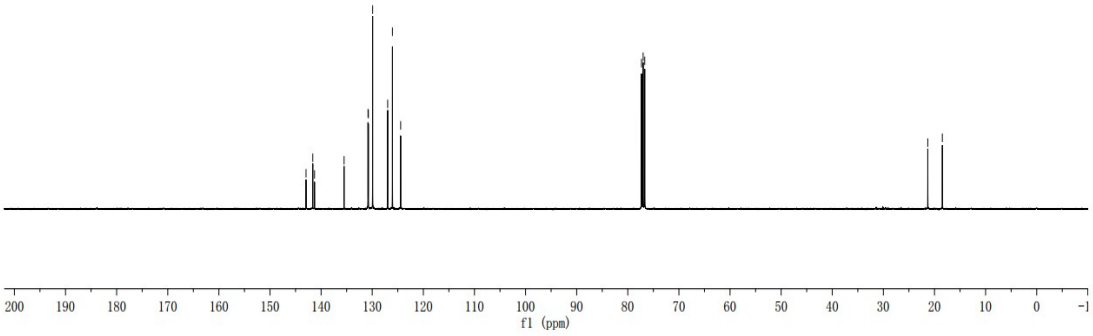


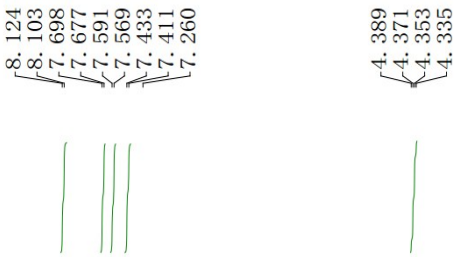
4l ^{1}H NMR ($CDCl_3$, 400 MHz)

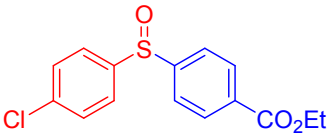




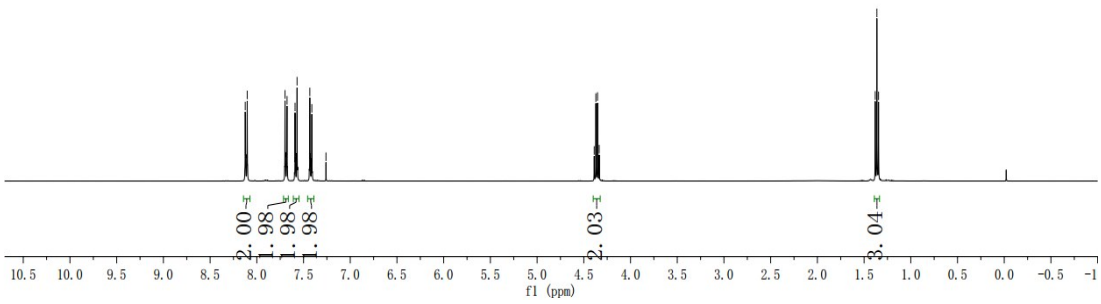
4l ^{13}C NMR ($CDCl_3$, 100 MHz)

