

Supporting Information for

Ligand-Free Copper-Catalyzed C(sp³)–H Imidation of Aromatic and Aliphatic
Methyl Sulfides with *N*-Fluorobenzenesulfonimide

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Content

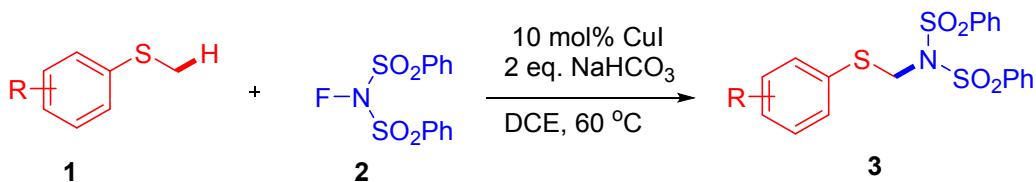
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1 Experimental Section

1.1 General information

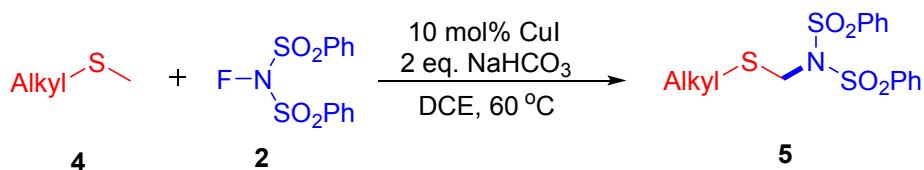
All chemicals were obtained from commercial suppliers and used without further purification. All reactions were conducted in oven-dried glasswares under air condition. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE DMX-400 spectrometry at 400MHz DMSO, respectively. Mass spectra were performed on a Bruker Esquire 3000plus mass spectrometer equipped with EI interface and ion trap analyzer. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source.

1.2 General procedure for the preparation of *N*-(phenylsulfonyl)-*N*-((phenylthio)methyl)benzenesulfonamide derivatives **3**



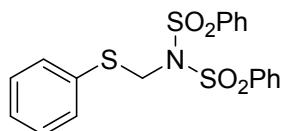
In a dry 25 mL round-bottom flask, aromatic methyl sulfide (0.5 mmol, 1 equiv), NFSI (0.6 mmol, 1.2 equiv), CuI (0.1 equiv) and NaHCO₃ (1 mmol, 2.0 equiv) were dissolved in 3 mL of DCE, the resulting mixture was heated to 60 °C for 8 h. The solution was then cooled to rt, diluted with CH₃COOC₂H₅, washed with a saturated aqueous solution of NaCl, dried over Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding benzenesulfonamide derivatives.

1.3 General procedure for the preparation of *N*-(alkylthio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamides **5**



In a dry 25 mL round-bottom flask, aliphatic methyl sulfide (0.5 mmol, 1 equiv), NFSI (0.6 mmol, 1.2 equiv), CuI (0.1 equiv) and NaHCO₃ (1 mmol, 2.0 equiv) were dissolved in 3 mL of DCE, the resulting mixture was heated to 60 °C for 8 h. The solution was then cooled to rt, diluted with CH₃COOC₂H₅, washed with a saturated aqueous solution of NaCl, dried over Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding benzenesulfonamide derivatives.

3a: *N*-(phenylsulfonyl)-*N*-((phenylthio)methyl)benzenesulfonamide: Isolated as white solid, yield 85%.



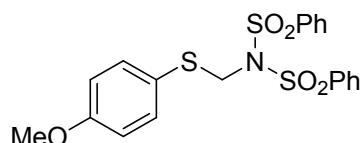
¹H NMR (400MHz, DMSO-*d*₆) δ: 7.98-7.95 (m, 4H), 7.81-7.77 (m, 2H), 7.68-7.64 (m, 4H), 7.33-7.30 (m, 5H), 5.42 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 139.1, 134.6, 133.1, 131.5, 129.4, 129.1, 127.9, 127.8, 54.2. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₇NO₄S₃: 419.0320; found: 419.0324.

3b: *N*-(phenylsulfonyl)-*N*-((*p*-tolylthio)methyl)benzenesulfonamide: Isolated as white solid, yield 88%.



¹H NMR (400MHz, DMSO-*d*₆) δ: 7.99-7.99 (m, 4H), 7.80-7.76 (m, 2H), 7.68-7.64 (m, 4H), 7.21-7.11 (m, 4H), 5.37 (s, 2H), 2.27 (s, 3H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 139.1, 137.6, 134.5, 132.0, 129.7, 129.4, 127.9, 54.7, 20.6. HRMS (EI, m/z) M⁺: calcd for C₂₀H₁₉NO₄S₃: 433.0476; found: 433.0478.

3c: *N*-(((4-methoxyphenyl)thio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as white solid, yield 90%.



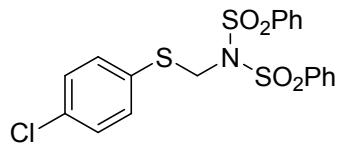
¹H NMR (400MHz, DMSO-*d*₆) δ: 8.03-8.01 (m, 4H), 7.83-7.80 (m, 2H), 7.80-7.79 (m, 4H), 7.26-7.24 (m, 2H), 6.91-6.88 (m, 2H), 5.32 (s, 2H), 3.76 (s, 3H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 159.5, 139.2, 134.7, 134.5, 129.4, 128.0, 123.0, 114.7, 55.6, 55.2. HRMS (EI, m/z) M⁺: calcd for C₂₀H₁₉NO₅S₃: 449.0425; found: 449.0430.

3d: *N*-(((4-fluorophenyl)thio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as light yellow solid, yield 76%.



¹H NMR (400MHz, DMSO-*d*₆) δ: 8.00-7.98 (m, 4H), 7.82-7.78 (m, 2H), 7.78-7.76 (m, 4H), 7.37-7.18 (m, 2H), 7.19-7.14 (m, 2H), 5.38 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 163.3, 160.8, 139.1, 134.8, 134.7, 134.6, 132.0, 129.4, 128.4, 128.3, 127.9, 116.3, 116.0, 55.0. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₆FNO₄S₃: 437.0220; found: 437.0221.

3e: *N*-(((4-chlorophenyl)thio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as light yellow solid, yield 81%.



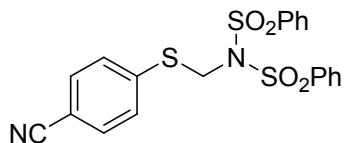
¹H NMR (400MHz, DMSO-*d*₆) δ: 7.98-7.95 (m, 4H), 7.82-7.78 (m, 2H), 7.69-7.65 (m, 4H), 7.40-7.33 (m, 4H), 5.42 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 138.9, 134.6, 133.4, 132.7, 132.0, 129.4, 129.0, 128.0, 54.2. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₆ClNO₄S₃: 452.9984; found: 452.9983.

3f: *N*-(((4-nitrophenyl)thio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as light yellow solid, yield 72%.



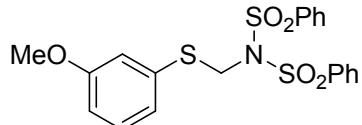
¹H NMR (400MHz, DMSO-*d*₆) δ: 8.15-8.13 (m, 2H), 7.98-7.95 (m, 4H), 7.82-7.78 (m, 2H), 7.68-7.61 (m, 6H), 5.61 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 145.9, 143.3, 138.7, 134.8, 129.8, 129.5, 127.9, 123.8, 52.1. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₆N₂O₆S₃: 464.0269; found: 464.0267.

3g: *N*-(((4-cyanophenyl)thio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as white solid, yield 77%.



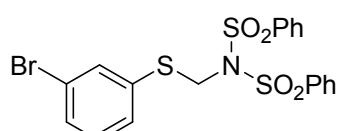
¹H NMR (400MHz, DMSO-*d*₆) δ: 7.98-7.96 (m, 4H), 7.86-7.77 (m, 3H), 7.68-7.64 (m, 4H), 7.41-7.35 (m, 2H), 7.02-6.98 (m, 1H), 5.46 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 139.4, 138.8, 138.3, 134.7, 130.7, 129.5, 128.9, 128.8, 127.9, 102.3, 53.3. HRMS (EI, m/z) M⁺: calcd for C₂₀H₁₆N₂O₄S₃: 444.0272; found: 444.0271.

3h: *N*-(((3-methoxyphenyl)thio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as white solid, yield 93%.



¹H NMR (400MHz, DMSO-*d*₆) δ: 7.99-7.97 (m, 4H), 7.82-7.78 (m, 2H), 7.68-7.64 (m, 4H), 7.25-7.22 (m, 1H), 6.92-6.84 (m, 3H), 5.44 (s, 2H), 3.71 (s, 3H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 159.3, 139.1, 134.5, 134.2, 129.9, 129.4, 127.9, 123.3, 116.2, 113.9, 55.1, 54.0. HRMS (EI, m/z) M⁺: calcd for C₂₀H₁₉NO₅S₃: 449.0425; found: 449.0425.

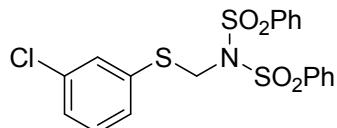
3i: *N*-(phenylsulfonyl)-*N*-((phenylthio)methyl)benzenesulfonamide: Isolated as light yellow solid, yield 82%.



¹H NMR (400MHz, DMSO-*d*₆) δ: 7.98-7.95 (m, 4H), 7.83-7.79 (m, 2H), 7.69-7.65 (m, 4H), 7.50-7.47 (m, 2H), 7.45-7.36 (m, 1H), 7.35-7.25 (m, 1H), 5.46 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ:

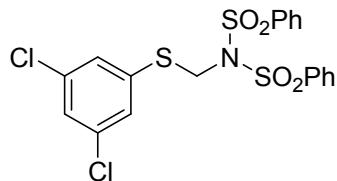
138.9, 135.5, 134.6, 130.8, 130.6, 130.3, 129.4, 127.9, 121.9, 53.8. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₆BrNO₄S₃: 496.9425; found: 496.9427.

3j: *N*-(((3-chlorophenyl)thio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as light yellow solid, yield 79%.



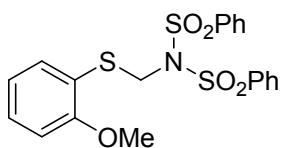
¹H NMR (400MHz, DMSO-d₆) δ: 7.98-7.95 (m, 4H), 7.82-7.78 (m, 2H), 7.69-7.65 (m, 4H), 7.36-7.31 (m, 4H), 5.46 (s, 2H). ¹³C NMR (100MHz, DMSO-d₆) δ: 138.9., 135.2, 134.6, 133.3, 130.7, 130.6, 129.8, 127.9, 127.7, 53.8. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₆ClNO₄S₃: 452.9930; found: 452.9930.

3k: *N*-(((3,5-dichlorophenyl)thio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as light yellow solid, yield 76%.



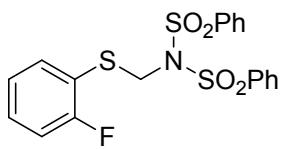
¹H NMR (400MHz, DMSO-d₆) δ: 8.00-7.97 (t, J = 7.8 Hz, 4H), 7.83-7.79 (t, J = 7.5 Hz, 2H), 7.70-7.66 (m, 4H), 7.53-7.51 (t, J = 1.8 Hz, 1H), 7.36-7.35 (d, J = 1.8 Hz, 2H), 5.52 (s, 2H). ¹³C NMR (100MHz, DMSO-d₆) δ: 138.9, 136.9, 134.6, 134.1, 129.4, 129.3, 127.9, 127.3, 53.4. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₅Cl₂NO₄S₃: 486.9540; found: 486.9538.

3l: *N*-(((2-methoxyphenyl)thio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as white solid, yield 91%.



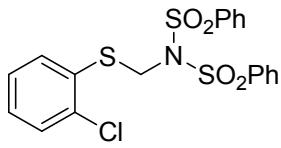
¹H NMR (400MHz, DMSO-*d*₆) δ: 7.97-7.94 (m, 4H), 7.82-7.77 (m, 2H), 7.69-7.65 (m, 4H), 7.32-7.31 (t, *J* = 0.8 Hz, 1H), 7.09-7.01 (m, 2H), 6.86-6.82 (m, 1H), 5.38 (s, 2H), 3.82 (s, 3H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 158.4, 139.1, 134.4, 133.1, 129.9, 129.3, 127.9, 120.6, 119.7, 111.4, 55.6, 52.1. HRMS (EI, m/z) M⁺: calcd for C₂₀H₁₉NO₅S₃: 449.0425; found: 449.0428.

3m: *N*-((2-fluorophenyl)thiomethyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as light yellow solid, yield 78%.



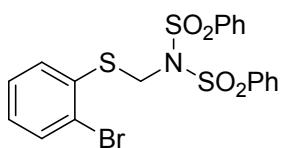
¹H NMR (400MHz, DMSO-*d*₆) δ: 7.98-7.96 (m, 4H), 7.80-7.79 (m, 2H), 7.67 (s, 4H), 7.39-7.13 (m, 4H), 5.39 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 138.9, 134.6, 134.5, 131.0, 130.9, 129.4, 127.9, 124.9, 116.0, 115.8, 53.2. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₆FNO₄S₃: 437.0225; found: 437.0225.

3n: *N*-((2-chlorophenyl)thiomethyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as light yellow solid, yield 75%.



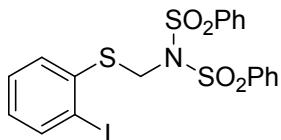
¹H NMR (400MHz, DMSO-*d*₆) δ: 7.99-7.96 (m, 4H), 7.83-7.78 (m, 2H), 7.69-7.64 (m, 4H), 7.51-7.40 (m, 2H), 7.32-7.29 (m, 2H), 5.48 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 138.8, 134.7, 134.6, 132.7, 131.9, 129.8, 129.4, 127.9, 127.7, 52.6. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₆ClNO₄S₃: 452.9930; found: 452.9933.

3o: *N*-((2-bromophenyl)thiomethyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as light yellow solid, yield 74%.



