Supporting Information

An Efficient Imidation of Thioethers with Nitrene in Water

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General Remarks. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Starting materials of *N*-Nosyloxycarbamates were prepared using conventional procedures known in the literature.[1] Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AV300 (300 MHz) or Bruker AV400 (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00). 1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are desig nated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV300 (75 MHz) or Bruker AV400 (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Waters Q TOF Premier mass spectrometer. IR Spectra were recorded on a MAGNA/IR-550 spectrometer and absorption bands were reported in cm^{-1}. Analytical thin layer chromatography (TLC) was carried out on Merck 60 F254 pre coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

General procedure for the preparation of sulfilimines. To a round bottom flask equipped with a magnetic stir bar, was added sulfide **1** (0.2 mmol), benzyl nosyloxycarbamates **2** (0.1 mmol), water (1.0 mL) and CaO (0.1 mmol). The flask was closed with a stopper, and was stirred at the room temperature till benzyl nosyloxycarbamates was completely consumed (monitored by TLC). Then the mixture was extracted with EtOAc (2 ml×3). The organic layer was dried over anhydrous $MgSO_4$ filtered and evaporated. The resulting crude residue was purified via column chromatography on silica gel to afford the desired product **3**.

Characterization Data for Isolated Products 3. *N-(benzyloxycarbonyl)-S-methyl-S-phenylsulfilimine (**3a**).* **3a** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from thioanisole. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 20.7mg (75%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.57-7.51 (m, 3H), 7.39 (d, J = 6.8 Hz, 2H), 7.34-7.25 (m, 3H), 5.11 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 137.3, 136.4, 132.3, 129.9, 128.2, 128.1, 127.6, 126.2, 67.6, 36.1. IR (KBr, cm^{-1}) 2975, 1717, 1649, 1381, 1270, 1080, 851, 749. HRMS (ESI+, m/z) for $C_{15}H_{16}NO_2S$ $[M+H]^+$: Calcd. 274.0896, Found: 274.0891.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-methylphenyl) sulfilimine (**3b**).* **3b** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from methyl-(4-methylphenyl) sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 24.4 mg (85%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.09 (m, 2H), 7.38 (d, J = 6.8 Hz, 2H), 7.32-7.26 (m, 3H), 7.02 (dt, J_1 = 10.0 Hz, J_2 = 2.8 Hz, 2H), 5.09 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 3.84 (s, 3H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 162.9, 137.3, 128.4, 128.2, 128.1, 127.59, 126.9, 115.4, 67.5, 55.6, 36.1. IR (KBr, cm^{-1}) 2978, 1717, 1650, 1380, 1260, 1085, 837, 752. HRMS (ESI+, m/z) for $C_{16}H_{18}NO_2S$ $[M+H]^+$: Calcd. 288.1053, Found: 288.1061.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-methoxyphenyl) sulfilimine (**3c**).* **3c** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from methyl-(4-methoxyphenyl) sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 17.6mg (58%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, CDCl3) δ 7.73 (d, J = 8Hz, 2H), 7.39-7.28 (m, 7H), 5.11 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 2.92 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.1, 130.7, 128.3, 128.1, 127.73, 126.7, 111.6, 67.8, 52.2, 35.6, 21.6. IR (KBr, cm^{-1}) 2978, 1717, 1650, 1381, 1271, 1079, 887, 782. HRMS (ESI+, m/z) for $C_{16}H_{18}NO_3S$ $[M+H]^+$: Calcd. 304.1002, Found: 304.1003.

*N-(benzyloxycarbonyl)-S-methyl-S-(3-methoxyphenyl) sulfilimine (**3d**).* **3d** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from 3-methoxythioanisole. The crude material was purified by flash

column chromatography (hexane / AcOEt = 1:1) to afford 14.2mg (57%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.26 (m, 8H), 7.07 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2H), 5.12-5.10 (m, 2H),3.83 (d, J = 2.8 Hz, 3H), 2.81 (d, J = 2.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 160.7, 137.7, 137.3, 130.8, 128.2, 128.1, 127.6, 118.8, 118.3, 110.5, 67.5, 55.7, 36.1. IR (KBr, cm^{-1}) 2935, 1643, 1593, 1479, 1254, 1083, 840, 781. HRMS (ESI+, m/z) for $C_{16}H_{18}NO_3S$ $[M+H]^+$: Calcd. 304.1002, Found: 304.1006.

*N-(benzyloxycarbonyl)-S-methyl-S-(2-methoxyphenyl) sulfilimine (**3e**)*. **3e** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from 2-methoxy thioanisole. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 13.6mg (45%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.42 (d, J = 32.4 Hz, 2H), 7.34-7.28 (m, 1H), 6.96 (d, J = 8.4 Hz, 1H), 5.14 (s, 2H), 3.93 (s, 3H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 156.1, 137.5, 133.1, 128.1, 127.6, 126.2, 123.6, 122.0, 111.4, 67.6, 56.1, 34.5. IR (KBr, cm^{-1}) 2920, 2840, 1636, 1587, 1481, 1263, 1065, 844, 755. HRMS (ESI+, m/z) for $C_{16}H_{18}NO_3S$ $[M+H]^+$: Calcd. 304.1002, Found: 304.1004.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-chlorobenzene) sulfilimine (**3f**)*. **3f** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from S-methyl-S-(4-chlorobenzene) sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 18.7mg (61%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.53-7.50 (m, 2H), 7.38 (d, J = 7.2 Hz, 2H), 7.33-7.27 (m, 3H), 5.10 (AB quartet, J_{AB} = 12. 0 Hz, 2H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 138.9, 137.2, 135.0 130.3, 128.3, 128.2, 127.7, 127.6, 67.7, 36.1. IR (KBr, cm^{-1}) 2975, 1718, 1634, 1378, 1265, 1092, 826, 743. HRMS (ESI+, m/z) for $C_{15}H_{15}ClNO_2S$ $[M+H]^+$: Calcd. 308.0507, Found: 308.0501.

*N-(benzyloxycarbonyl)-S-methyl-S-(3-chlorobenzene) sulfilimine (**3g**)*. **3g** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from 3-chlorothioanisole. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 18.4mg (60%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (t, J = 1.6 Hz, 1H), 7.65-7.63 (m, 1H), 7.53 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 1H), 7.48-7.44 (m, 1H), 7.39-7.27 (m, 5H), 5.11 (AB quartet, J_{AB} = 12. 8 Hz, 2H), 2.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 160.8, 137.7, 137.3, 130.8, 128.2, 128.1, 127.6, 118.8, 118.3, 110.5, 67.5, 55.7, 36.1. IR (KBr, cm^{-1}) 2924, 1716, 1630, 1459, 1250, 1077, 853, 799. HRMS (ESI+, m/z) for $C_{15}H_{15}ClNO_2S$ $[M+H]^+$: Calcd. 308.0507, Found: 308.0504.

*N-(benzyloxycarbonyl)-S-methyl-S-(3-chlorobenzene) sulfilimine (**3h**)*. **3h** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from 2-chlorothioansole. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 13.5mg (44%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 1H), 7.50-7.47 (m, 3H), 7.40 (d, J = 7.2 Hz, 2H), 7.35-7.28 (m, 3H), 5.13 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 2.87 (s, 3H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 137.3, 134.9, 130.0, 129.6, 128.5, 128.3, 128.2, 127.7, 126.8, 67.8, 34.7. IR (KBr, cm^{-1}) 2920, 1630, 1453, 1375, 1251, 1091, 973, 851, 759. HRMS (ESI+, m/z) for $C_{15}H_{15}ClNO_2S$ $[M+H]^+$: Calcd. 308.0507, Found: 308.0509.

*N-(benzyloxycarbonyl)-S-methyl-S-(3,5-dichlorobenzene) sulfilimine (**3i**)*. **3i** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from 3,5- dichloro thioanisole. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 29.1mg (80%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 0.4 Hz, 2H), 7.39-7.27 (m, 5H), 5.11 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl^3$) δ 164.4, 140.2, 137.0, 136.8, 132.5, 128.4, 127.8, 124.4, 67.9, 36.1. IR (KBr, cm^{-1}) 2922, 1632, 1563, 1418, 1263, 1087, 855, 736. HRMS (ESI+, m/z) for $C_{15}H_{14}Cl_2NO_2S$ $[M+H]^+$: Calcd. 342.0117, Found: 342.0114.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-bromophenyl) sulfilimine (**3j**).* **3j** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from methyl-(4-bromophenyl) sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 18.3mg (52%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.63 (m, 4H), 7.38 (d, J = 8 Hz, 2H), 7.34-7.27 (m, 3H), 5.13 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 137.2, 135.7, 133.2, 128.7, 128.3, 128.3, 127.7, 127.2, 126.8, 76.7, 67.8, 36.0. IR (KBr, cm^{-1}) 2978, 1717, 1650, 1380, 1270, 1068, 886, 782. HRMS (ESI+, m/z) for $C_{15}H_{15}BrNO_2S$ $[M+H]^+$: Calcd. 352.0001, Found: 352.0005.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-fluorophenyl) sulfilimine (**3k**).* **3k** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from 4-fluorothioanisole. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 24.4mg (68%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.39-7.21 (m, 7H), 5.10 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 164.3, 163.8, 137.2, 132.0, 131.9, 131.1, 128.8, 128.3, 128.1, 127.7, 117.5, 117.3, 67.7, 36.2. IR (KBr, cm^{-1}) 2969, 1632, 1489, 1379, 1259, 1075, 836, 742. HRMS (ESI+, m/z) for $C_{15}H_{15}NO_3FS$ $[M+H]^+$: Calcd. 292.0802, Found: 292.0806.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-hydroxyphenyl) sulfilimine (**3l**).* **3l** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from 4-Hydroxyphenyl methyl sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 22.3mg (77%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.24 (m, 7H), 6.74 (d, J = 8.4 Hz, 2H), 5.11 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 161.7, 136.9, 128.5, 128.4, 127.9, 127.8, 123.9, 117.4, 67.9, 35.2. IR (KBr, cm^{-1}) 2930, 1577, 1438, 1375, 1271, 1079, 973, 832, 742. HRMS (ESI+, m/z) for $C_{15}H_{16}NO_3S$ $[M+H]^+$: Calcd. 290.0845, Found: 290.0841.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-formylphenyl) sulfilimine (**3m**).* **3m** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from Methyl 4-formylphenyl sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 19.3mg (76%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.1(s, 1H), 7.99 (m, 4H). 7.40-7.28 (m, 5H), 5.12 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 164.5, 142.9, 138.9, 137.1, 130.8, 128.3, 128.1, 127.8, 126.8, 67.9, 35.9. IR (KBr, cm^{-1}) 3393, 2926, 1706, 1606, 1453, 1381, 1261, 1085, 977, 836, 691. HRMS (ESI+, m/z) for $C_{16}H_{16}NO_3S$ $[M+H]^+$: Calcd. 302.0845, Found: 302.0844.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-acetophenone) sulfilimine (**3n**).* **3n** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from 4-(Methylthio) acetophenone. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 21.8mg (73%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.39-7.27 (m, 5H), 5.11 (AB quartet, J_{AB} = 12. 0 Hz, 2H), 2.87 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 164.5, 141.4, 139.9, 137.1, 130.8, 129.6, 128.3, 128.1, 127.8, 126.4, 67.9, 35.9, 26.8. IR (KBr, cm^{-1}) 3044, 2928, 1683, 1630, 1393, 1257, 1081, 961, 836, 744, 598. HRMS (ESI+, m/z) for $C_{17}H_{18}NO_3S$ $[M+H]^+$: Calcd. 316.1002, Found: 316.1004.

*N-(benzyloxycarbonyl)-S-ethyl-S-phenylsulfilimine (**3o**).* **3o** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from S-ethy-S-phenyl sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 14.9mg (52%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.63 (m, 2H), 7.50-7.42 (m, 3H), 7.32-7.31 (d, J = 7.2 Hz, 2H), 7.25-7.16 (m, 3H), 5.04 (AB quartet, J_{AB} = 12. 4

Hz, 2H), 3.08-2.9 (m, 2H), 1.17 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 137.4, 134.4, 132.3, 129.8, 128.2, 128.1, 127.6, 126.9, 126.2, 67.6, 45.2, 7.9. IR (KBr, cm^{-1}) 2977, 1718, 1643, 1381, 1264, 1080, 851, 749. HRMS (ESI+, m/z) for $C_{16}H_{18}NO_2S$ $[M+H]^+$: Calcd. 288.1053, Found: 288.1049.

*N-(benzyloxycarbonyl)-S-phenyl-S-benzylsulfilimine (**3p**)*. **3p** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from S-pheny-S-benzyl sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 21.0 mg (63%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 3H), 7.43-7.36 (m, 4H), 7.33-7.27 (m, 4H), 7.22 (t, J = 8.0 Hz, 2H), 6.96 (d, J = 7.2 Hz, 2H), 5.17-5.09 (m, 2H), 4.50 (d, J = 12.4 Hz, 1H), 4.10 (d, J = 12.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 137.5, 133.1, 132.5, 130.6, 129.4, 129.0, 128.7, 128.2, 128.1, 127.6, 127.5, 67.7, 57.7. IR (KBr, cm^{-1}) 2979, 1717, 1603, 1374, 1269, 1078, 930, 887. HRMS (ESI+, m/z) for $C_{21}H_{20}NO_2S$ $[M+H]^+$: Calcd. 350.1209, Found: 350.1213.

*N-(benzyloxycarbonyl)-S-methyl-S-benzylsulfilimine (**3q**)*. **3q** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from Benzyl methyl sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 23.8mg (83%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.26 (m, 10H), 5.11 (S, 2H), 4.41 (d, J = 12.8 Hz), 4.03 (d, J = 12.8 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 137.4, 130.3, 129.3, 129.2, 128.4, 128.3, 127.9, 127.6, 67.4, 53.3, 28.9. IR (KBr, cm^{-1}) 2929, 1717, 1623, 1413, 1265, 1078, 842, 698. HRMS (ESI+, m/z) for $C_{16}H_{17}NO_2S$ $[M+H]^+$: Calcd. 288.1053, Found: 288.1052.

*N-(benzyloxycarbonyl)-S-benzyl-S-benzylsulfilimine (**3r**)*. **3r** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from S-benzyl-S-benzyl sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 18.2mg (50%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 10H), 7.31-7.28 (m, 3H), 7.25-7.24 (m, 2H), 5.10 (s, 2H), 4.28 (d, J = 13.2 Hz, 2H), 4.10 (d, J = 12.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 137.5, 130.4, 129.1, 129.0, 128.9, 128.24, 127.9, 127.5, 76.4, 50.2. IR (KBr, cm^{-1}) 2972, 1717, 1541, 1379, 1263, 1077, 887, 700. HRMS (ESI+, m/z) for $C_{22}H_{22}NO_2S$ $[M+H]^+$: Calcd. 364.1366, Found: 364.1364.

*N-(benzyloxycarbonyl)-tetrahydrothiophene sulfilimine (**3s**)*. **3s** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from tetrahydrothiophene sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 15.6mg (66%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 5H), 5.09 (s, 2H), 3.64-3.57 (m, 2H), 3.32-3.25 (m, 2H), 2.36-2.21 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 137.4, 128.3, 128.2, 127.6, 67.5, 49.0, 26.8. IR (KBr, cm^{-1}) 2939, 1615, 1382, 1279, 913, 843, 740, 643. HRMS (ESI+, m/z) for $C_{12}H_{16}NO_2S$ $[M+H]^+$: Calcd. 238.0896, Found: 238.0899.

*N-(benzyloxycarbonyl)-S-phenyl-S-phenylsulfilimine (**3t**)*. **3t** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from S-pheny-S-pheny sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 25.1mg (30%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 4H), 7.50-7.44 (m, 6H), 7.41 (d, J = 6.8 Hz, 2H), 7.33-7.28 (m, 3H), 5.16 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 137.4, 136.6, 132.0, 129.8, 128.3, 127.7, 127.6, 67.9. IR (KBr, cm^{-1}) 2980, 1920, 1716, 1373, 1268, 1077, 887, 751. HRMS (ESI+, m/z) for $C_{20}H_{18}NO_2S$ $[M+H]^+$: Calcd. 336.1053, Found: 336.1058.

*N-(benzyloxycarbonyl)-S-phenyl-S-cyclopropylsulfilimine (**3u**)*. **3u** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from S-phenyl-S-cyclopropyl sulfide. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 8.0mg (27%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, 2H), 7.57-7.51 (m, 3H), 7.39 (d, J = 7.2 Hz, 2H), 7.33-7.28 (m, 3H), 5.12 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 2.56-2.50 (m, 1H), 1.44-1.33 (m, H), 1.14-1.02 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 137.4, 136.3,

132.1, 129.7, 128.2, 127.60, 126.7, 67.6, 29.2, 5.2, 4.9. IR (KBr, cm^{-1}) 2975, 1717, 1558, 1381, 1269, 1079, 885, 781. HRMS (ESI+, m/z) for $C_{17}H_{18}NO_2S$ $[M+H]^+$: Calcd. 300.1053, Found: 300.1050.

Characterization Data for Isolated Products 4. *N-(benzyloxycarbonyl)triphenylphosphoranimine (**4**)*. **4** was obtained following the general procedure for the preparation of *N*-(benzyloxycarbonyl)sulfilimine starting from triphenylphosphine. The crude material was purified by flash column chromatography (hexane / AcOEt = 1:1) to afford 35.1mg (85%) of the desired product as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.70 (m, 6H), 7.57-7.51 (m, 3H), 7.46-7.38 (m, 6H), 7.27-7.24 (m, 5H), 5.06 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 137.3, 134.4, 133.3, 128.9, 128.8, 128.2, 127.1, 127.0, 67.62. IR (KBr, cm^{-1}) 2974, 1719, 1647, 1381, 1270, 1080, 851. HRMS (ESI+, m/z) for $C_{26}H_{23}NO_2P$ $[M+H]^+$: Calcd. 412.1461, Found: 412.1464.

General procedure for the preparation sulfoximines 5. *Method a:* To a round bottom flask equipped with a magnetic stir bar, was added sulfilimine **3** (0.1 mmol), K_2CO_3 (0.1 mmol), water (2.0 mL) and $KMnO_4$ (1 mmol). The resulting mixture was stirred for 24h at room temperature. Then the reaction mixture was extracted with EtOAc (2 ml×3) and concentrated in vacuo and the resulting residue was purified by flash chromatography to give the sulfoximine **5**. *Method b*: To a round bottom flask equipped with a magnetic stir bar, was added sulfilimine **3** (0.1 mmol), K_2CO_3 (0.1 mmol), EtOH (2.0 mL) and *m*CPBA (1 mmol). The resulting mixture was stirred for 24h at room temperature. Then the reaction mixture was concentrated in vacuo and the resulting residue was purified by flash chromatography to give the sulfoximine **5**.

Characterization Data for Isolated Products 5. *N-(benzyloxycarbonyl)-S-methyl-S-phenylsulfoximine (**5a**)*. **5a** was obtained following the general method a: 86%; method b: 83%. The crude material was purified by flash column chromatography (hexane / AcOEt = 3:1) to afford product as light yellow oils. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 4.8 Hz, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.59 (t, J = 6.0 Hz, 2H), 7.29 (s, 5H), 5.08 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 3.3 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 138.3, 136.2, 133.9, 129.7, 128.3, 128.24, 127.9, 127.4, 67.8, 44.6. IR (KBr, cm^{-1}) 2980, 1719, 1558, 1384, 1271, 1050, 886, 784. HRMS (ESI+, m/z) for $C_{15}H_{16}NO_3S$ $[M+H]^+$: Calcd. 290.0845, Found: 290.0840.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-methylphenyl) sulfoximine (**5b**)*. **5b** was obtained following the general method a: 92%; method b: 56%. The crude material was purified by flash column chromatography (hexane / AcOEt = 3:1) to afford product as light yellow oils. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H), 7.37(d, J = 8.0 Hz, 2H), 7.29 (s, 5H), 5.07 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 3.29 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 162.9, 137.3, 128.4, 128.2, 128.1, 127.5, 126.9, 67.5, 55.6, 36.0. IR (KBr, cm^{-1}): 2980, 1717, 1635, 1381, 1266, 1080, 885, 773. HRMS (ESI+, m/z) for $C_{16}H_{18}NO_3S$ $[M+H]^+$: Calcd. 304.1002, Found: 304.1008.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-methoxyphenyl) sulfoximine (**5c**)*. **5c** was obtained following the general method a: 68%; method b: 82%. The crude material was purified by flash column chromatography (hexane / AcOEt = 3:1) to afford product as light yellow oils. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.87 (m, 2H), 7.31-7.27 (m, 5H), 7.04-7.00 (m, 2H), 5.08 (AB quartet, J_{AB} = 12. 0 Hz, 2H), 3.88 (s, 3H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.6, 136.2, 129.6, 129.2, 128.3, 128.2, 127.5, 114.9, 67.7, 55.7, 45.0. IR (KBr, cm^{-1}) 2976, 1717, 1592, 1382, 1261, 1092, 886, 781. HRMS (ESI+, m/z) for $C_{16}H_{18}NO_4S$ $[M+H]^+$: Calcd. 320.0951, Found: 320.0949.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-chlorobenzene) sulfoximine (**5f**)*. **5f** was obtained following the general method a: 79%; method b: 79%. The crude material was purified by flash column chromatography (hexane / AcOEt = 3:1) to afford product as light yellow oils. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.87 (m, 2H), 7.54-7.52 (m, 2H), 7.30-7.26 (m, 5H) 5.06 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 140.8, 136.7, 135.9, 130.0, 128.9, 128.4, 128.3, 128.1, 67.9,

44.5. IR (KBr, cm^{-1}) 2975, 1718, 1634, 1378, 1265, 1092, 826, 743. HRMS (ESI+, m/z) for $C_{15}H_{15}ClNO_3S$ $[M+H]^+$: Calcd. 324.0456, Found: 324.0454.

*N-(benzyloxycarbonyl)-S-methyl-S-(4-bromophenyl) sulfoximine (**5j**)*. **5j** was obtained following the general method a: 92%; method b: 68%. The crude material was purified by flash column chromatography (hexane / AcOEt = 3:1) to afford product as light yellow oils. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.33-7.28 (m, 5H), 5.07 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 137.2, 135.9, 133.0, 129.4, 128.9, 128.4, 128.3, 128.0, 67.9, 44.5. IR (KBr, cm^{-1}): 2978, 1717, 1650, 1380, 1272, 1068, 886, 782. HRMS (ESI+, m/z) for $C_{15}H_{15}BrNO_3S$ $[M+H]^+$: Calcd. 367.9951, Found: 367.9955.

*N-(benzyloxycarbonyl)-S-ethyl-S-phenylsulfoximine (**5o**)*. **5o** was obtained following the general method a: 37%; method b: 78%. The crude material was purified by flash column chromatography (hexane / AcOEt = 3:1) to afford product as light yellow oils. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H), 7.76-7.50 (m, 3H), 7.39 (d, J = 6.8 Hz, 2H), 7.33-7.26 (m, 3H), 5.12 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 3.12-2.99 (m, 2H), 12.5 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 136.2, 133.3, 129.6, 128.3 128.2, 128.1, 127.9, 127.4, 67.8, 50.8, 6.9. IR (KBr, cm^{-1}) 2978, 1716, 1557, 1383, 1257, 1121, 887, 737. HRMS (ESI+, m/z) for $C_{16}H_{18}NO_3S$ $[M+H]^+$: Calcd. 304.1002, Found: 304.1006.

*N-(benzyloxycarbonyl)-S-phenyl-S-benzylsulfoximine (**5p**)*. **5p** was obtained following the general method a: 28%; method b: 63%. The crude material was purified by flash column chromatography (hexane / AcOEt = 3:1) to afford product as light yellow oils. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.58(m, 3H), 7.44-7.40 (m, 2H), 7.35-7.26 (m, 6H), 7.19-7.16 (m, 2H), 6.91 (d, J = 7.2 Hz, 2H), 5.14 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 4.73 (d, J = 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 136.3, 135.0, 131.2, 129.2, 129.1, 128.7, 128.5, 128.4, 128.3, 127.9, 67.9, 62.2. IR (KBr, cm^{-1}) 2987, 1717, 1542, 1383, 1270, 1048, 881, 810. HRMS (ESI+, m/z) for $C_{21}H_{20}NO_3S$ $[M+H]^+$: Calcd. 366.1158, Found: 366.1153.

