Construction of oxindole spiro medium-sized *S*-heterocycles via ring expansion [2,3]-sigmatropic rearrangement

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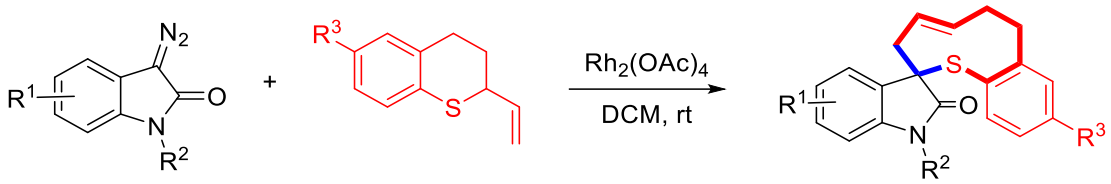
Contents

1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (200~300 mesh). All ^{1}H NMR spectra were recorded on a Bruker Avance Ⅱ 400 MHz, ^{13}C NMR spectra were recorded on a Bruker Avance Ⅱ 101 MHz, and ^{19}F NMR spectra were recorded on a Bruker Avance Ⅱ 377 MHz with chemical shifts reported as ppm (in CDCl3, TMS as an internal standard),. Data for 1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XL TM). The substrates diazooxindoles[1] and vinyl/ethynyl thiochromanes[2] were prepared based on literature procedures.

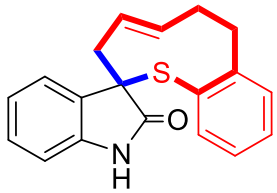
2. Experimental procedures and characterization of compounds 3



1 **2** **3**

Substrates **2** (0.2 mmol, 1 equiv) and $Rh_2(OAc)_4$ (2 mol%) were introduced into a dried glass tube and add 2 mL dry DCM as solvent, then the diazooxindoles **1** (0.24 mmol, 1.2 equiv) was added dropwise at room temperature. The reaction was monitored by TLC. The product was directly purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 3:1) to give the product **3**.

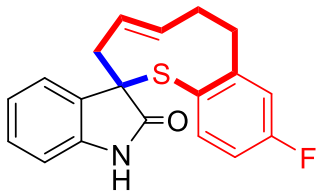
Compound 3a



3a

Prepared according to the procedure as pink solid (56.3 mg, 92% yield, 2.3:1 dr); mp 168.7-169.4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.69 (s, 1H), 7.30 – 7.27 (m, 2H), 7.14 – 7.01 (m, 2H), 6.85 (dd, *J* = 6.3 Hz, 1H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.29 (d, *J* = 7.8 Hz, 1H), 6.22 (ddd, *J* = 15.5, 11.2, 4.6 Hz, 1H), 6.06 (d, *J* = 7.8 Hz, 1H), 5.19 (ddd, *J* = 15.4, 11.3, 4.0 Hz, 1H), 3.16 (t, *J* = 12.5 Hz, 1H), 2.90 – 2.79 (m, 2H), 2.72 – 2.62 (m, 1H), 2.49 (dd, *J* = 12.1, 4.0 Hz, 1H), 2.04 – 1.95 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 146.1, 142.8, 141.4, 139.4, 132.2, 131.9, 130.7, 130.0, 128.8, 127.2, 125.9, 124.6, 121.4, 110.3, 69.5, 42.0, 37.1, 33.6; HRMS (ESI) m/z Calcd. for $C_{19}H_{16}NOS^-$ ([M-H]$^-$) 306.0958, Found 306.0957.

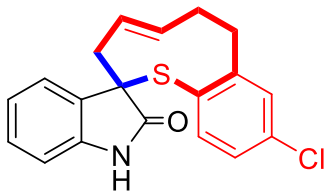
Compound 3b



3b

Prepared according to the procedure as pink solid (61.5 mg, 95% yield, 2.2:1 dr); mp 171.2-172.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 7.38 – 7.28 (m, 2H), 7.01 (dd, *J* = 10.7, 7.4 Hz, 2H), 6.58 (td, *J* = 8.3, 2.9 Hz, 1H), 6.21 (ddd, *J* = 24.1, 9.8, 5.4 Hz, 2H), 6.12 (d, *J* = 7.5 Hz, 1H), 5.21 (ddd, *J* = 15.4, 11.4, 4.1 Hz, 1H), 3.19 – 3.09 (m, 1H), 2.88 – 2.79 (m, 2H), 2.66 (dd, *J* = 12.9, 4.3 Hz, 1H), 2.49 (dd, *J* = 12.1, 4.1 Hz, 1H), 2.01 (d, *J* = 12.2 Hz, 1H); ^{13}C NMR(101 MHz, $CDCl_3$) δ 177.8, 163.7 (d, *J* = 250.3 Hz), 148.8 (d, *J* = 8.0 Hz), 144.5 (d, *J* = 8.2 Hz), 139.8, 139.1, 130.5, 128.9, 127.5 (d, *J* = 3.1 Hz), 127.1, 124.8, 121.5, 118.8 (d, *J* = 21.2 Hz), 113.0 (d, *J* = 20.7 Hz), 110.3, 69.5, 41.8, 37.4, 33.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.42; HRMS (ESI) m/z Calcd. for $C_{19}H_{16}FNOS^-$ ([M-H]$^-$) 324.0864, Found 324.0862.

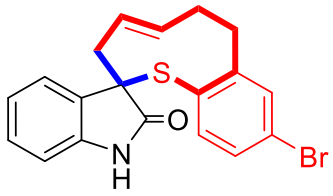
Compound 3c



3c

Prepared according to the procedure as pink solid (61.9 mg, 91% yield, 2.2:1 dr); mp 190.6-191.7 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68 (s, 1H), 7.28 (d, *J* = 2.9 Hz, 2H), 7.12 – 7.05 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.88 – 6.79 (m, 2H), 6.17 (m, 2H), 5.20 (ddd, *J* = 15.5, 11.4, 4.1 Hz, 1H), 3.18 – 3.07 (m, 1H), 2.80 (d, *J* = 11.1 Hz, 2H), 2.66 (dd, *J* = 13.0, 4.4 Hz, 1H), 2.49 (dd, *J* = 12.2, 4.1 Hz, 1H), 2.00 (d, *J* = 12.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 147.9, 143.8, 142.5, 139.7, 139.1, 136.0, 132.0, 130.4, 129.0, 127.1, 126.0, 124.8, 121.6, 110.3, 69.7, 41.8, 37.1, 33.3; HRMS (ESI) m/z Calcd. for $C_{19}H_{16}ClNOS^-$ ([M-H]$^-$) 340.0568, Found 340.0568.

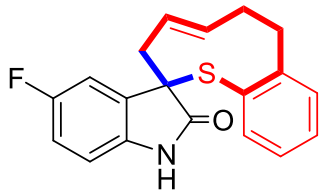
Compound 3d



3d

Prepared according to the procedure as pink solid (73.6 mg, 96% yield, 1.9:1 dr); mp 196.9-198.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 7.34 – 7.28 (m, 2H), 7.02 – 6.97 (m, 2H), 6.84 (dd, *J* = 7.6 Hz, 1H), 6.25 – 6.14 (m, 2H), 6.12 (d, *J* = 8.2 Hz, 1H), 5.21 (ddd, *J* = 15.4, 11.4, 4.1 Hz, 1H), 3.18 – 3.07 (m, 1H), 2.84 – 2.78 (m, 2H), 2.69 – 2.63 (m, 1H), 2.50 (dd, *J* = 12.1, 4.0 Hz, 1H), 2.02 – 1.96 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 148.2, 144.0, 139.1, 136.9, 134.9, 131.1, 130.4, 129.0, 129.0, 127.1, 124.9, 124.5, 121.6, 110.3, 69.6, 41.9, 37.0, 33.3; HRMS (ESI) m/z Calcd. for $C_{19}H_{16}BrNOS^-$ ([M-H]$^-$) 384.0063, Found 384.0066.

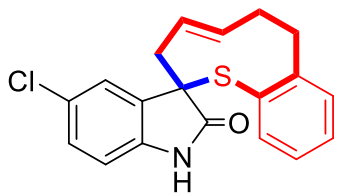
Compound 3e



3e

Prepared according to the procedure as pink solid (57.3 mg, 88% yield, 2.8:1 dr); mp 178.5-179.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 7.38 – 7.30 (m, 3H), 6.97 – 6.93 (m, 2H), 6.31 (d, *J* = 7.8 Hz, 1H), 6.22 (ddd, *J* = 15.5, 11.1, 4.6 Hz, 1H), 5.75 (dd, *J* = 8.6, 2.4 Hz, 1H), 5.12 (ddd, *J* = 15.4, 11.4, 4.1 Hz, 1H), 3.19 – 3.09 (m, 1H), 2.93 – 2.87 (m, 1H), 2.76 (d, *J* = 11.8 Hz, 2H), 2.48 (dd, *J* = 12.2, 4.0 Hz, 1H), 2.04 – 1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 158.0 (d, *J* = 239.9 Hz), 146.2, 142.6, 139.8, 135.5 (d, *J* = 2.0 Hz), 132.5, 132.0 (d, *J* = 8.8 Hz), 131.5, 130.5, 125.9, 123.9, 115.2 (d, *J* = 25.1 Hz), 114.9 (d, *J* = 23.5 Hz), 110.4 (d, *J* = 8.1 Hz), 69.5, 41.7, 37.1, 33.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -120.93; HRMS (ESI) m/z Calcd. for $C_{19}H_{16}FNOS^-$ ([M-H]$^-$) 324.0864, Found 324.0861.