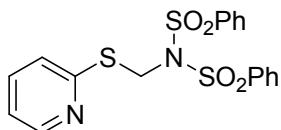
¹H NMR (400MHz, DMSO-*d*₆) δ: 7.99-7.96 (m, 4H), 7.82-7.78 (m, 2H), 7.69-7.64 (m, 5H), 7.46-7.33 (m, 2H), 7.24-7.19 (m, 1H), 5.49 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 138.8, 134.6, 134.2, 133.0, 132.0, 129.4, 129.1, 128.2, 127.9, 124.9, 52.6. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₆BrNO₄S₃: 496.9425; found: 496.9427.

3p: *N*-((2-iodophenyl)thiomethyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as white solid, yield 80%.



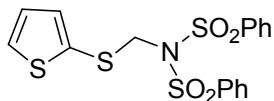
¹H NMR (400MHz, DMSO-*d*₆) δ: 8.00-7.98 (m, 4H), 7.82-7.78 (m, 4H), 7.69-7.65 (m, 4H), 7.58-7.56 (m, 2H), 5.59 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 140.6, 138.7, 134.6, 132.5, 130.1, 129.4, 127.9, 118.5, 109.3, 52.4. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₆INO₄S₃: 544.9286; found: 544.9286.

3q: *N*-(phenylsulfonyl)-*N*-((pyridin-2-ylthio)methyl)benzenesulfonamide: Isolated as white solid, yield 83%.



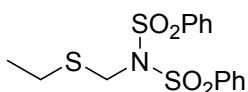
¹H NMR (400MHz, DMSO-*d*₆) δ: 8.53-8.50 (m, 1H), 7.91-7.88 (m, 4H), 7.75 (m, 2H), 7.61-7.57 (m, 5H), 7.22-7.15 (m, 2H), 5.91 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 155.0, 149.2, 138.6, 137.1, 134.6, 129.3, 127.7, 122.5, 120.9, 47.8. HRMS (EI, m/z) M⁺: calcd for C₁₈H₁₆N₂O₄S₃: 420.0272; found: 420.0275.

3r: *N*-(phenylsulfonyl)-*N*-((thiophen-2-ylthio)methyl)benzenesulfonamide: Isolated as white solid, yield 84%.



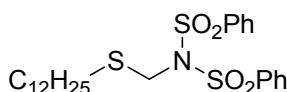
¹H NMR (400MHz, DMSO-*d*₆) δ: 8.04-8.01 (m, 4H), 7.84-7.79 (m, 2H), 7.72-7.67 (m, 5H), 7.04-6.94 (m, 2H), 5.24 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 139.1, 135.8, 134.6, 132.1, 129.5, 129.4, 128.0, 127.9, 51.1. HRMS (EI, m/z) M⁺: calcd for C₁₇H₁₅NO₄S₄: 424.9884; found: 424.9885.

5a: *N*-((ethylthio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as colorless liquid, yield 76%.



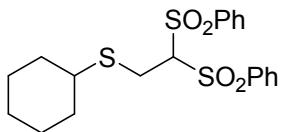
¹H NMR (400MHz, DMSO-*d*₆) δ: 8.06-8.04 (t, *J* = 8.0 Hz, 4H), 7.81-7.77 (m, 2H), 7.70-7.66 (m, 4H), 5.05 (s, 2H), 2.54-2.50 (m, 2H), 1.50-1.45 (m, 2H), 0.85-0.80 (m, 3H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 139.2, 134.4, 129.3, 127.9, 51.7, 22.2, 13.1. HRMS (EI, m/z) M⁺: calcd for C₁₆H₁₉NO₄S₃: 385.0476; found: 385.0475.

5b: *N*-((dodecylthio)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as colorless liquid, yield 81%.



¹H NMR (400MHz, DMSO-*d*₆) δ: 8.07-8.05 (d, *J* = 6.0 Hz, 4H), 7.77-7.75 (d, *J* = 6.6 Hz, 2H), 7.67-7.64 (t, *J* = 6.6 Hz, 4H), 5.06 (s, 2H), 1.42-0.83 (m, 25H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 139.3, 134.2, 129.2, 127.9, 51.8, 31.3, 31.0, 29.0, 28.8, 28.7, 28.5, 28.1, 22.1, 13.8. HRMS (EI, m/z) M⁺: calcd for C₂₅H₃₇NO₄S₃: 511.1885; found: 511.1883.

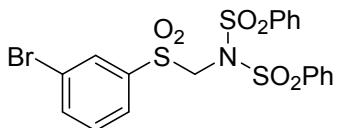
5c: (2,2-bis(phenylsulfonyl)ethyl)(cyclohexyl)sulfane: Isolated as white solid, yield 72%.



¹H NMR (400MHz, DMSO-*d*₆) δ: 8.09-8.07 (t, *J* = 8.6 Hz, 4H), 7.80-7.75 (m, 2H), 7.69-7.66 (m, 4H), 5.08 (s, 2H), 1.81-1.79 (m, 2H), 1.47-1.59 (m, 3H), 2.01-1.14 (m, 6H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 139.4, 134.3, 129.3, 127.9, 50.5, 42.6, 32.9, 25.3, 25.1.

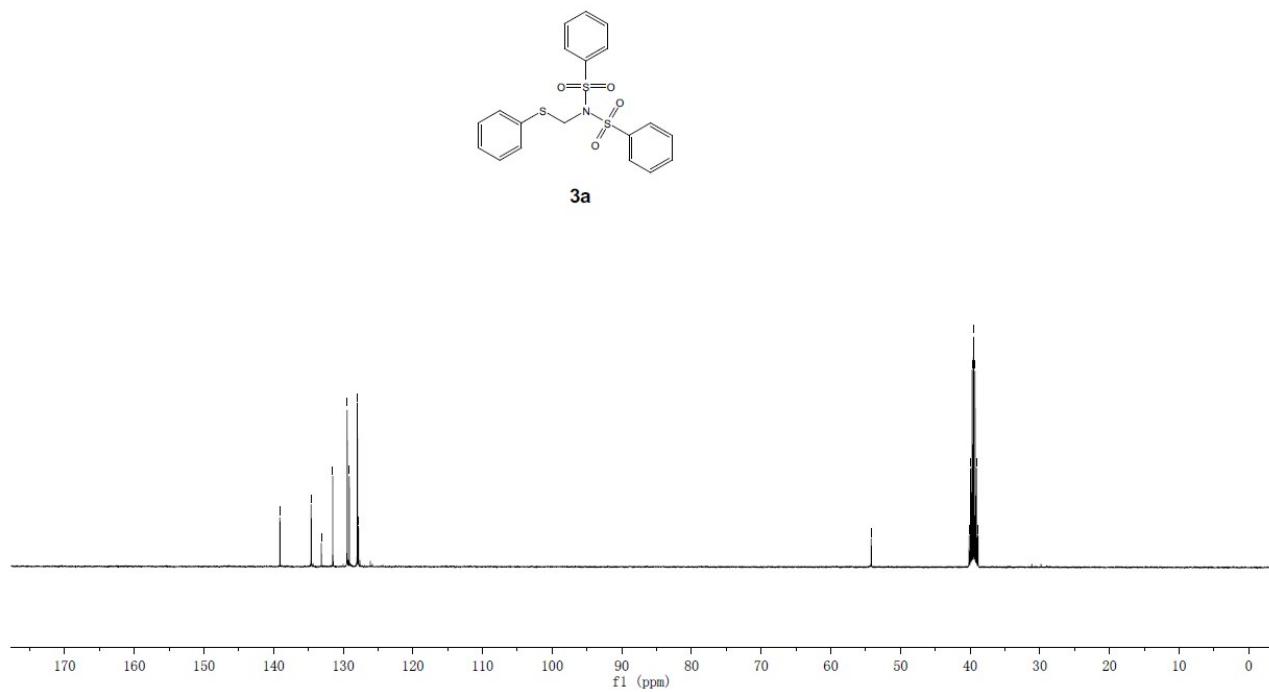
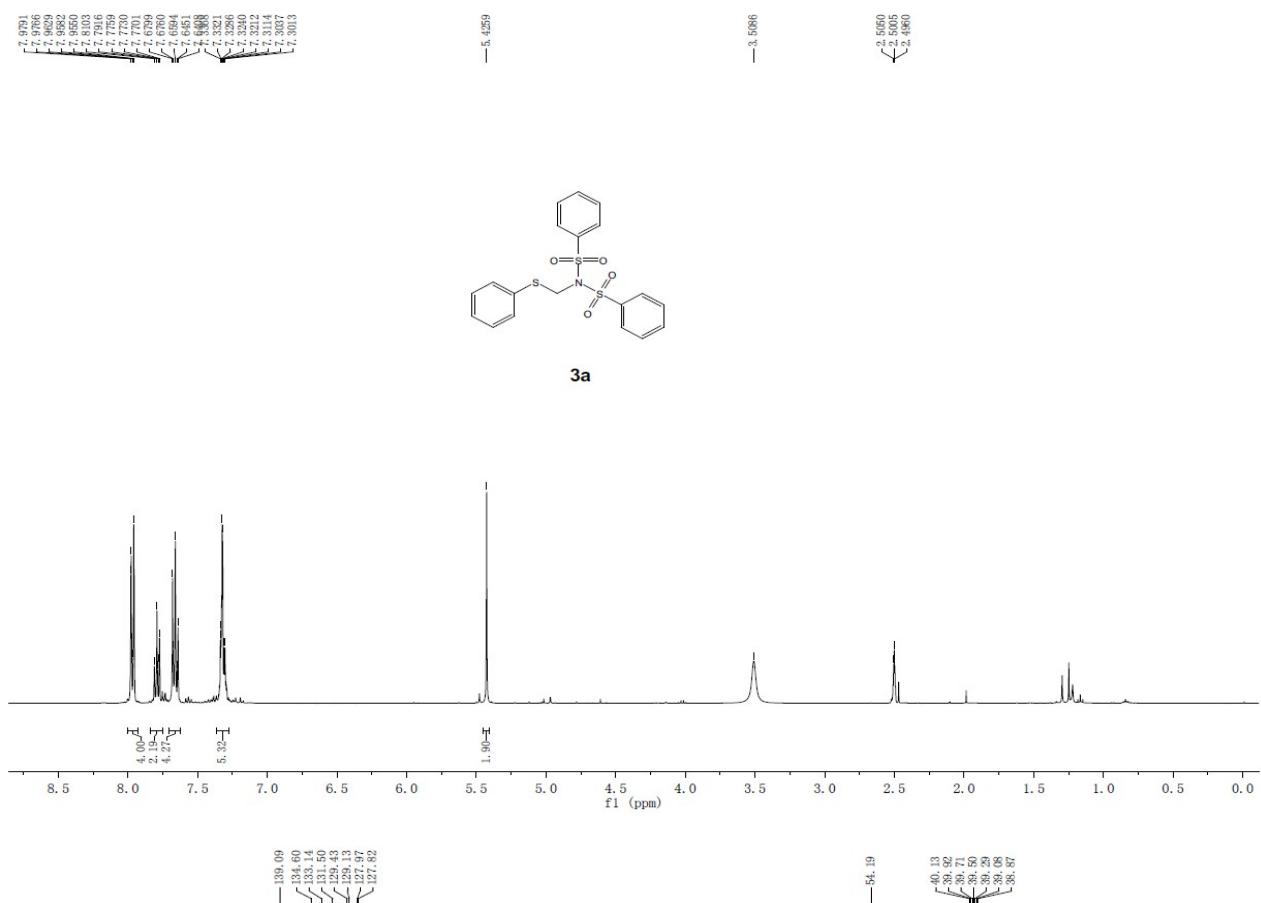
HRMS (EI, m/z) M⁺: calcd for C₁₉H₂₃NO₄S₃: 425.0789; found: 425.0788.

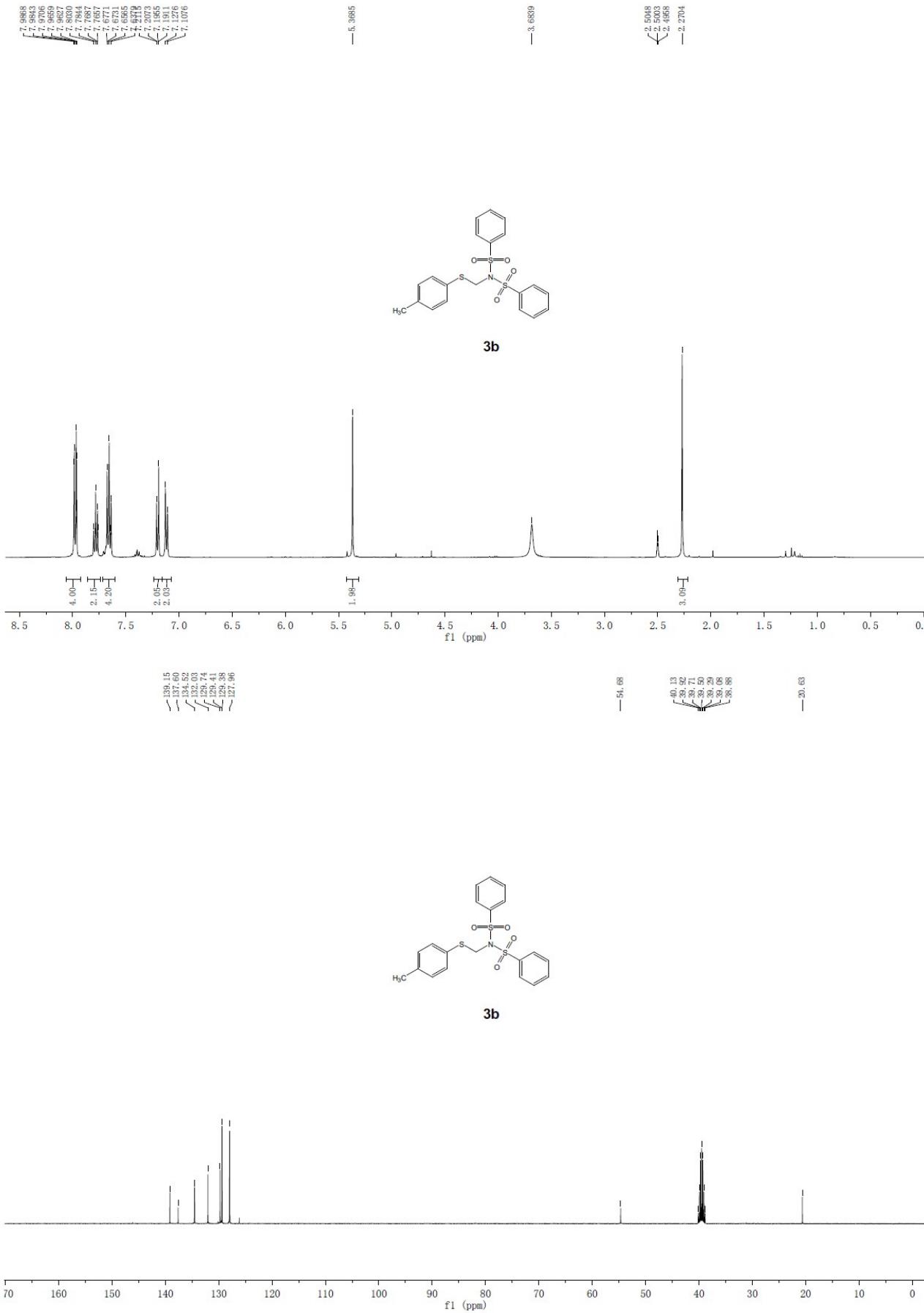
6: *N*-((3-bromophenyl)sulfonyl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide: Isolated as white solid, yield 72%.