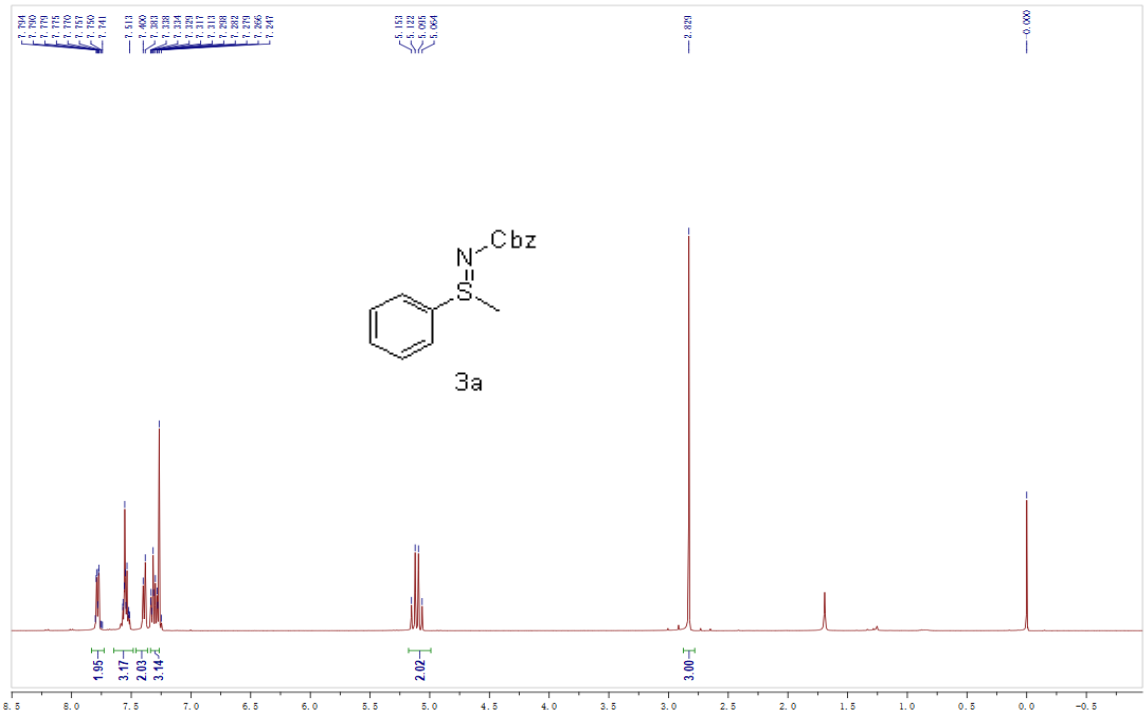
*N-(benzyloxycarbonyl)-tetrahydrothiophene sulfoximine (**5s**)*. **5s** was obtained following the general method a: 58%; method b: 79%. The crude material was purified by flash column chromatography (hexane / AcOEt = 3:1) to afford product as light yellow oils. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 6.8 Hz, 2H), 7.33-7.26 (m, 3H), 5.09 (s, 2H), 3.13-3.12 (m, 2H), 2.46-2.45 (m, 2H), 2.06-2.03 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 137.4, 128.5, 128.3, 128.1, 67.5, 49.0, 26.8. IR (KBr, cm^{-1}) 2938, 2392, 1653, 1558, 1259, 1210, 913, 740. HRMS (ESI+, m/z) for $C_{12}H_{16}NO_3S$ $[M+H]^+$: Calcd. 254.0845, Found: 254.0846.

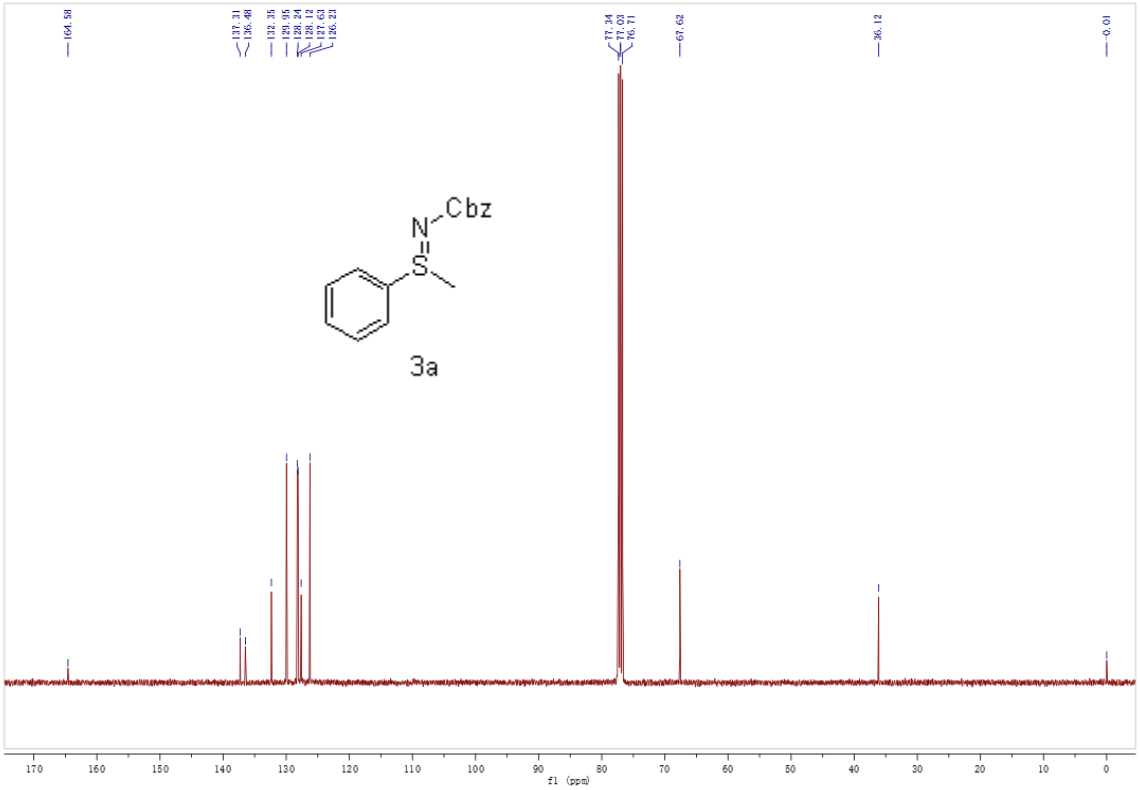
*N-(benzyloxycarbonyl)-S-phenyl-S-cyclopropyl sulfoximine (**5u**)*. **5u** was obtained following the general method a: 31%; method b: 76%. The crude material was purified by flash column chromatography (hexane / AcOEt = 3:1) to afford product as light yellow oils. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91-7.89 (m, 2H), 7.67-7.63 (m, 1H), 7.58-7.54 (m, 2H), 5.04 (AB quartet, J_{AB} = 12. 4 Hz, 2H), 2.67-2.61 (m, 1H), 1.67-1.58 (m, 4H), 1.33-1.13 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 138.8, 136.2, 133.6, 129.6, 128.3, 128.2, 127.9, 127.5, 67.8, 33.5, 6.7, 5.2. IR (KBr, cm^{-1}) 2978, 1716, 1558 1375, 1257, 1079, 887, 780. HRMS (ESI+, m/z) for $C_{17}H_{18}NO_3S$ $[M+H]^+$: Calcd. 316.1002, Found: 316.1005.