Compound 3f

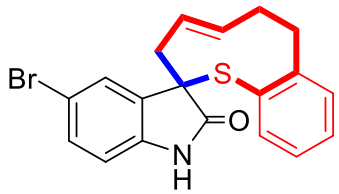


3f

Prepared according to the procedure as pink solid (58.0 mg, 85% yield, 3.5:1 dr); mp 176.6-177.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 7.35 (dd, *J* = 16.5, 9.0 Hz, 3H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.27 (d, *J* = 8.2 Hz, 1H), 6.20 (d, *J* = 15.3 Hz, 1H), 5.91 (s, 1H), 5.19 – 5.06 (m, 1H), 3.14 (t, *J* = 12.6 Hz, 1H), 2.91 (d, *J* = 5.7 Hz, 1H),

2.77 (t, *J* = 11.4 Hz, 2H), 2.48 (dd, *J* = 12.3, 4.0 Hz, 1H), 2.07 – 1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 146.1, 142.6, 139.7, 138.1, 132.5, 132.1, 131.4, 130.5, 128.5, 127.5, 126.9, 125.8, 124.0, 111.1, 69.4, 41.6, 37.1, 33.4; HRMS (ESI) m/z Calcd. for $C_{19}H_{16}ClNOS^-$ ([M-H]$^-$) 340.0568, Found 340.0569.

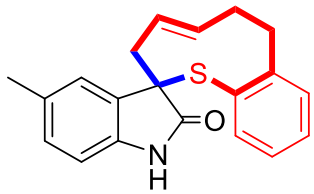
Compound 3g



3g

Prepared according to the procedure as pink solid (62.5 mg, 81% yield, 3.5:1 dr); mp 176.4-177.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.44 (s, 1H), 7.42 (ddd, *J* = 10.6, 8.8, 2.1 Hz, 2H), 7.31 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.99 (td, *J* = 7.6, 1.7 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.29 – 6.25 (m, 1H), 6.21 (td, *J* = 11.0, 5.5 Hz, 1H), 6.03 (d, *J* = 1.9 Hz, 1H), 5.11 (ddd, *J* = 15.4, 11.4, 4.1 Hz, 1H), 3.13 (td, *J* = 12.6, 1.9 Hz, 1H), 2.90 (dt, *J* = 7.7, 3.9 Hz, 1H), 2.81 – 2.72 (m, 2H), 2.51 – 2.45 (m, 1H), 2.04 (d, *J* = 11.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 146.1, 142.7, 139.7, 138.6, 132.5, 131.4, 131.4, 130.5, 130.2, 125.9, 124.0, 114.2, 111.6, 69.5, 41.6, 37.0, 33.4; HRMS (ESI) m/z Calcd. for $C_{19}H_{16}BrNOS^-$ ([M-H]$^-$) 384.0063, Found 384.0065.

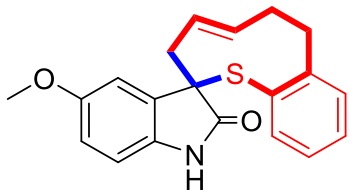
Compound 3h



3h

Prepared according to the procedure as pink solid (61.6 mg, 96% yield, 3:1 dr); mp 147.8-149.1 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.58 (s, 1H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.07 (dd, *J* = 12.7, 7.7 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.23 (dd, *J* = 18.2, 9.2 Hz, 2H), 5.76 (s, 1H), 5.18 (ddd, *J* = 15.4, 11.3, 4.0 Hz, 1H), 3.16 (s, 1H), 2.89 (d, *J* = 5.5 Hz, 1H), 2.76 (dd, *J* = 12.0, 6.5 Hz, 2H), 2.48 (dd, *J* = 12.2, 4.0 Hz, 1H), 2.10 (s, 3H), 2.06 – 1.98 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 146.2, 143.0, 139.1, 137.3, 132.1, 132.0, 130.6, 130.5, 129.9, 128.8, 128.1, 125.3, 124.7, 110.0, 69.7, 41.9, 37.1, 33.5, 21.1; HRMS (ESI) m/z Calcd. for $C_{20}H_{18}NOS^-$ ([M-H]$^-$) 320.1115, Found 320.1115.

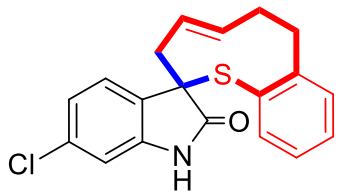
Compound 3i



3i

Prepared according to the procedure as pink solid (61.9 mg, 92% yield, 2.9:1 dr); mp 171.4-172.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.61 (s, 1H), 7.30 (td, *J* = 8.7, 8.1, 4.6 Hz, 3H), 6.94 – 6.88 (m, 2H), 6.35 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.29 – 6.17 (m, 1H), 5.63 (d, *J* = 2.6 Hz, 1H), 5.23 – 5.10 (m, 1H), 3.55 (s, 3H), 3.16 (t, *J* = 12.6 Hz, 1H), 2.89 (t, *J* = 6.5 Hz, 1H), 2.77 (d, *J* = 11.6 Hz, 2H), 2.49 (dt, *J* = 12.2, 2.9 Hz, 1H), 2.03 – 1.96 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 154.5, 146.2, 142.8, 139.4, 133.3, 132.3, 131.8, 131.7, 130.0, 125.8, 124.4, 113.8, 110.8, 69.9, 55.6, 41.9, 37.1, 33.6; HRMS (ESI) m/z Calcd. for $C_{20}H_{18}NO_2S^-$ ([M-H]$^-$) 336.1064, Found 336.1065.

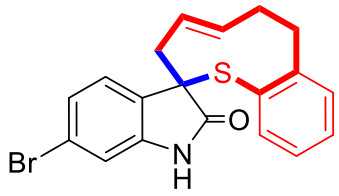
Compound 3j



3j

Prepared according to the procedure as pink solid (53.3 mg, 78% yield, 2.6:1 dr); mp 190.0-191.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.31 (s, 1H), 7.36 – 7.28 (m, 3H), 7.12 – 7.03 (m, 2H), 6.34 (d, *J* = 7.8 Hz, 1H), 6.22 (ddd, *J* = 15.7, 10.9, 4.4 Hz, 1H), 5.96 (dd, *J* = 8.1, 1.8 Hz, 1H), 5.19 – 5.06 (m, 1H), 3.14 (t, *J* = 12.6 Hz, 1H), 2.90 (d, *J* = 5.8 Hz, 1H), 2.77 (t, *J* = 11.4 Hz, 2H), 2.46 (dd, *J* = 11.4, 3.4 Hz, 1H), 2.00 (d, *J* = 11.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 146.2, 142.7, 140.9, 139.7, 134.6, 132.4, 131.7, 130.2, 129.0, 128.0, 126.1, 124.1, 121.4, 110.9, 69.0, 42.0, 37.1, 33.5; HRMS (ESI) m/z Calcd. for $C_{19}H_{16}ClNOS^-$ ([M-H]$^-$) 340.0568, Found 340.0570.

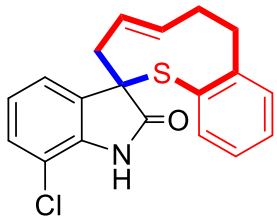
Compound 3k



3k

Prepared according to the procedure as pink solid (69.8 mg, 91% yield, 2.6:1 dr); mp 201.3-202.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.46 (s, 1H), 7.28 (d, *J* = 15.2 Hz, 3H), 6.92 (d, *J* = 7.8 Hz, 2H), 6.35 (d, *J* = 7.7 Hz, 1H), 6.29 – 6.16 (m, 1H), 5.90 (d, *J* = 8.0 Hz, 1H), 5.13 (d, *J* = 11.3 Hz, 1H), 3.15 (t, *J* = 12.6 Hz, 1H), 2.92 – 2.86 (m, 1H), 2.81 – 2.72 (m, 2H), 2.51 – 2.41 (m, 1H), 2.00 (d, *J* = 11.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 146.2, 142.7, 141.2, 139.7, 132.4, 132.4, 130.3, 129.6, 128.3, 126.1, 124.3, 124.1, 122.5, 113.9, 69.1, 42.0, 37.1, 33.6; HRMS (ESI) m/z Calcd. for $C_{19}H_{16}BrNOS^-$ ([M-H]$^-$) 384.0063, Found 384.0065.

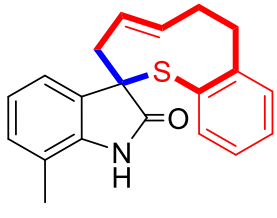
Compound 3l



3l

Prepared according to the procedure as pink solid (56.1 mg, 82% yield, 1.7:1 dr); mp 196.7-197.4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 3H), 6.73 (t, *J* = 7.9 Hz, 1H), 6.33 – 6.26 (m, 1H), 6.20 (dd, *J* = 9.8, 5.4 Hz, 1H), 5.96 (d, *J* = 7.5 Hz, 1H), 5.12 (ddd, *J* = 15.4, 11.4, 4.1 Hz, 1H), 3.13 (td, *J* = 12.6, 2.0 Hz, 1H), 2.92 – 2.80 (m, 2H), 2.67 (dd, *J* = 12.5, 4.4 Hz, 1H), 2.48 (dd, *J* = 12.4, 4.0 Hz, 1H), 1.99 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 146.2, 142.7, 141.2, 139.7, 132.3, 131.9, 131.7, 130.2, 128.6, 125.9, 125.5, 124.1, 122.2, 115.1, 70.1, 41.8, 37.1, 33.5; HRMS (ESI) m/z Calcd. for $C_{19}H_{16}ClNOS^-$ ([M-H]$^-$) 340.0568, Found 340.0568.

Compound 3m

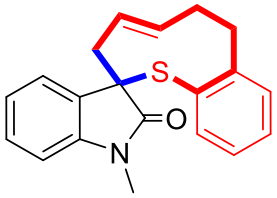


3m

Prepared according to the procedure as pink solid (60.8 mg, 95% yield, 1.9:1 dr); mp 201.8-202.7 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.80 (s, 1H), 7.31 – 7.26 (m, 3H), 7.07 (q, *J* = 5.8, 3.9 Hz, 2H), 6.29 (d, *J* = 7.8 Hz, 1H), 6.22 (ddd, *J* = 15.5, 11.1, 4.6 Hz, 1H), 5.90 (d, *J* = 7.5 Hz, 1H), 5.19 (ddd, *J* = 15.3, 11.4, 4.1 Hz, 1H), 3.20 – 3.12 (m, 1H), 2.87 (d, *J* = 6.3 Hz, 1H), 2.81 – 2.73 (m, 2H), 2.48 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.33 (s, 3H), 2.03 – 1.97 (m, 1H); ^{13}C NMR (101

MHz, $CDCl_3$) δ 178.5, 146.0, 142.9, 141.3, 139.2, 136.9, 132.1, 132.0, 130.0, 129.9, 125.8, 124.7, 124.6, 121.2, 119.7, 70.0, 42.0, 37.1, 33.6, 16.7; HRMS (ESI) m/z Calcd. for $C_{20}H_{18}NOS^-$ ($[M-H]^-$) 320.1115, Found 320.1112.