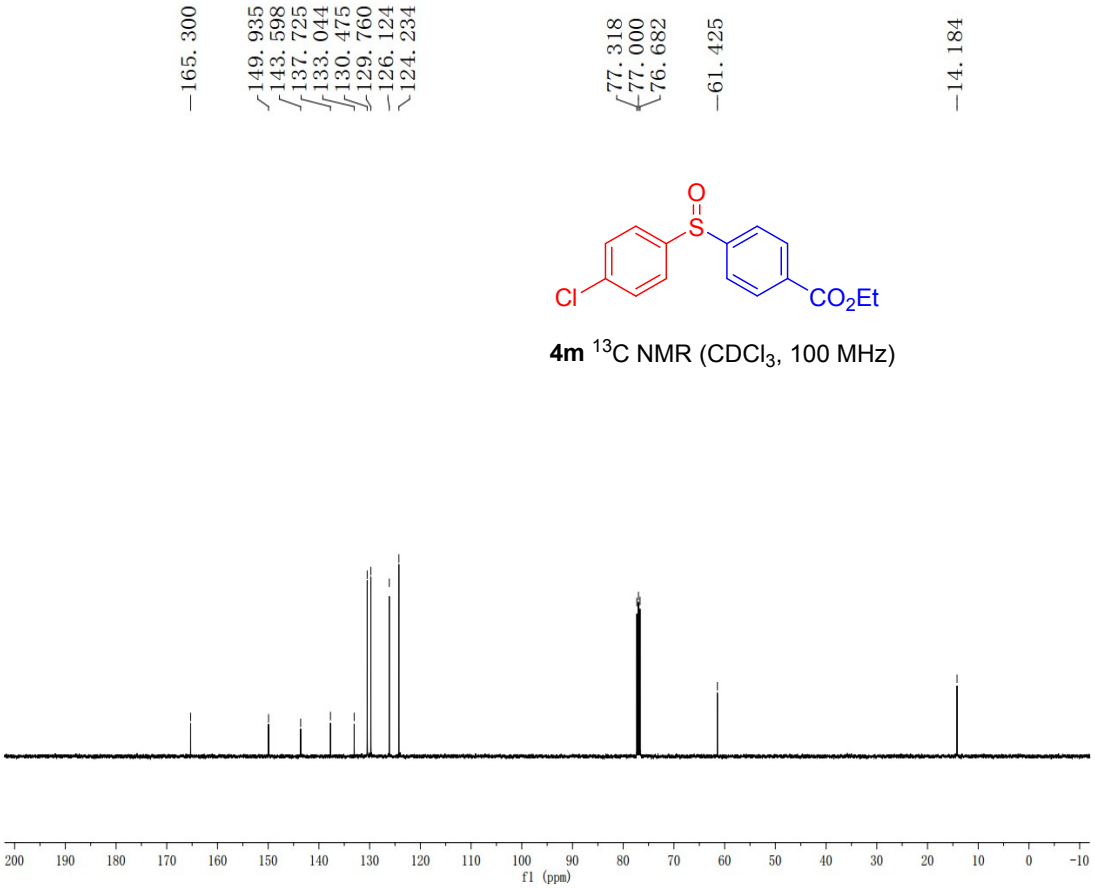