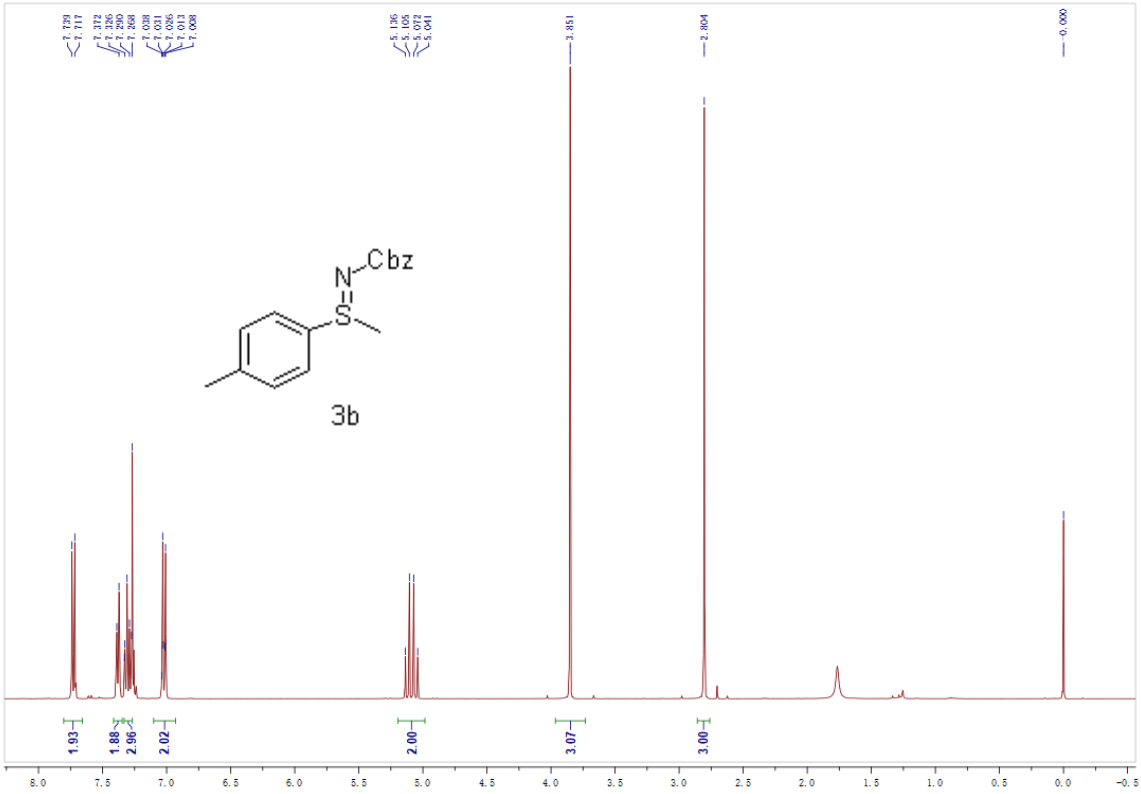
References

1 K. H.Ng, A. S. C.Chan, W. Y. J. Yu, *J. Am. Chem. Soc.*2010, 132, 12862-12864.

^{1}H and ^{13}C NMR spectra of 3



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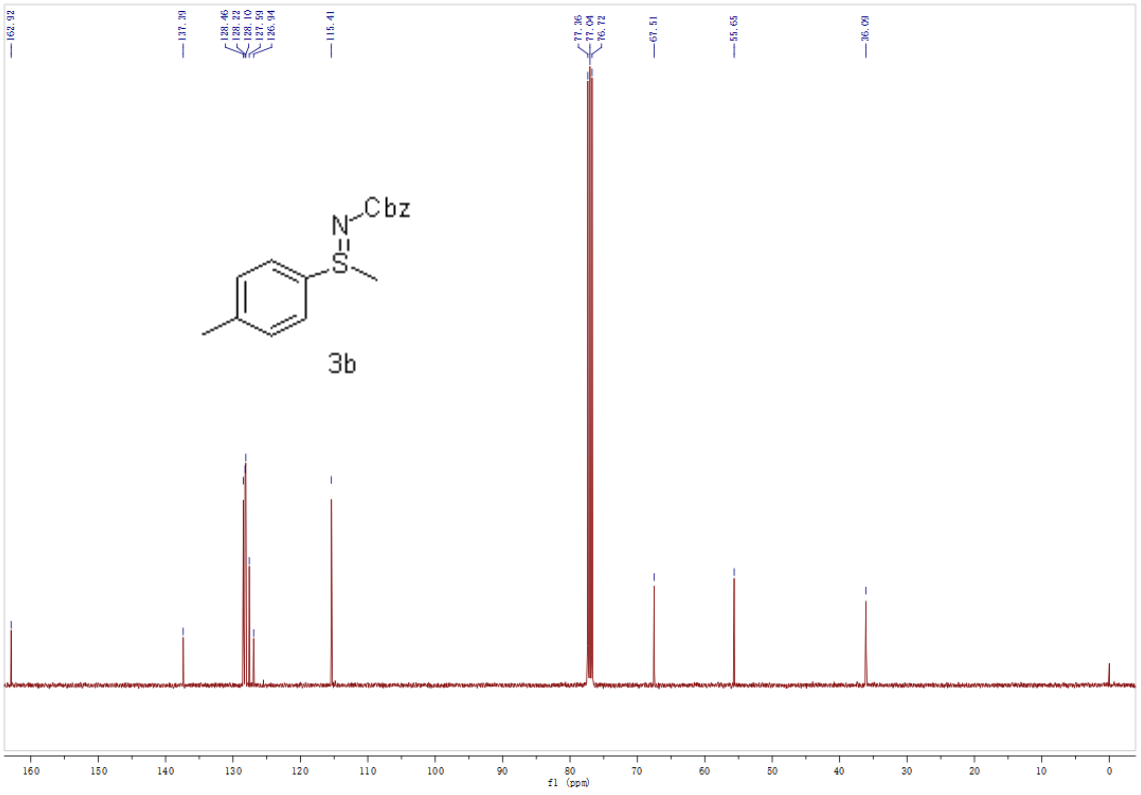
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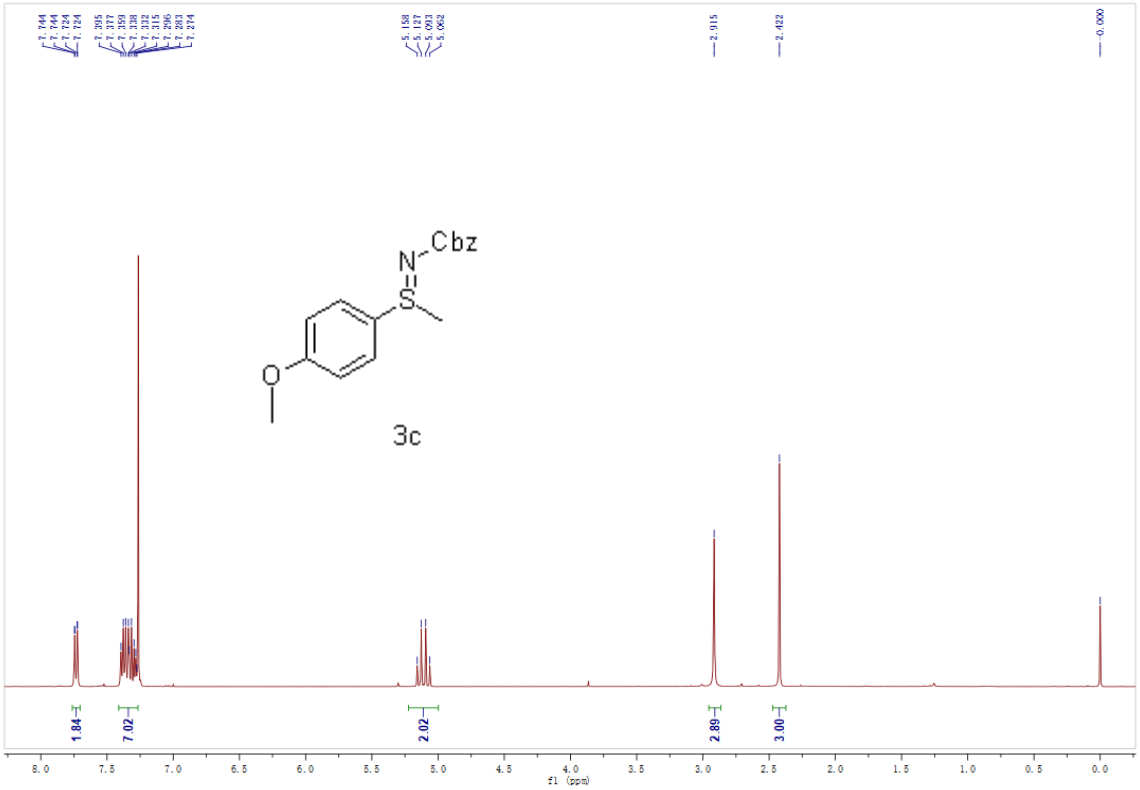
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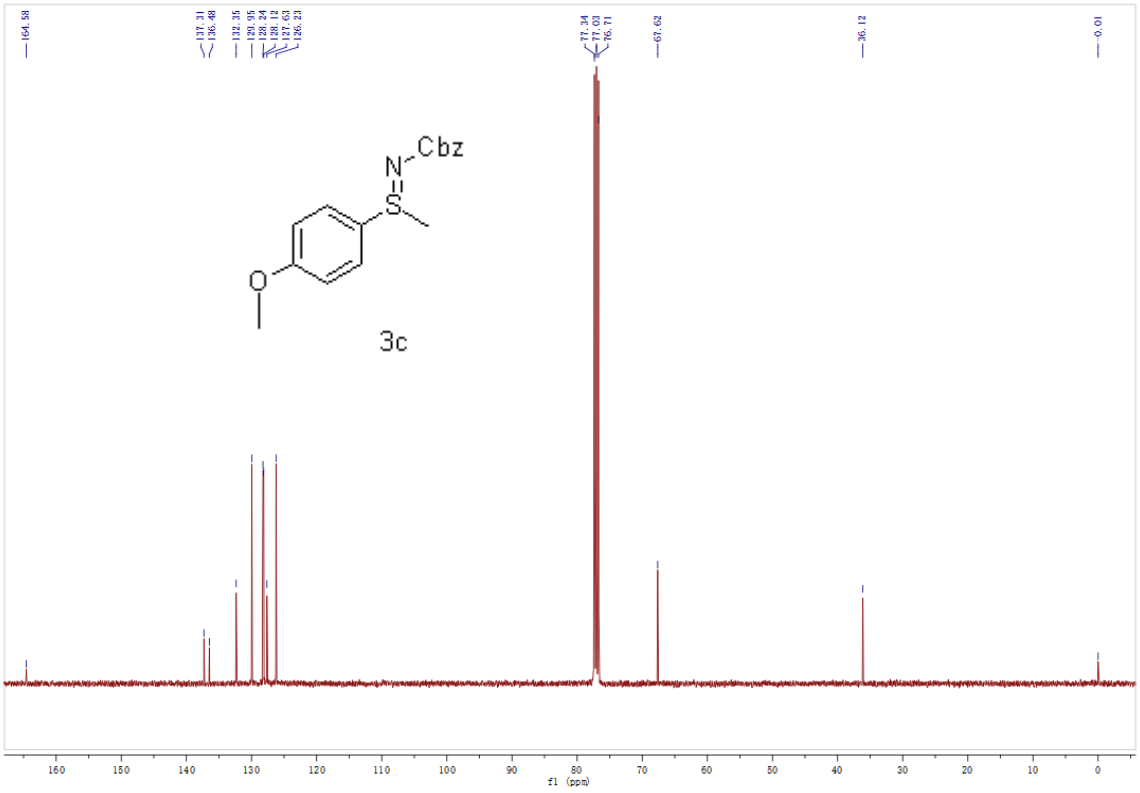
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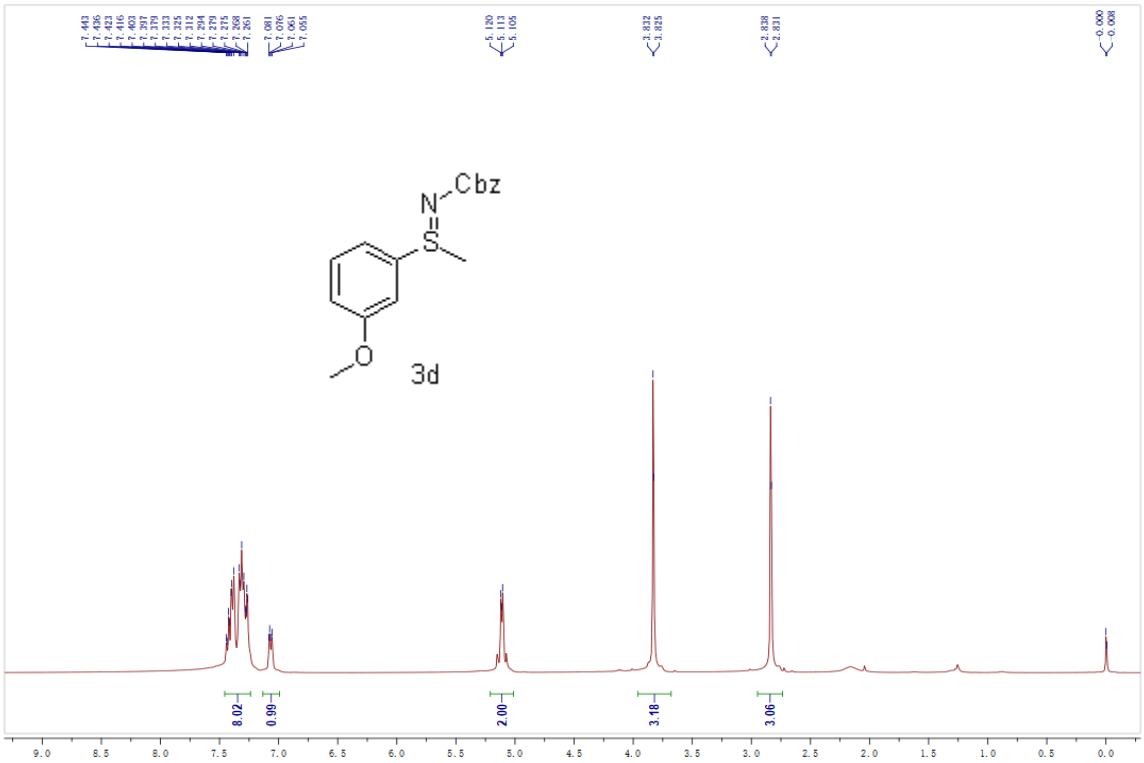
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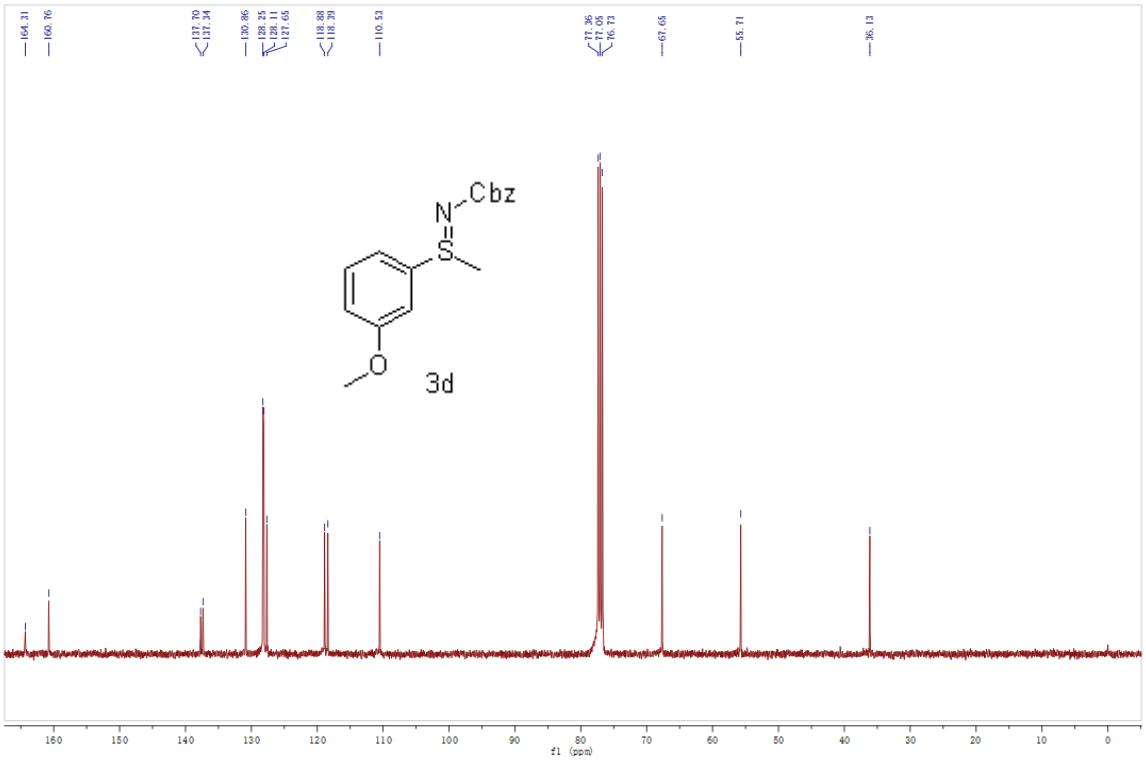
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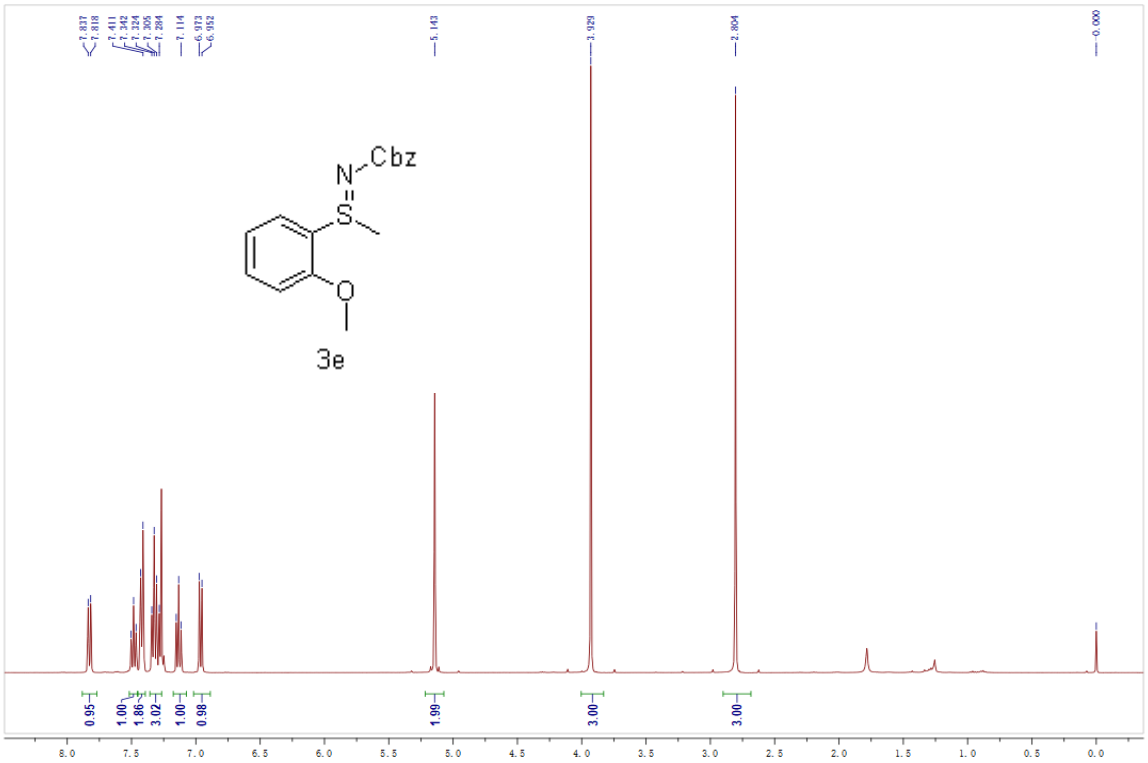
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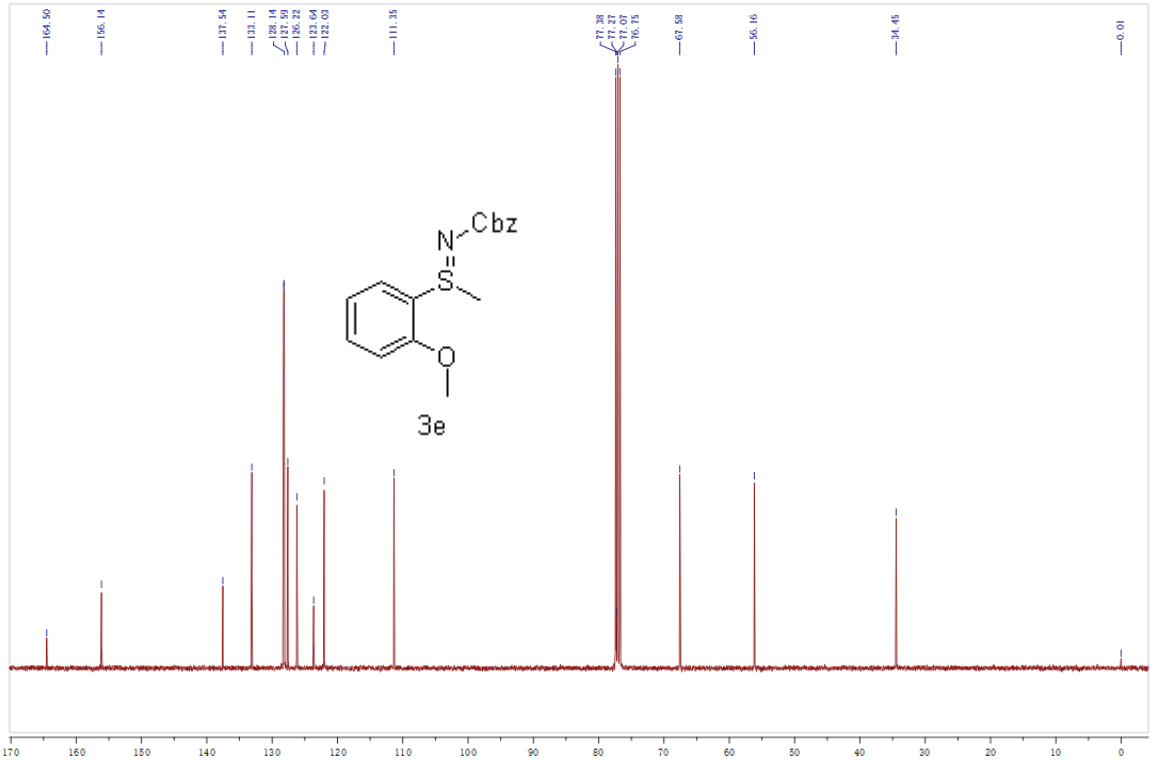
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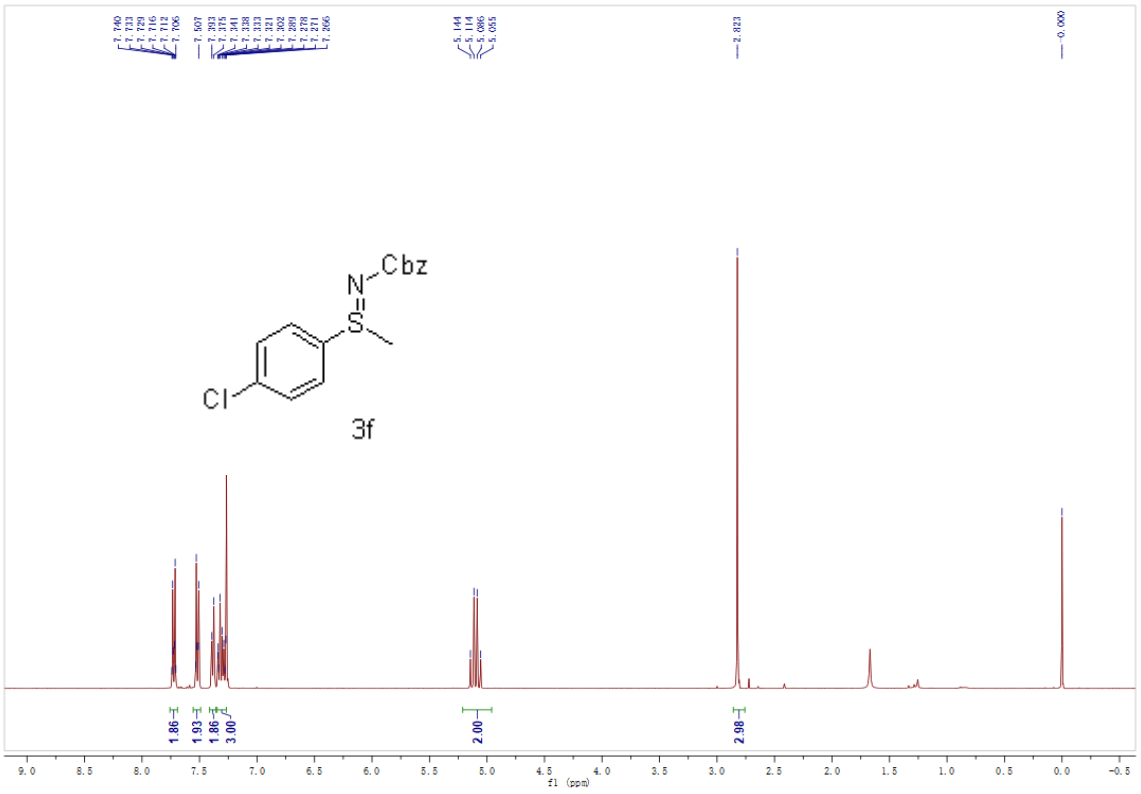
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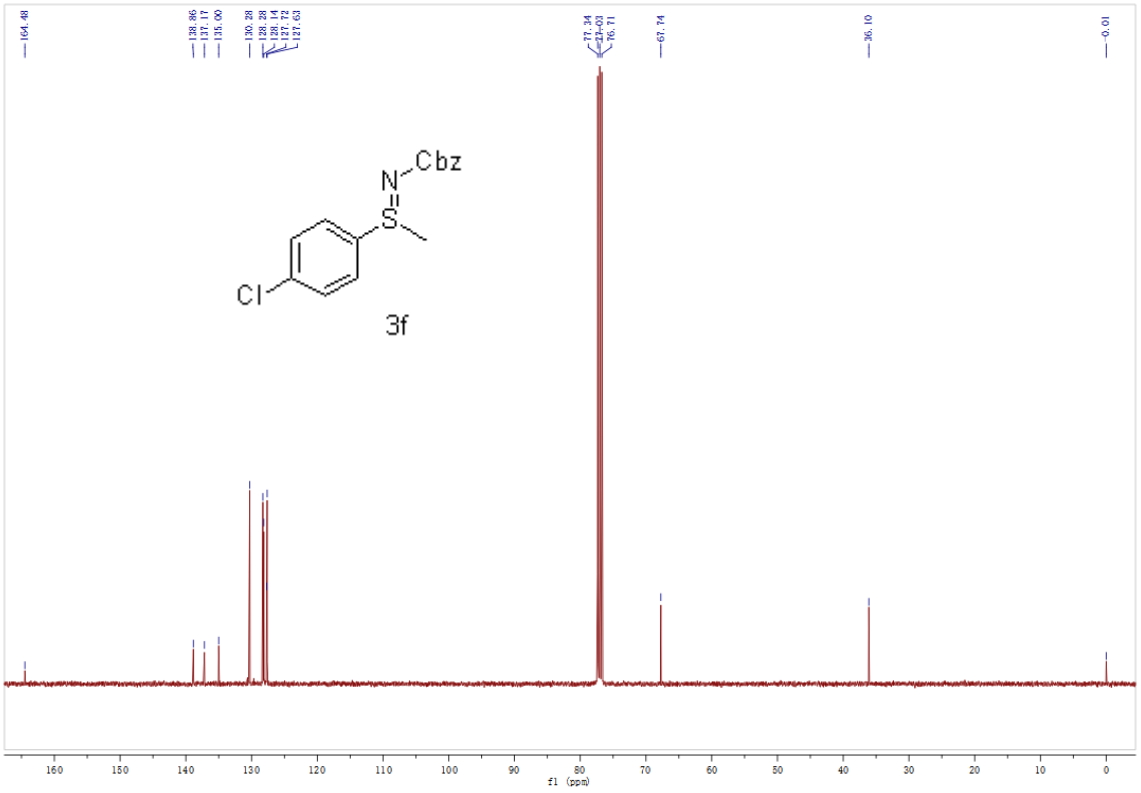
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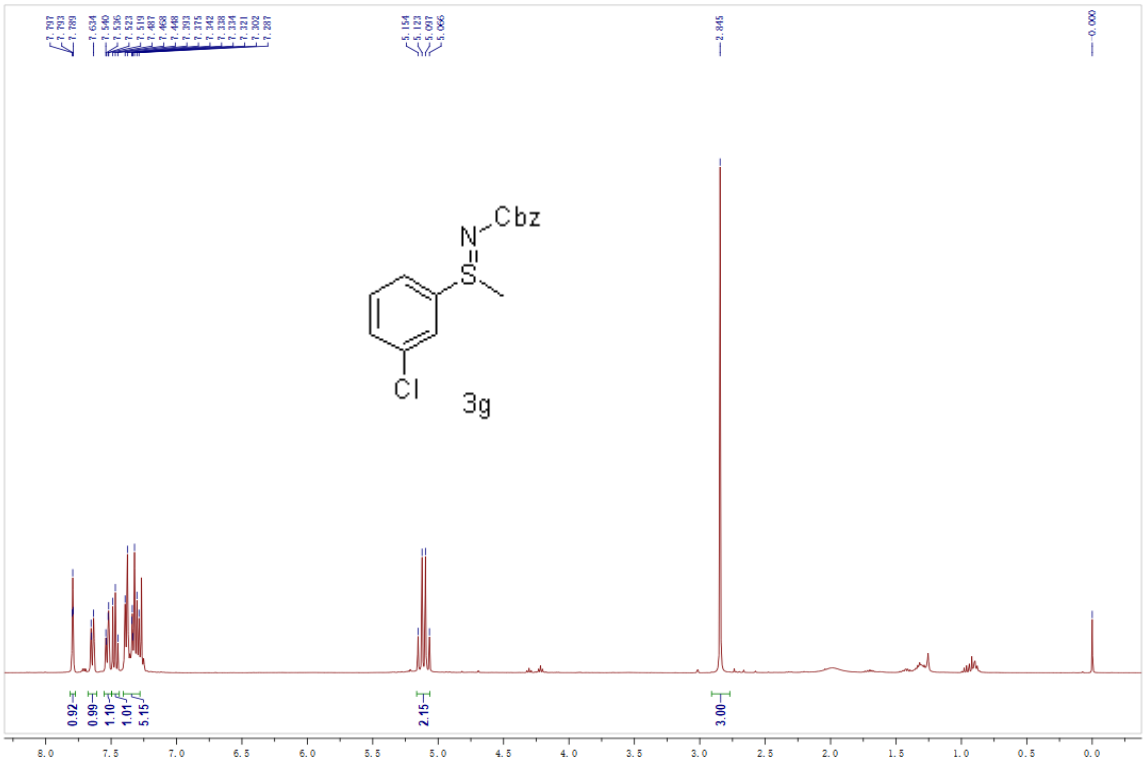
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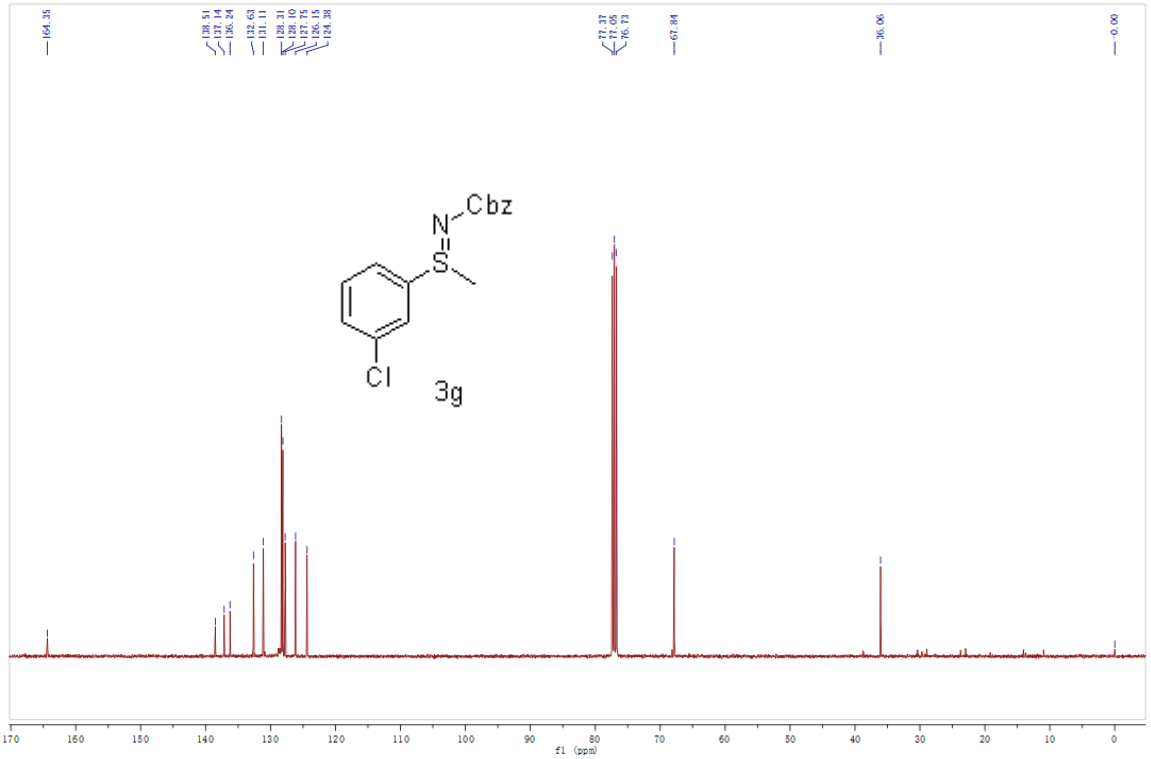
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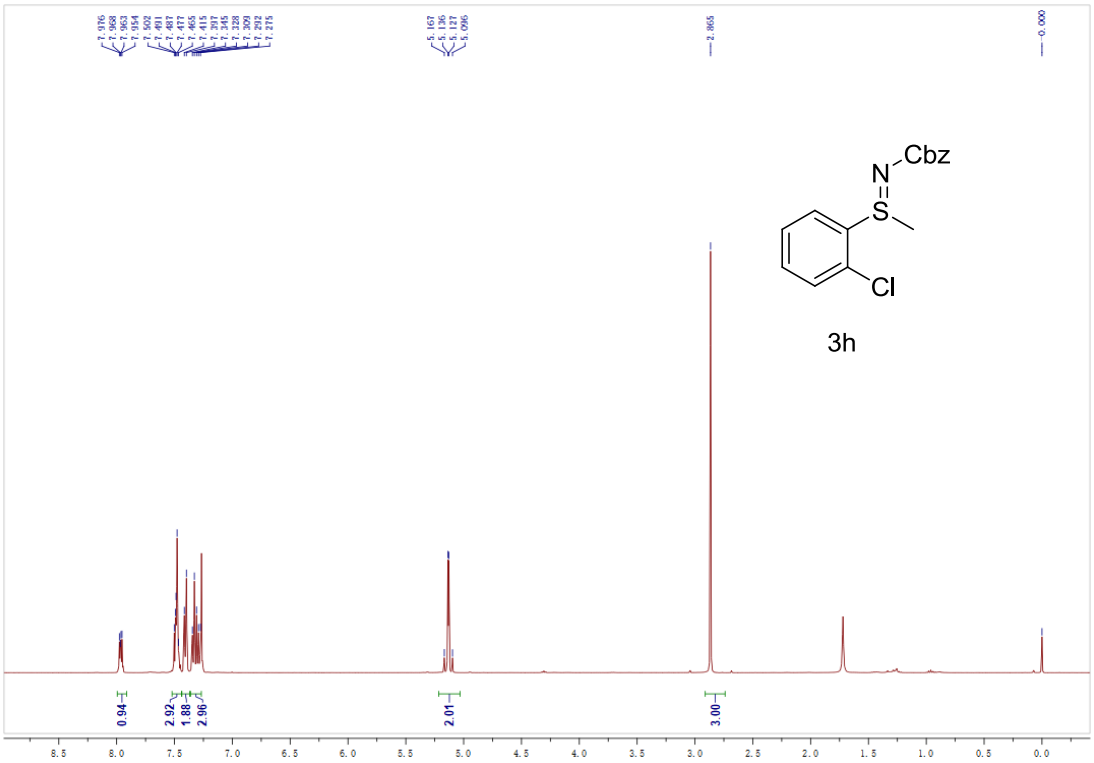
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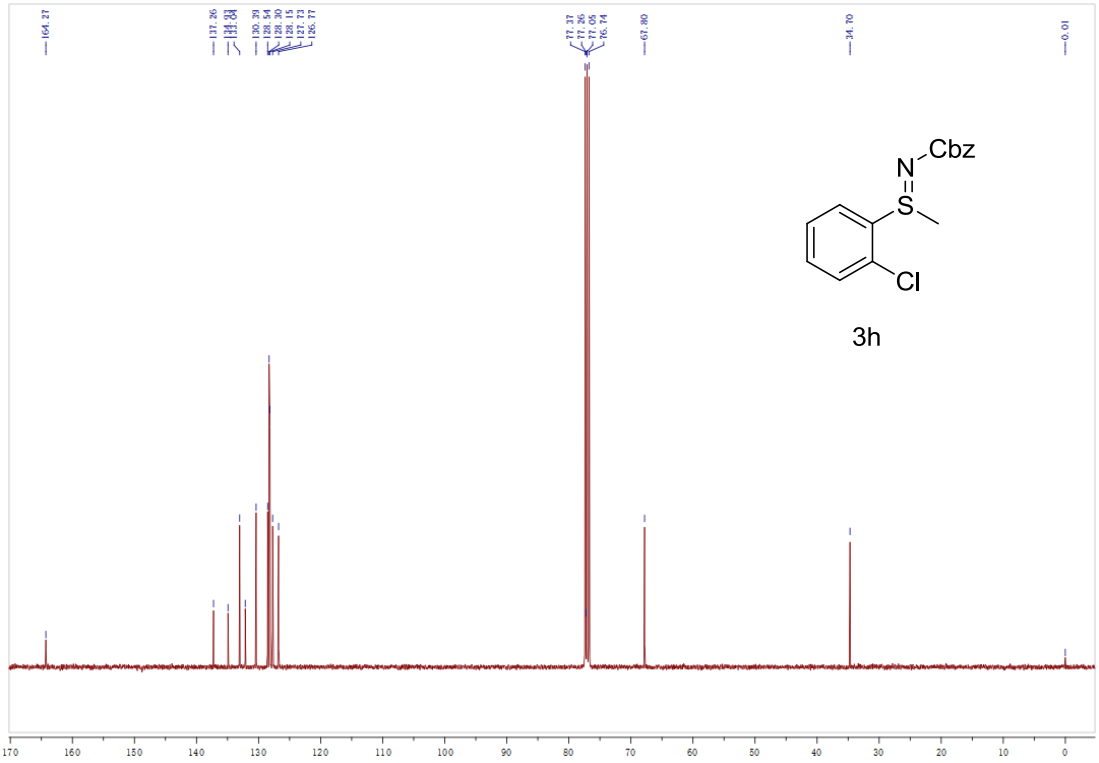
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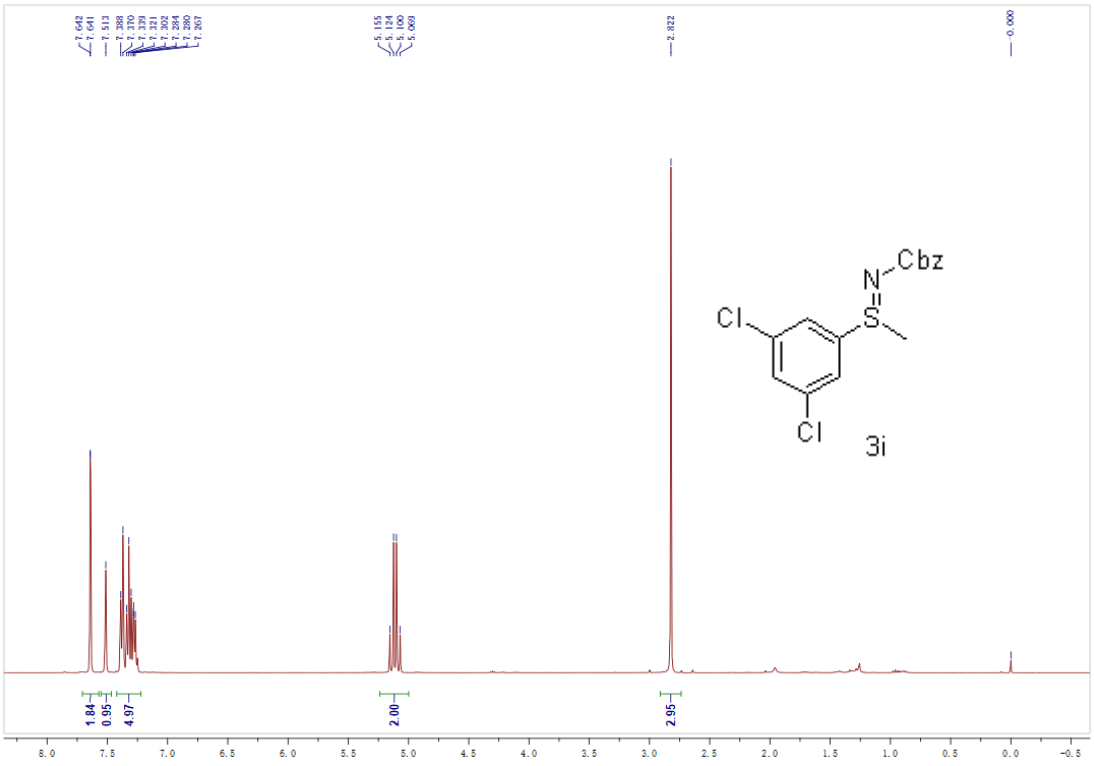
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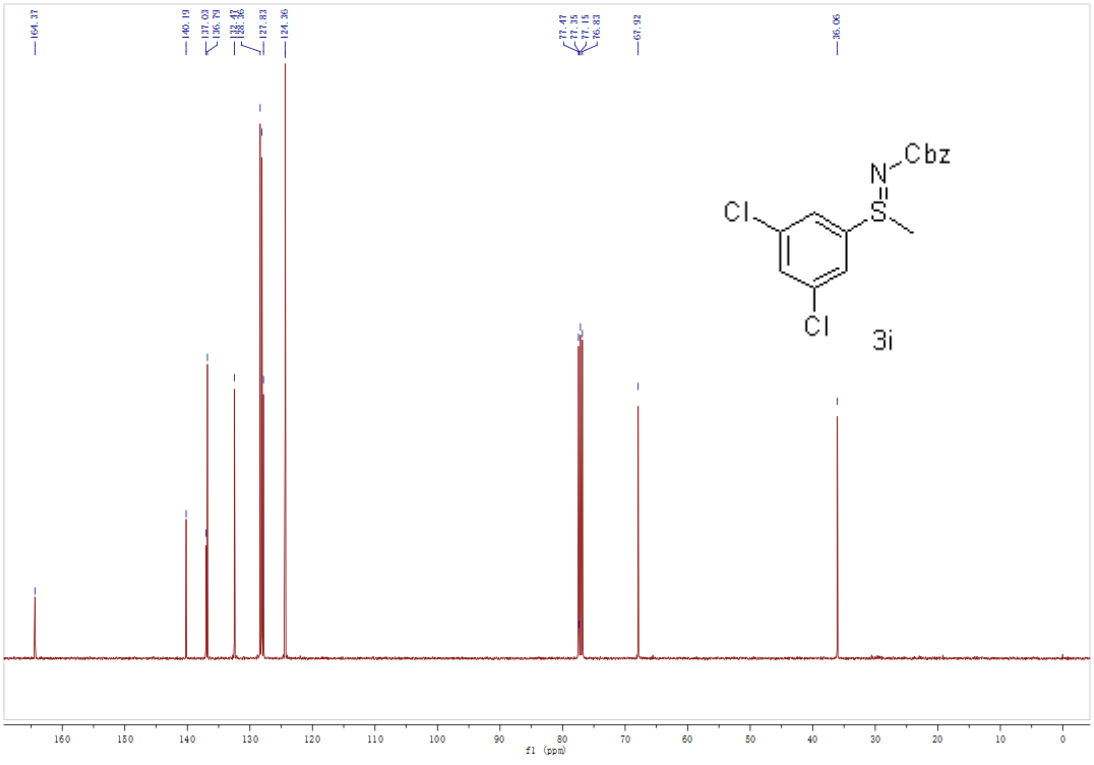
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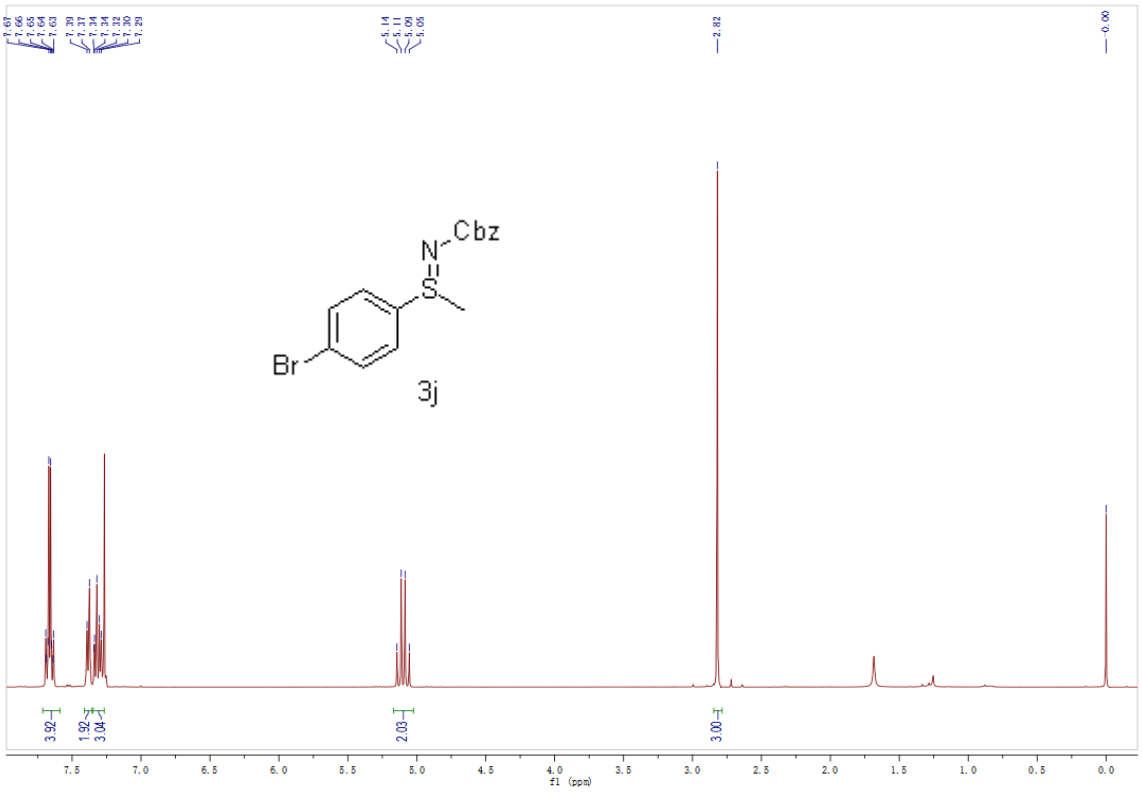
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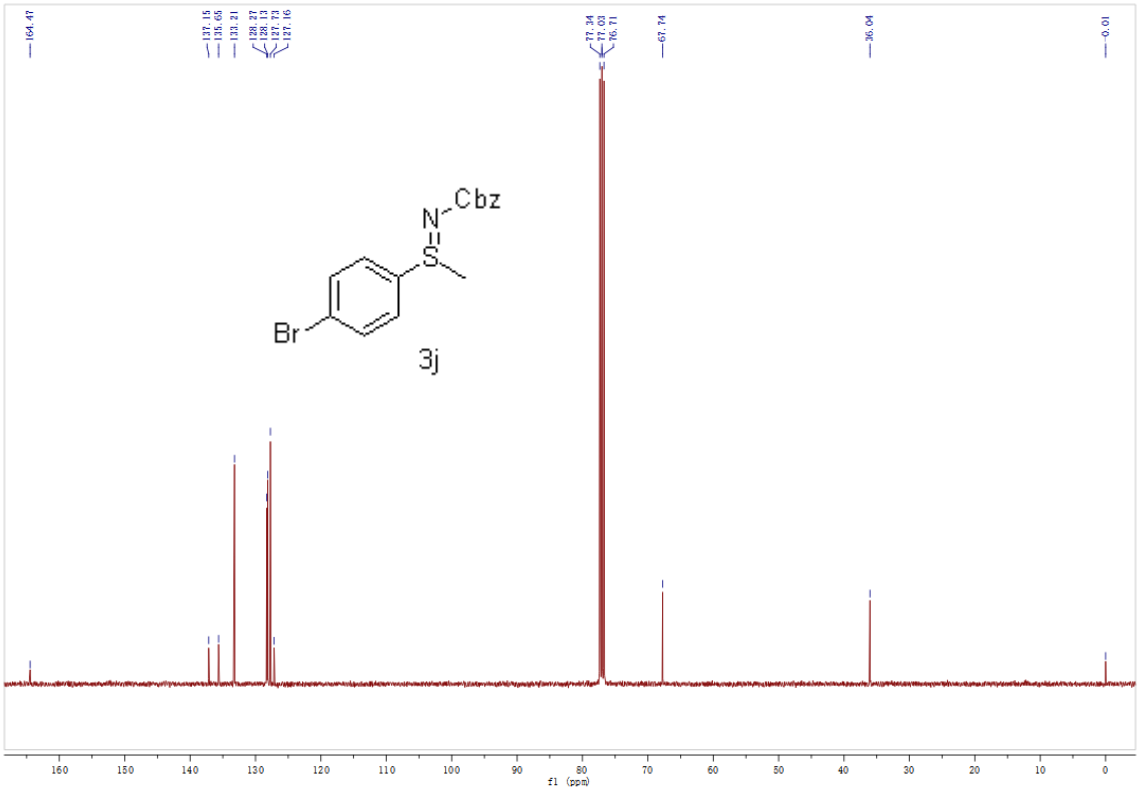
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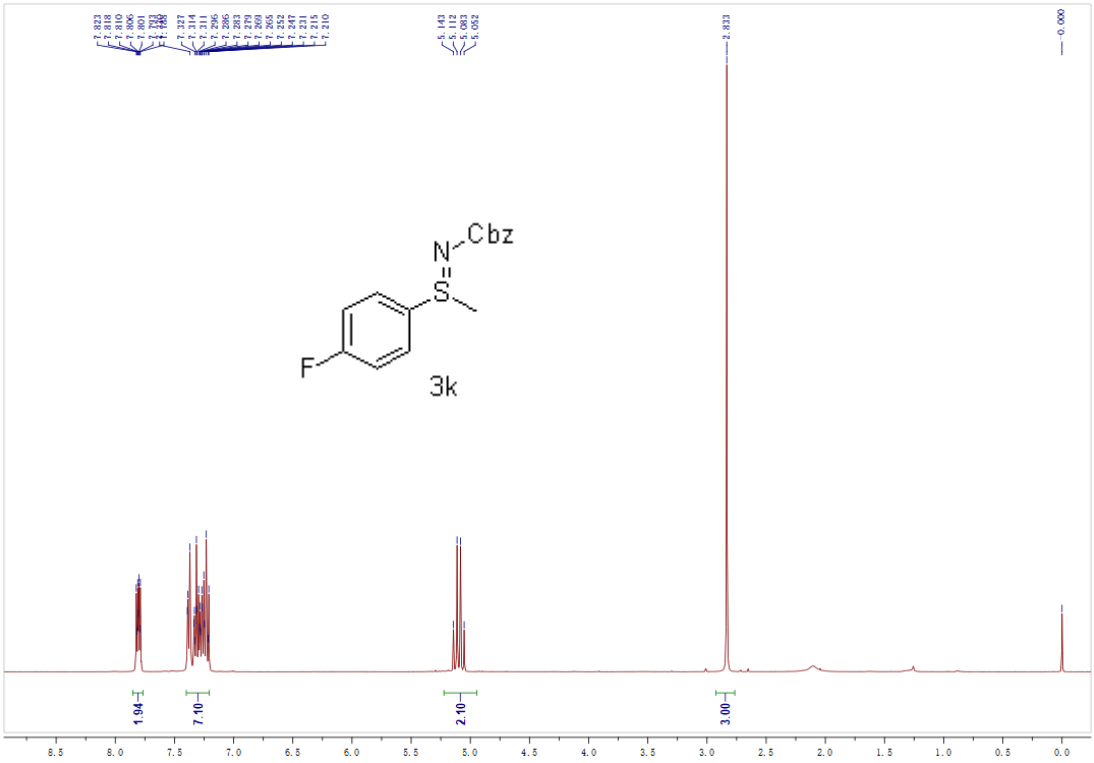
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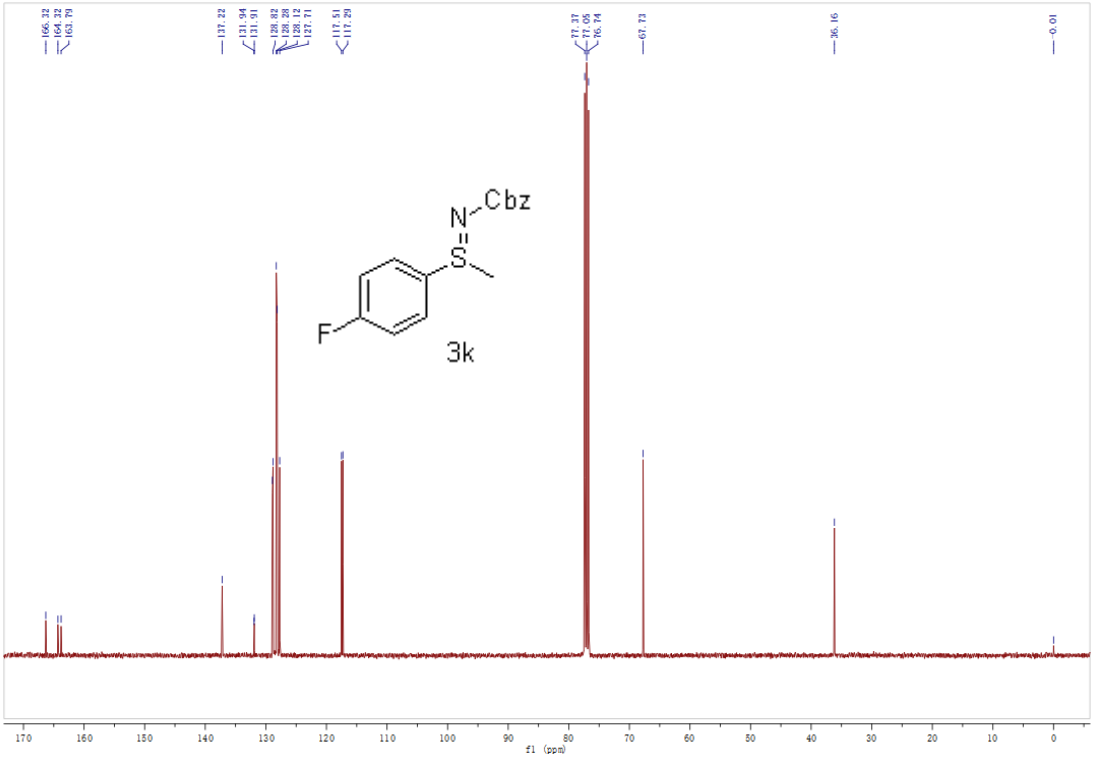
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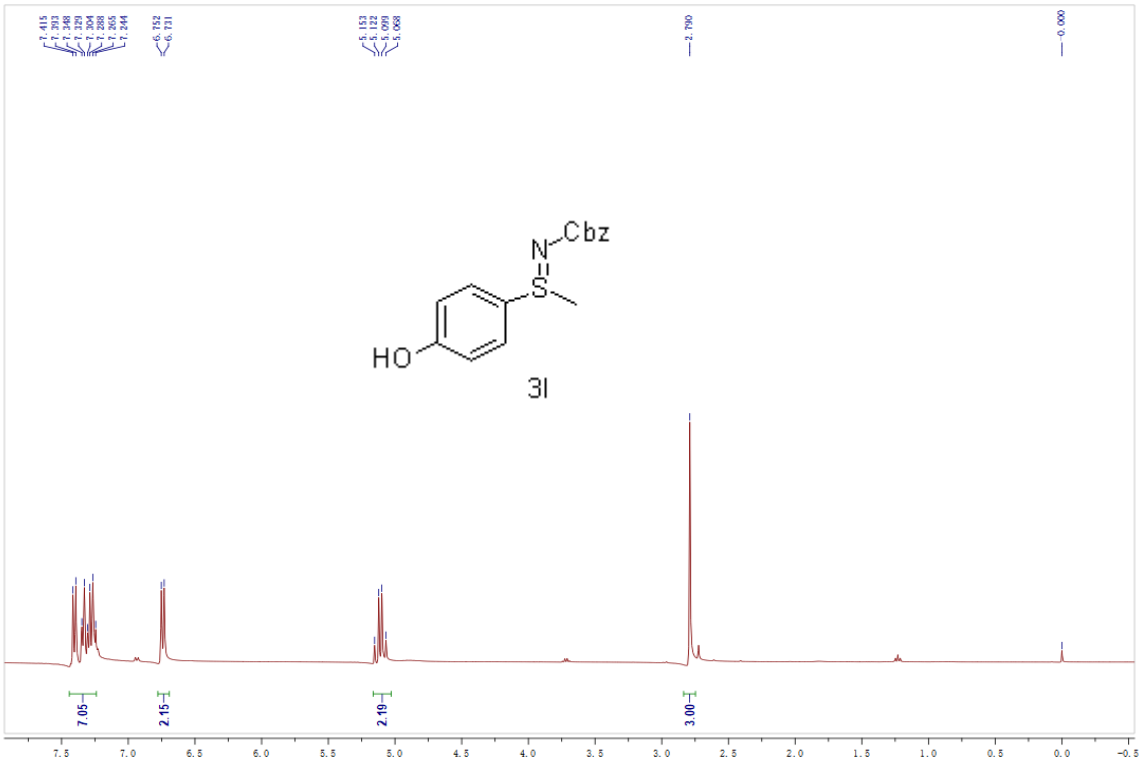
N
S
F
3k
f1 (ppm)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7.348
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7.244
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6.731
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5.122
5.099
5.068
2.790
0.000
Cbz
N
S
HO
3l
7.05
2.15
2.19
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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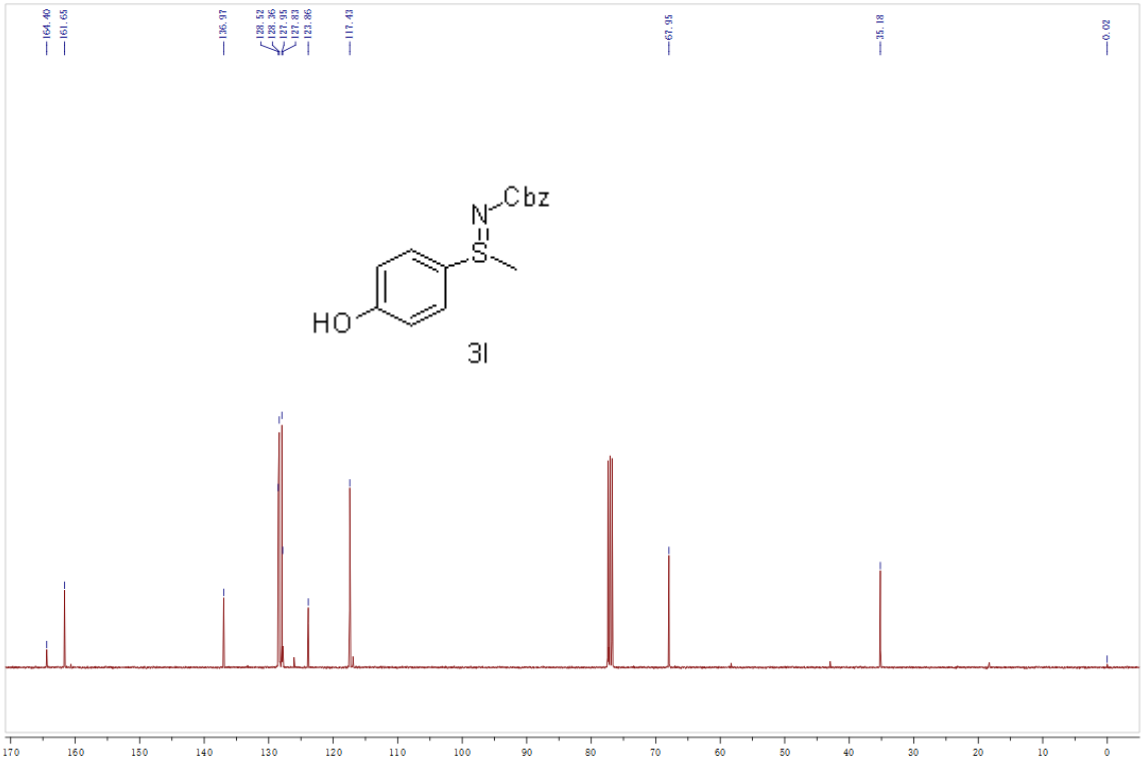
0.0
-0.5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161.65
136.97
128.52
128.36
127.95
127.83
123.86
117.43
67.95
35.18
0.02
Cbz
N
S
HO
3l
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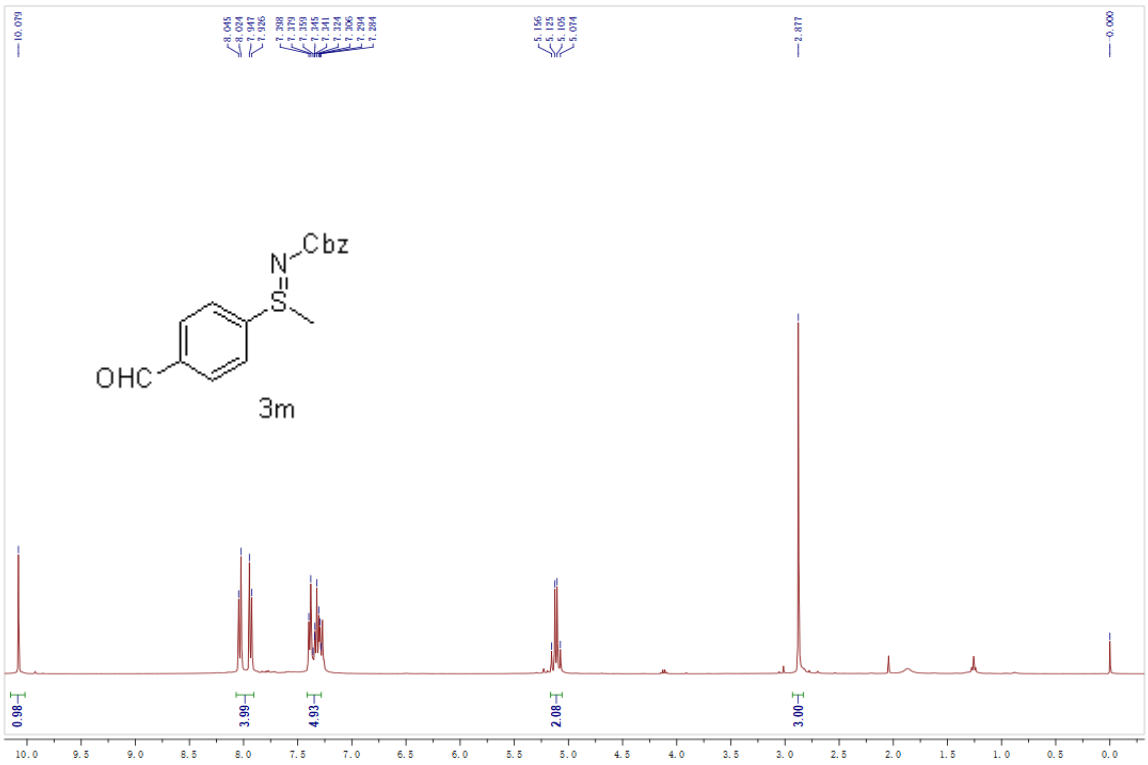
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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8.045
8.024
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7.398
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7.353
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7.341
7.324
7.306
7.294
7.284
5.156
5.125
5.105
5.074
2.877
0.000
Cbz
N
S
OHC
3m
0.98
3.99
4.93
2.08
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
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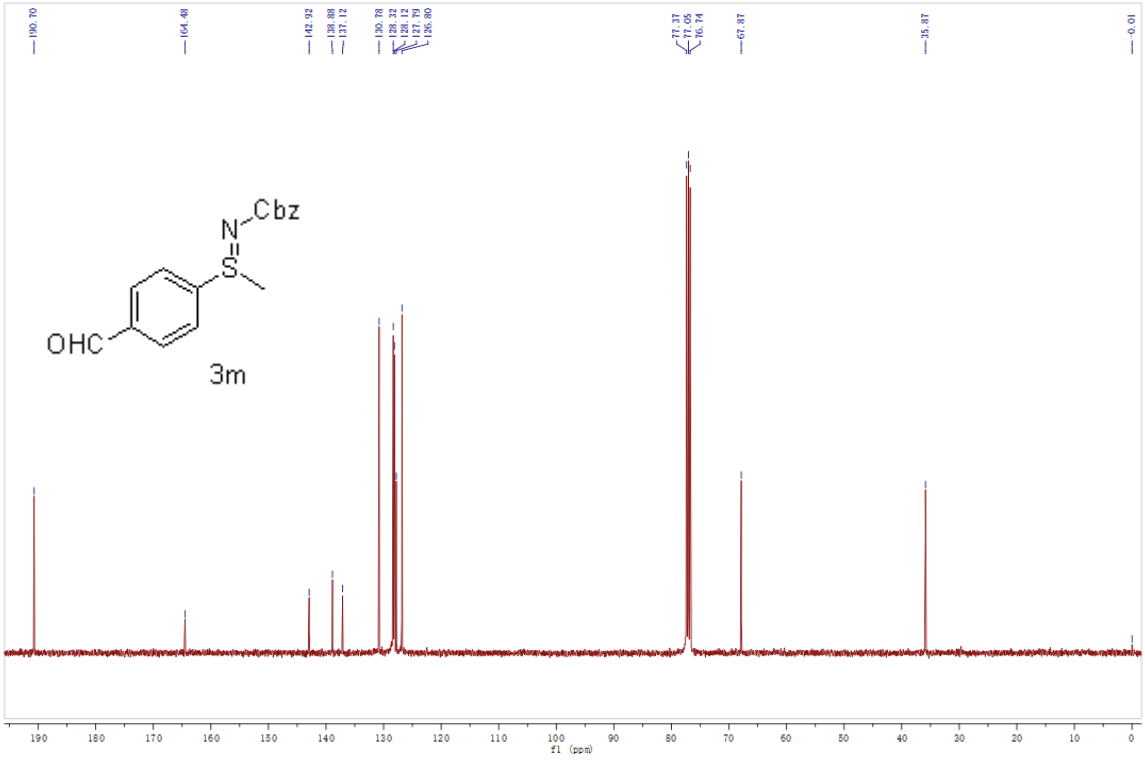
3.0
2.5
2.0
1.5
1.0
0.5
0.0