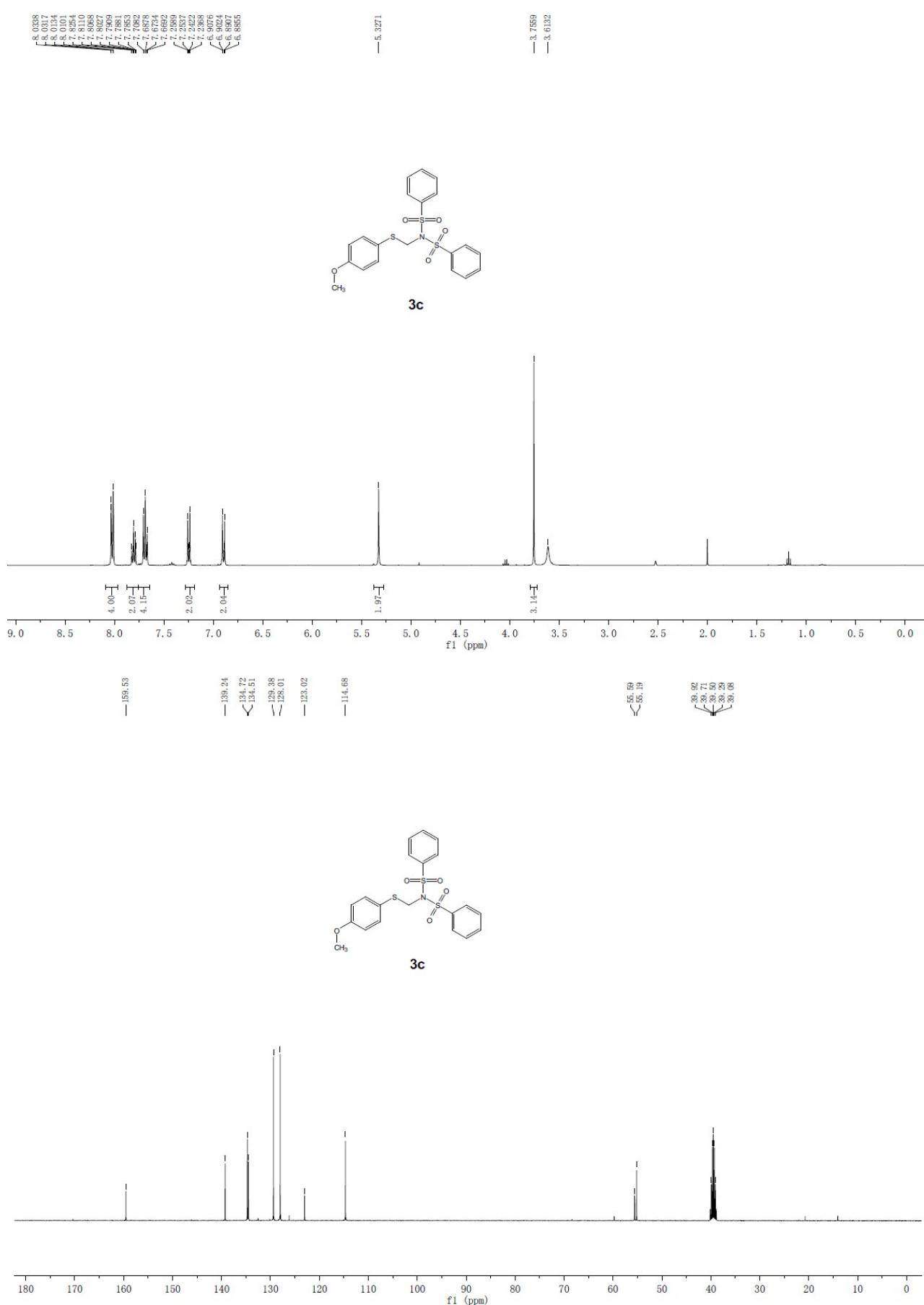


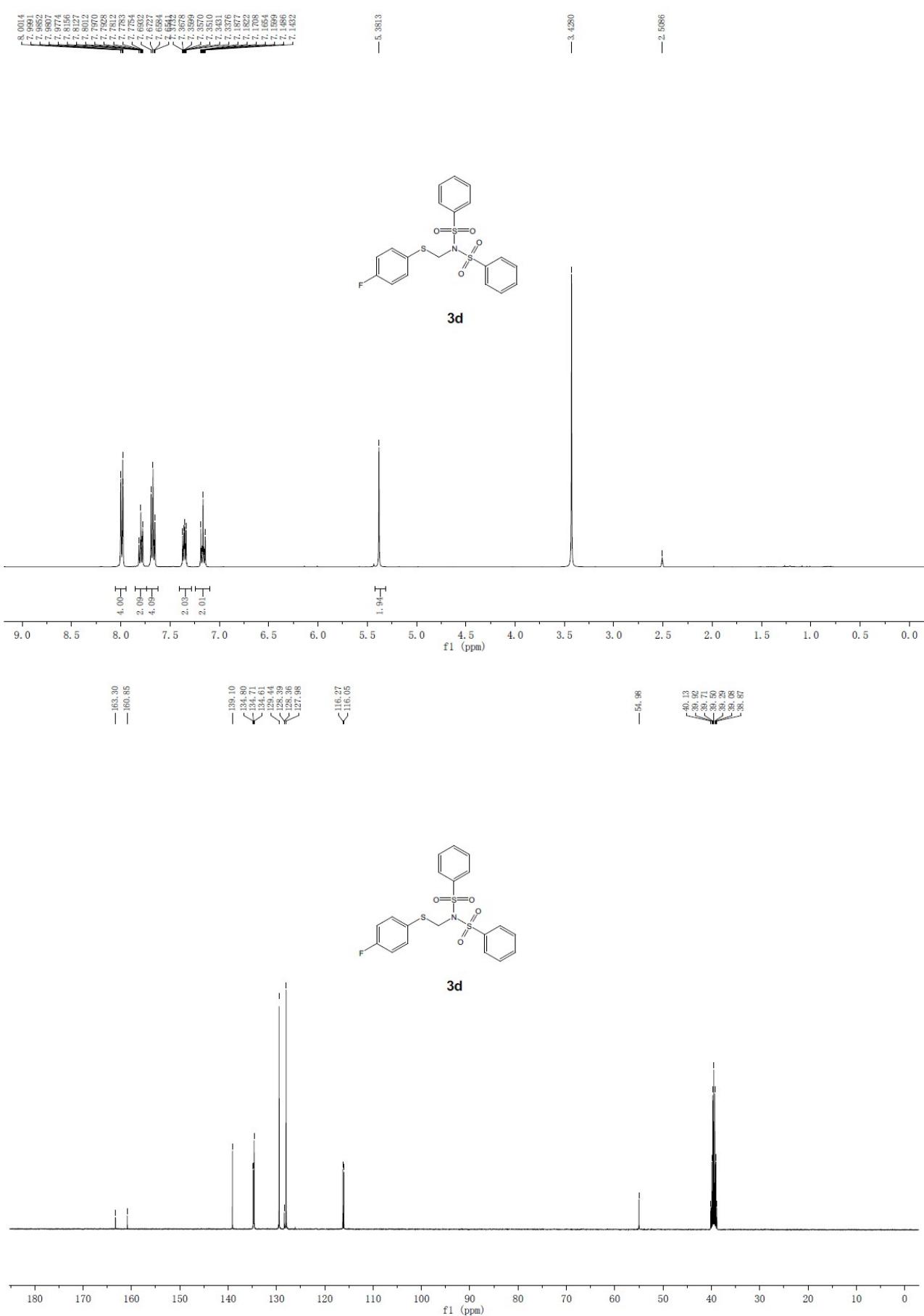
¹H NMR (400MHz, DMSO-*d*₆) δ: 7.98-7.96 (d, *J* = 8.4 Hz, 4H), 7.77-7.74 (t, *J* = 7.6 Hz, 4H), 7.62-7.53 (m, 6H), 5.56 (s, 2H). ¹³C NMR (100MHz, DMSO-*d*₆) δ: 139.8, 138.6, 137.9, 135.4, 129.8, 129.1, 128.3, 128.2, 122.6, 67.6. HRMS (EI, m/z) M⁺: calcd for C₁₉H₁₆BrNO₆S₃: 528.9323; found: 528.9323.