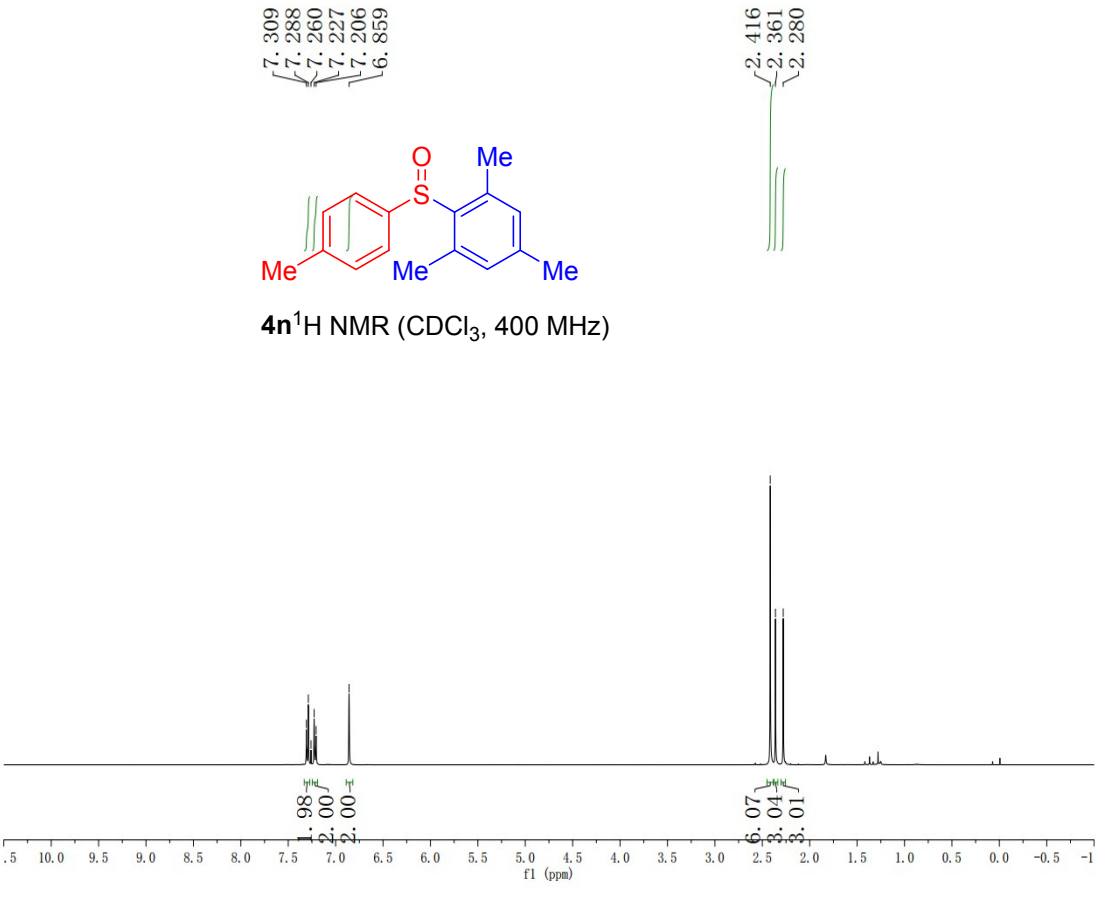


4m ^{1}H NMR ($CDCl_3$, 400 MHz)