190.70
164.48
142.92
138.88
137.12
130.78
128.32
128.12
127.79
126.80
77.37
77.05
76.74
67.87
35.87
0.01
Cbz
N
S
OHC
3m
190
180
170
160
150
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130
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110
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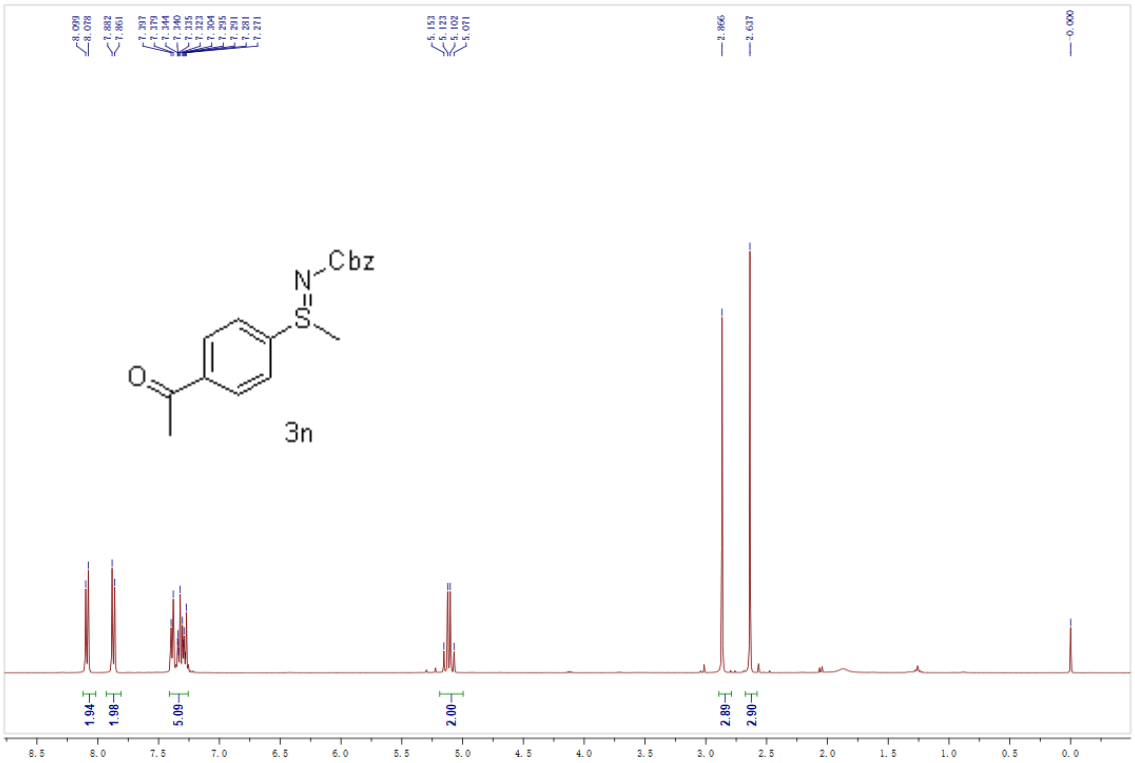
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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S
O
3n
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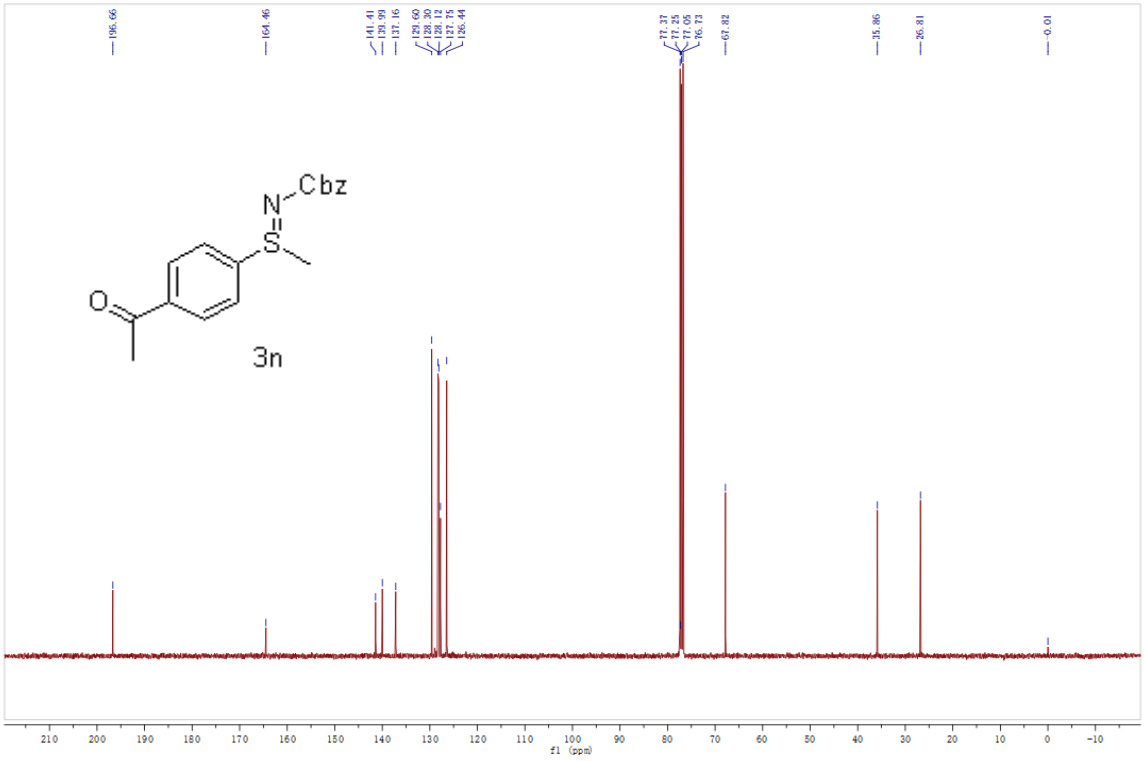
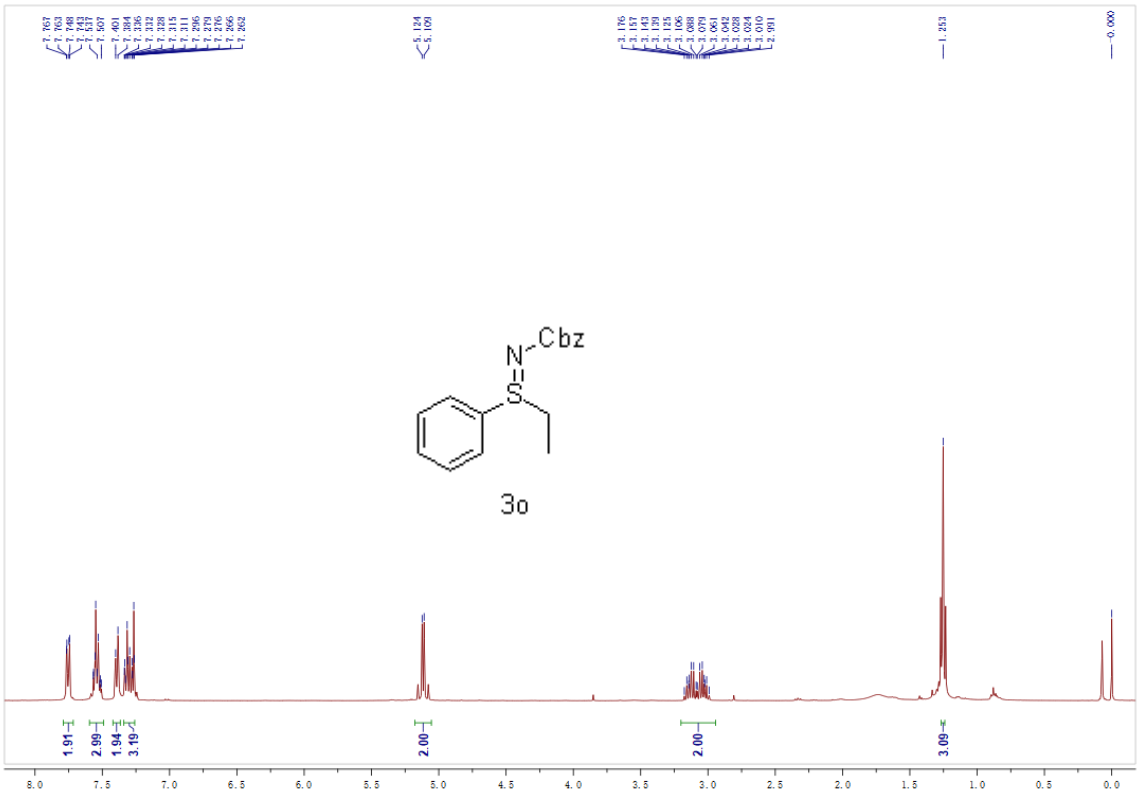
1.98
5.09
2.00
2.89
2.90