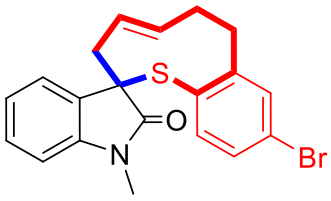
Compound 3n



3n

Prepared according to the procedure as pink solid (63.6 mg, 99% yield, 2.8:1 dr); mp 136.3-137.2 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 3H), 6.94 – 6.90 (m, 1H), 6.89 – 6.82 (m, 1H), 6.81 – 6.76 (m, 1H), 6.28 – 6.15 (m, 2H), 6.07 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.16 (ddd, *J* = 15.4, 11.4, 4.0 Hz, 1H), 3.31 (s, 3H), 3.14 (td, *J* = 12.6, 1.9 Hz, 1H), 2.87 – 2.71 (m, 3H), 2.40 (dd, *J* = 12.1, 4.0 Hz, 1H), 2.02 – 1.94 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 146.1, 142.7, 141.4, 139.2, 132.1, 132.1, 130.1, 129.9, 128.7, 126.9, 125.7, 124.7, 121.3, 108.2, 68.9, 42.1, 37.0, 33.6, 26.7; HRMS (ESI) m/z Calcd. for $C_{20}H_{20}NOS^+$ ($[M+H]^+$) 322.1260, Found 322.1257.

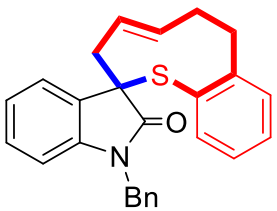
Compound 3o



3o

Prepared according to the procedure as pink solid (76.4 mg, 96% yield, 2.4:1 dr); mp 163.1-164.0 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 2.3 Hz, 1H), 7.37 – 7.30 (m, 2H), 6.98 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.85 (td, *J* = 7.6, 1.0 Hz, 1H), 6.16 (d, *J* = 7.2 Hz, 1H), 6.07 (d, *J* = 8.3 Hz, 1H), 5.19 (ddd, *J* = 15.4, 11.5, 4.1 Hz, 1H), 3.31 (s, 3H), 3.09 (td, *J* = 12.6, 1.8 Hz, 1H), 2.78 (dd, *J* = 13.3, 10.2 Hz, 3H), 2.40 (dd, *J* = 12.2, 4.1 Hz, 1H), 1.98 (d, *J* = 12.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 148.2, 143.9, 142.4, 138.9, 134.8, 131.3, 129.8, 128.9, 128.8, 126.8, 125.0, 124.3, 121.5, 108.4, 69.1, 41.9, 36.9, 33.2, 26.7; HRMS (ESI) m/z Calcd. for $C_{20}H_{19}BrNOS^+$ ($[M+H]^+$) 400.0365, Found 400.0364.

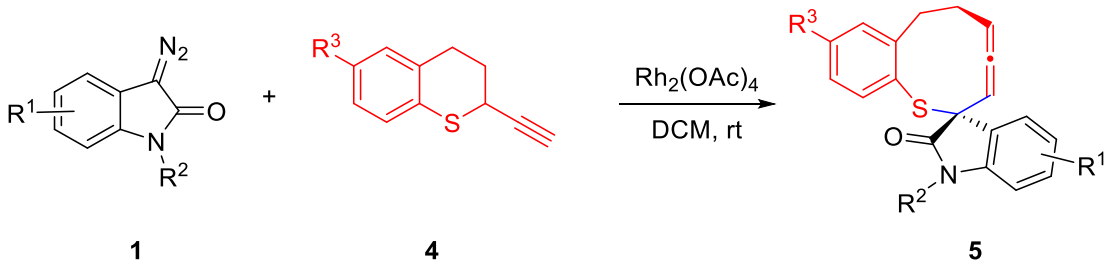
Compound 3p



3p

Prepared according to the procedure as pink solid (73.5 mg, 93% yield, 2:1 dr); mp 148.9-150.2 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.26 (m, 8H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.78 (ddd, *J* = 20.7, 13.9, 7.9 Hz, 3H), 6.25 (td, *J* = 14.1, 12.6, 7.2 Hz, 1H), 6.09 (d, *J* = 7.5 Hz, 1H), 5.18 (dd, *J* = 28.8, 13.8 Hz, 2H), 4.89 (d, *J* = 15.9 Hz, 1H), 3.16 (t, *J* = 12.5 Hz, 1H), 2.87 (t, *J* = 11.1 Hz, 2H), 2.76 (dt, *J* = 10.4, 5.0 Hz, 1H), 2.48 (dd, *J* = 12.2, 4.0 Hz, 1H), 2.03 – 1.94 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 146.1, 142.8, 139.3, 135.7, 132.1, 130.1, 129.9, 128.8, 128.5, 127.6, 127.6, 127.1, 127.0, 125.8, 124.7, 124.5, 121.4, 109.2, 69.1, 43.8, 41.9, 37.1, 33.6; HRMS (ESI) m/z Calcd. for $C_{26}H_{24}NOS^+$ ($[M+H]^+$) 398.1573, Found 398.1573.

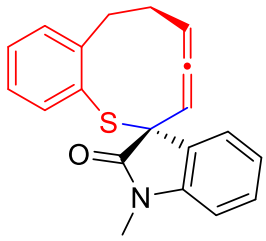
3. Experimental procedures and characterization of compounds 5



1 **4** **5**

Substrates **4** (0.2 mmol, 1 equiv) and $Rh_2(OAc)_4$ (2 mol%) were introduced into a dried glass tube and add 2 mL dry DCM as solvent, then the diazooxindoles **1** (0.24 mmol, 1.2 equiv) was added dropwise at room temperature. The reaction was monitored by TLC. The product was directly purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 3:1) to give the product **5**.

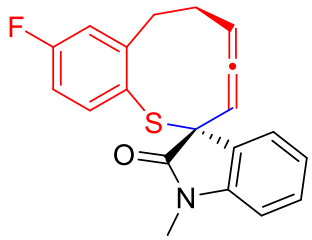
Compound 5a



5a

Prepared according to the procedure as pink solid (60.5 mg, 95% yield); mp 158.3-159.4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.07 – 6.91 (m, 1H), 6.88 – 6.53 (m, 3H), 6.31 (s, 1H), 5.99 (s, 1H), 5.33 (s, 1H), 3.60 (s, 1H), 3.30 (s, 3H), 3.16 – 2.76 (m, 2H), 2.69 – 2.55 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 174.4, 149.8, 142.5, 141.9, 130.3, 130.0, 128.5, 125.7, 125.2, 121.7, 108.0, 97.0, 93.3, 54.6, 35.5, 30.6, 26.7; HRMS (ESI) m/z Calcd. for $C_{20}H_{18}NOS^+$ ([M+H]$^+$) 320.1104, Found 320.1100.

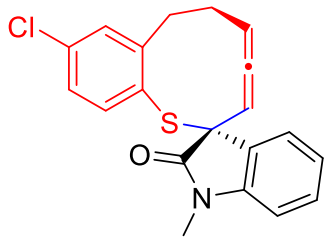
Compound 5b



5b

Prepared according to the procedure as pink solid (49.4 mg, 73% yield); mp 147.2-148.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (s, 1H), 7.11 – 7.07 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.71 (s, 3H), 6.31 (s, 1H), 6.04 (s, 1H), 5.33 (s, 1H), 3.60 (s, 1H), 3.30 (s, 3H), 3.07 (s, 1H), 2.86 (s, 1H), 2.64 – 2.55 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 174.2, 164.0 (d, *J* = 251.9 Hz), 152.6, 144.4, 142.0, 128.6, 126.0, 125.1, 121.7, 116.7 (d, *J* = 21.2 Hz), 113.3 (d, *J* = 21.1 Hz), 97.1, 93.1, 54.7, 35.5, 31.0, 26.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -109.85; HRMS (ESI) m/z Calcd. for $C_{20}H_{17}FNOS^+$ ([M+H]$^+$) 338.1009, Found 338.1005.

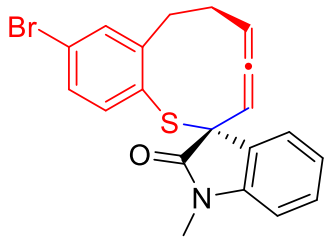
Compound 5c



5c

Prepared according to the procedure as pink solid (60.9 mg, 86% yield); mp 169.1-170.4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 2.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.06 – 6.93 (m, 1H), 6.89 – 6.58 (m, 3H), 6.31 (s, 1H), 6.08 (s, 1H), 5.35 (s, 1H), 3.57 (s, 1H), 3.30 (s, 3H), 3.06 (s, 1H), 2.86 (s, 1H), 2.64 – 2.55 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 174.1, 151.6, 143.5, 142.0, 136.6, 130.1, 128.7, 126.1, 125.1, 121.8, 108.2, 97.0, 93.2, 54.7, 35.4, 30.8, 26.7; HRMS (ESI) m/z Calcd. for $C_{20}H_{17}ClNOS^+$ ([M+H]$^+$) 354.0714, Found 354.0716.