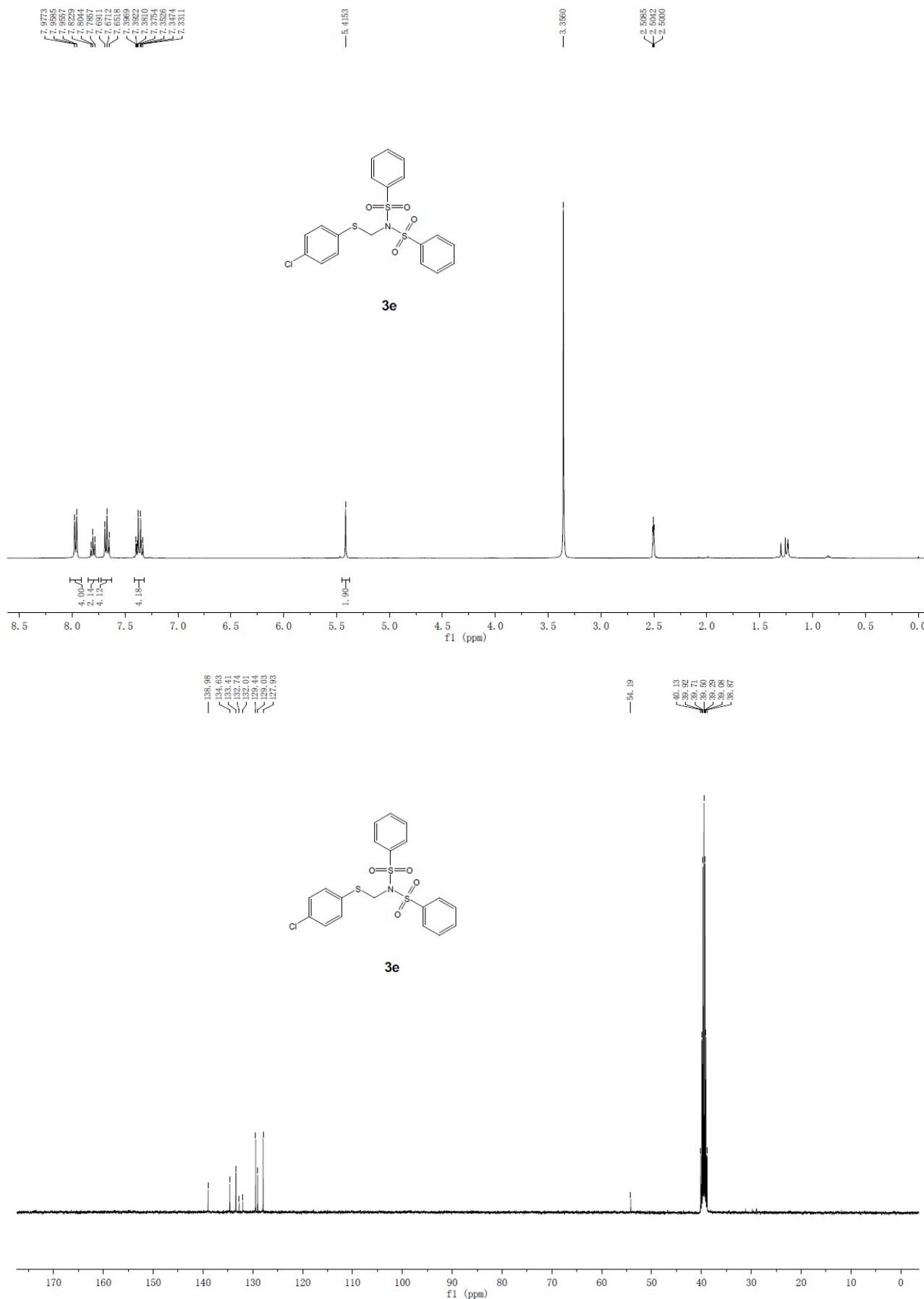
2 ^1H and ^{13}C NMR Data

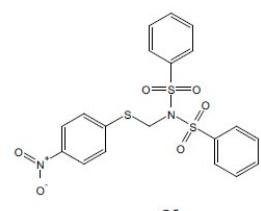
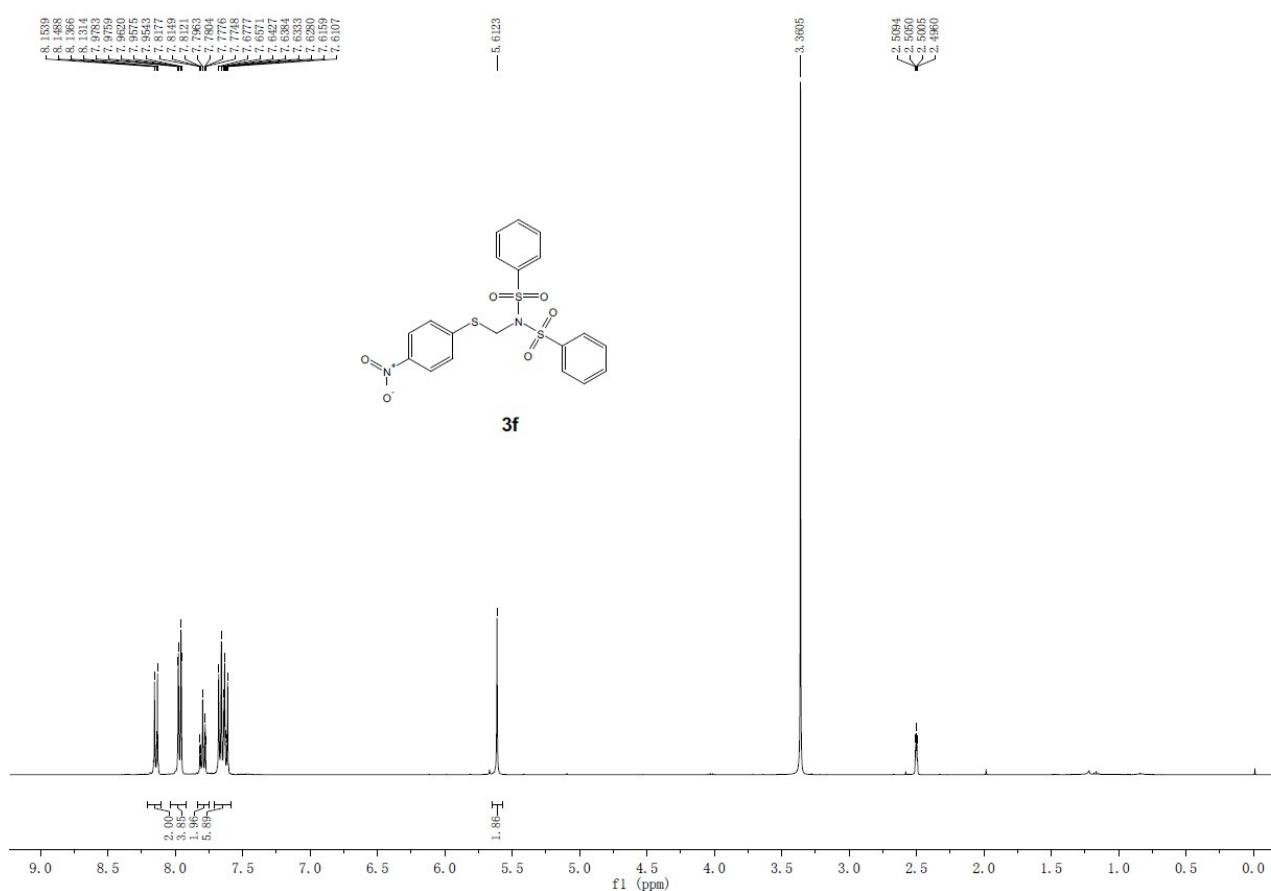