Cbz
N
S
O
3n
f1 (ppm)


Cbz
N
S
3o
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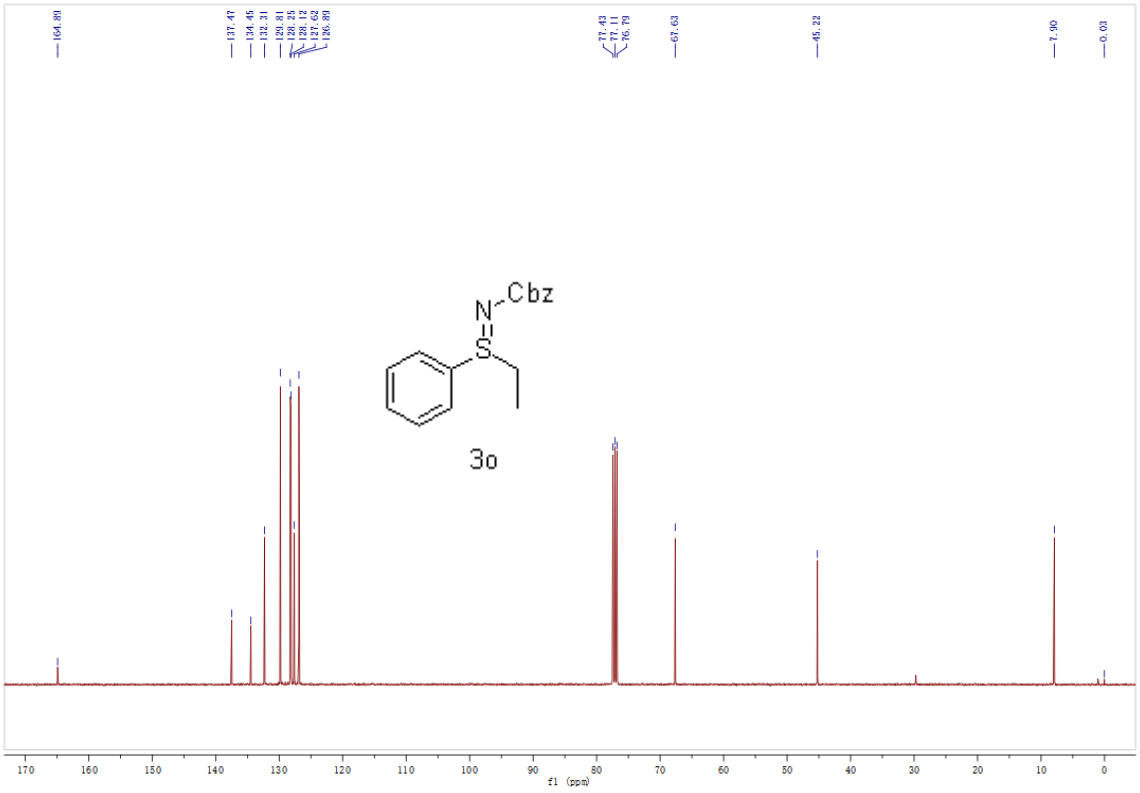
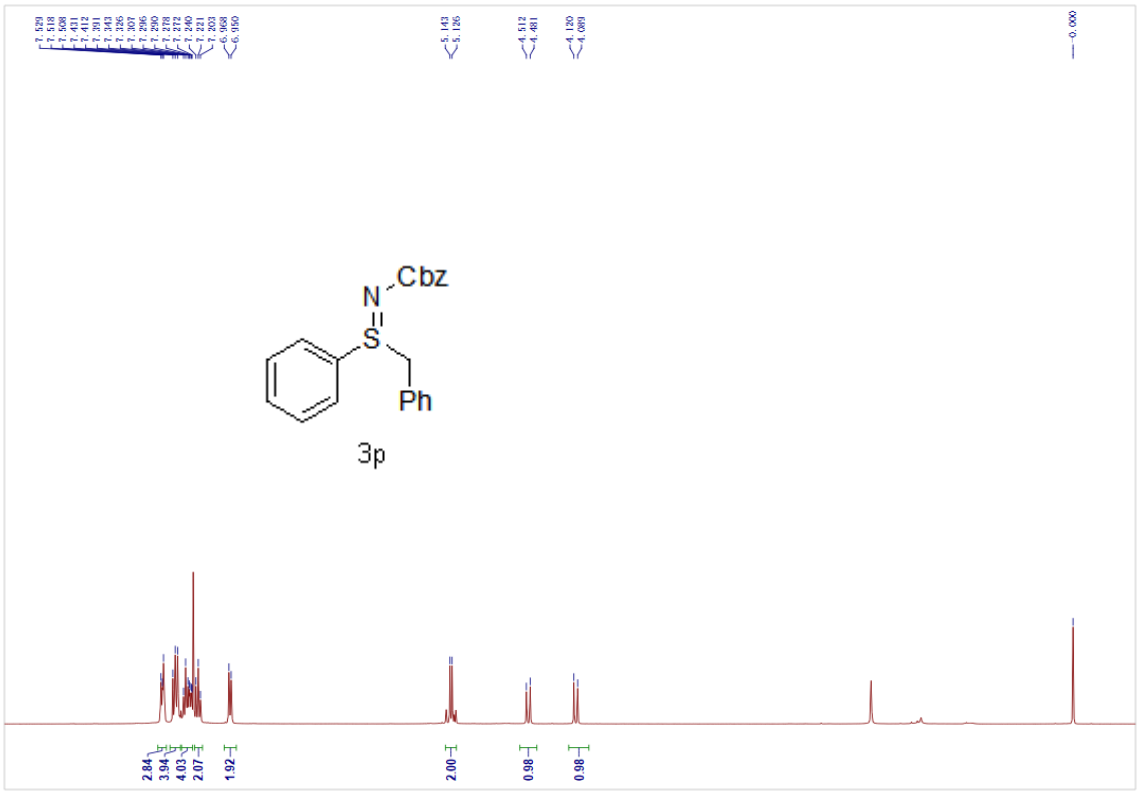
2.99
1.94
3.19
2.00
2.00
3.09


Cbz
N
S
3o
f1 (ppm)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7.508
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7.412
7.391
7.343
7.325
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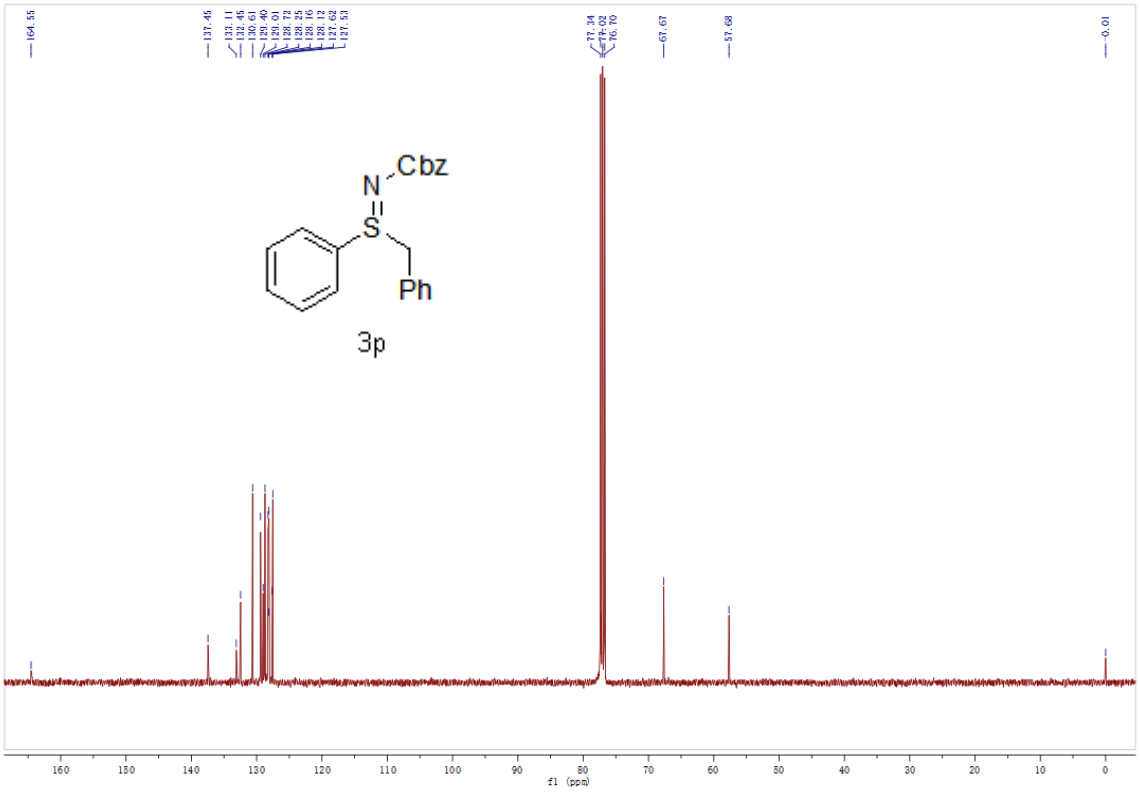
7.295
7.290
7.278
7.272
7.260
7.231
7.203
6.968
6.950
5.143
5.126
4.512
4.481
4.120
4.089
0.000
Cbz
N
S
Ph
3p
2.84
3.94
4.03
2.07
1.92
2.00
0.98
0.98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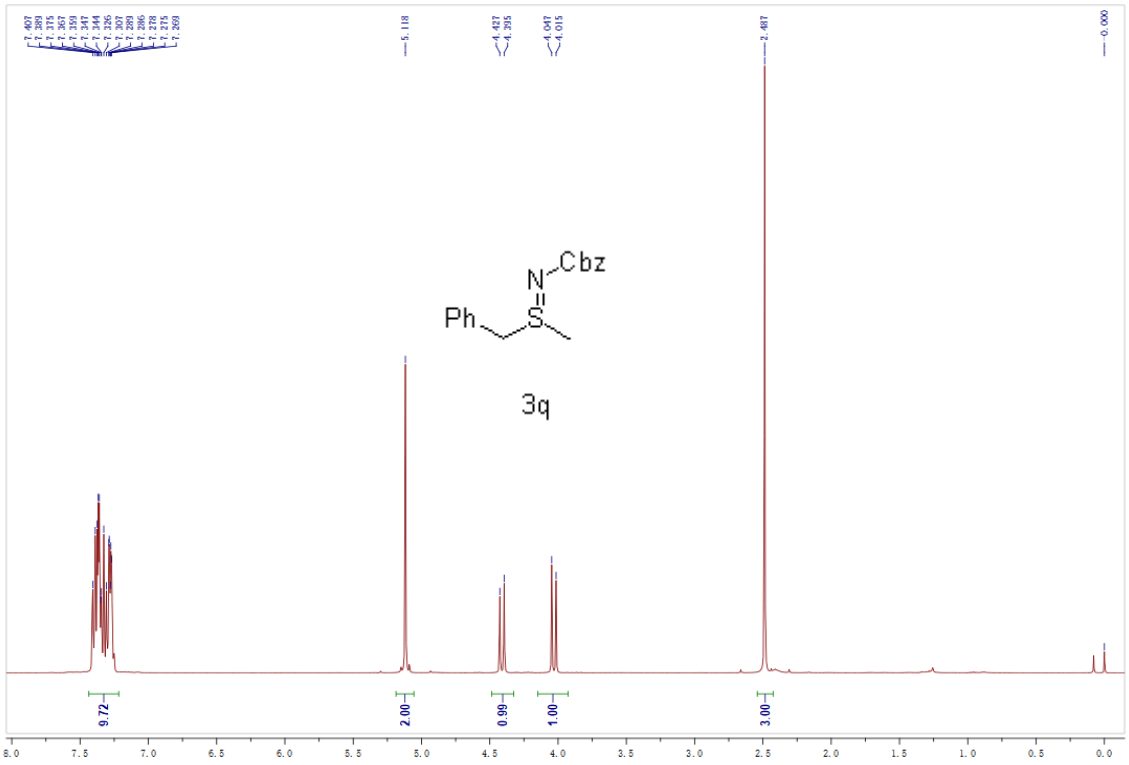
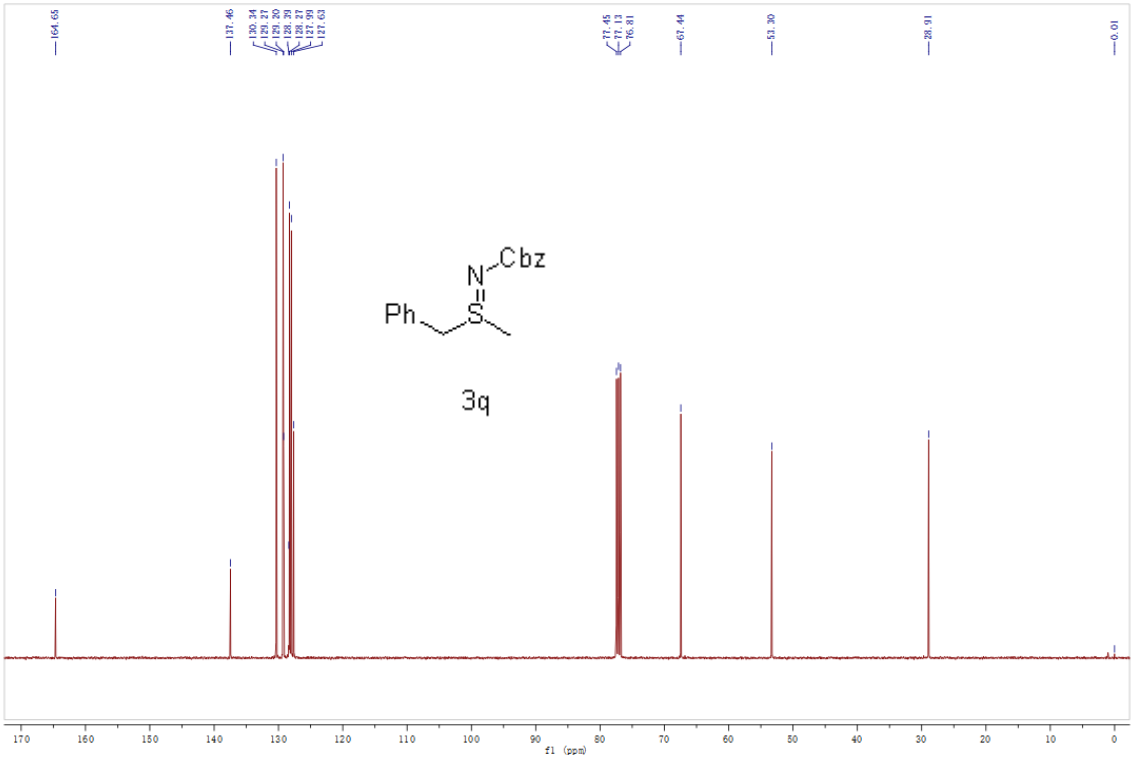
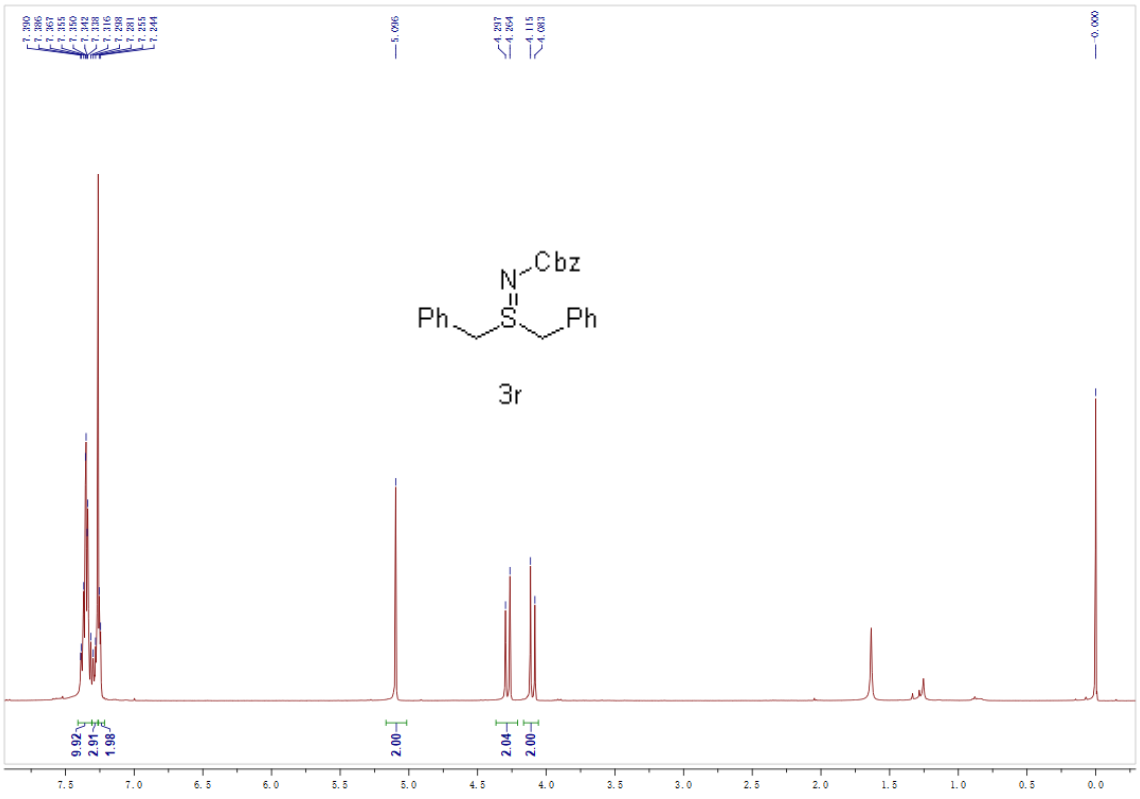
137.45
133.11
132.45
130.61
129.40
129.01
128.72
128.25
128.16
128.12
127.62
127.53
77.34
77.02
76.70
67.67
57.68
0.01
Cbz
N
S
Ph
3p
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cbz
N
S
Ph
3q
9.72
2.00
0.99
1.00
3.00