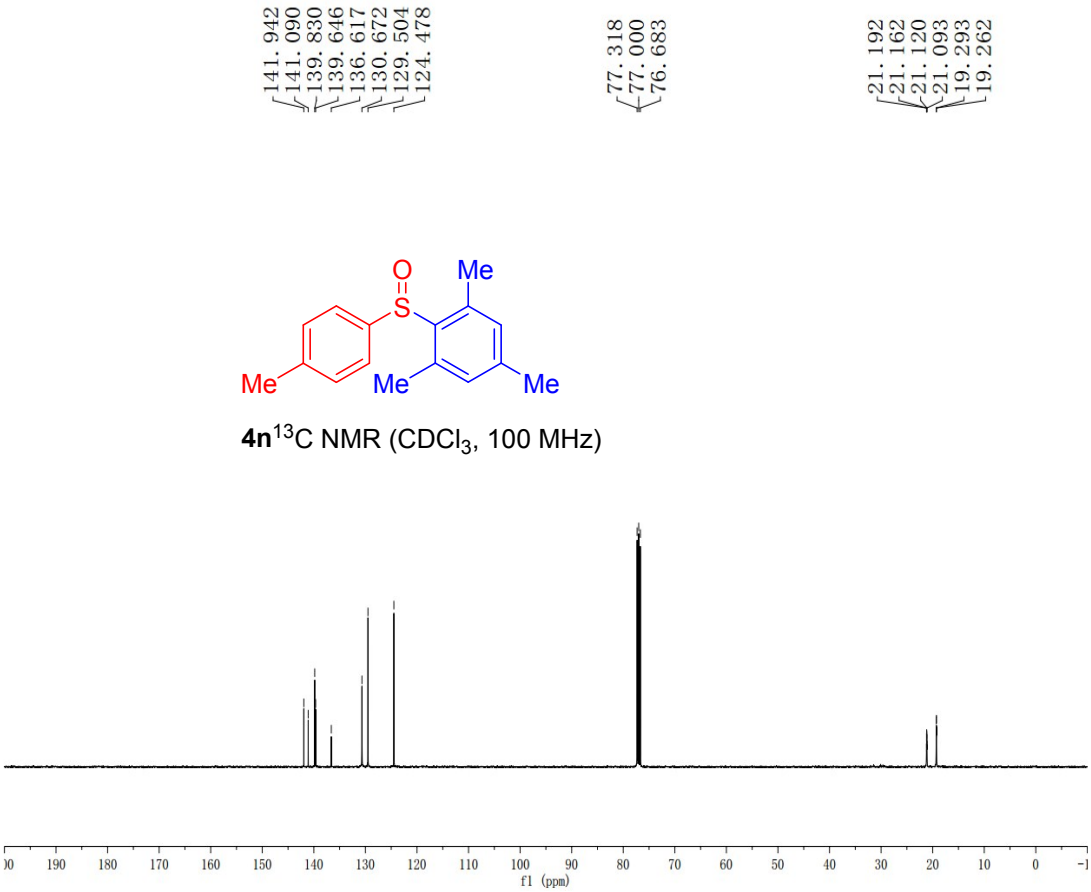




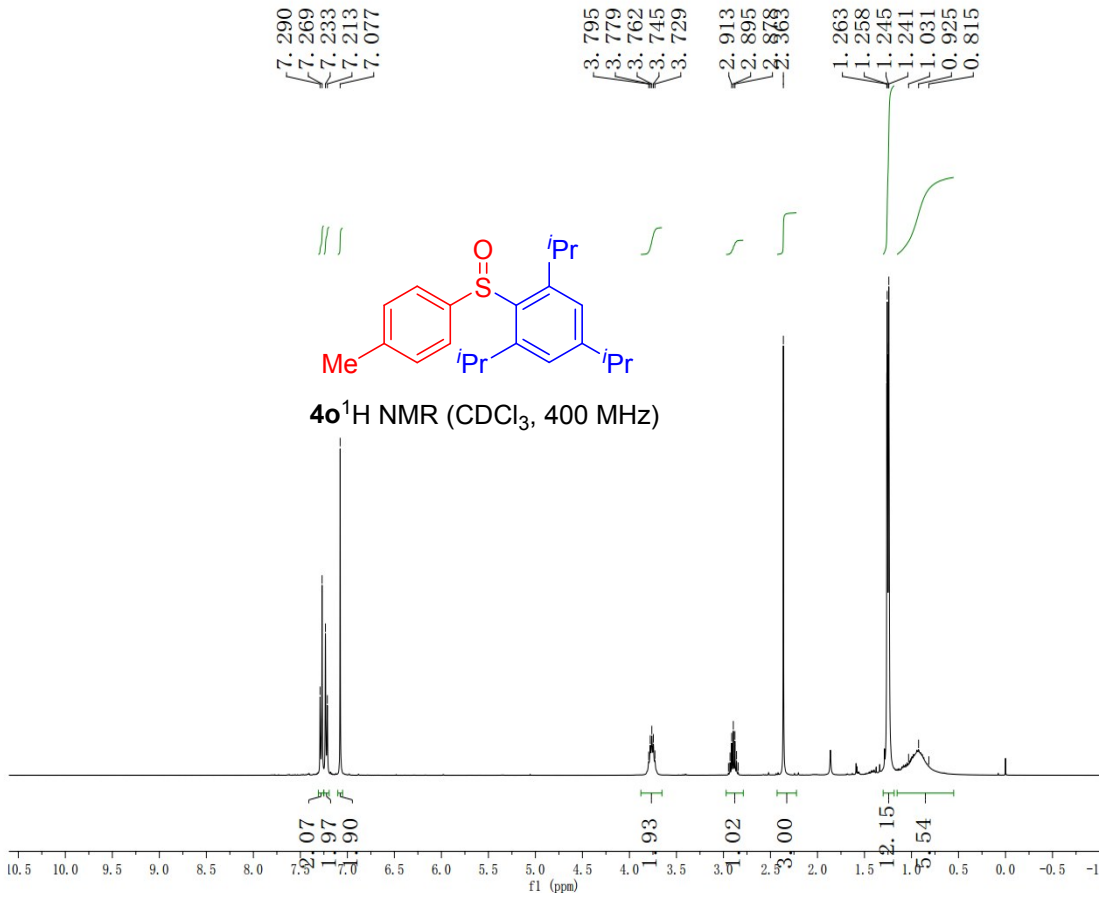
4m ^{13}C NMR ($CDCl_3$, 100 MHz)