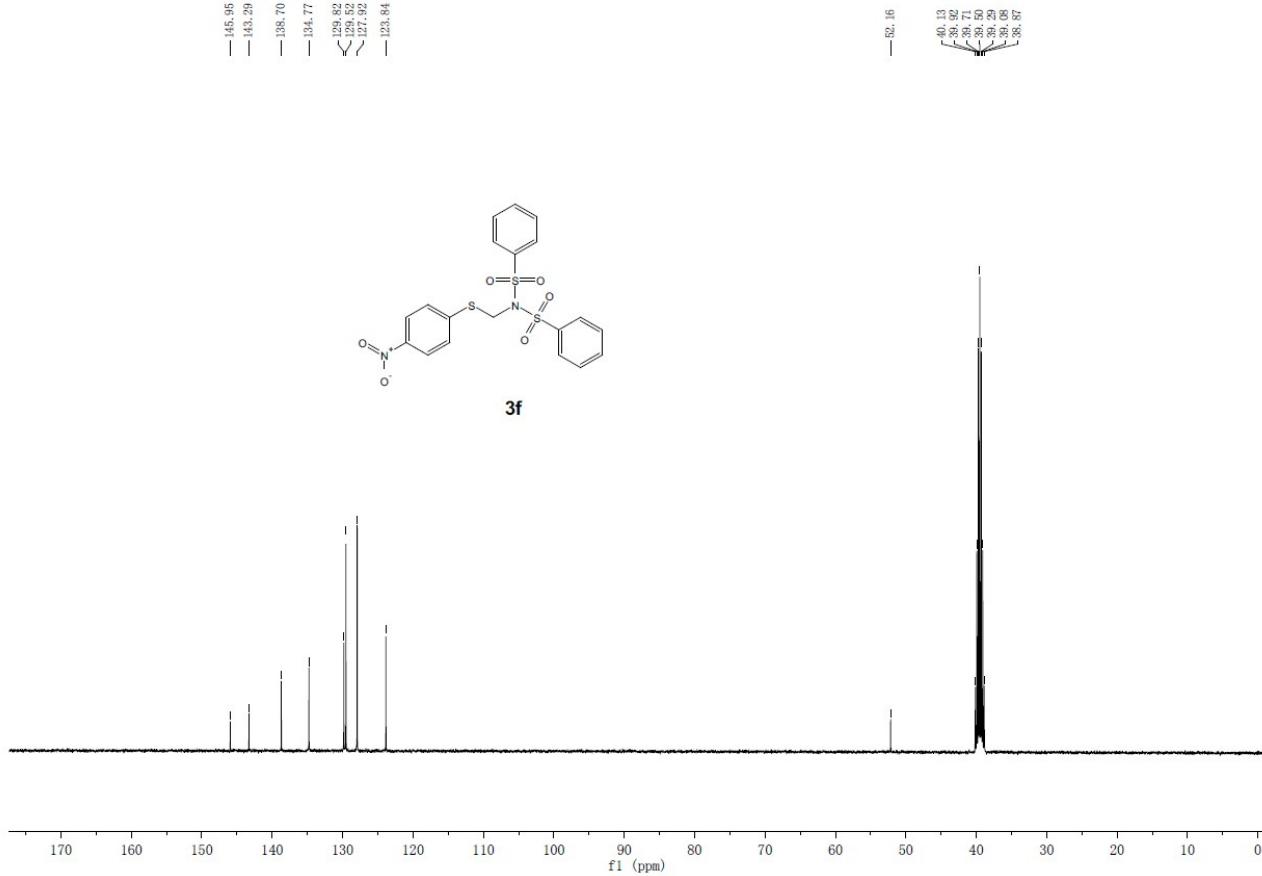


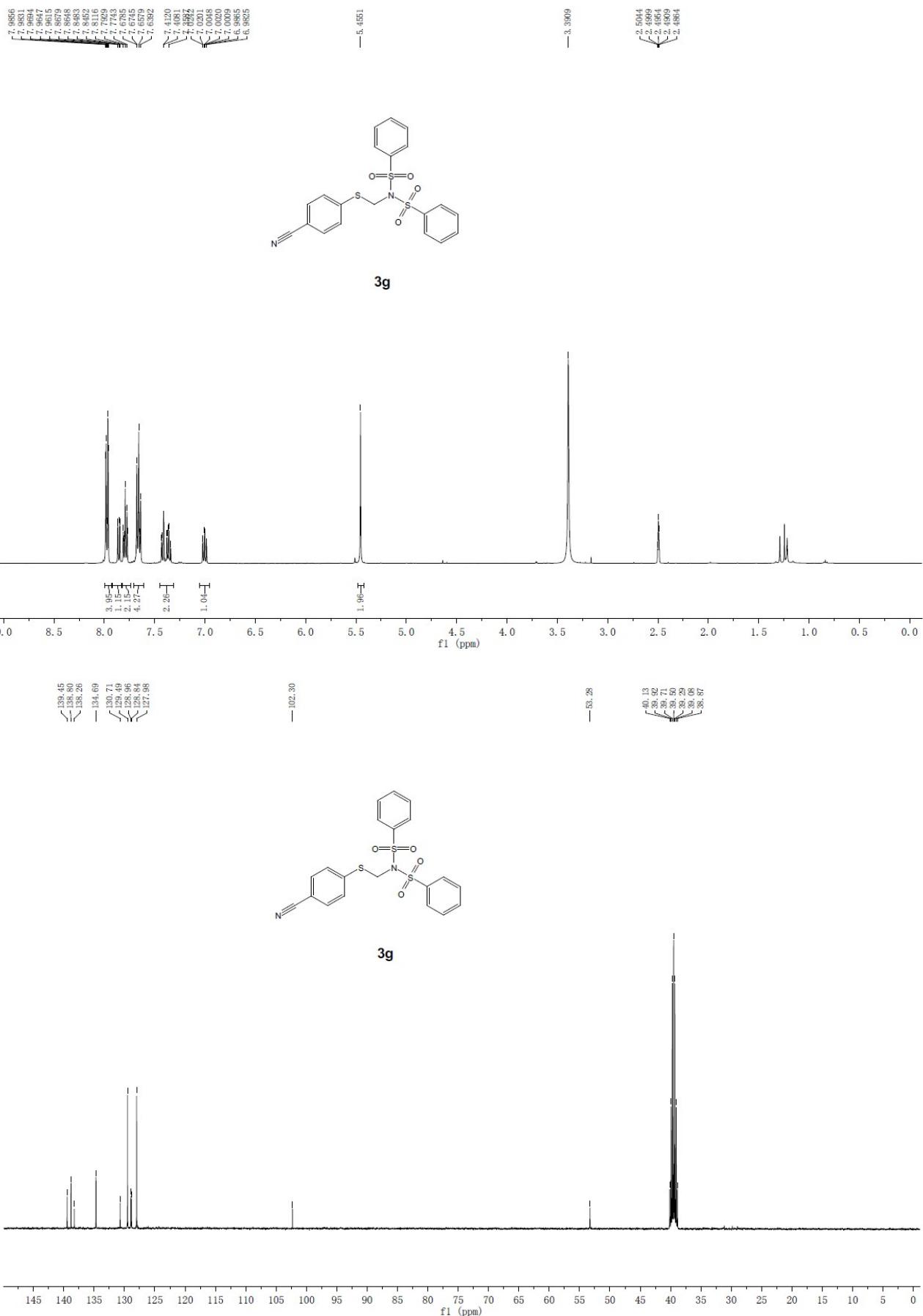


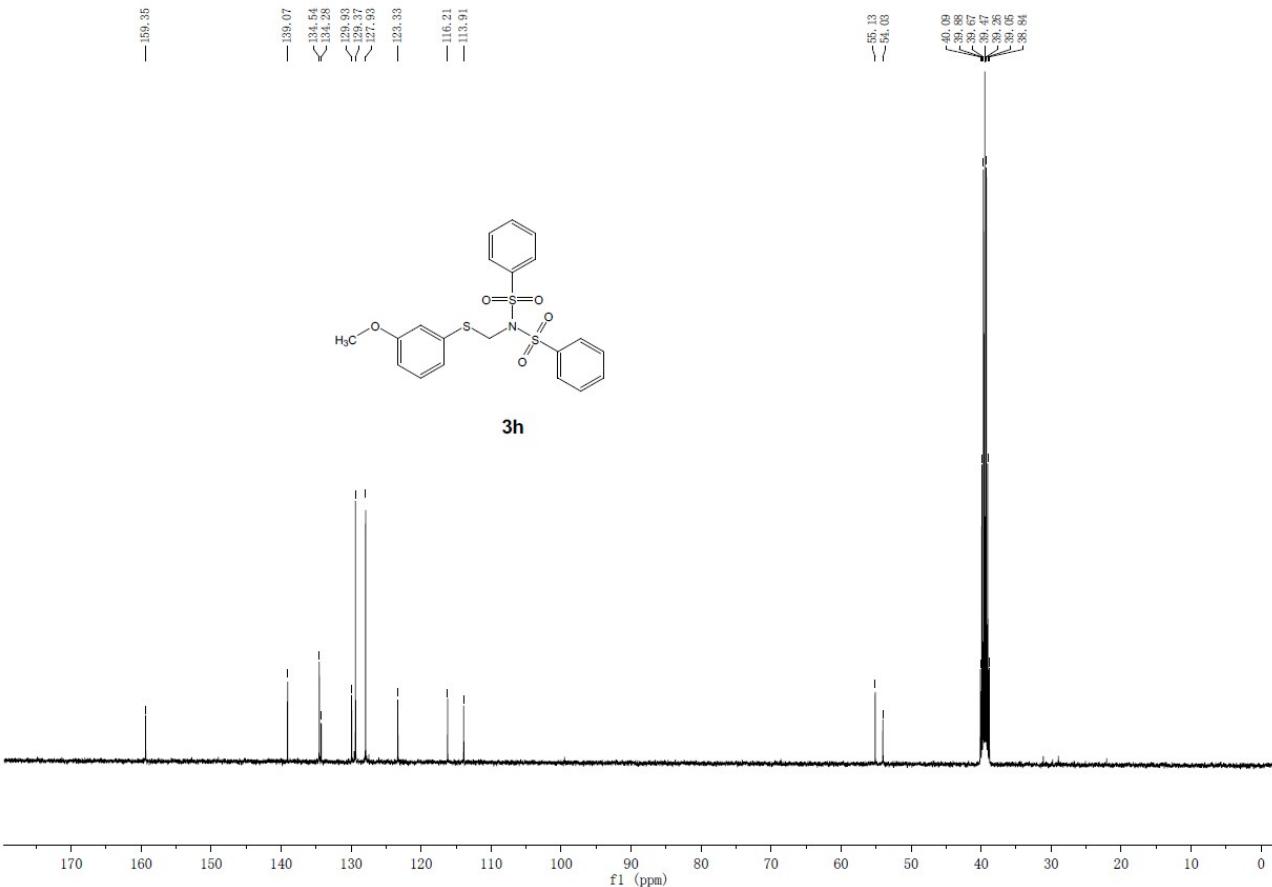
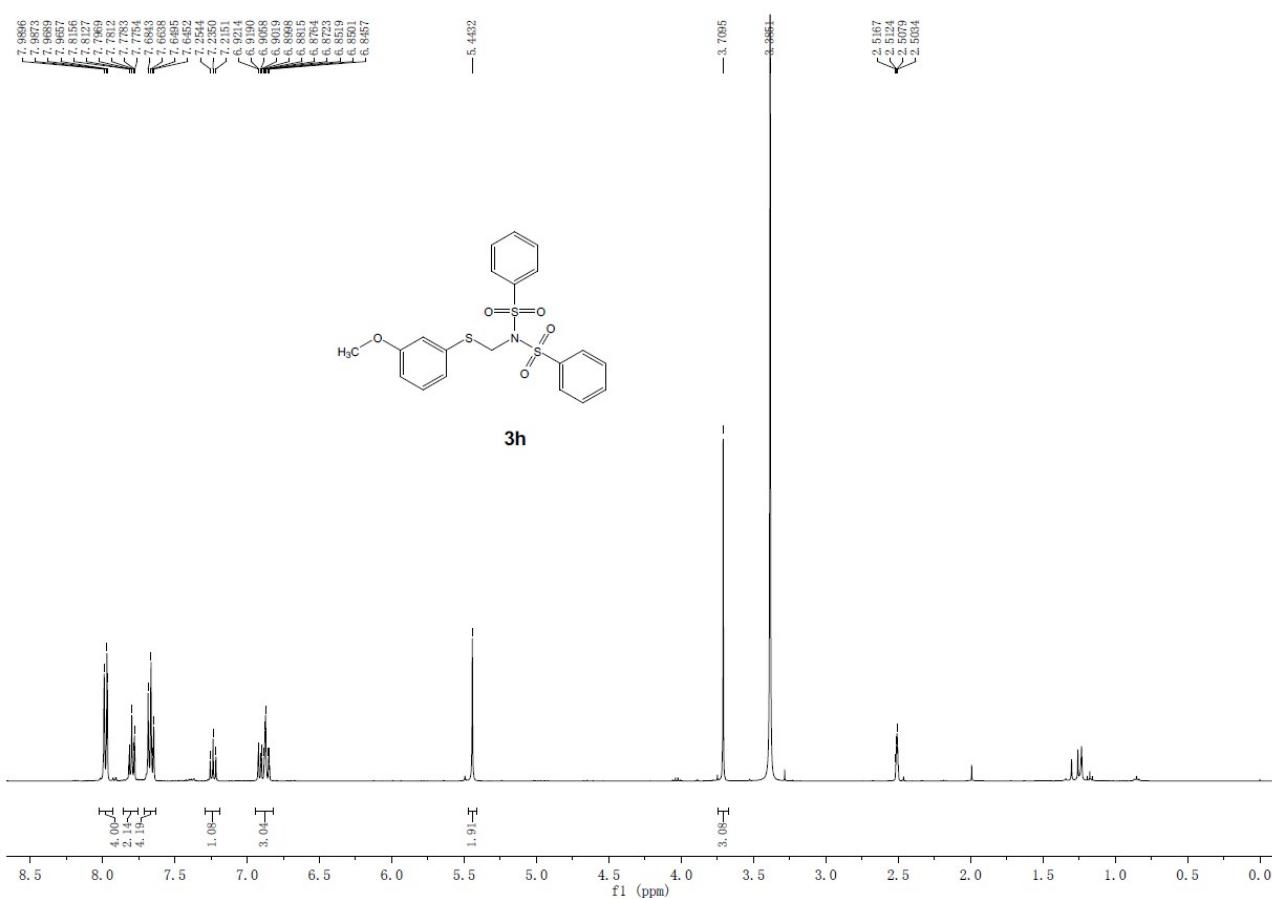


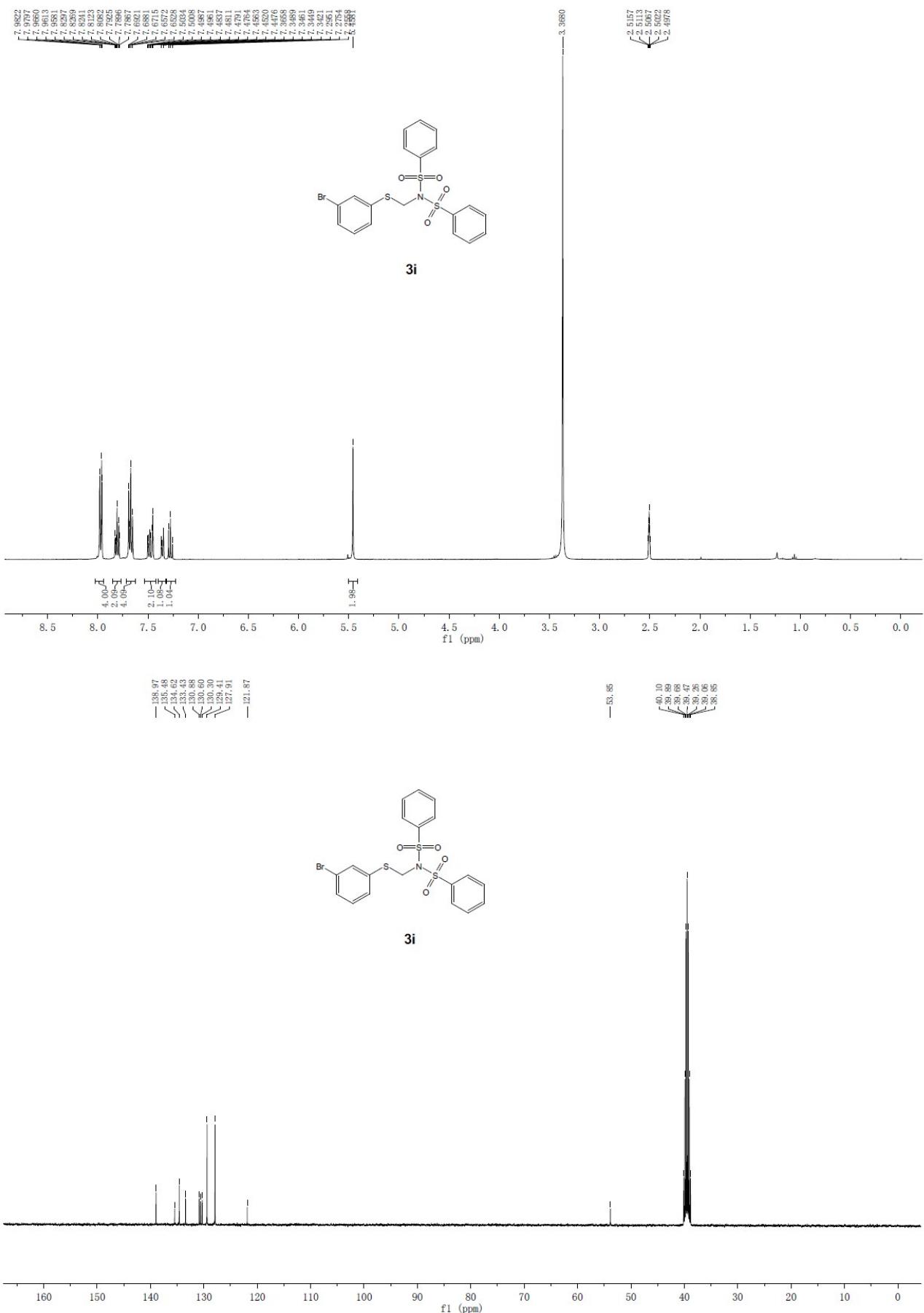


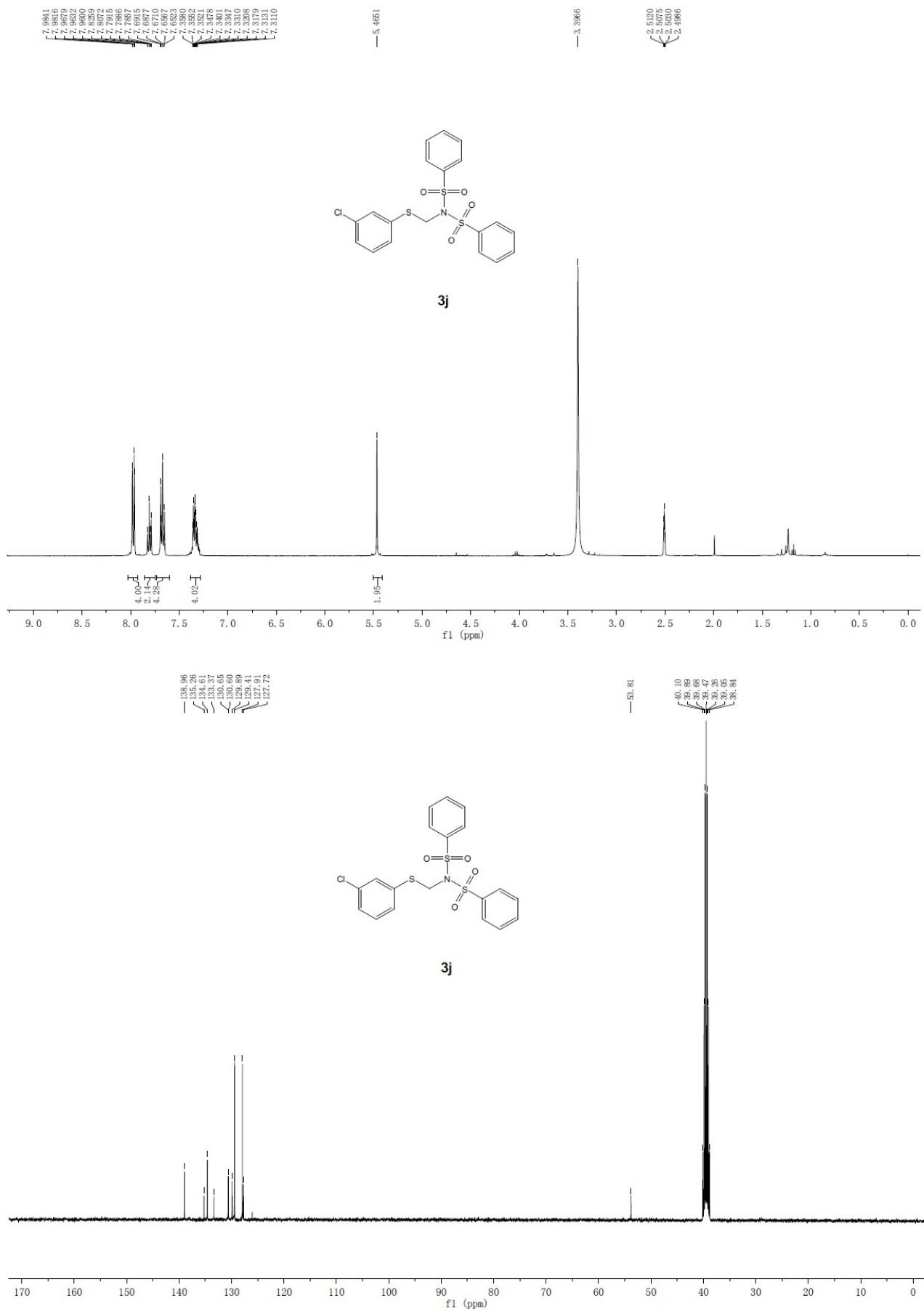
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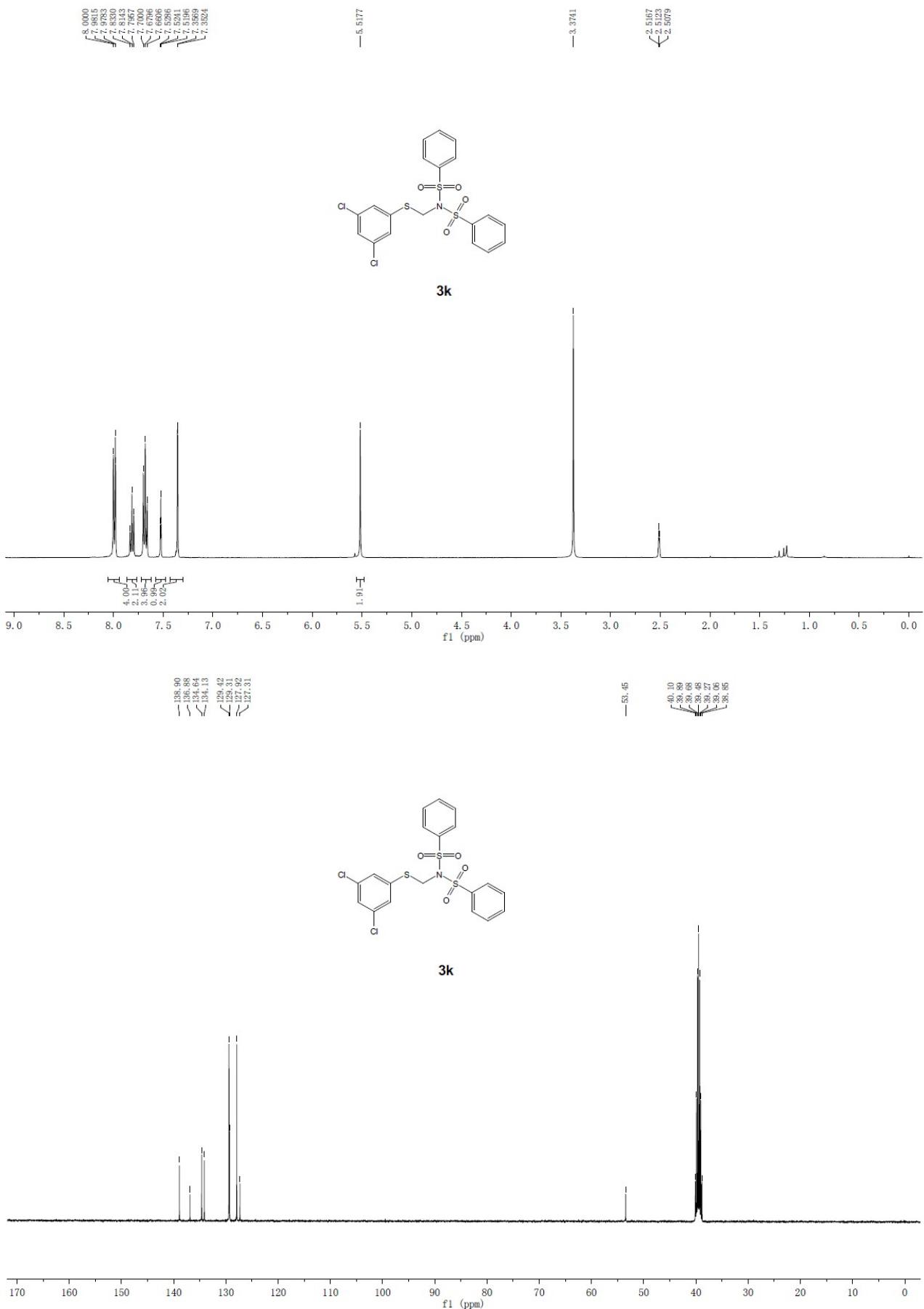