Cbz
N
S
Ph
3q
f1 (ppm)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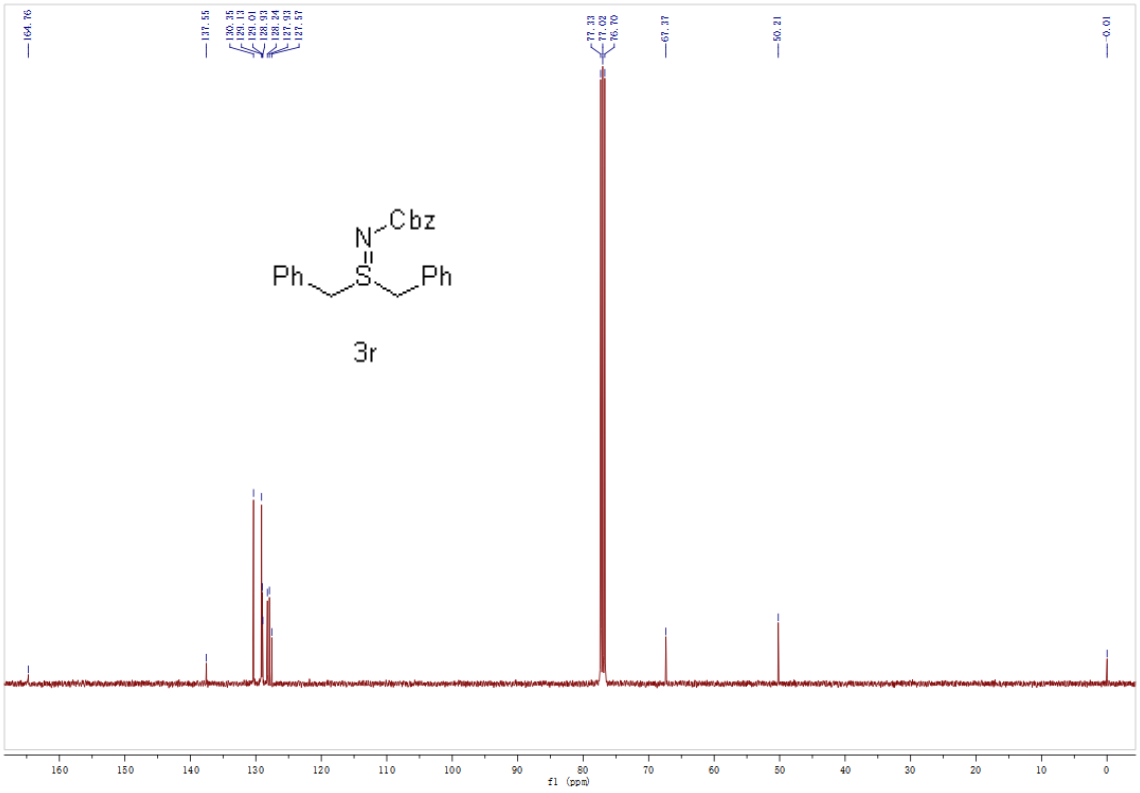
7.350
7.342
7.338
7.316
7.288
7.281
7.255
7.244
5.096
4.257
4.254
4.115
4.083
0.000
N
Cbz
Ph
S
Ph
3r
9.92
2.91
1.98
2.00
2.04
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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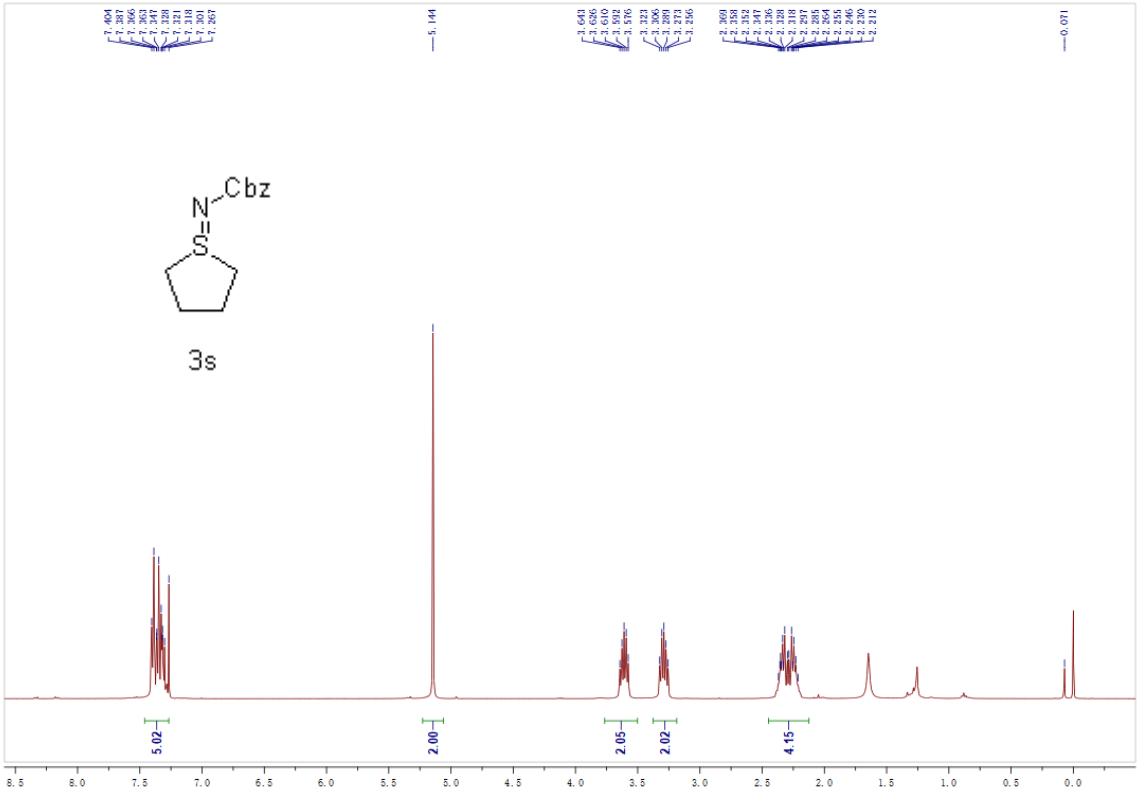
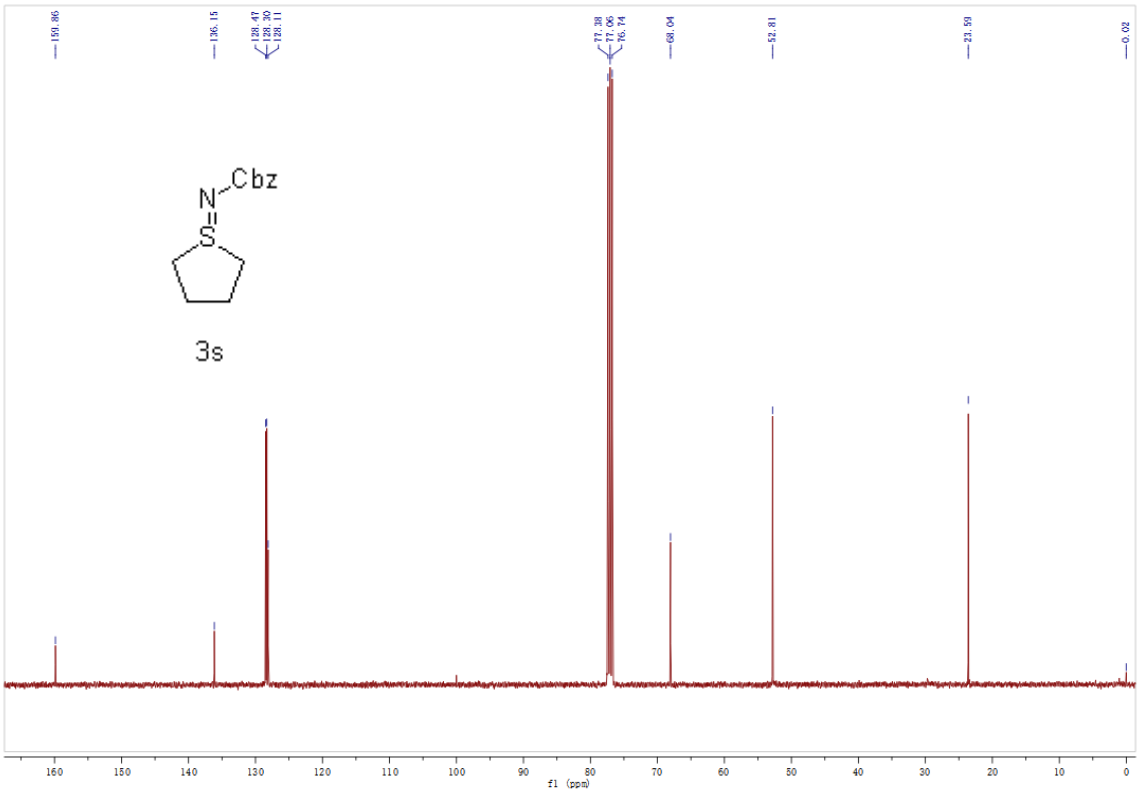
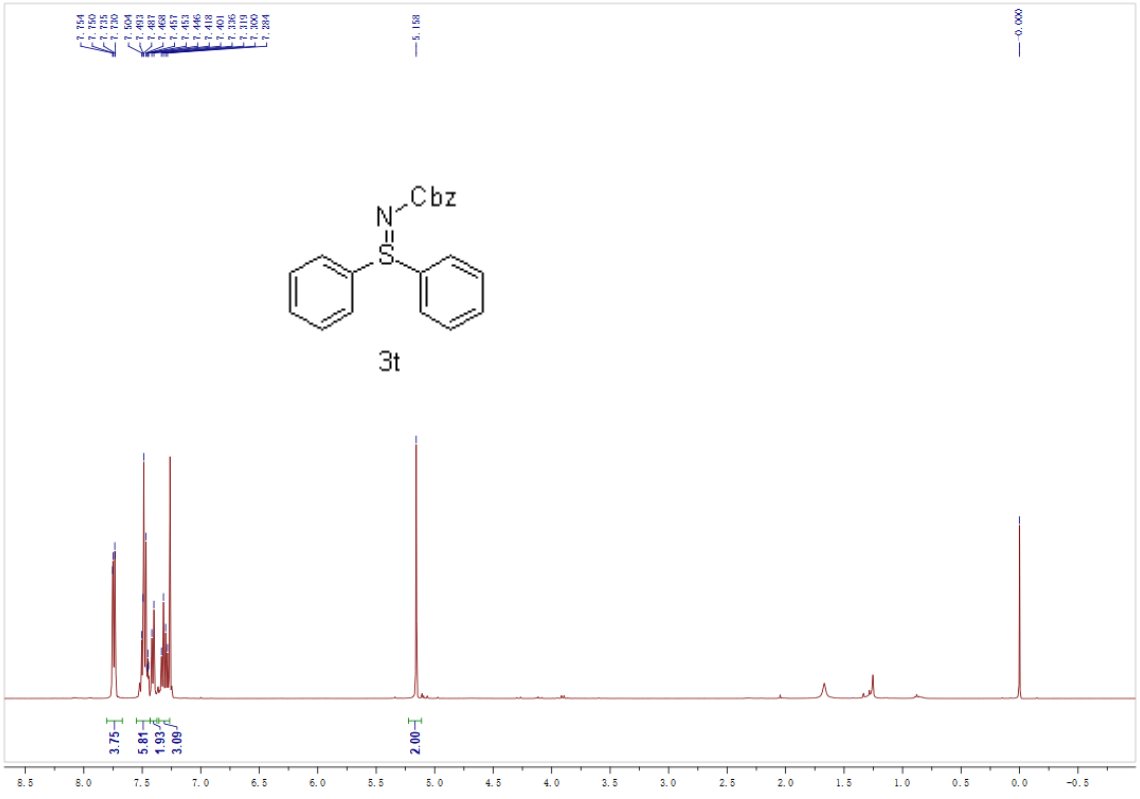
130.35
129.13
129.01
128.93
128.24
127.93
127.87
77.33
77.02
76.70
67.37
50.21
0.01
N
Cbz
Ph
S
Ph
3r
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cbz
N
S
3s
5.02
2.00
2.05
2.02
4.15


Cbz
N
S
3s
f1 (ppm)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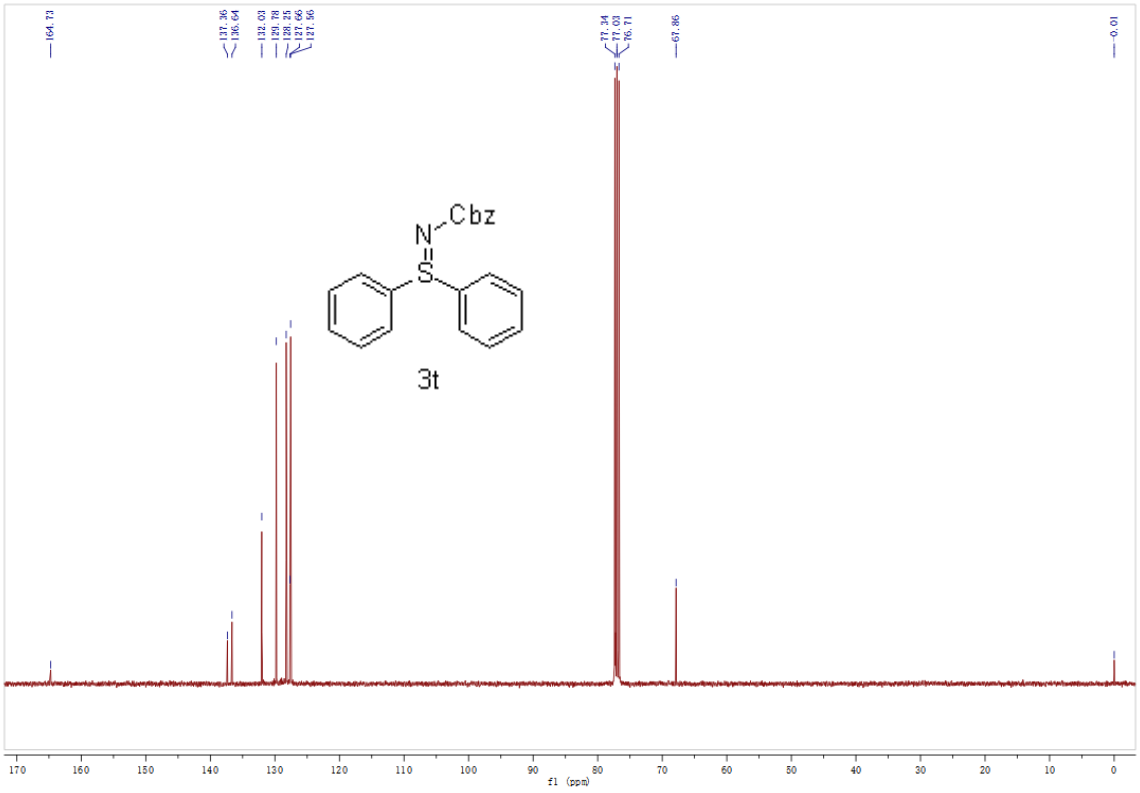
7.730
7.504
7.493
7.487
7.468
7.457
7.453
7.446
7.418
7.401
7.335
7.310
7.300
7.284
5.158
0.000
Cbz
N
S
3t
3.75
5.81
1.93
3.09
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


164.73
137.36
136.64
132.03
129.78
128.25
127.86
127.56
77.34
77.03
76.71
67.86
0.01
Cbz
N
S
3t
170
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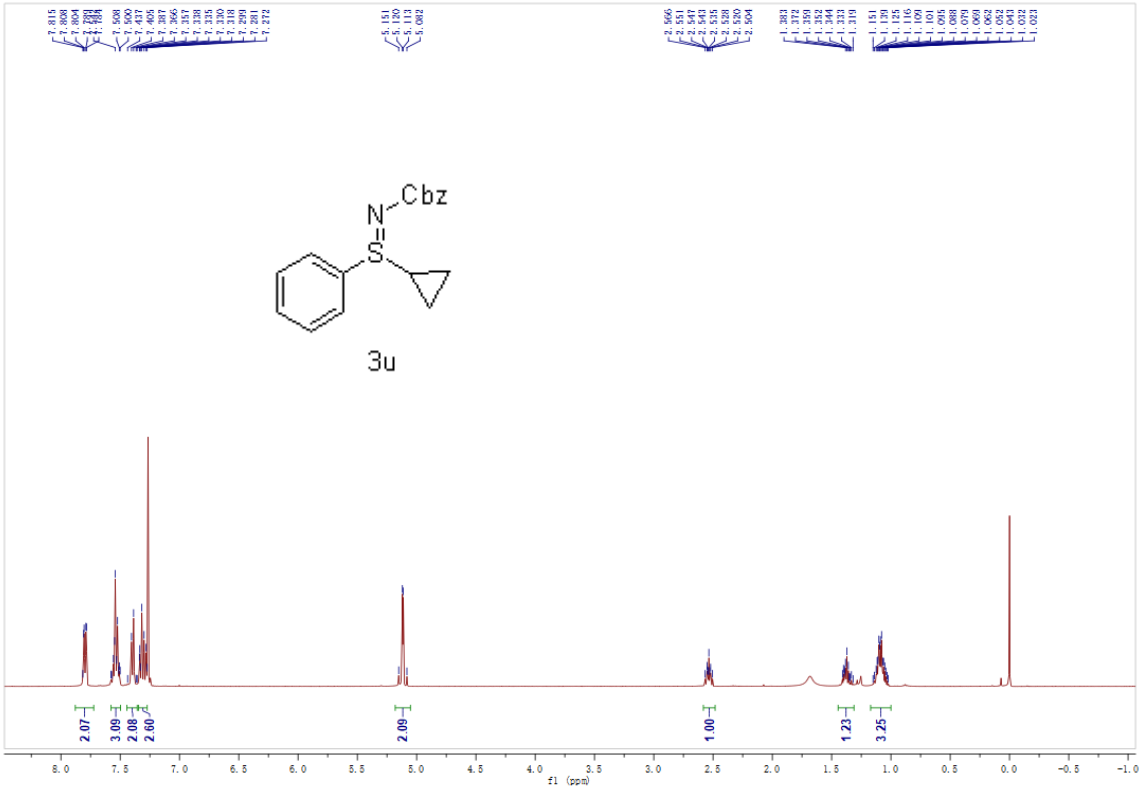
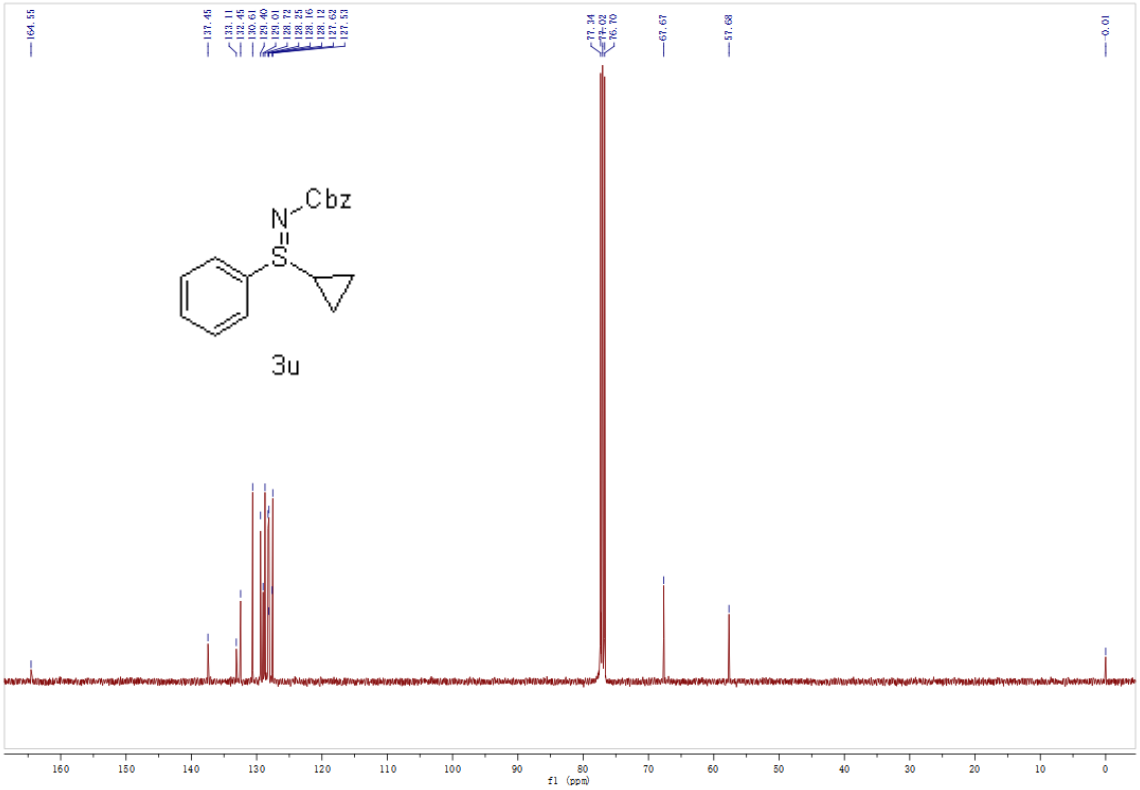
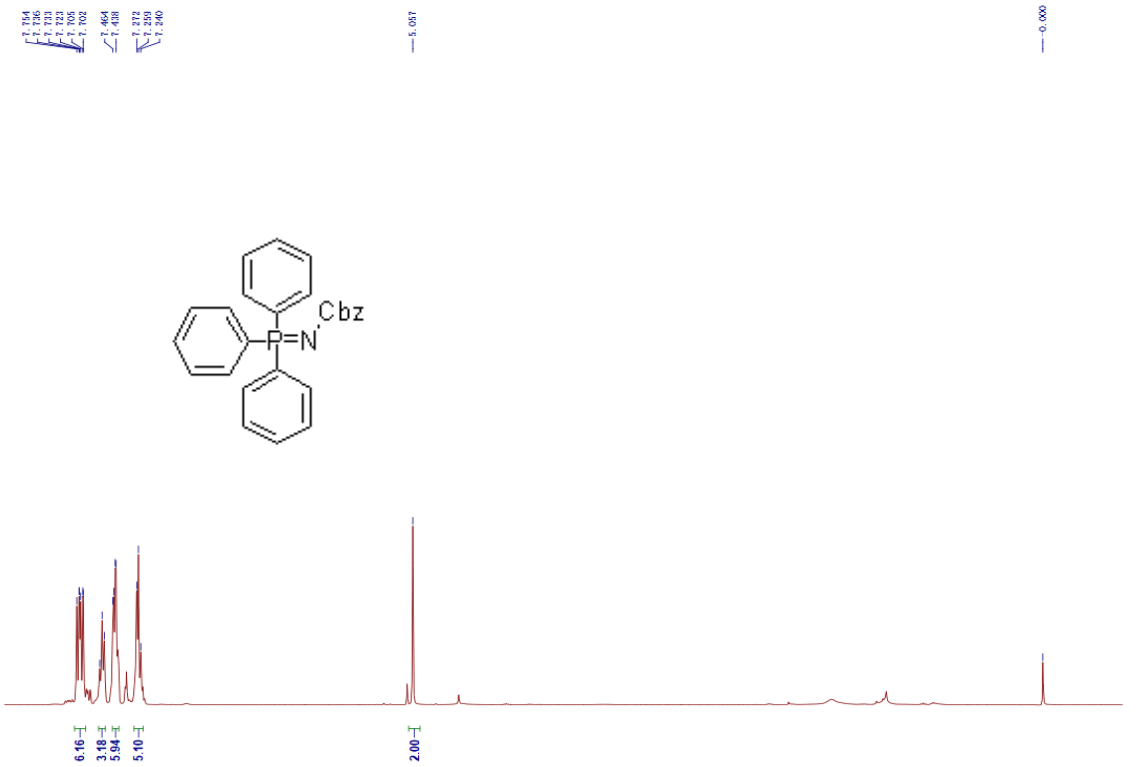
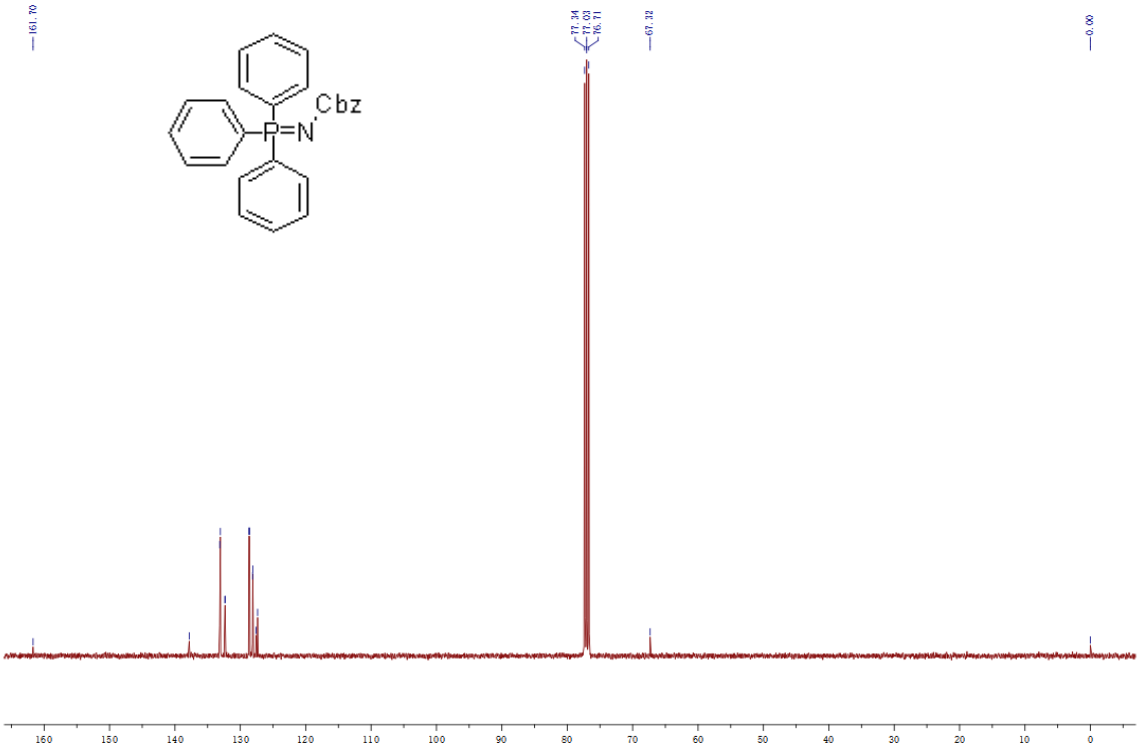
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cbz
N
S
3u
2.07
3.09
2.08
2.60
2.09
1.00
1.23
3.25
f1 (ppm)