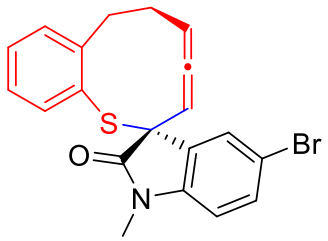
Compound 5d



5d

Prepared according to the procedure as pink solid (73.8 mg, 93% yield); mp 178.7-179.6 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.33 (m, 3H), 7.32 – 7.26 (m, 2H), 7.13 (dd, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.87 (s, 1H), 5.30 (s, 1H), 3.52 (d, *J* = 13.9 Hz, 1H), 3.24 (s, 3H), 3.01 (d, *J* = 15.8 Hz, 1H), 2.85 (d, *J* = 13.1 Hz, 1H), 2.53 – 2.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 171.6, 150.9, 142.5, 142.3, 133.1, 132.9, 129.6, 129.5, 129.1, 129.0, 125.0, 123.3, 122.8, 108.3, 108.2, 94.4, 92.4, 52.9, 34.5, 31.7, 26.5; HRMS (ESI) m/z Calcd. for $C_{20}H_{17}BrNOS^+$ ([M+H]$^+$) 398.0209, Found 398.0210.

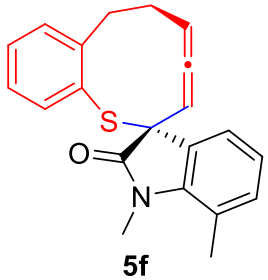
Compound 5e



5e

Prepared according to the procedure as pink solid (67.0 mg, 84% yield); mp 173.3-174.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.33 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 8.3 Hz, 2H), 6.20 (s, 1H), 5.85 (s, 1H), 5.29 (s, 1H), 3.50 (s, 1H), 3.21 (s, 3H), 3.07 – 2.76 (m, 2H), 2.64 – 2.55 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 173.8, 149.7, 142.6, 140.9, 131.0, 130.7, 130.1, 128.4, 125.9, 114.5, 109.4, 96.4, 93.7, 54.4, 35.3, 30.5, 26.8; HRMS (ESI) m/z Calcd. for $C_{20}H_{17}BrNOS^+$ ([M+H]$^+$) 398.0209, Found 398.0208.

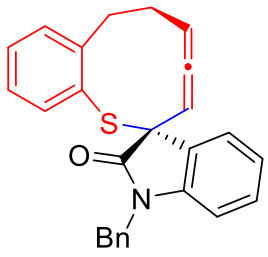
Compound 5f



5f

Prepared according to the procedure as pink solid (64.4 mg, 97% yield); mp 164.7-165.9 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.33 (m, 2H), 7.06 – 6.89 (m, 2H), 6.65 (d, *J* = 78.1 Hz, 2H), 6.29 (s, 1H), 5.89 (s, 1H), 5.33 (s, 1H), 3.58 (s, 4H), 3.16 – 2.80 (m, 2H), 2.58 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 175.3, 149.9, 142.6, 139.7, 132.3, 130.3, 130.0, 129.2, 125.7, 123.3, 121.6, 119.5, 97.1, 93.3, 54.2, 35.5, 30.7, 30.1, 19.2; HRMS (ESI) m/z Calcd. for $C_{21}H_{20}NOS^+$ ([M+H]$^+$) 334.1260, Found 334.1261.

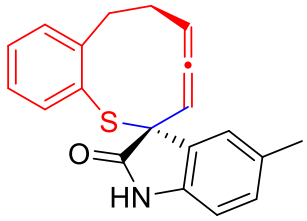
Compound 5g



5g

Prepared according to the procedure as pink solid (70.4 mg, 89% yield); mp 139.4-140.6 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.31 (m, 4H), 7.28 (dd, *J* = 5.9, 2.9 Hz, 1H), 7.13 – 7.07 (m, 1H), 7.03 – 6.93 (m, 1H), 6.83 – 6.55 (m, 3H), 6.38 (s, 1H), 6.02 (s, 1H), 5.36 (s, 1H), 5.12 (d, *J* = 15.9 Hz, 1H), 4.88 (d, *J* = 15.9 Hz, 1H), 3.62 (s, 1H), 3.15 – 2.80 (m, 2H), 2.69 – 2.58 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 174.5, 149.8, 142.6, 141.0, 135.6, 130.3, 130.0, 128.8, 128.4, 127.6, 127.1, 125.7, 125.3, 121.7, 109.1, 96.9, 93.4, 54.9, 43.9, 35.5, 30.7; HRMS (ESI) m/z Calcd. for $C_{26}H_{22}NOS^{+}$ ([M+H]$^{+}$) 396.1417, Found 396.1420.

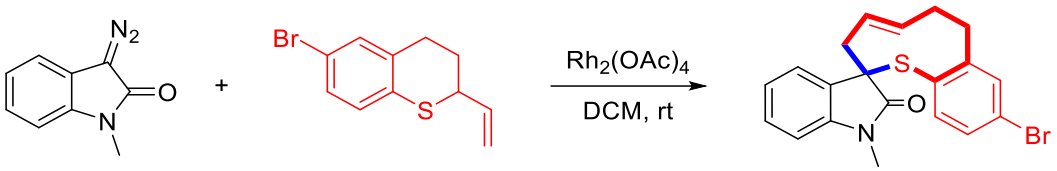
Compound 5h



5h

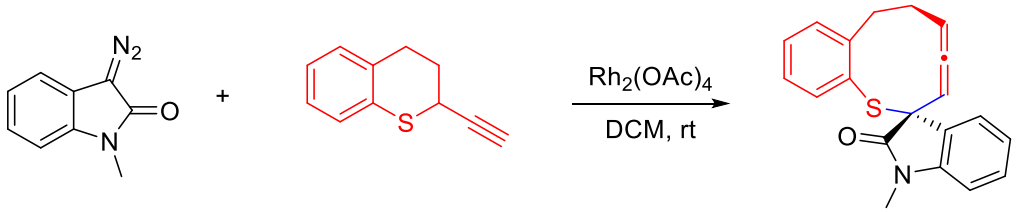
Prepared according to the procedure as pink solid (59.8 mg, 94% yield); mp 144.7-145.9 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 7.44 – 7.37 (m, 2H), 7.06 – 6.96 (m, 2H), 6.86 – 6.66 (m, 2H), 6.31 (s, 1H), 5.67 (s, 1H), 5.35 (s, 1H), 3.61 (s, 1H), 3.14 – 2.80 (m, 2H), 2.66 (s, 1H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 207.6, 175.6, 149.9, 142.5, 138.1, 130.9, 130.7, 130.3, 129.9, 129.1, 126.3, 127.0, 109.7, 109.7, 96.7, 94.0, 55.4, 35.3, 30.7, 21.2; HRMS (ESI) m/z Calcd. for $C_{20}H_{17}NNaOS^{+}$ ([M+Na]$^{+}$) 342.0923, Found 342.0925.

4. Scale-up reactions and transformations



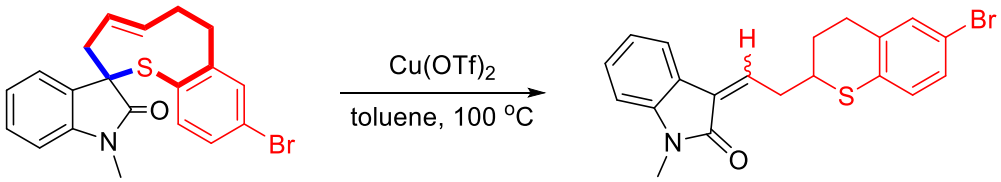
1k **2d** **3o**

Substrates **2d** (4 mmol, 1 equiv) and $Rh_2(OAc)_4$ (2 mol%) were introduced into a dried glass tube and add 40 mL dry DCM as solvent, then the diazooxindole **1k** (4.8 mmol, 1.2 equiv) was added dropwise at room temperature. The reaction was monitored by TLC. The product was directly purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 3:1) to give the product **3o** (1.52 g, 95% yield).



1k **4a** **5a**

Substrates **4a** (2 mmol, 1 equiv) and $Rh_2(OAc)_4$ (2 mol%) were introduced into a dried glass tube and add 20 mL dry DCM as solvent, then the diazooxindoles **1k** (2.4 mmol, 1.2 equiv) was added dropwise at room temperature. The reaction was monitored by TLC. The product was directly purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 3:1) to give the product **5a** (586 mg, 92% yield).

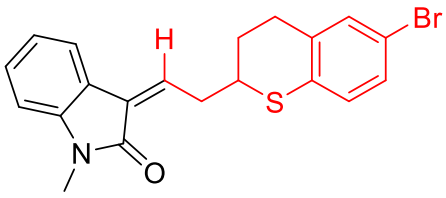


3o

(*Z*)-**6**, 18.3 mg, 46% yield
(*E*)-**6**, 17.1 mg, 43% yield

Compund **3o** (0.1 mmol) and $Cu(OTf)_2$ (10 mol%) were introduced into a dried glass tube and add 1 mL dry toluene as solvent, then the reaction was conducted at 100 °C. The reaction was monitored by TLC. The product was directly purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 3:1) to give the desired products.

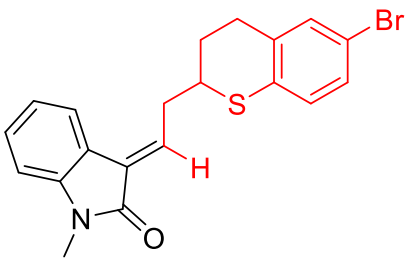
Compound (*Z*)-6



(*Z*)-**6**

Prepared according to the procedure as yellow solid (18.3 mg, 46% yield); mp 105.4-106.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.4 Hz, 1H), 7.31 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.05 (td, *J* = 7.5, 0.9 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.66 – 3.49 (m, 2H), 3.31 (q, *J* = 7.3 Hz, 1H), 3.26 (s, 3H), 2.97 – 2.77 (m, 2H), 2.37 – 2.25 (m, 1H), 1.92 (dtd, *J* = 13.8, 9.7, 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 142.4, 136.9, 135.8, 132.3, 132.3, 129.4, 129.1, 129.0, 128.0, 122.6, 122.0, 119.3, 117.3, 108.0, 41.9, 33.7, 29.1, 29.0, 25.7; HRMS (ESI) m/z Calcd. for $C_{20}H_{18}BrNNaOS^+$ ([M+Na]$^+$) 422.0185, Found 422.0179.