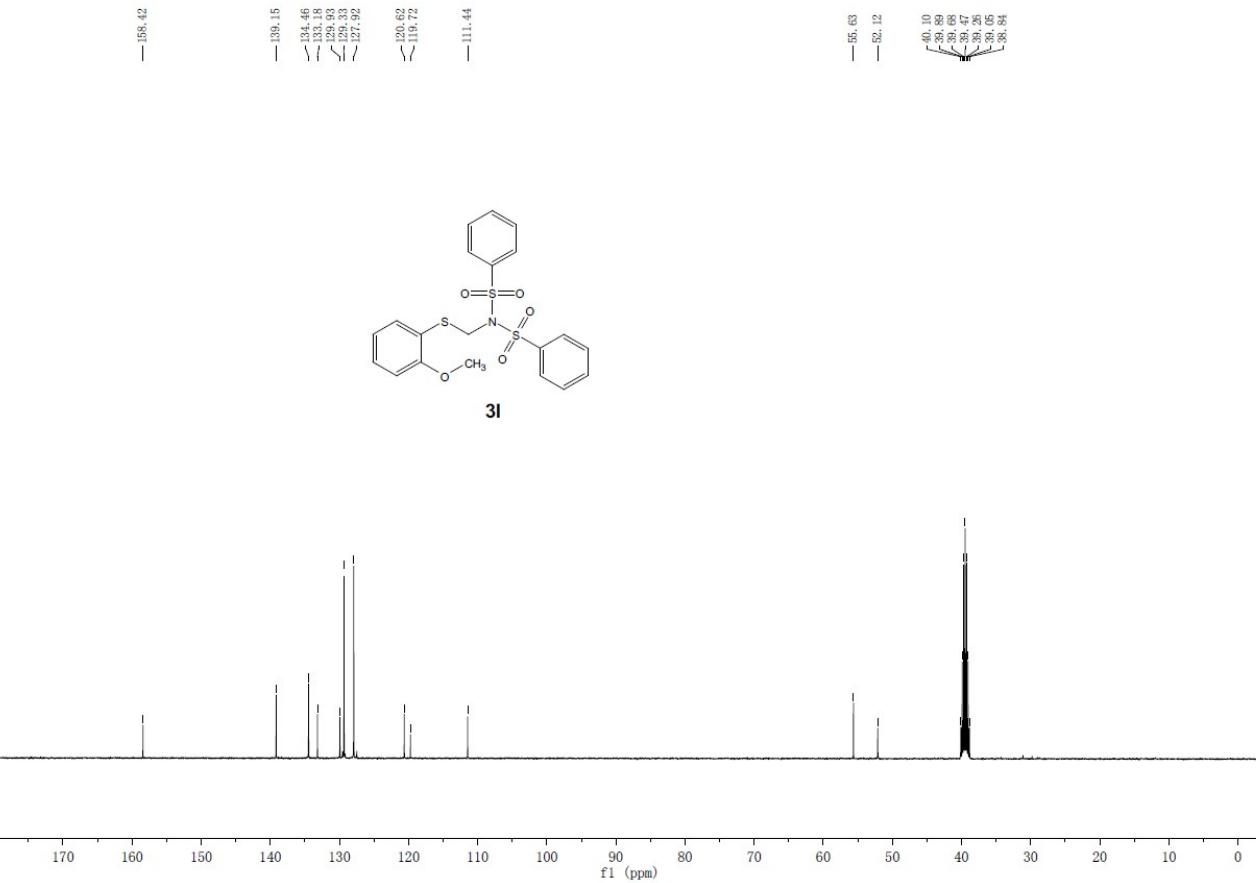
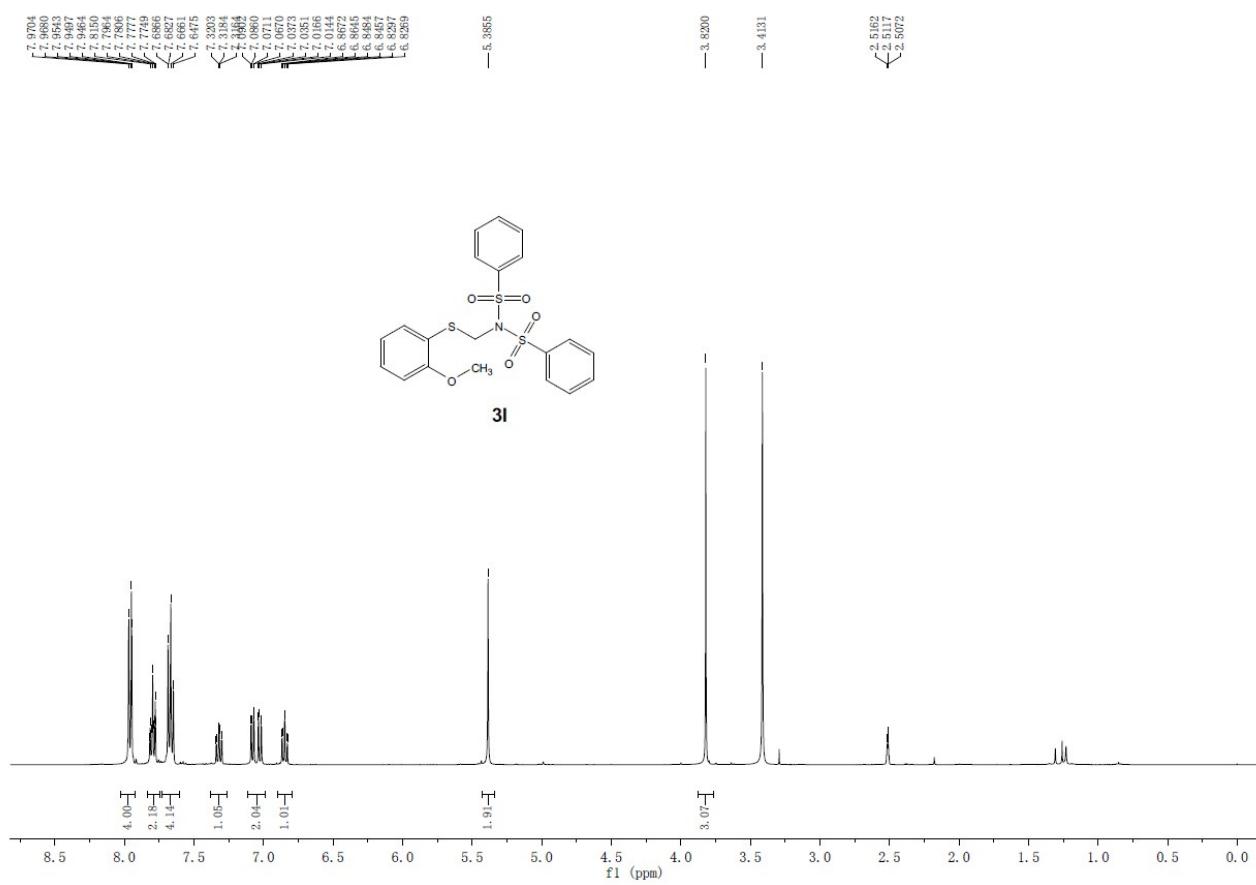