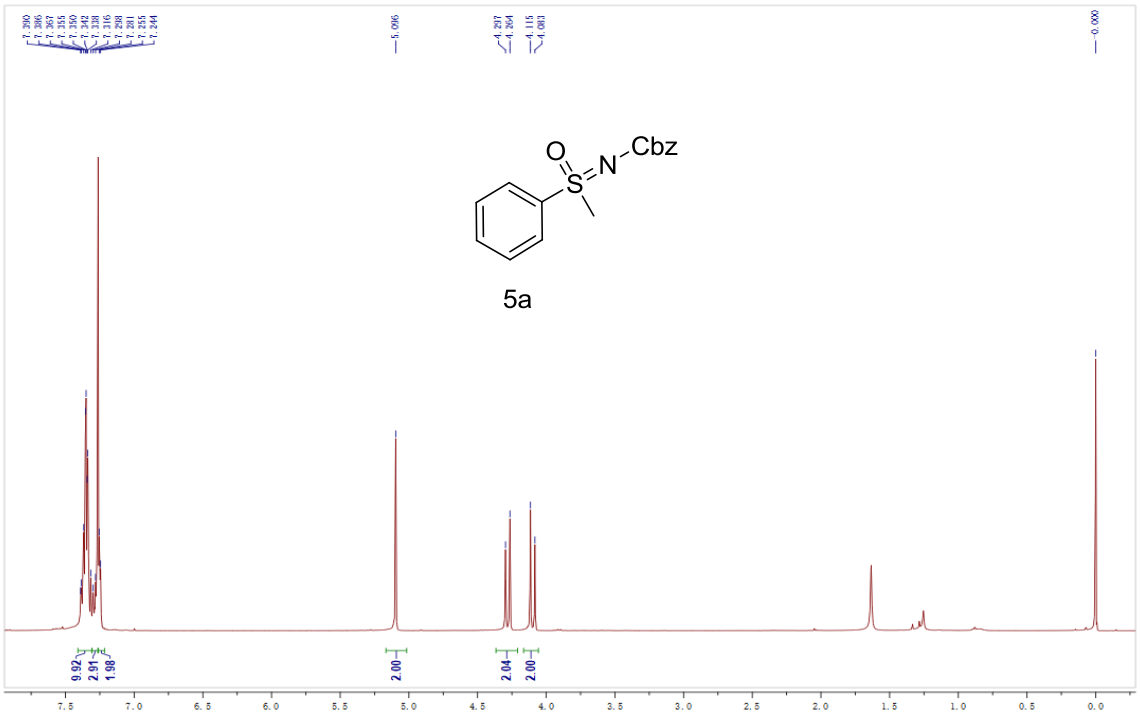

Cbz
N
S
3u
f1 (ppm)

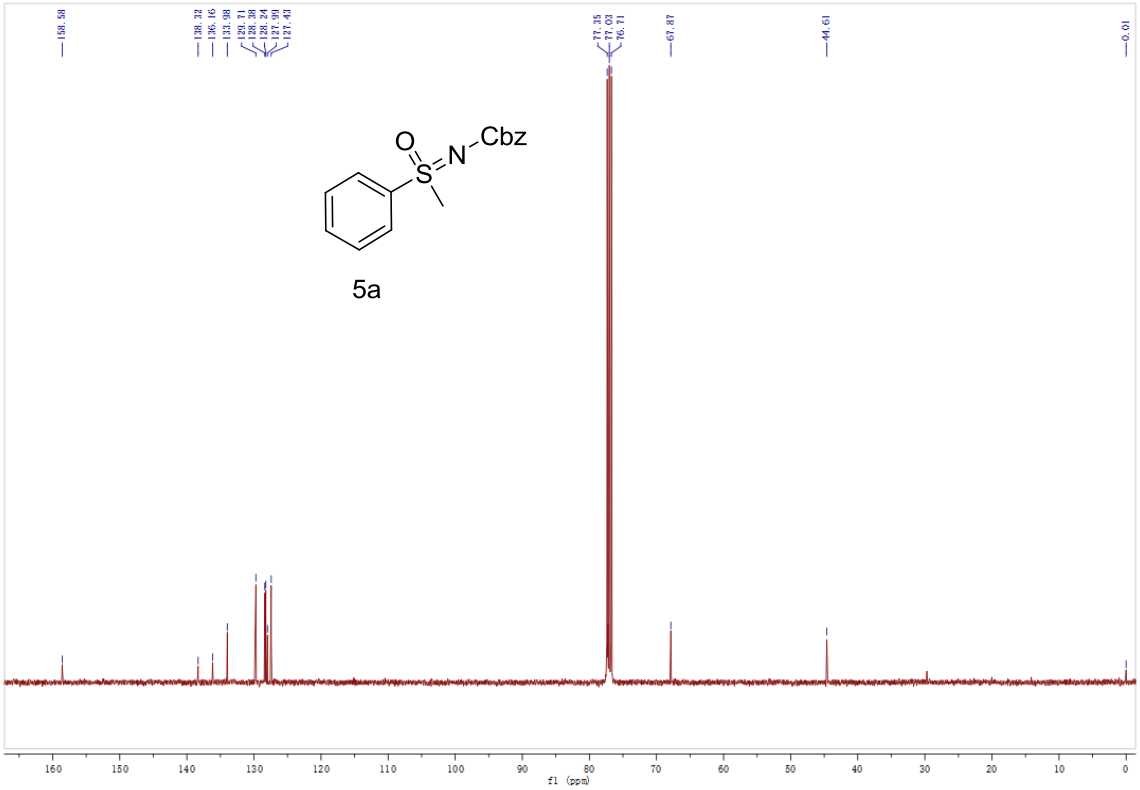
^{1}H and ^{13}C NMR spectra of 4

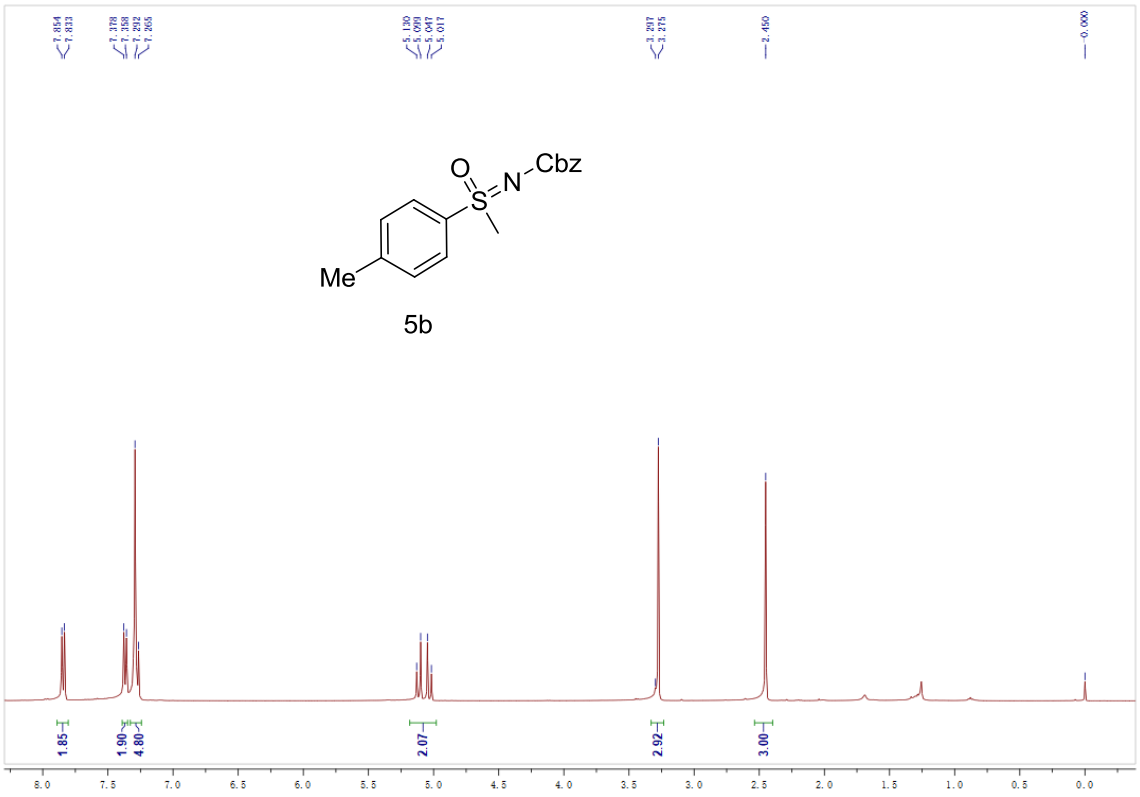




^{1}H and ^{13}C NMR spectra of 5



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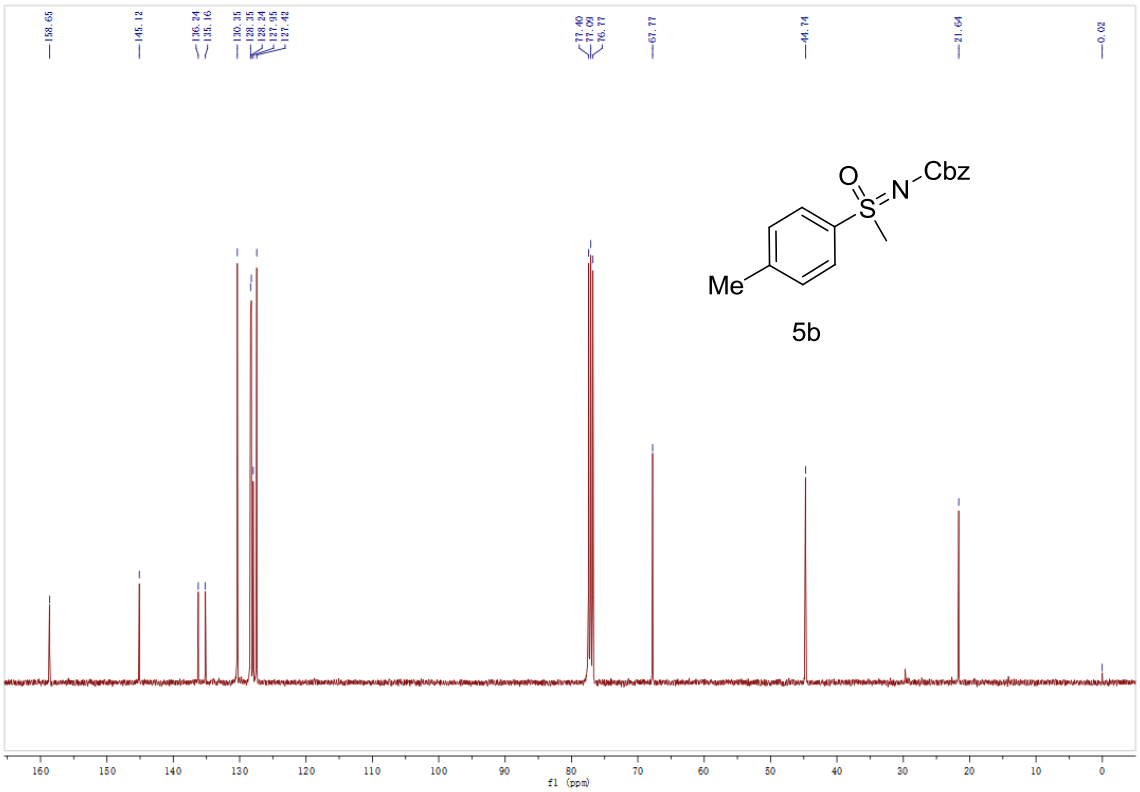
7.292
7.266
5.130
5.099
5.047
5.017
3.297
3.275
2.450
0.000
O
S
N
Cbz
Me
5b
1.85
1.90
4.80
2.07
2.92
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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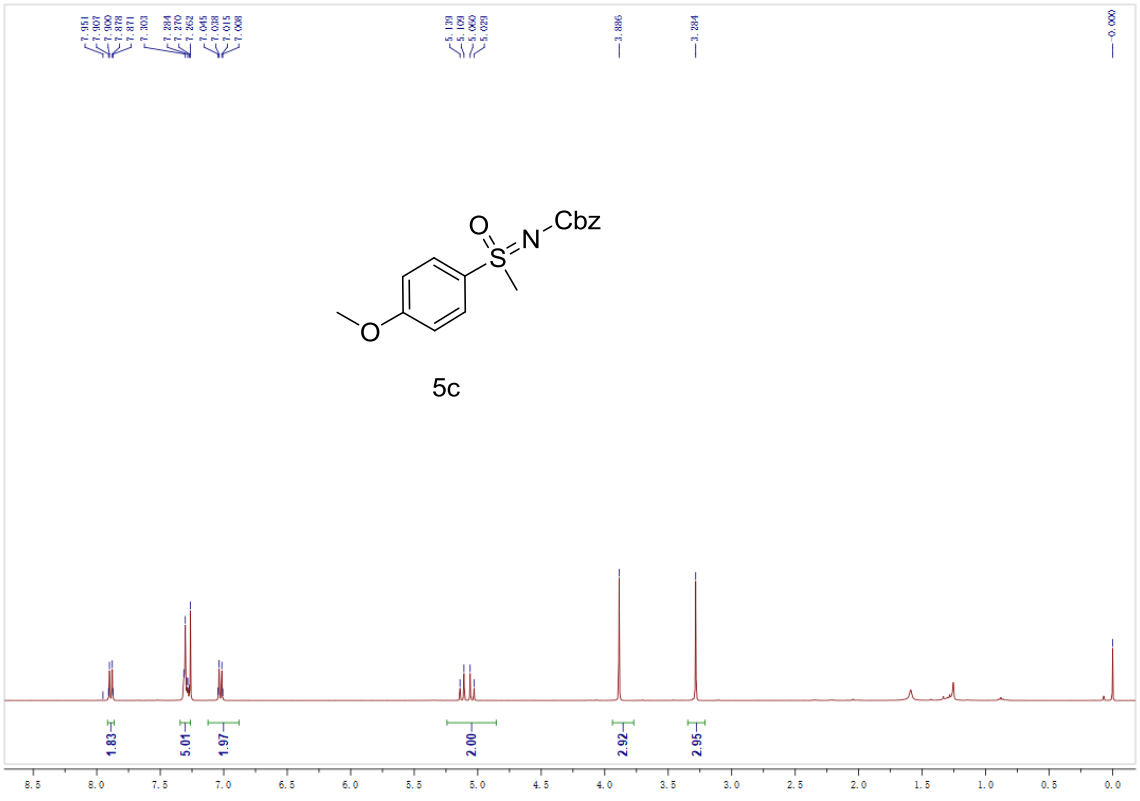
145.12
136.24
135.16
130.35
128.35
128.24
127.93
127.91
121.42
77.40
77.09
76.77
67.77
44.74
21.64
0.02
O
S
N
Cbz
Me
5b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.270
7.262
7.045
7.038
7.015
7.008
5.139
5.109
5.060
5.029
3.886
3.284
0.000
O
S
N
Cbz
O
1.83
5.01
1.97
2.00
2.92
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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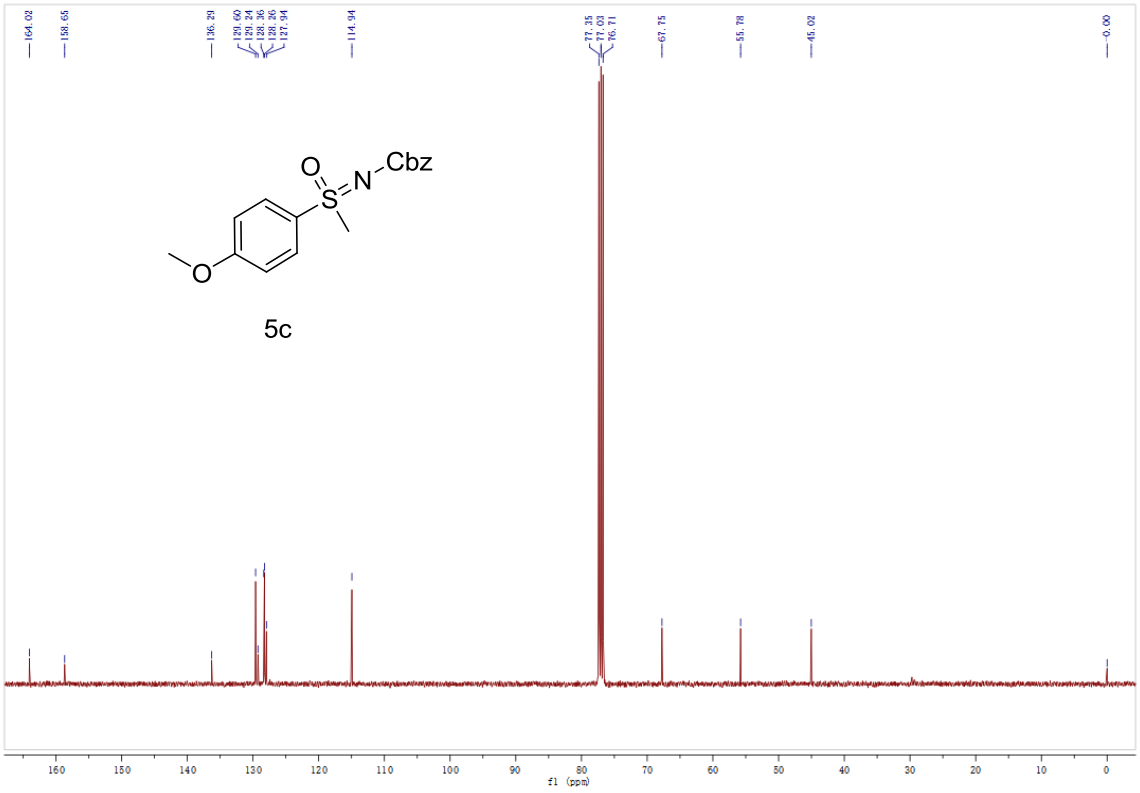
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

5c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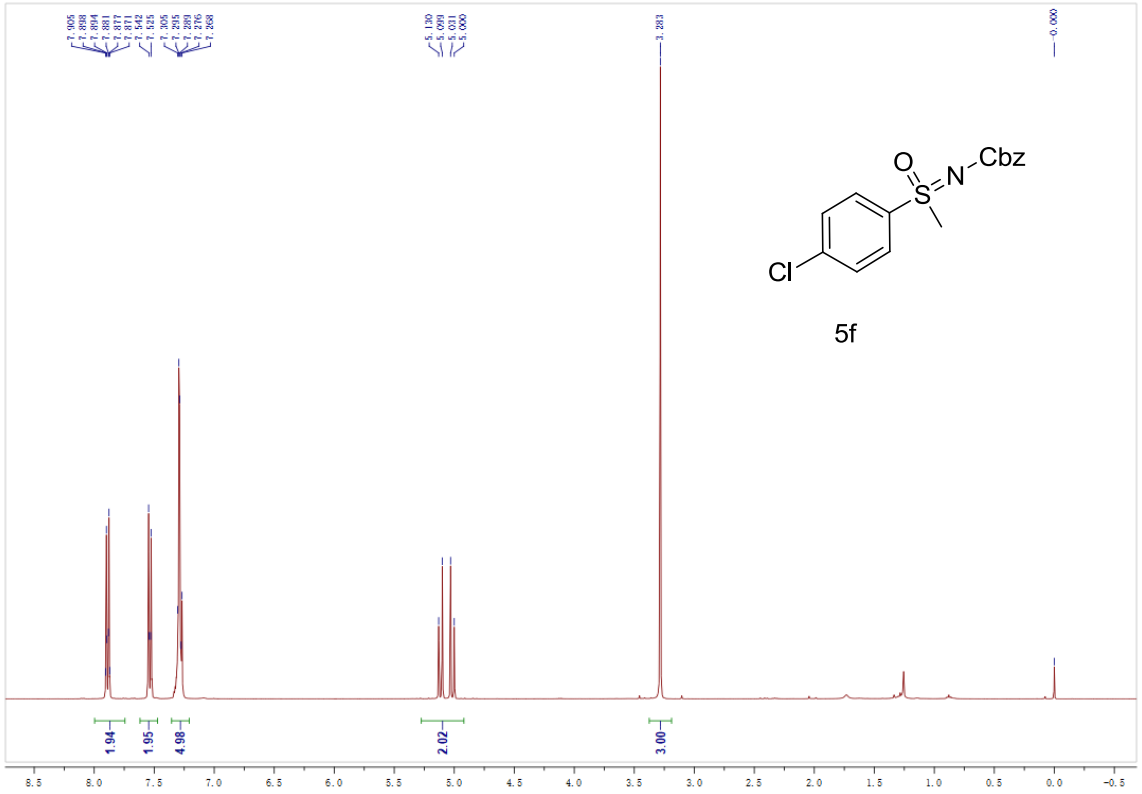
129.24
128.36
128.36
127.94
114.94
77.35
77.03
76.71
67.75
55.78
45.02
0.00
O
S
N
Cbz
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5c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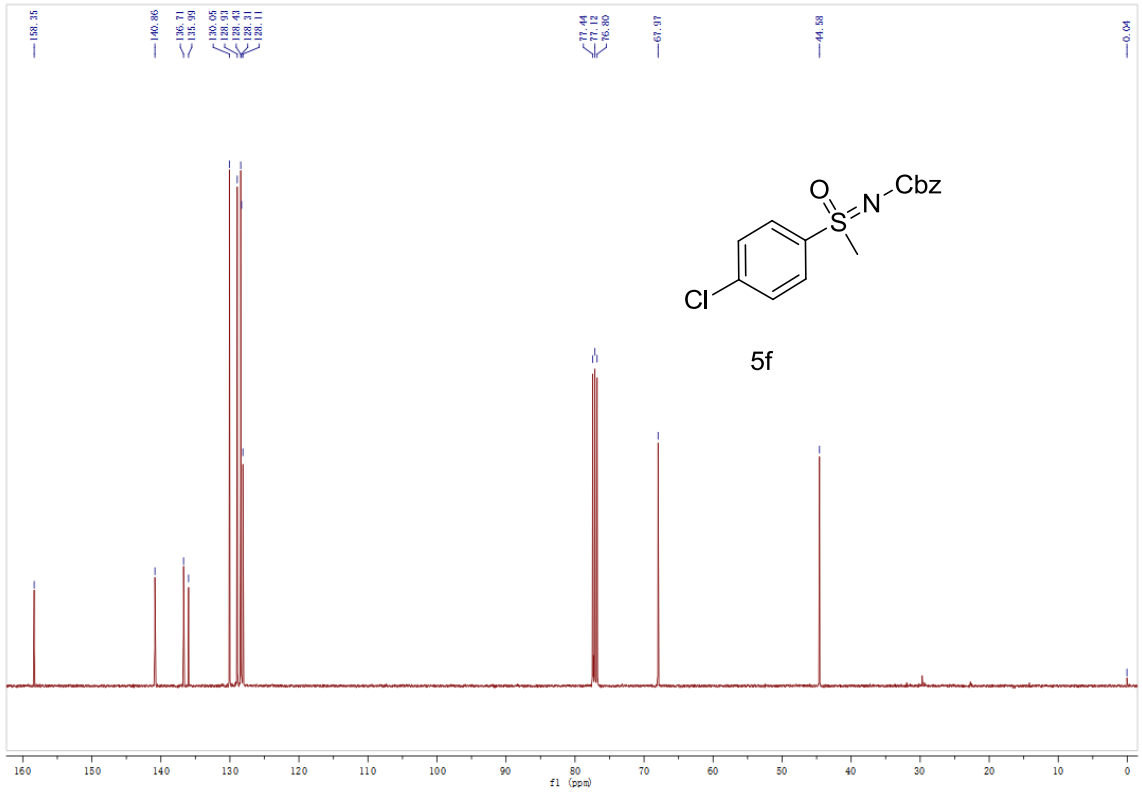
7.525
7.305
7.295
7.289
7.276
7.268
5.139
5.099
5.031
5.000
2.283
-0.000
O
S
N
Cbz
Cl
1.94
1.95
4.98
2.02
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