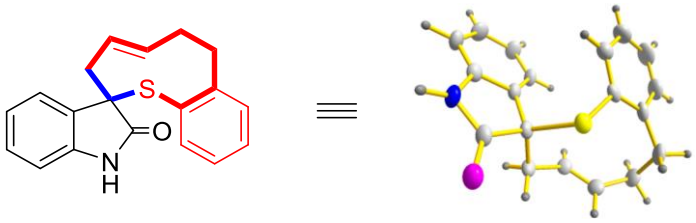
Compound (*E*)-6



(*E*)-**6**

Prepared according to the procedure as yellow solid (17.1 mg, 43% yield); mp 107.6-108.4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 12.1 Hz, 2H), 7.06 (ddd, *J* = 8.3, 4.2 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.61 (d, *J* = 7.5 Hz, 1H), 3.27 (s, 3H), 3.04 (t, *J* = 7.3 Hz, 2H), 2.95 – 2.77 (m, 2H), 2.42 – 2.26 (m, 1H), 2.01 – 1.79 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 144.0, 136.4, 135.5, 132.3, 132.1, 129.6, 129.4, 128.0, 123.6, 122.2, 121.8, 117.5, 108.2, 41.0, 35.6, 28.9, 28.9, 26.1; HRMS (ESI) m/z Calcd. for $C_{20}H_{18}BrNNaOS^+$ ([M+Na]$^+$) 422.0185, Found 422.0179.

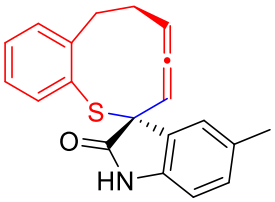
4. X-ray crystal structures



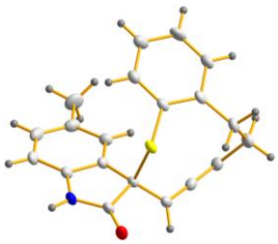
3a CCDC 2423576

Crystal data and structure refinement for **3a**.

Identification code	**3a**
Empirical formula	$C_{19}H_{17}NOS$
Formula weight	307.39
Temperature/K	173.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.2703(15)
b/Å	9.7437(12)
c/Å	17.104(2)
α/°	90
β/°	94.312(3)
γ/°	90
Volume/Å^3	1872.9(4)
Z	4
ρ_{calc}g/cm^3	1.090
μ/mm^{-1}	0.174
F(000)	648.0
Crystal size/mm^3	0.24 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.776 to 50.054
Index ranges	-13 ≤ h ≤ 13, -11 ≤ k ≤ 11, -20 ≤ l ≤ 20
Reflections collected	16332
Independent reflections	3271 [R_{int} = 0.0863, R_{sigma} = 0.0679]
Data/restraints/parameters	3271/0/203
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0688, wR_2 = 0.1463
Final R indexes [all data]	R_1 = 0.0975, wR_2 = 0.1602
Largest diff. peak/hole / e Å^{-3}	0.41/-0.30



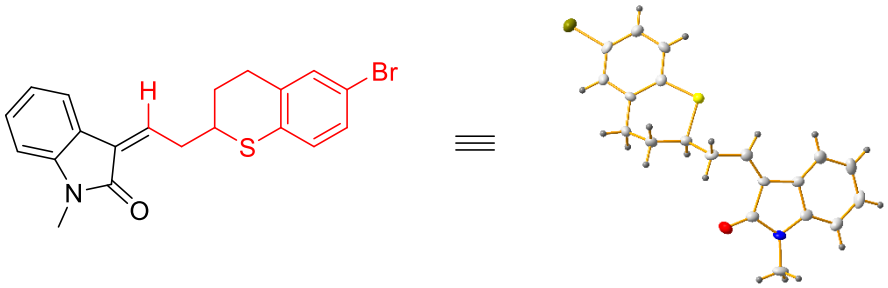
5h



CCDC 2423577

Crystal data and structure refinement for **5h**.

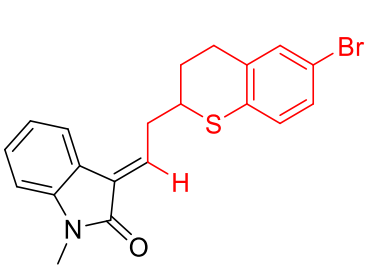
Identification code	**5h**
Empirical formula	$C_{20}H_{17}NOS$
Formula weight	319.40
Temperature/K	120.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.0368(6)
b/Å	14.1257(11)
c/Å	14.1169(11)
α/°	90
β/°	95.904(2)
γ/°	90
Volume/Å^3	1594.1(2)
Z	4
ρ_{calc}g/cm^3	1.331
μ/mm^{-1}	0.207
F(000)	672.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.09 to 58.81
Index ranges	-11 ≤ h ≤ 11, -19 ≤ k ≤ 19, -19 ≤ l ≤ 19
Reflections collected	24917
Independent reflections	4332 [R_{int} = 0.0782, R_{sigma} = 0.0738]
Data/restraints/parameters	4332/0/209
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0686, wR_2 = 0.1561
Final R indexes [all data]	R_1 = 0.1119, wR_2 = 0.2076
Largest diff. peak/hole / e Å^{-3}	0.82/-0.83

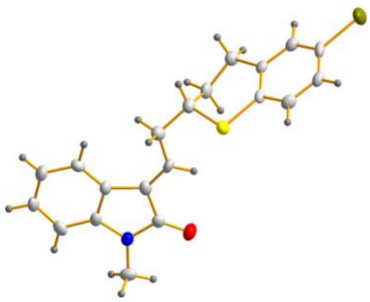


(*Z*)-**6** CCDC 2423578

Crystal data and structure refinement for (*Z*)-**6**.

Identification code	(*Z*)-**6**
Empirical formula	$C_{20}H_{18}BrNOS$
Formula weight	400.32
Temperature/K	120.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.640(5)
b/Å	13.250(4)
c/Å	7.717(2)
α/°	90
β/°	95.778(8)
γ/°	90
Volume/Å^3	1692.8(9)
Z	4
ρ_{calc}g/cm^3	1.571
μ/mm^{-1}	2.558
F(000)	816.0
Crystal size/mm^3	0.4 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.938 to 51.456
Index ranges	-20 ≤ h ≤ 20, -16 ≤ k ≤ 16, -9 ≤ l ≤ 9
Reflections collected	29292
Independent reflections	3228 [R_{int} = 0.1601, R_{sigma} = 0.1168]
Data/restraints/parameters	3228/0/218
Goodness-of-fit on F^2	0.977
Final R indexes [I>=2σ (I)]	R_1 = 0.0579, wR_2 = 0.1220
Final R indexes [all data]	R_1 = 0.1176, wR_2 = 0.1510
Largest diff. peak/hole / e Å^{-3}	1.28/-0.74





(*E*)-**6** CCDC 2423579

Crystal data and structure refinement for (*E*)-**6**.

Identification code	(*E*)-**6**
Empirical formula	$C_{20}H_{18}BrNOS$
Formula weight	400.32
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	7.0549(11)
b/Å	15.033(3)
c/Å	17.847(4)
α/°	65.113(6)
β/°	87.985(5)
γ/°	89.238(6)
Volume/Å^3	1716.0(5)
Z	4
ρ_{calc}g/cm^3	1.550
μ/mm^{-1}	2.523
F(000)	816.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.646 to 49.998
Index ranges	-8 ≤ h ≤ 8, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21
Reflections collected	34519
Independent reflections	6044 [R_{int} = 0.1142, R_{sigma} = 0.0810]
Data/restraints/parameters	6044/0/436
Goodness-of-fit on F^2	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.0730, wR_2 = 0.1970
Final R indexes [all data]	R_1 = 0.1049, wR_2 = 0.2179
Largest diff. peak/hole / e Å^{-3}	0.93/-1.14