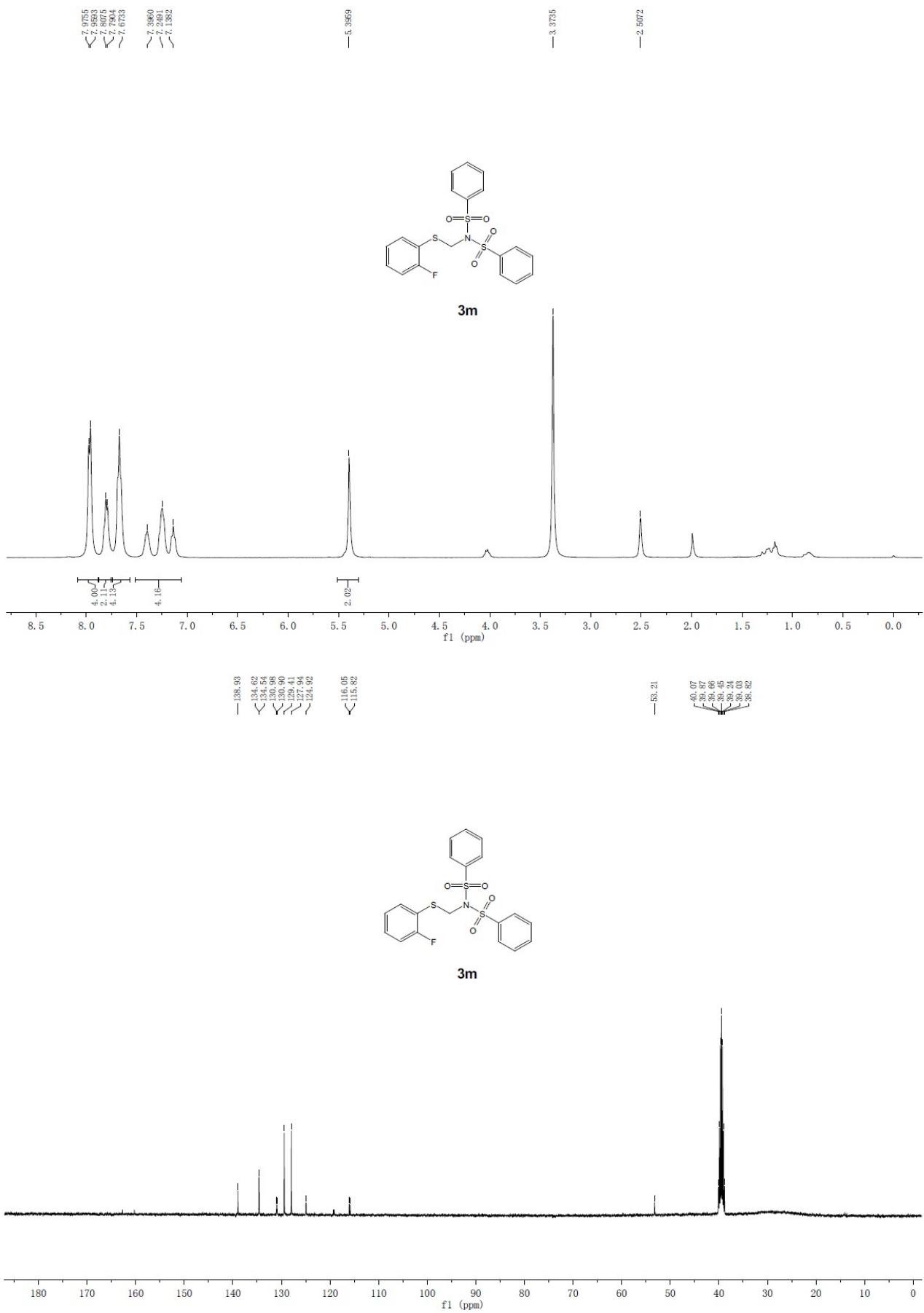


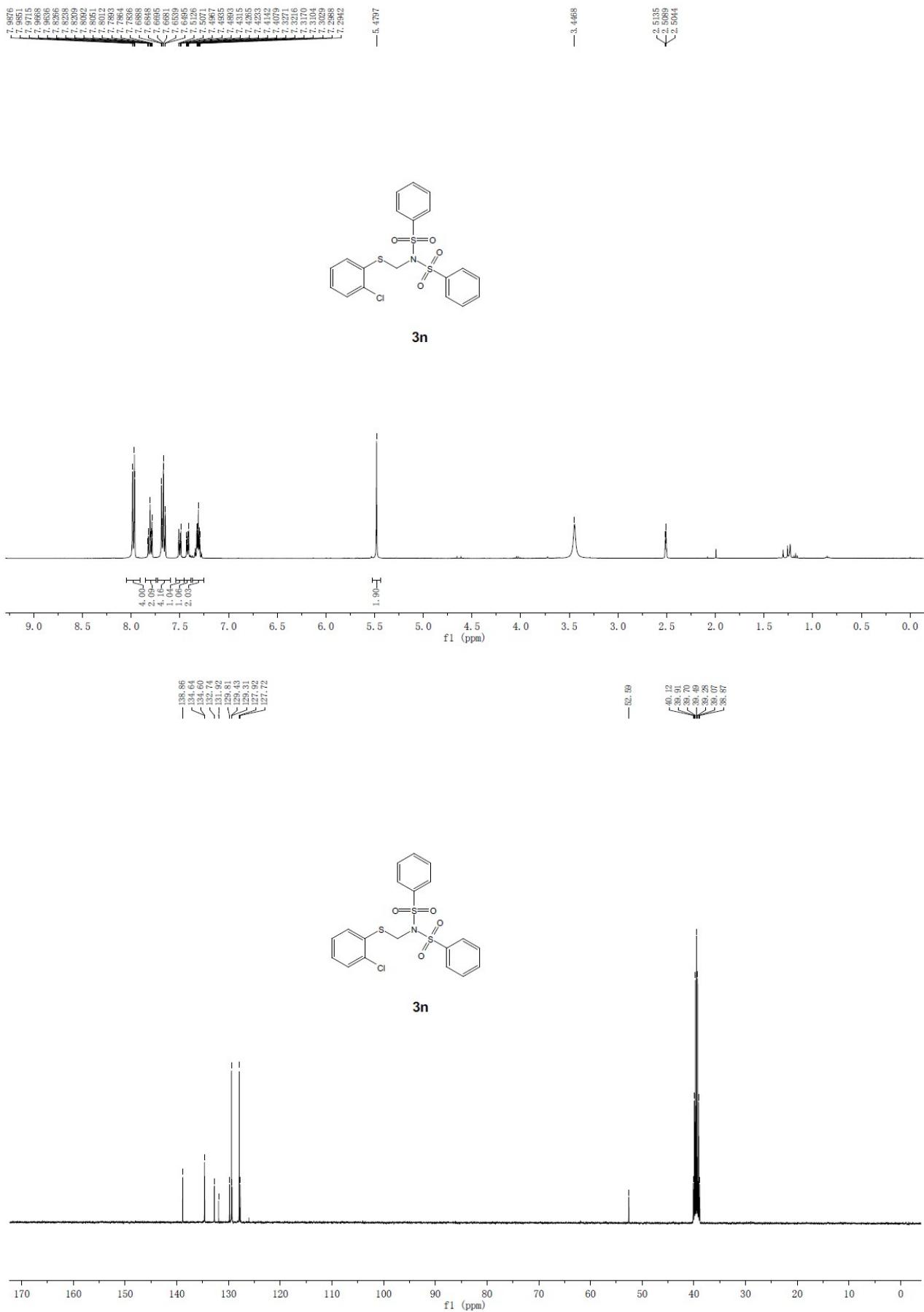


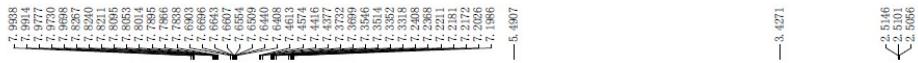




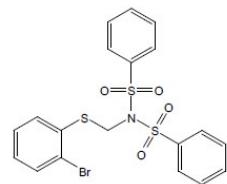
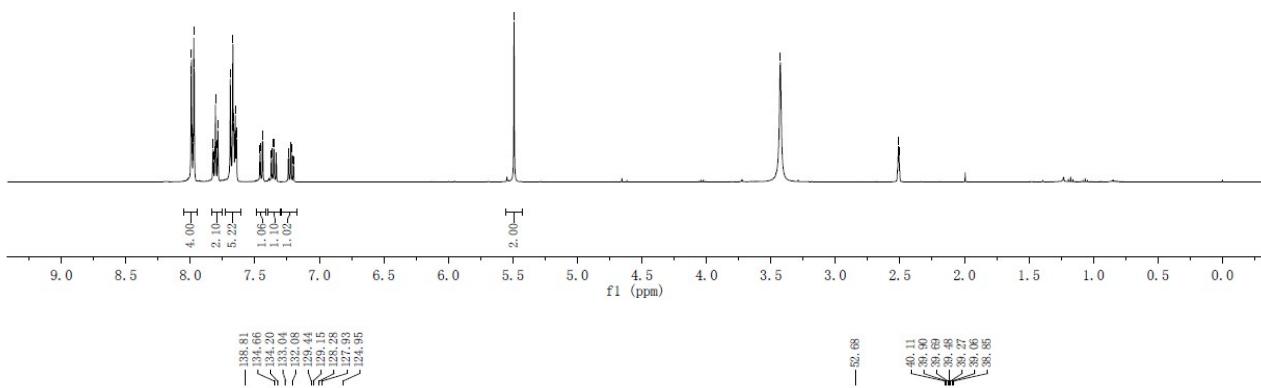




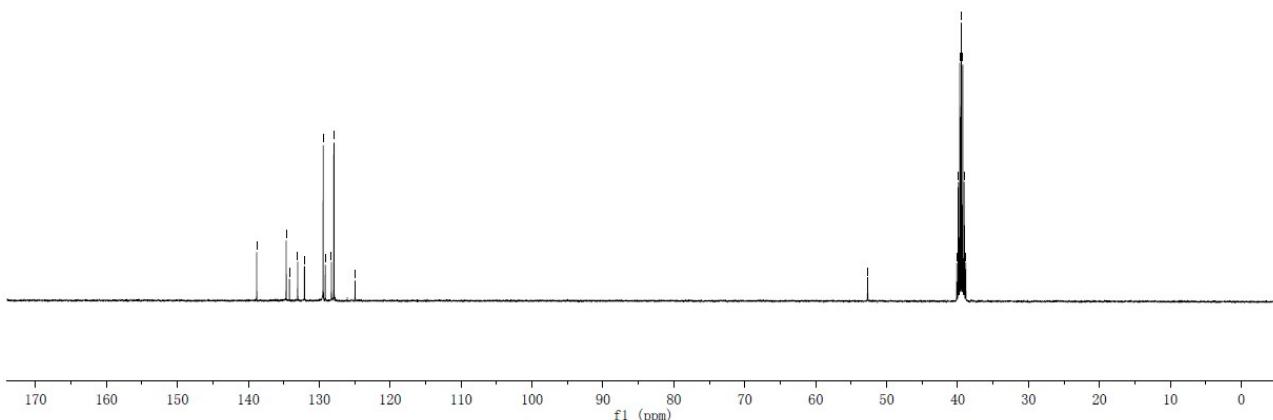




3o



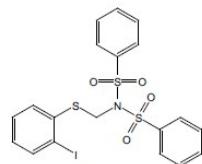
3o



8.060
8.0027
7.9843
7.9811
7.8296
7.8099
7.8099
7.8058
7.8023
7.5976
7.5945
7.5941
7.5912
7.5882
7.5858
7.5809
7.5733
7.5693
7.5650
7.5622
7.5600
7.5582
7.5582
7.5584
7.5563
7.5517

— 5.5941

— 3.5981



3p

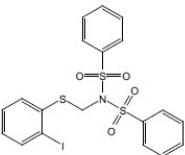


9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

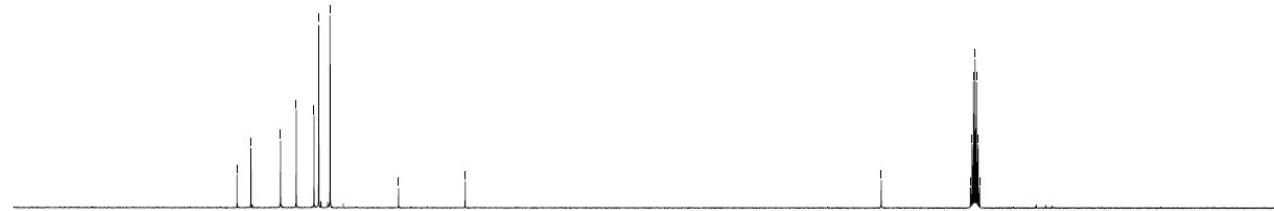
— 140.66
— 138.75
— 136.69
— 132.94
— 132.94
— 129.45
— 127.90

— 118.51
— 109.38

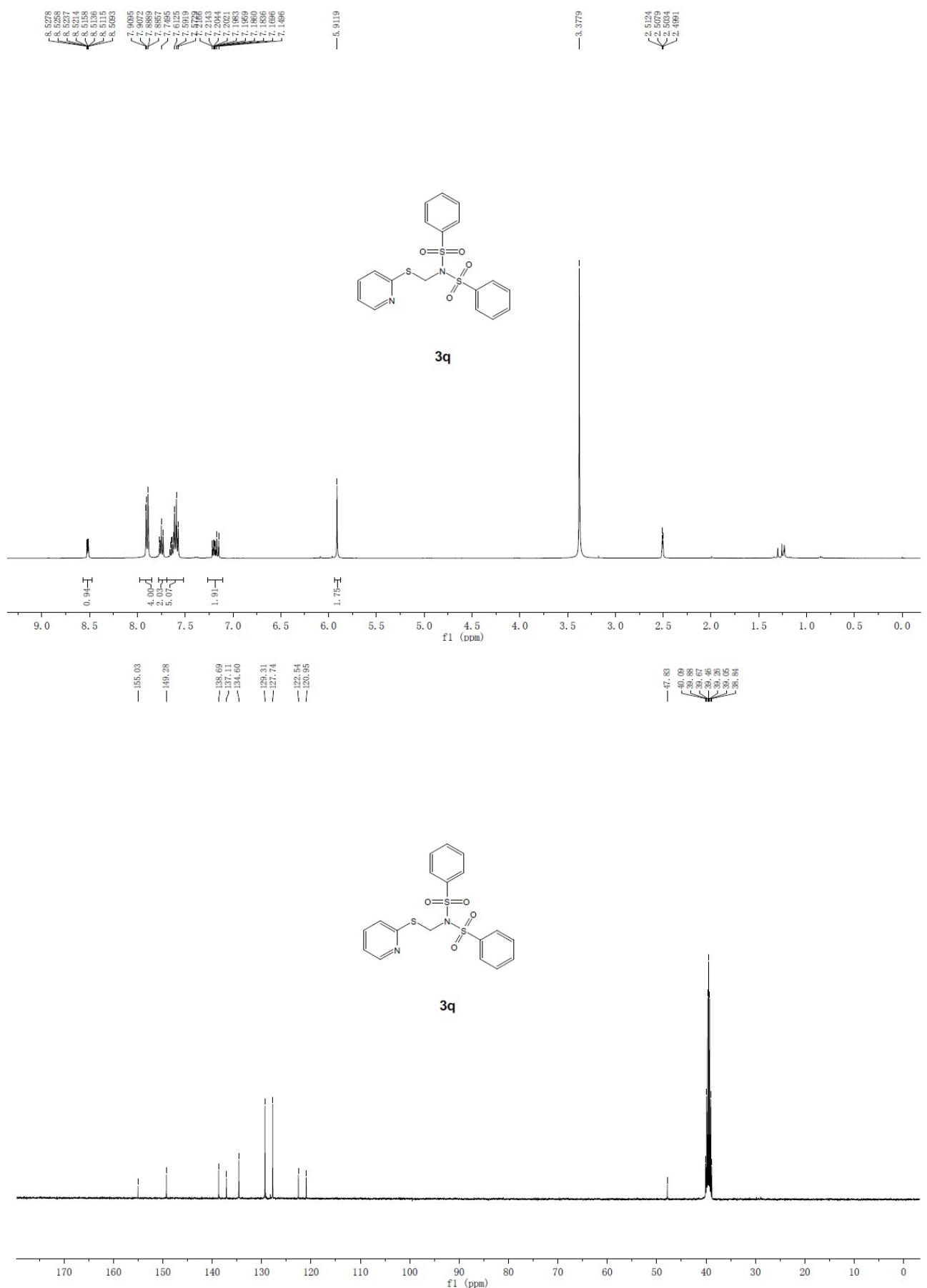
— 52.35



3p



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

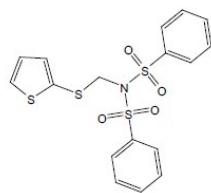


8.0375
 8.0311
 8.0215
 8.0205
 8.0167
 8.0155
 7.8353
 7.8167
 7.8124
 7.8010
 7.7981
 7.7952
 7.7173
 7.1154
 7.1099
 7.6938
 7.6895
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 6.9434

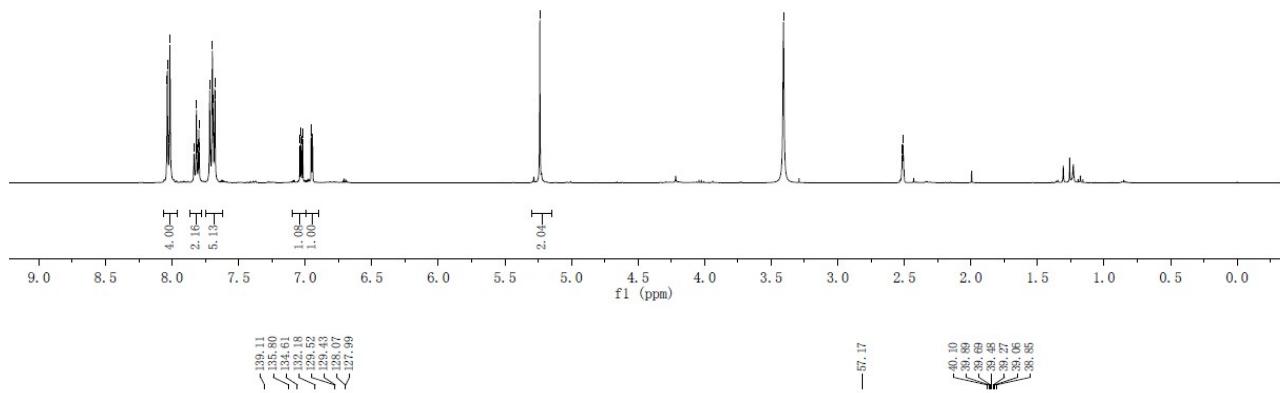
— 5.2378

2.1517
 2.1512
 2.1502

— 3.4077



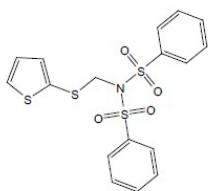
3r



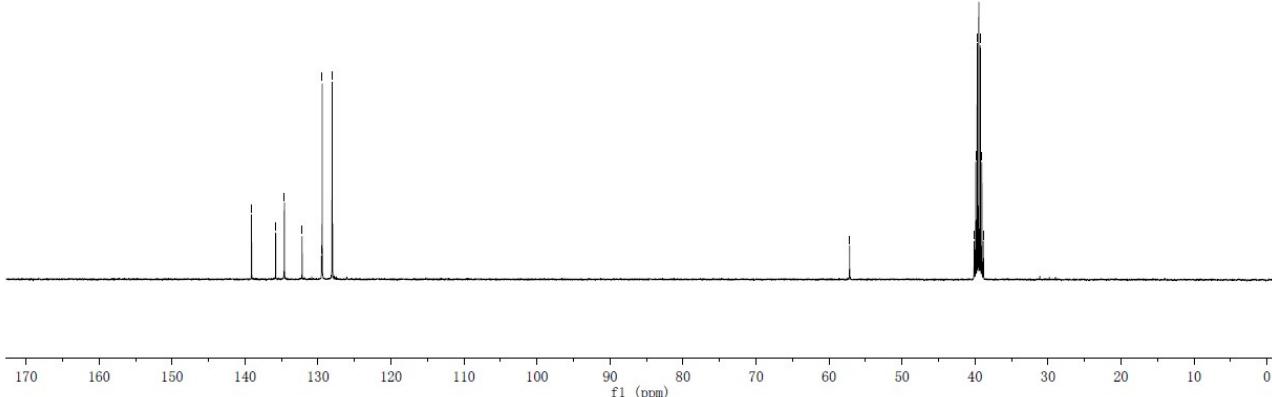
139.11
 135.80
 135.18
 132.52
 132.43
 129.43
 128.07
 127.99