5f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140.86
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135.99
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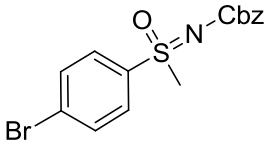
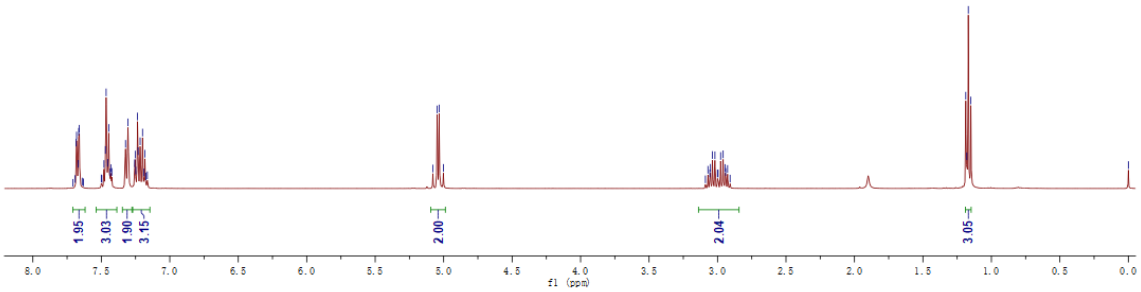
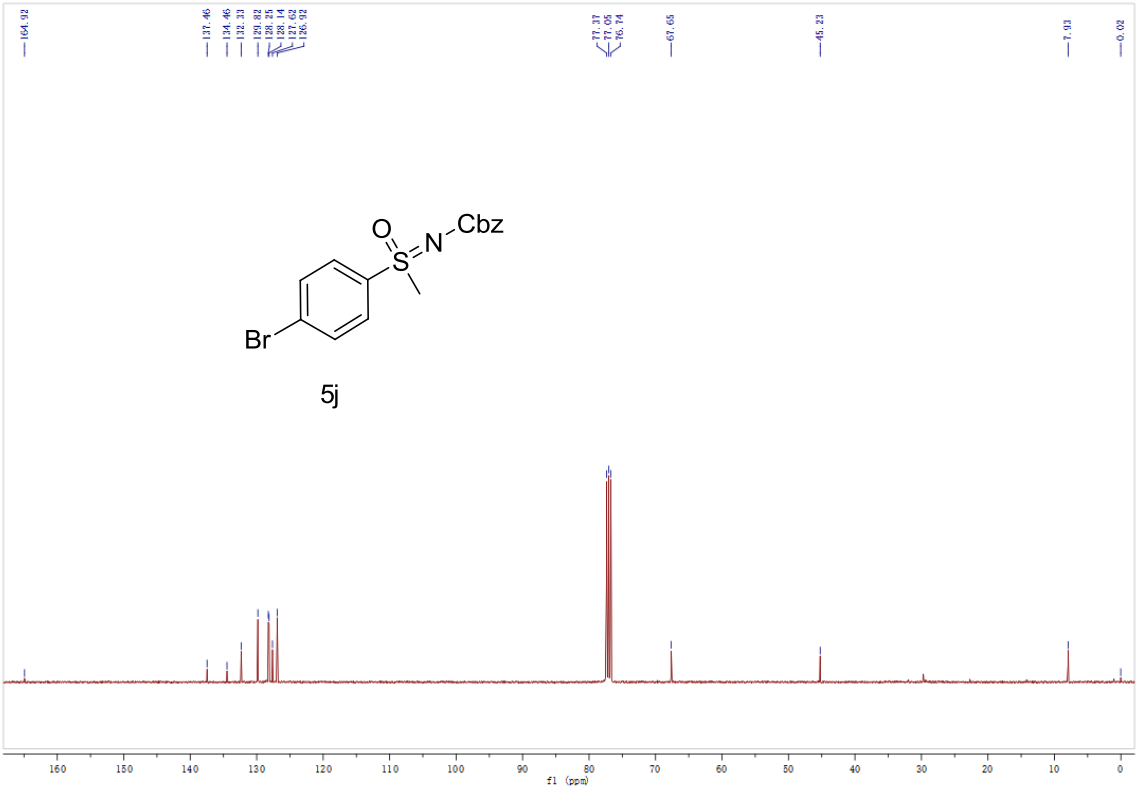
128.93
128.43
128.31
128.11
77.44
77.12
76.80
67.97
44.58
0.04
O
S
N
Cbz
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5f

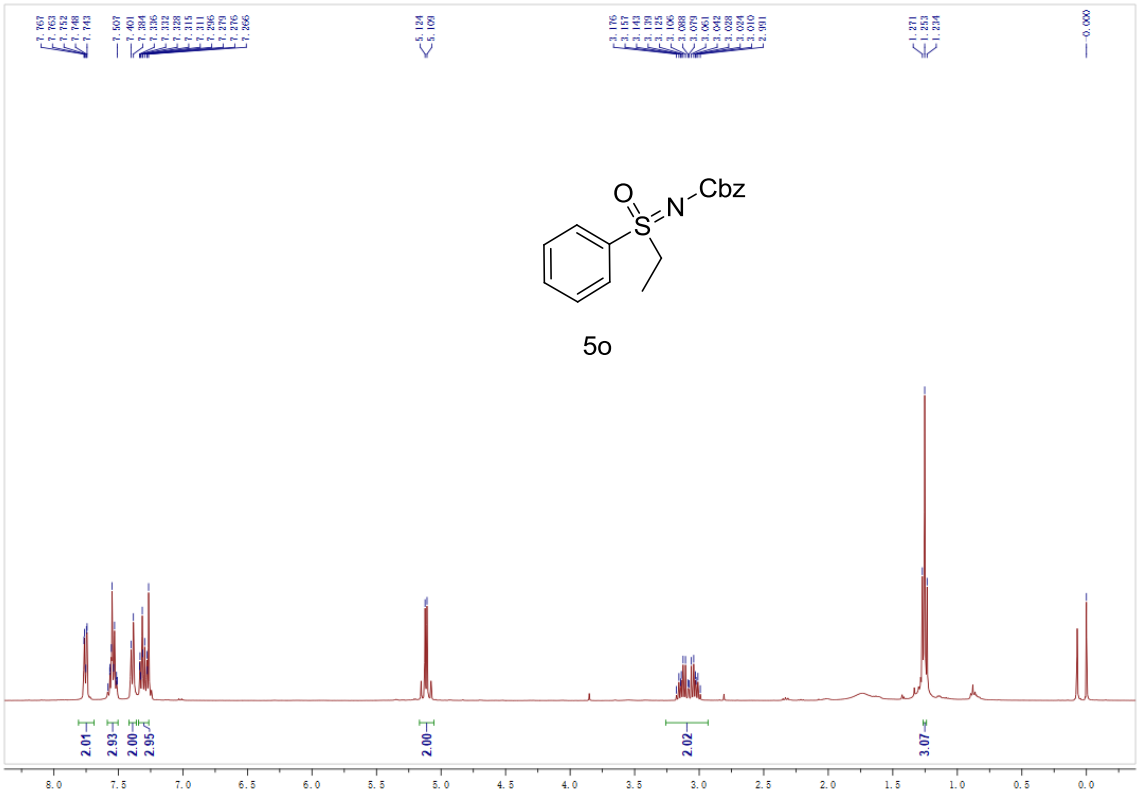


5j





5j



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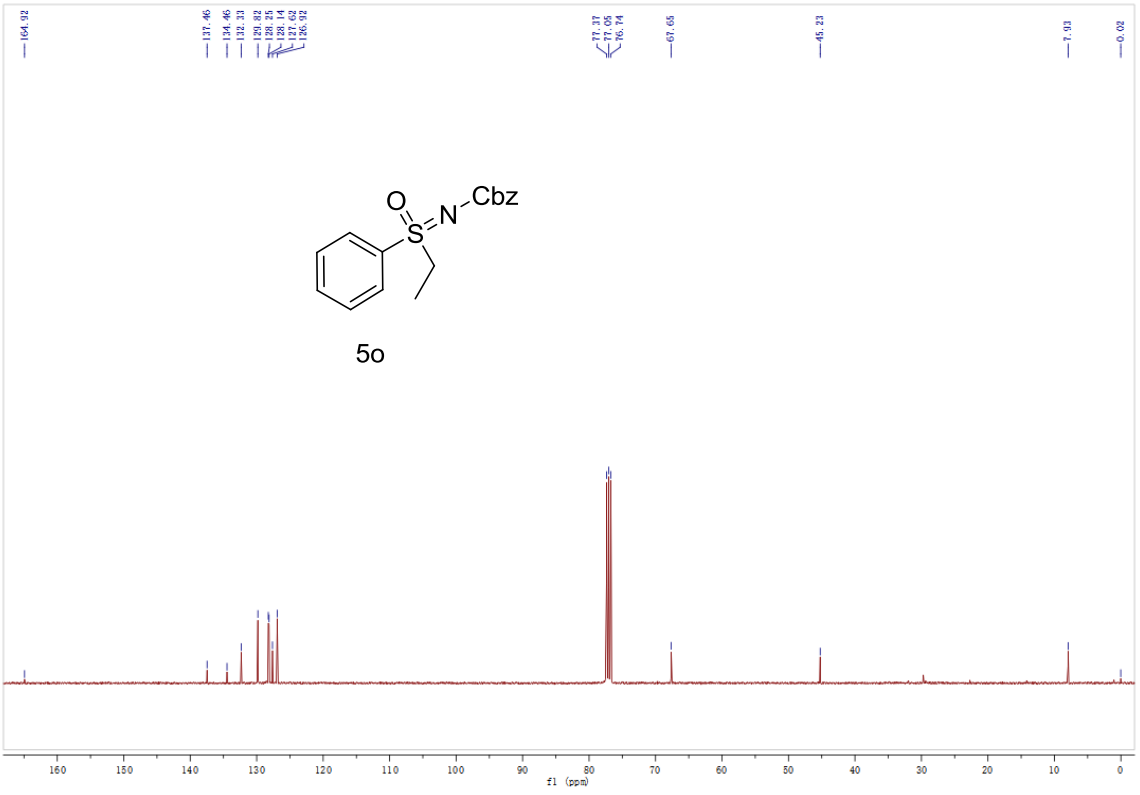
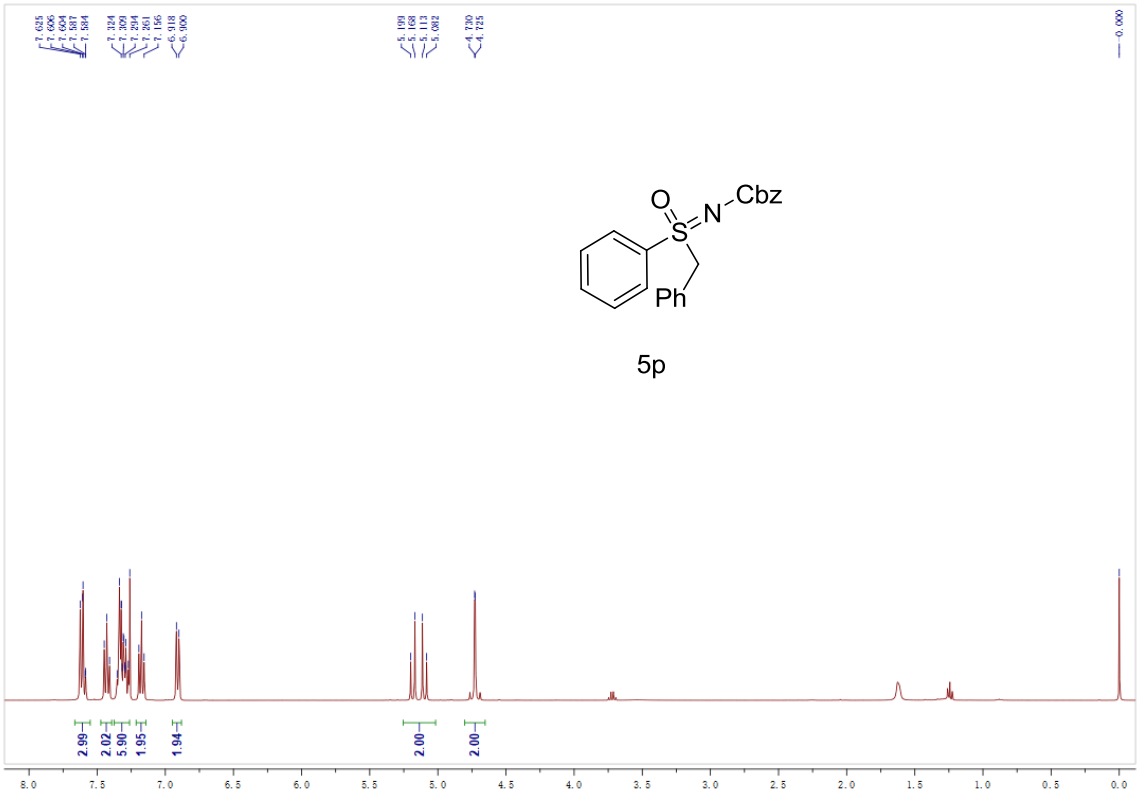


5o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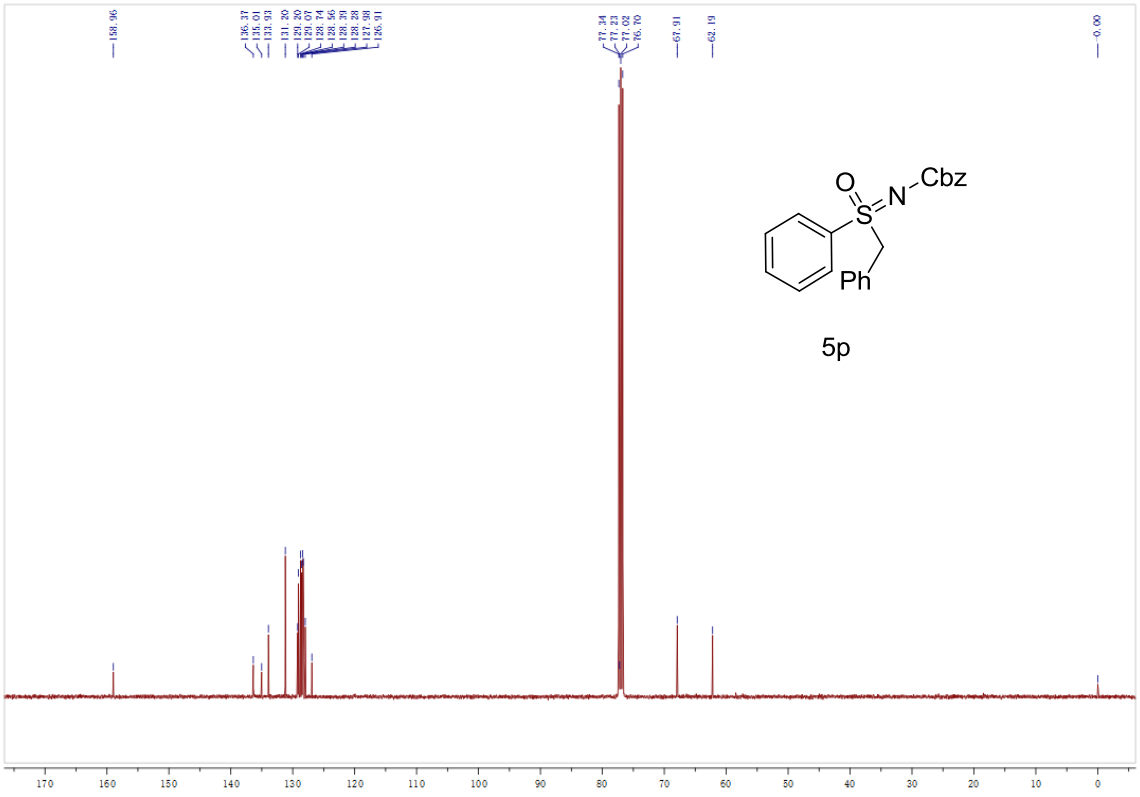
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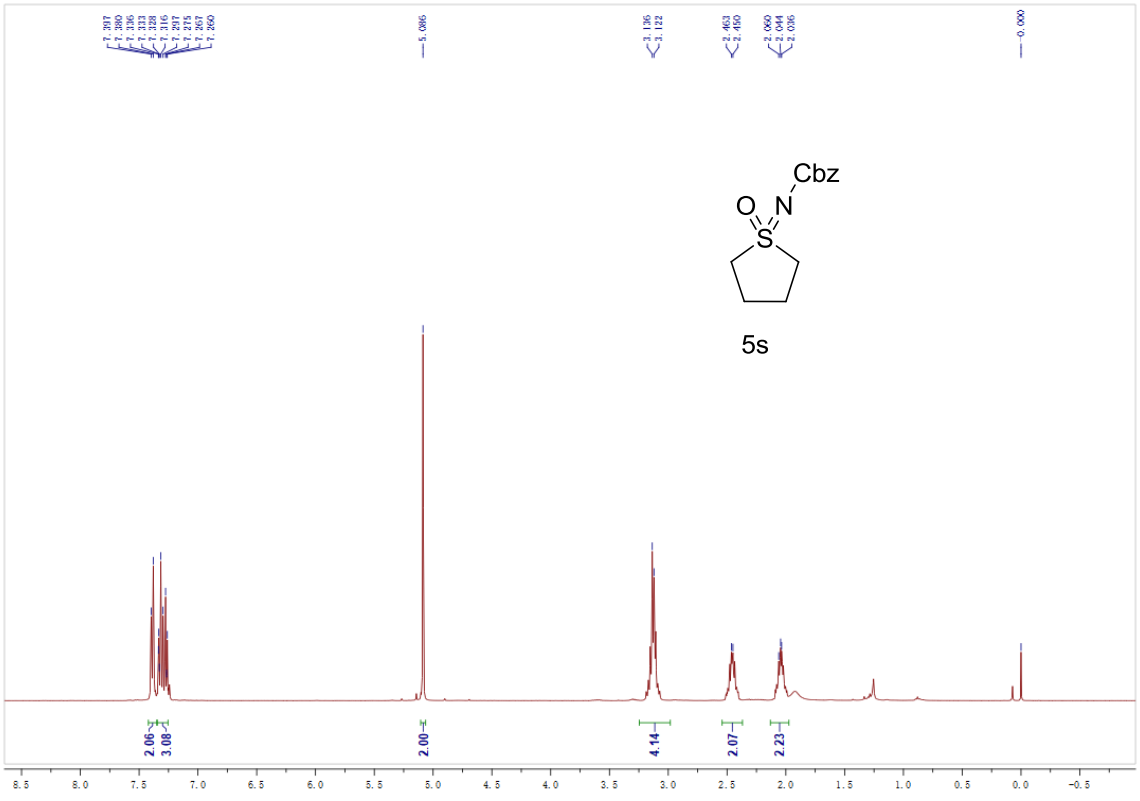
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O
N
S
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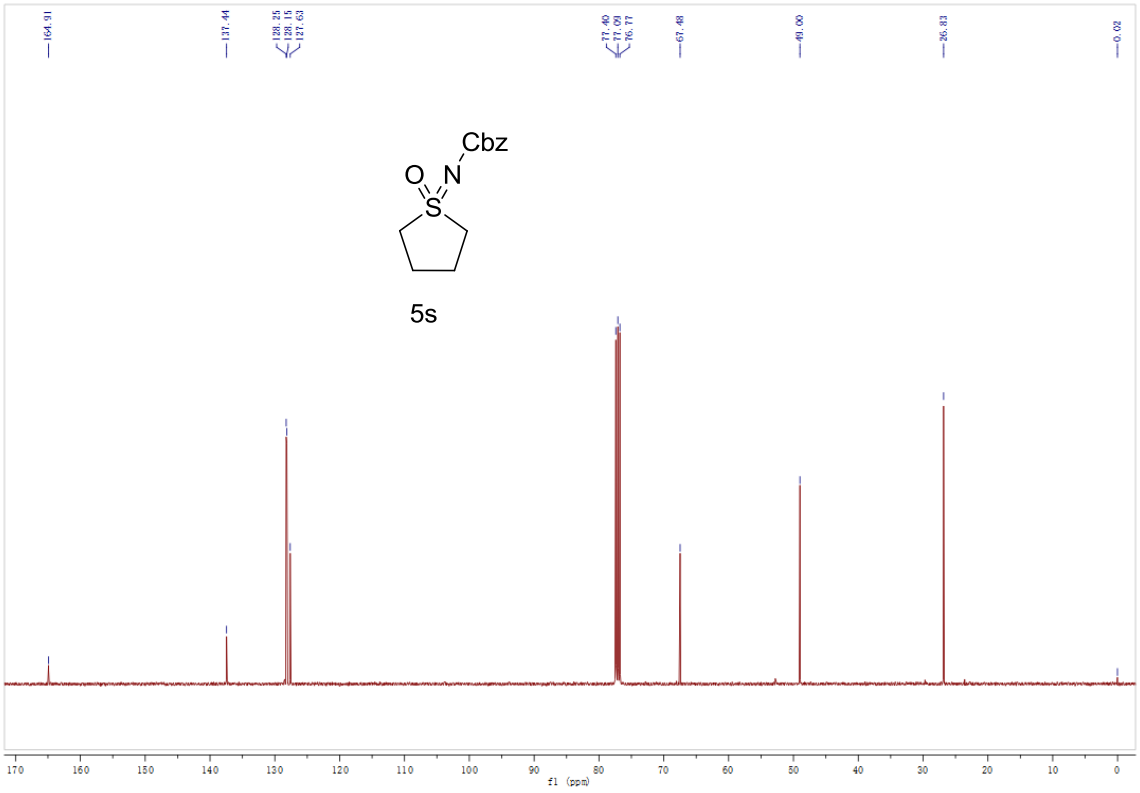
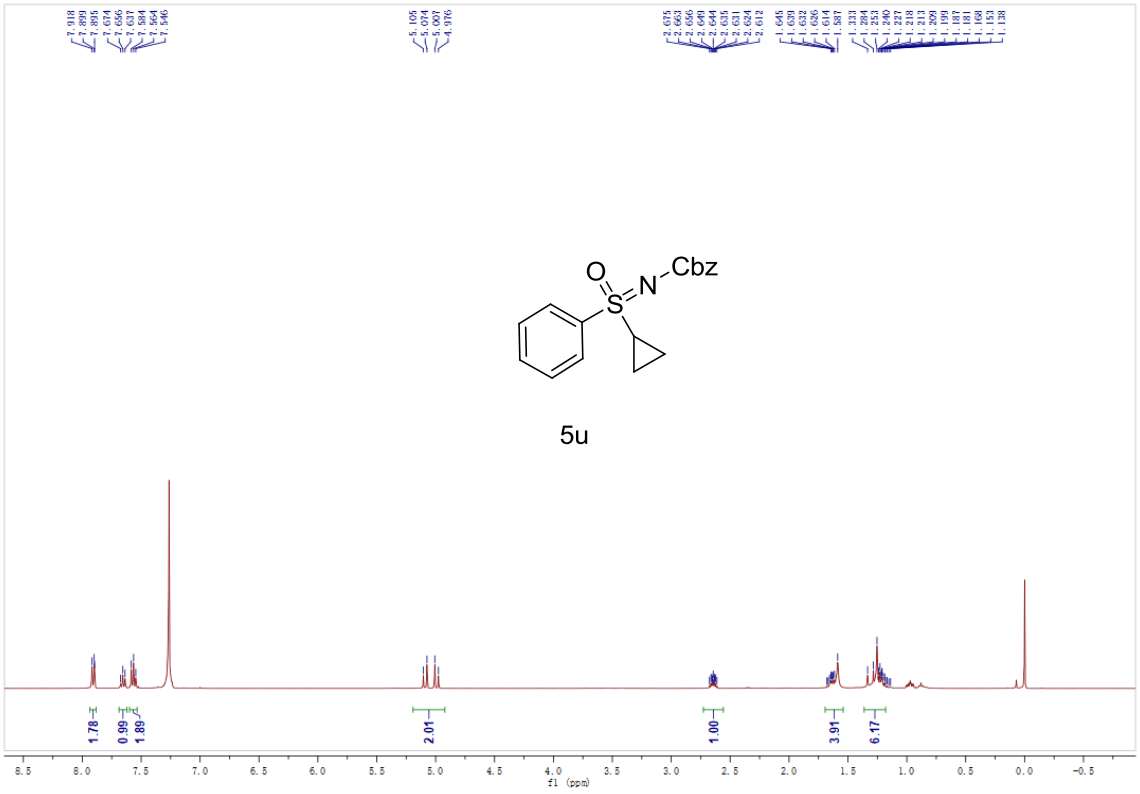

Cbz
O
N
S
5s
f1 (ppm)



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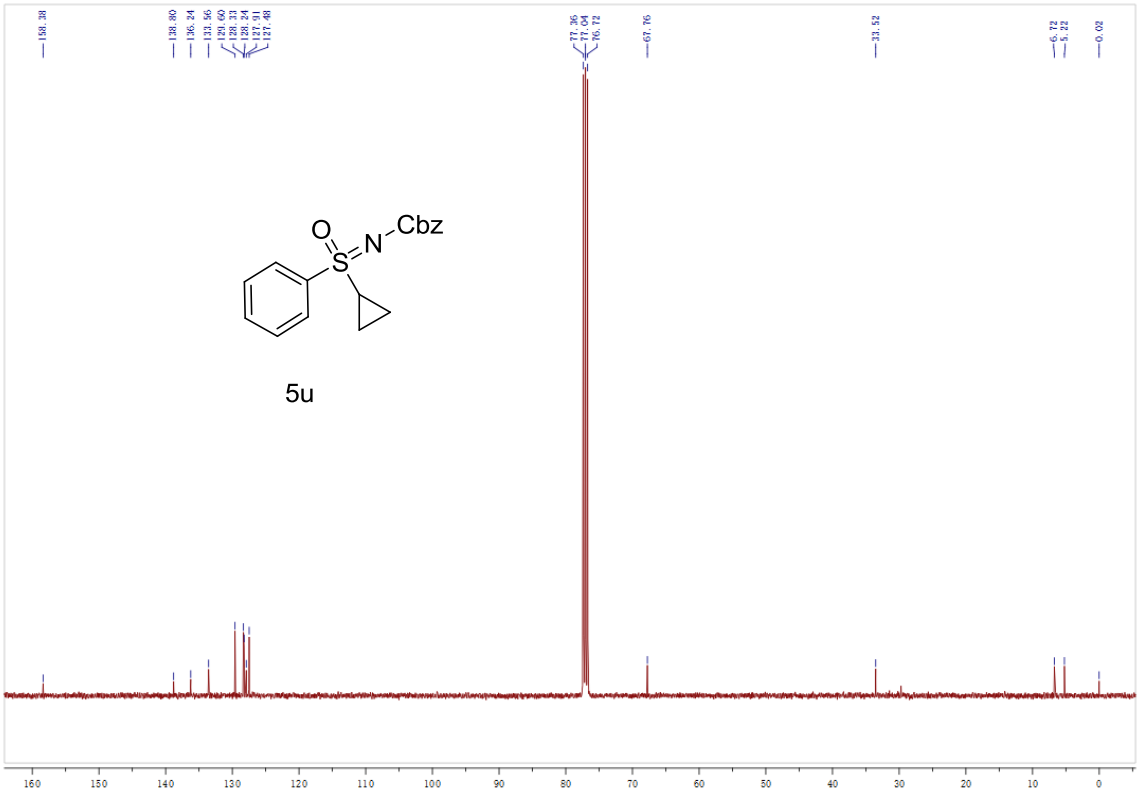

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