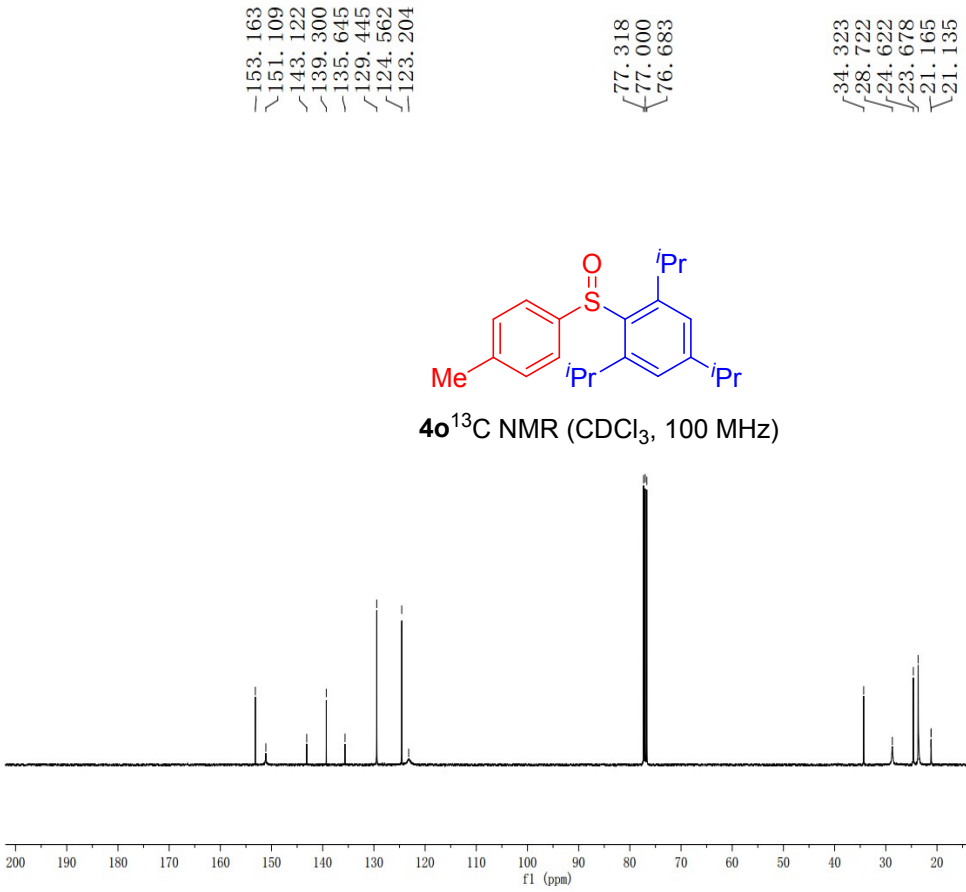
4n^{1}H NMR ($CDCl_3$, 400 MHz)