5. Proposed model for the diastereoselective formation of compound 5a

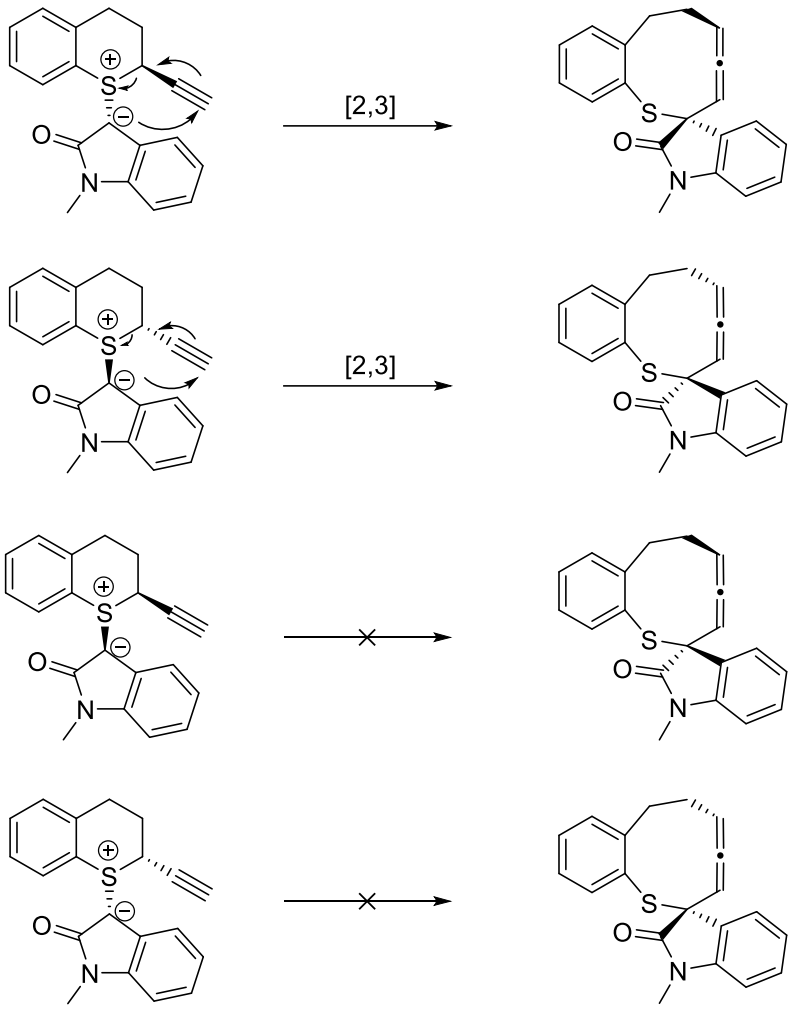


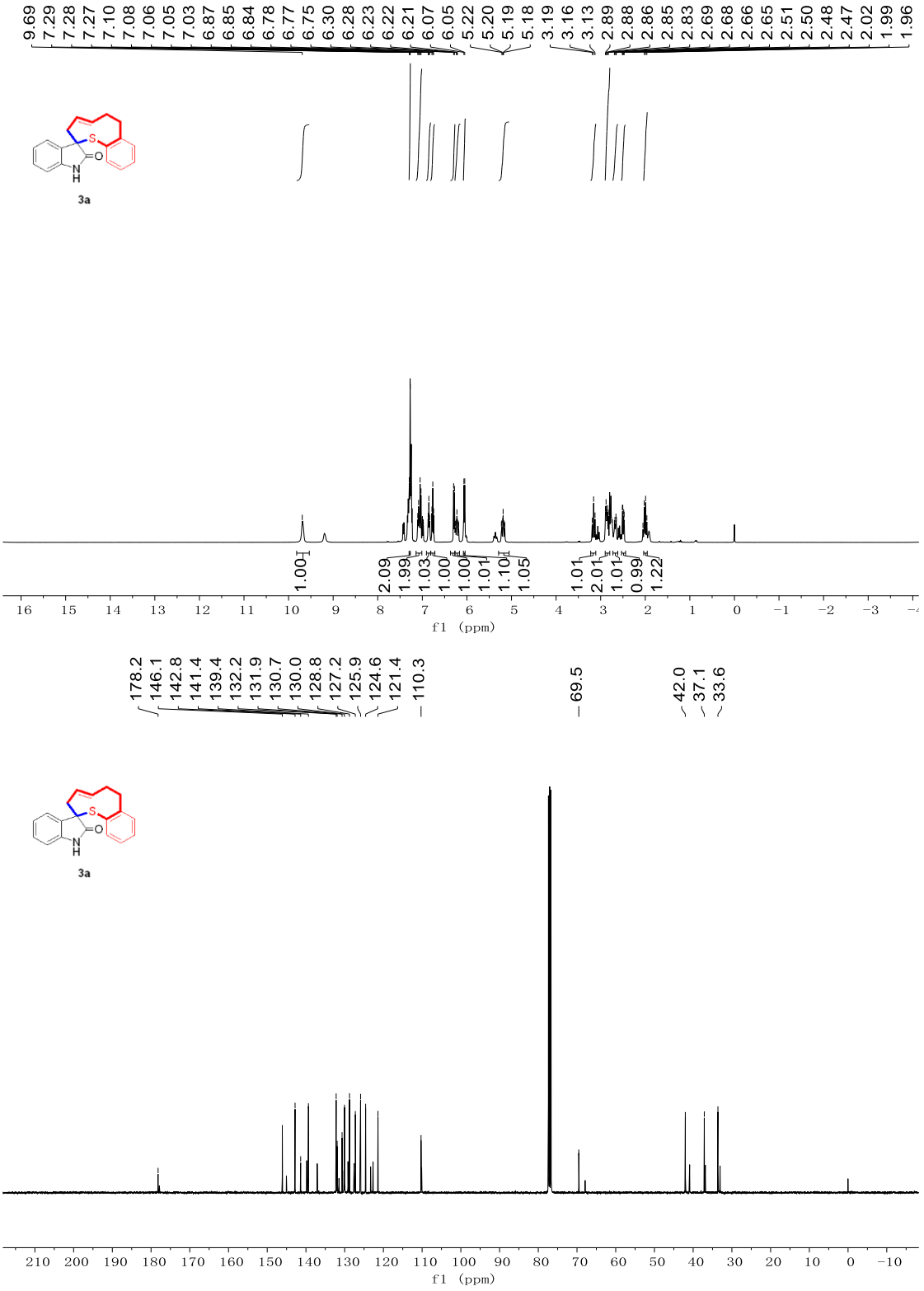
Figure S1 Diastereoselectivity model for the formation of compound **5a**

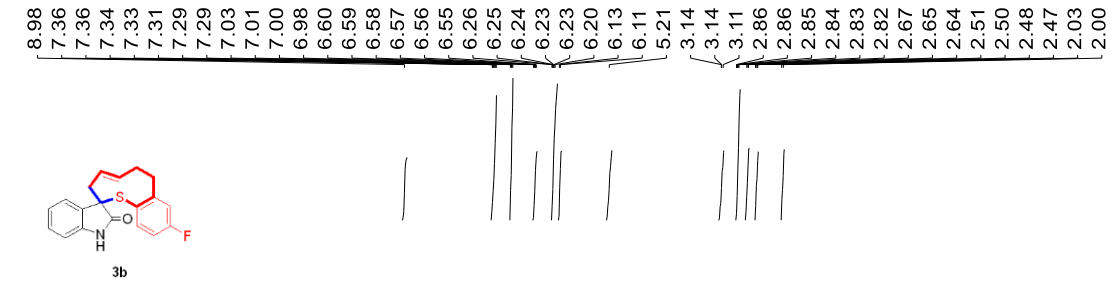
6. References

[1] (a) C. Zhai, D. Xing, C. Jing, J. Zhou, C. Wang, D. Wang and W. Hu, *Org. Lett.*, 2014, **16**, 2934–2937; (b) B. Ma, P. Wu, X. Wang, Z. Wang, H.-X. Lin and H.-X. Dai, *Angew. Chem. Int. Ed.*, 2019, **58**, 13335–13339; (c) A. V. Sasane, T.-C. Kuo, M.-J. Cheng and R.-S. Liu, *Org. Lett.*, 2022, **24**, 5220–5225.

[2] (a) V. Cere, C. Paolucci, S. Pollicino, E. Sandri and A. Fava, *J. Org. Chem.*, 1978, **43**, 4826–4831; (b) E. Vedejs, M. J. Arco, D. W. Powell, J. M. Renga and S. P. Singer, *J. Org. Chem.,* 1978, **43**, 4831–4837; (c) H. Sashida and T. Tsuchiya, *Chem. Pharm. Bull.*, 1986, **34**, 3644–3652; (d) H. Sashida and T. Tsuchiya, *Chem. Pharm. Bull.*, 1986, **34**, 3682–3687.

7. NMR spectra of product

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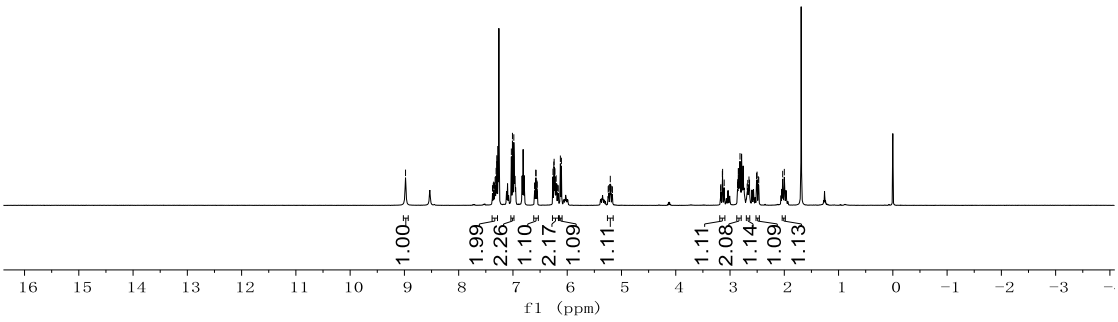
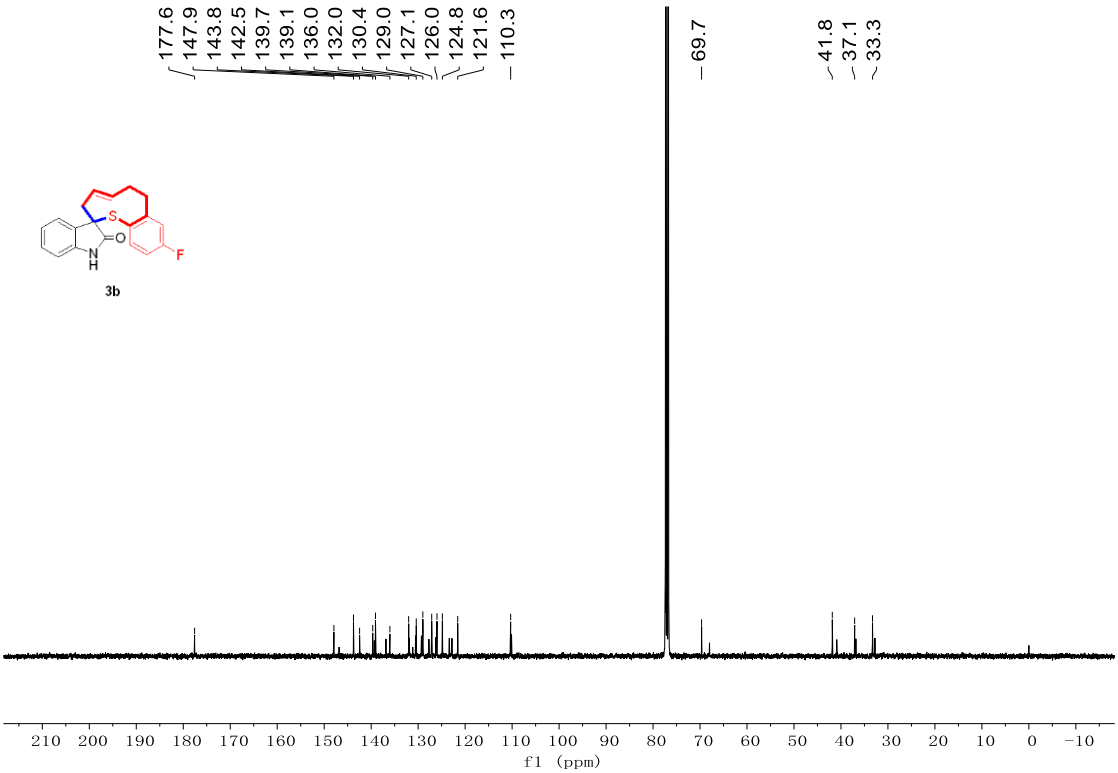
7.36
7.34
7.33
7.31
7.29
7.29
7.03
7.01
7.00
6.98
6.60
6.59
6.58
6.57
6.56
6.55
6.26
6.25
6.24
6.23
6.23
6.20
6.13
6.11
5.21
3.14
3.14
3.11
2.86
2.86
2.85
2.84
2.83
2.82
2.67
2.65
2.64
2.51
2.50
2.48
2.47
2.03
2.00
S
O
N
H
F