— 53.17

2.1517
 2.1512
 2.1502



3r



8.059
8.036
8.035
7.810
7.798
7.772
7.701
7.680
7.663

— 6.053

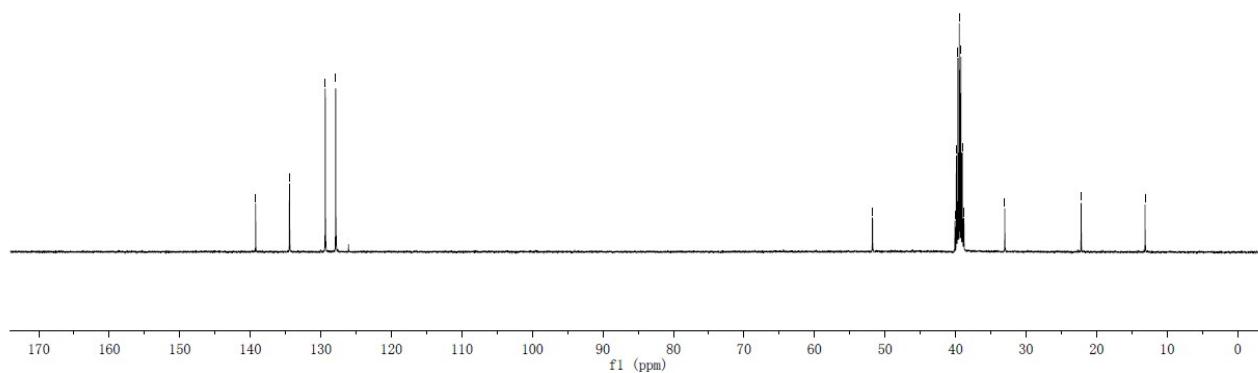
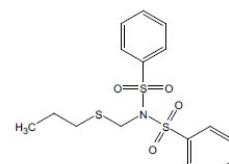
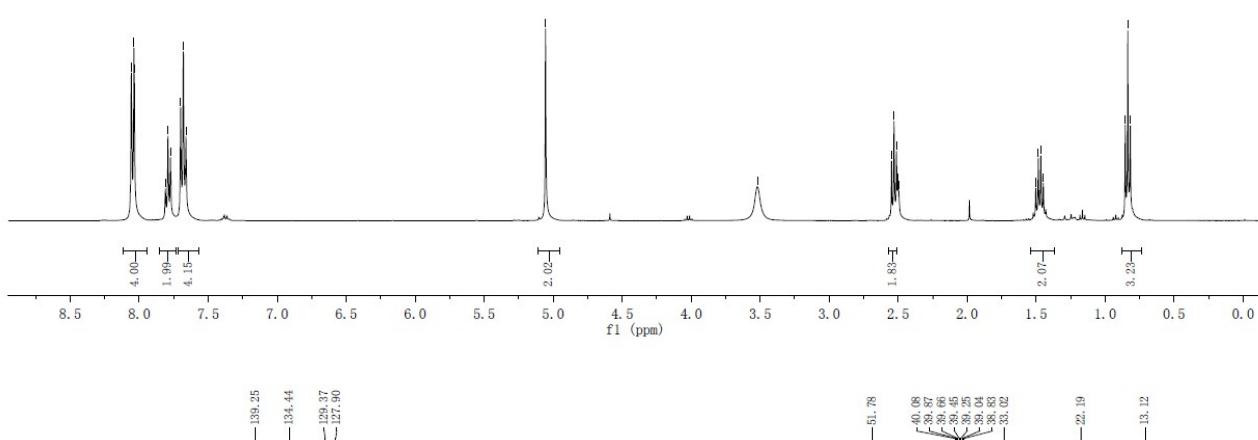
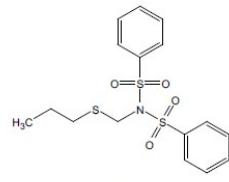
2.597
2.529
2.511
2.493
2.496
2.495

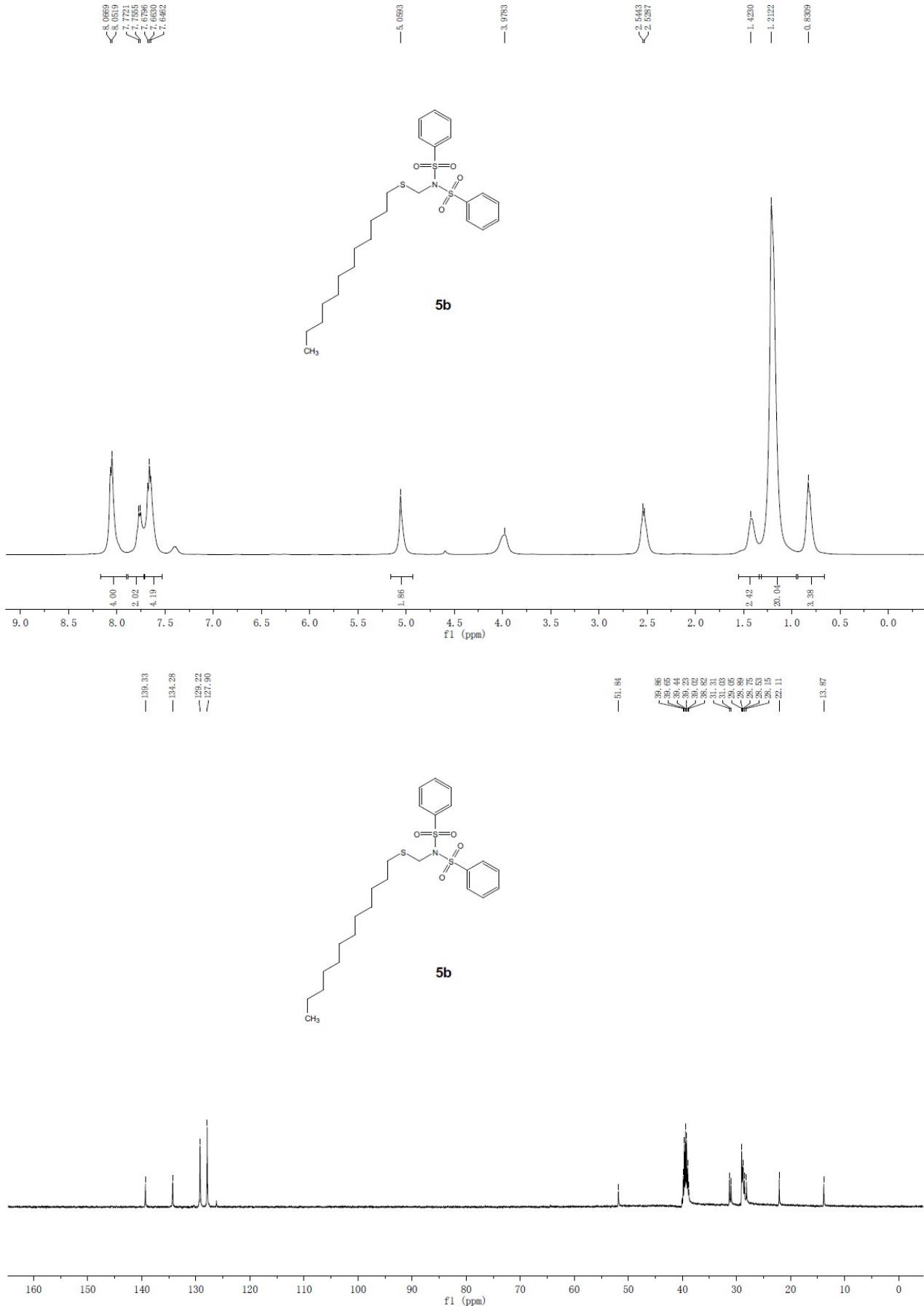
1.502
1.483
1.468
1.447

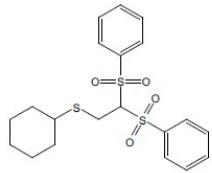
0.853

0.855

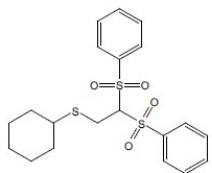
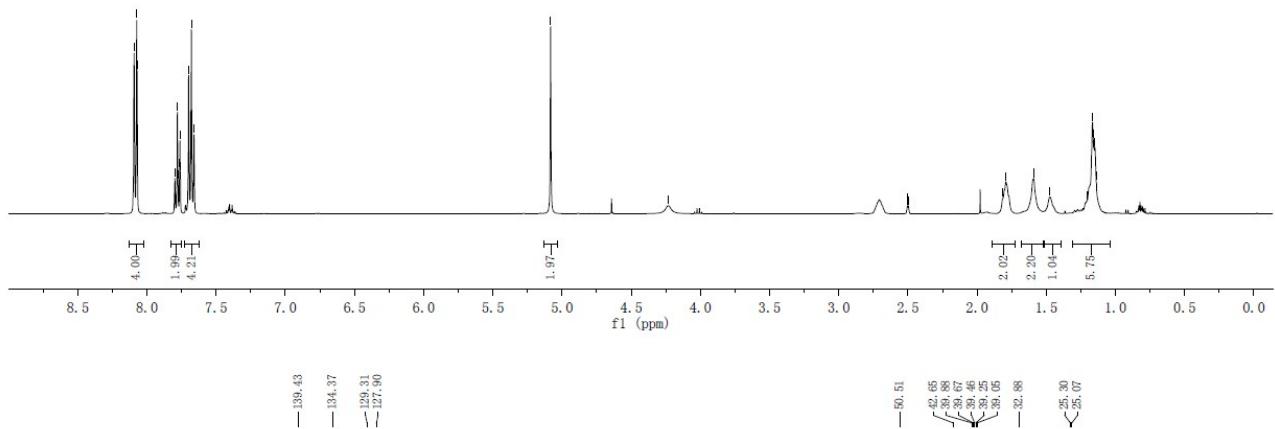
0.817



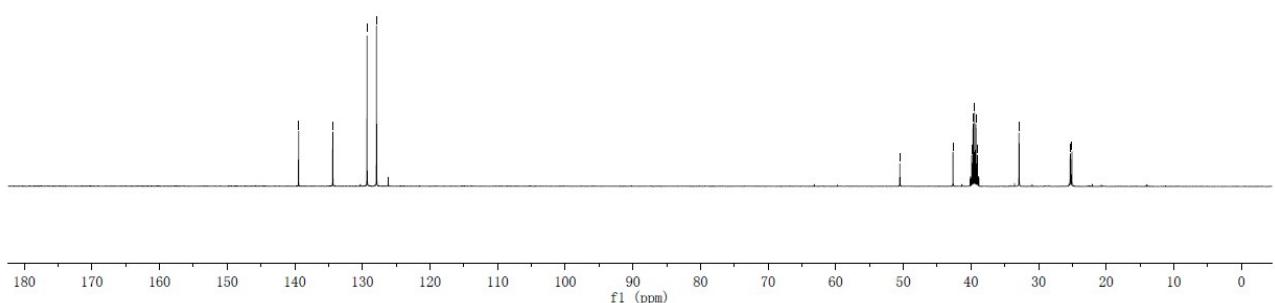




5c

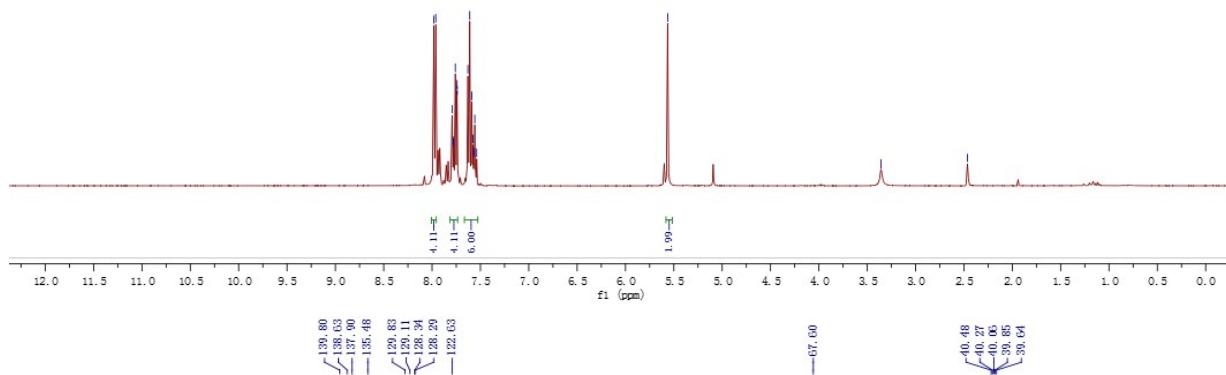


5c





6



6