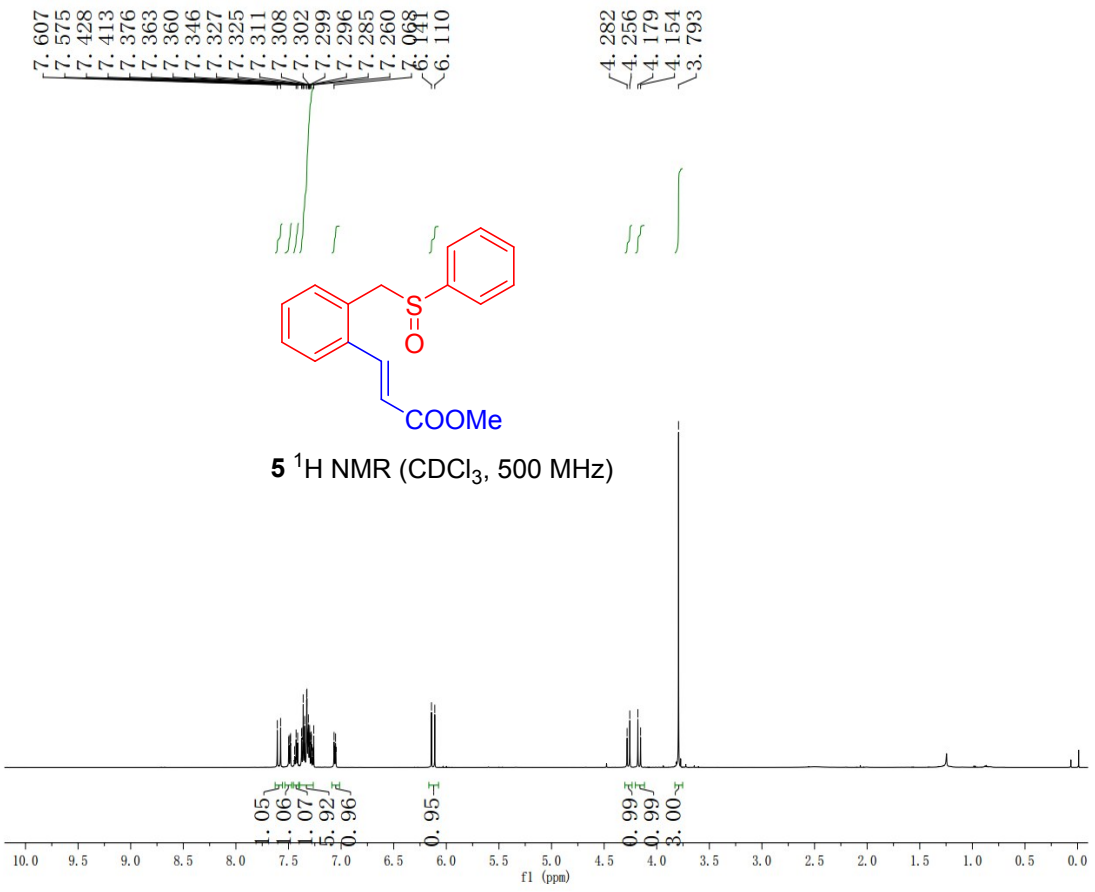
4n ^{13}C NMR ($CDCl_3$, 100 MHz)



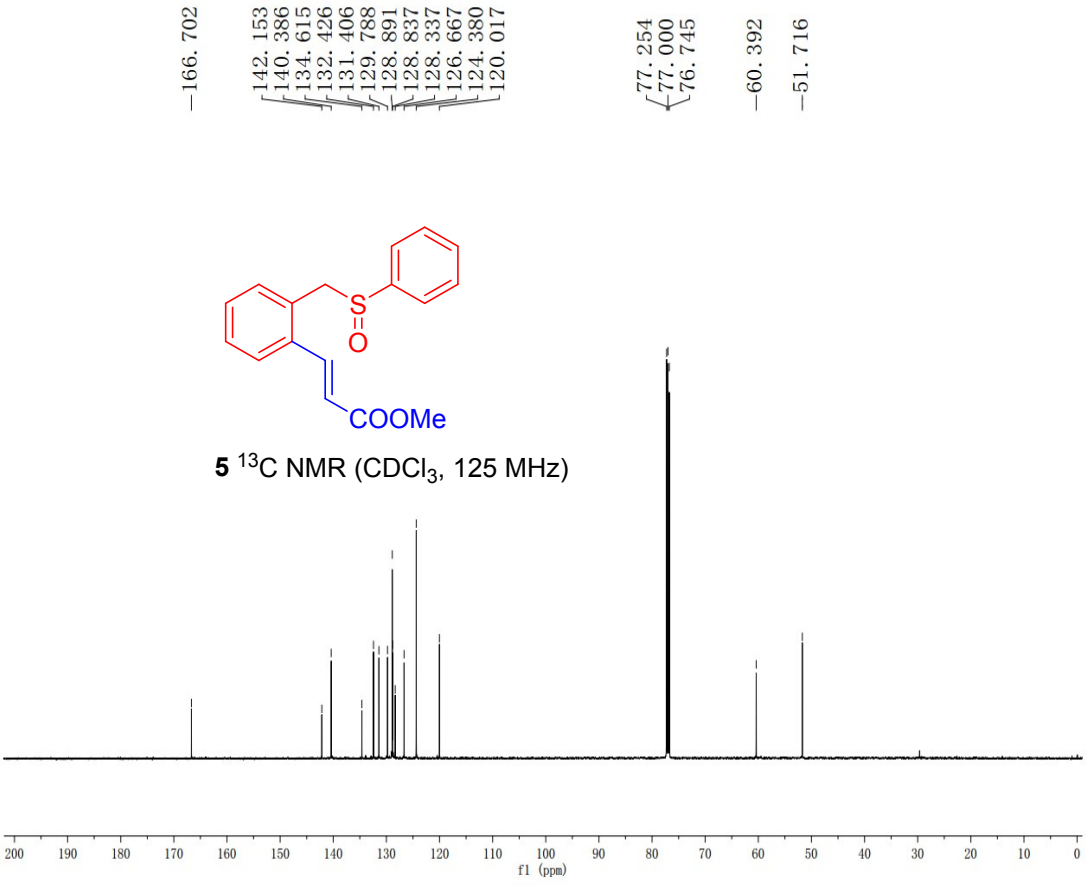
4o ^{1}H NMR ($CDCl_3$, 400 MHz)