3b


1.00
1.99
2.26
1.10
2.17
1.09
1.11
1.11
2.08
1.14
1.09
1.13
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)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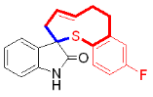
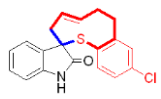
147.9
143.8
142.5
139.7
139.1
136.0
132.0
130.4
129.0
127.1
126.0
124.8
121.6
110.3
69.7
41.8
37.1
33.3
S
O
N
H
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

3b


S
O
N
H
F

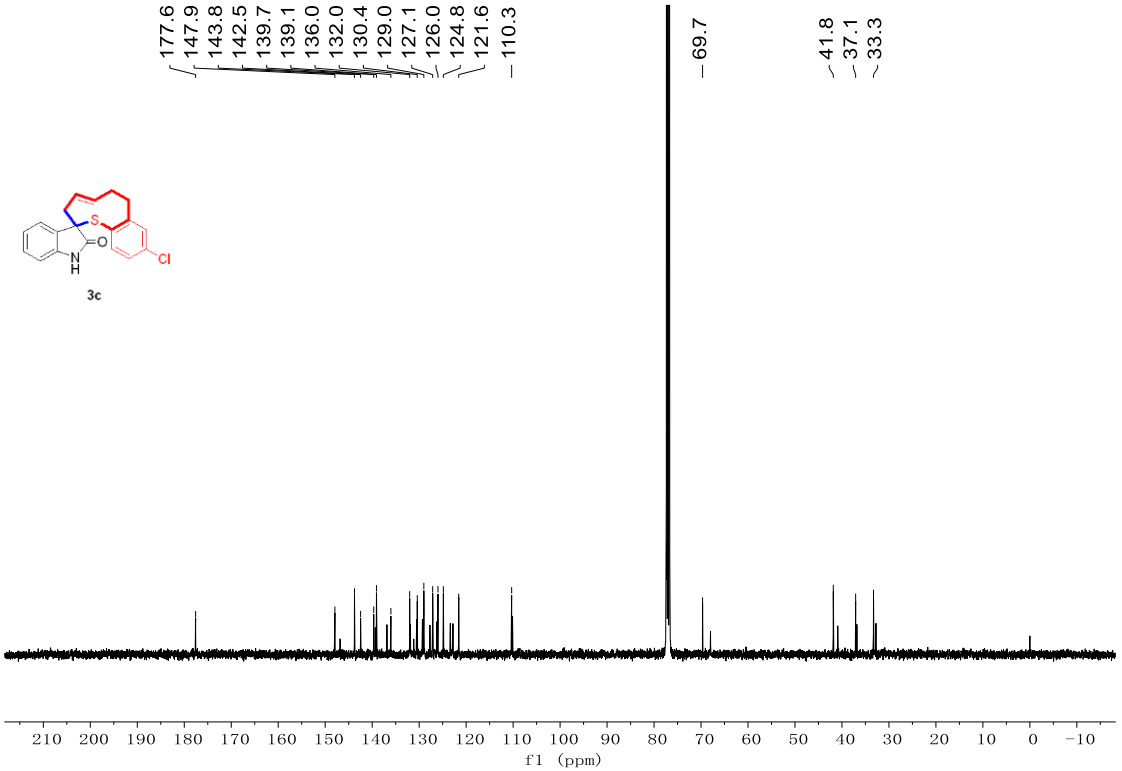
3b

-111.42
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


S
O
N
H
Cl

3c

8.68
6.20
6.19
6.18
6.16
6.15
5.21
5.20
5.19
3.12
3.12
3.09
2.83
2.81
2.78
2.77
2.69
2.67
2.66
2.65
2.64
2.51
2.50
2.48
2.47
2.02
1.00
2.00
1.24
1.04
1.99
2.29
1.04
1.02
2.11
1.17
1.00
1.08
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)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132.0
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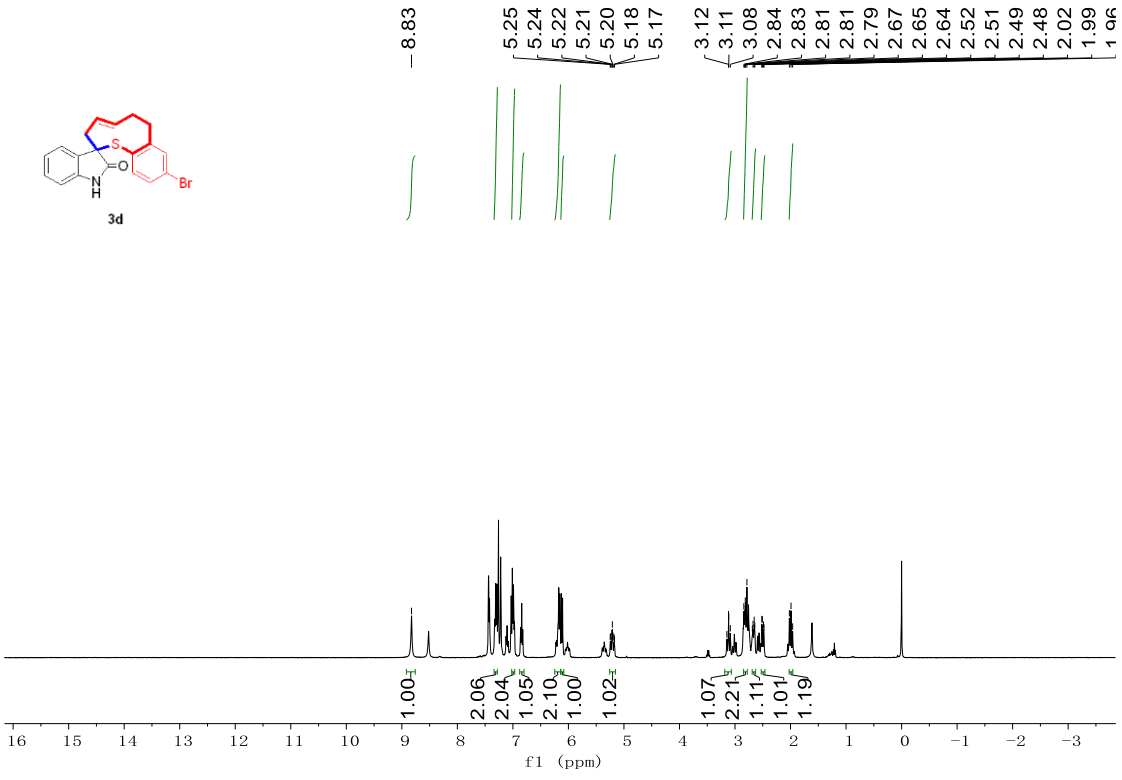
127.1
126.0
124.8
121.6
110.3
69.7
41.8
37.1
33.3
S
O
N
H
Cl
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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5.20
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5.17
3.12
3.11
3.08
2.84
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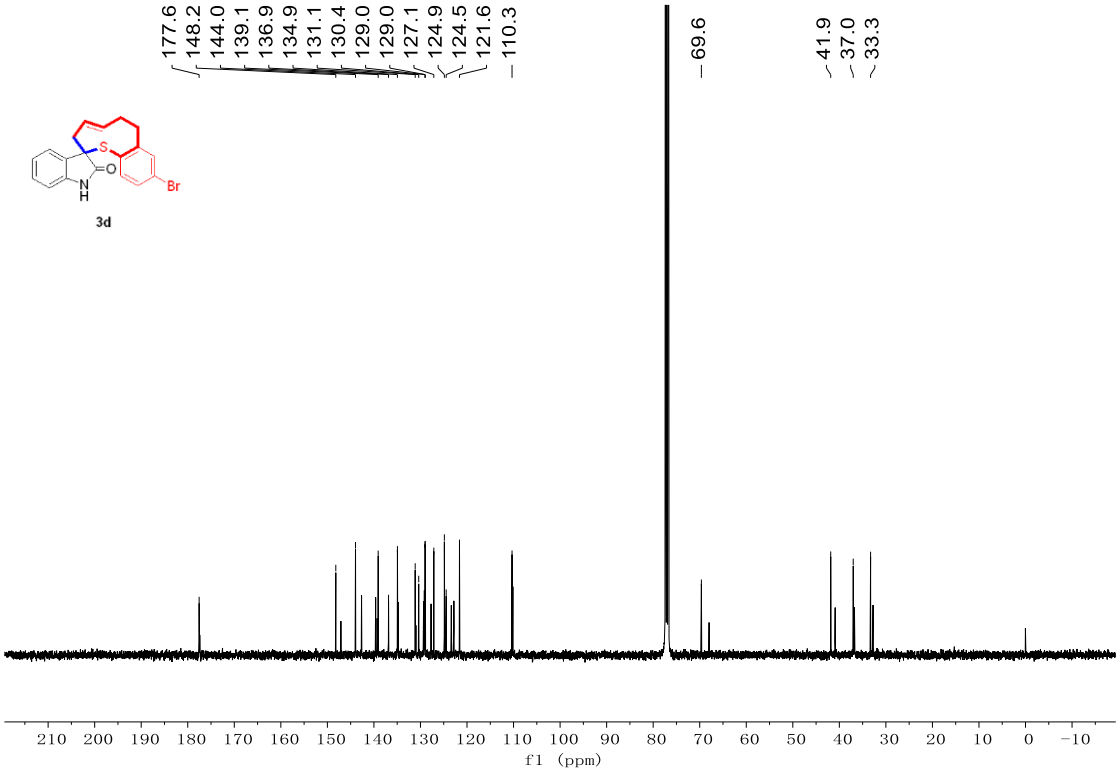