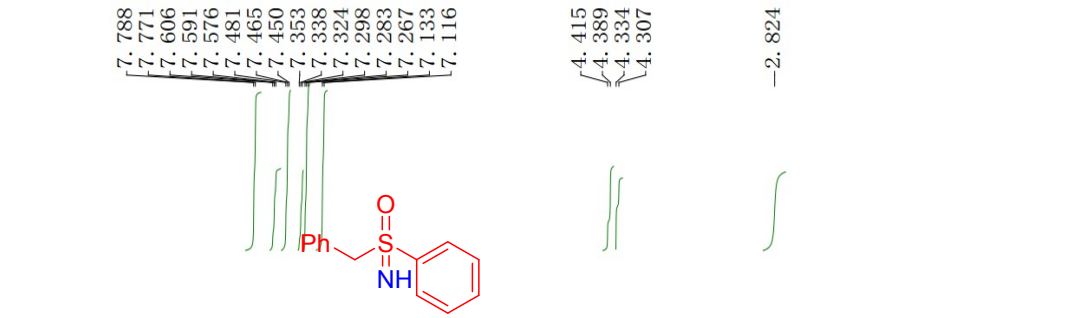
4o ^{13}C NMR ($CDCl_3$, 100 MHz)



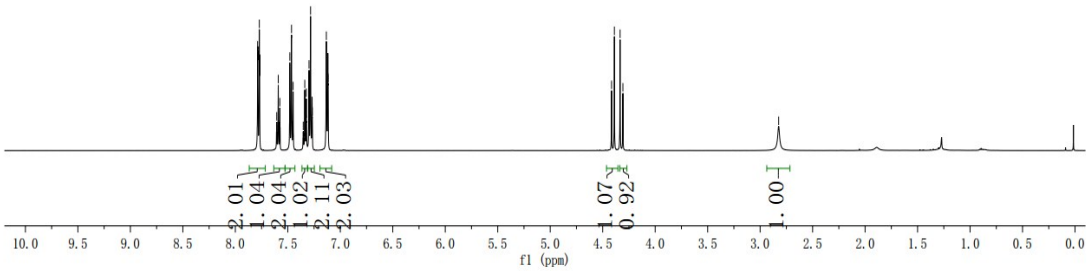
5 ^{1}H NMR ($CDCl_3$, 500 MHz)



5 ^{13}C NMR ($CDCl_3$, 125 MHz)



6^{1}H NMR ($CDCl_3$, 500 MHz)



6 ^{13}C NMR ($CDCl_3$, 125 MHz)