2.81
2.81
2.79
2.67
2.65
2.64
2.52
2.51
2.49
2.48
2.02
1.99
S
O
N
H
Br
3d
1.00
2.06
2.04
1.05
2.10
1.00
1.02
1.07
2.21
1.11
1.01
1.19
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)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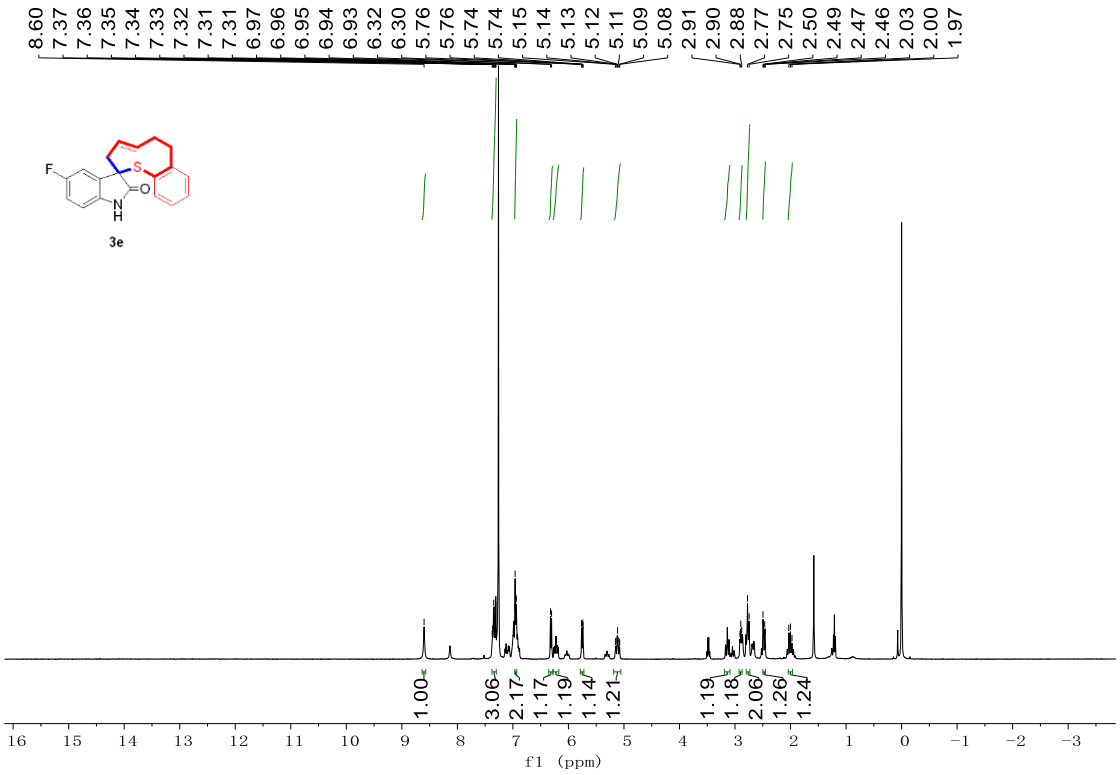
144.0
139.1
136.9
134.9
131.1
130.4
129.0
129.0
127.1
124.9
124.5
121.6
110.3
69.6
41.9
37.0
33.3
S
O
N
H
Br
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.33
7.32
7.31
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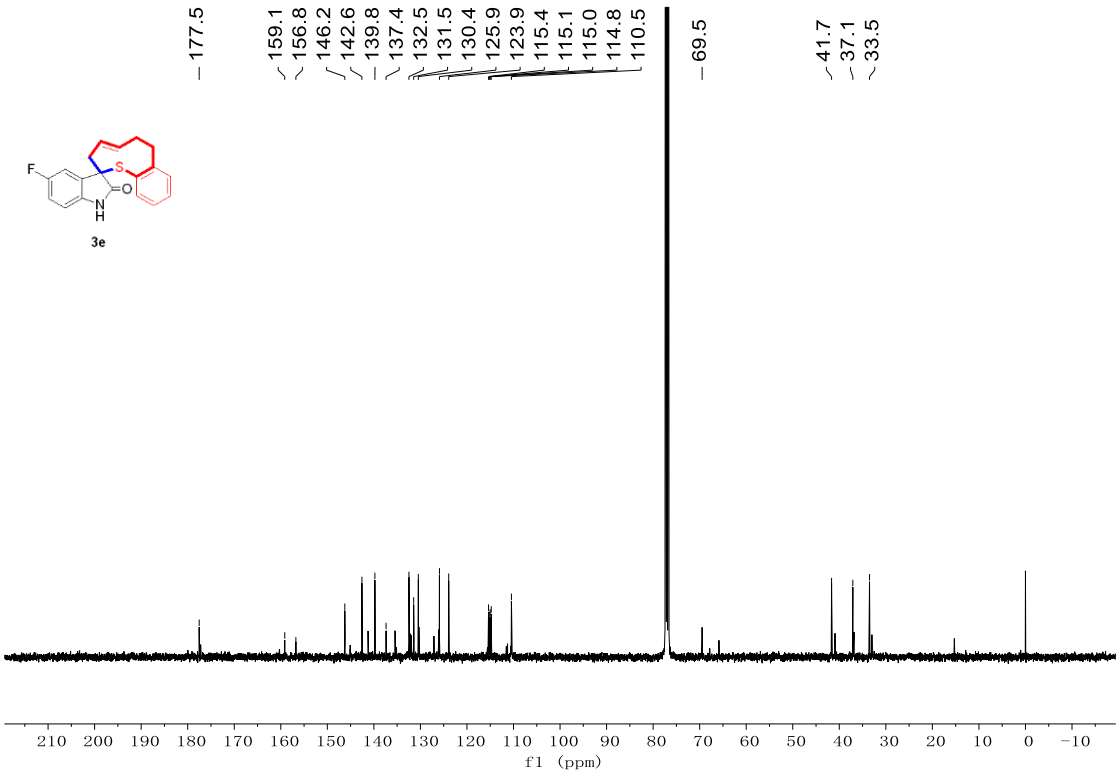
6.97
6.96
6.95
6.94
6.93
6.32
6.30
5.76
5.76
5.74
5.74
5.15
5.14
5.13
5.12
5.11
5.09
5.08
2.91
2.90
2.88
2.77
2.75
2.50
2.49
2.47
2.46
2.03
2.00
1.97
F
S
O
N
H
3e
1.00
3.06
2.17
1.17
1.19
1.14
1.21
1.19
1.18
2.06
1.26
1.24
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)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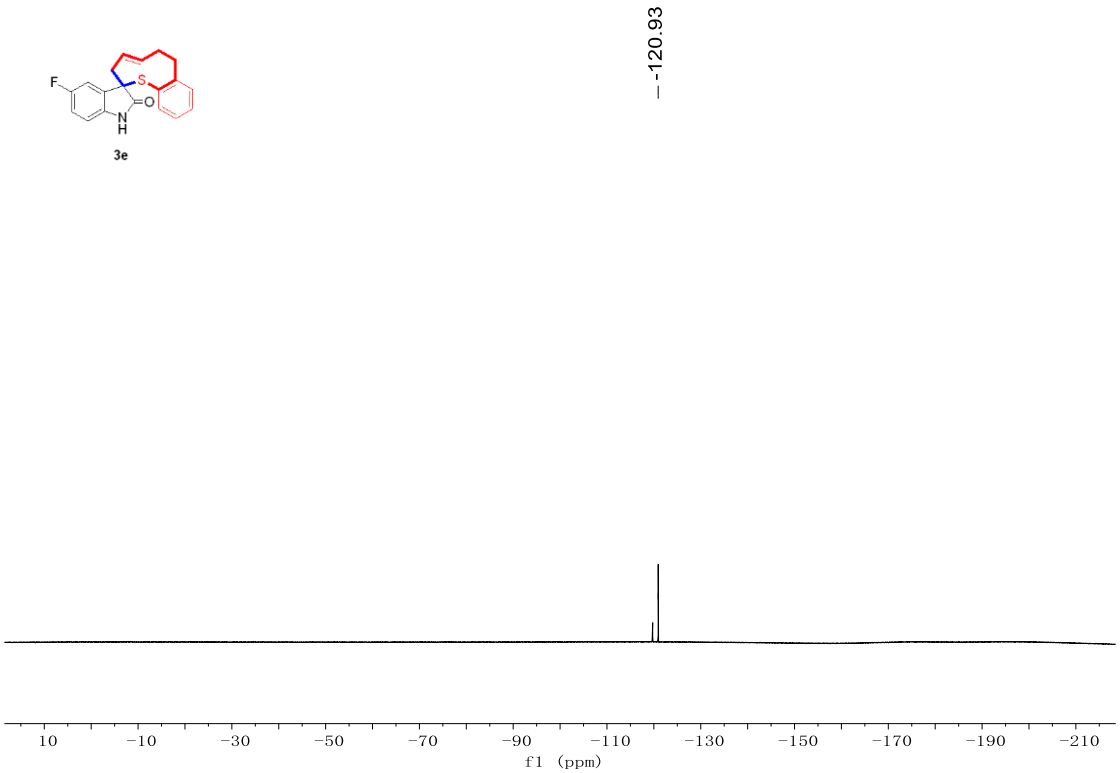
146.2
142.6
139.8
137.4
132.5
131.5
130.4
125.9
123.9
115.4
115.1
115.0
114.8
110.5
69.5
41.7
37.1
33.5
F
S
O
N
H
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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F
S
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N
H
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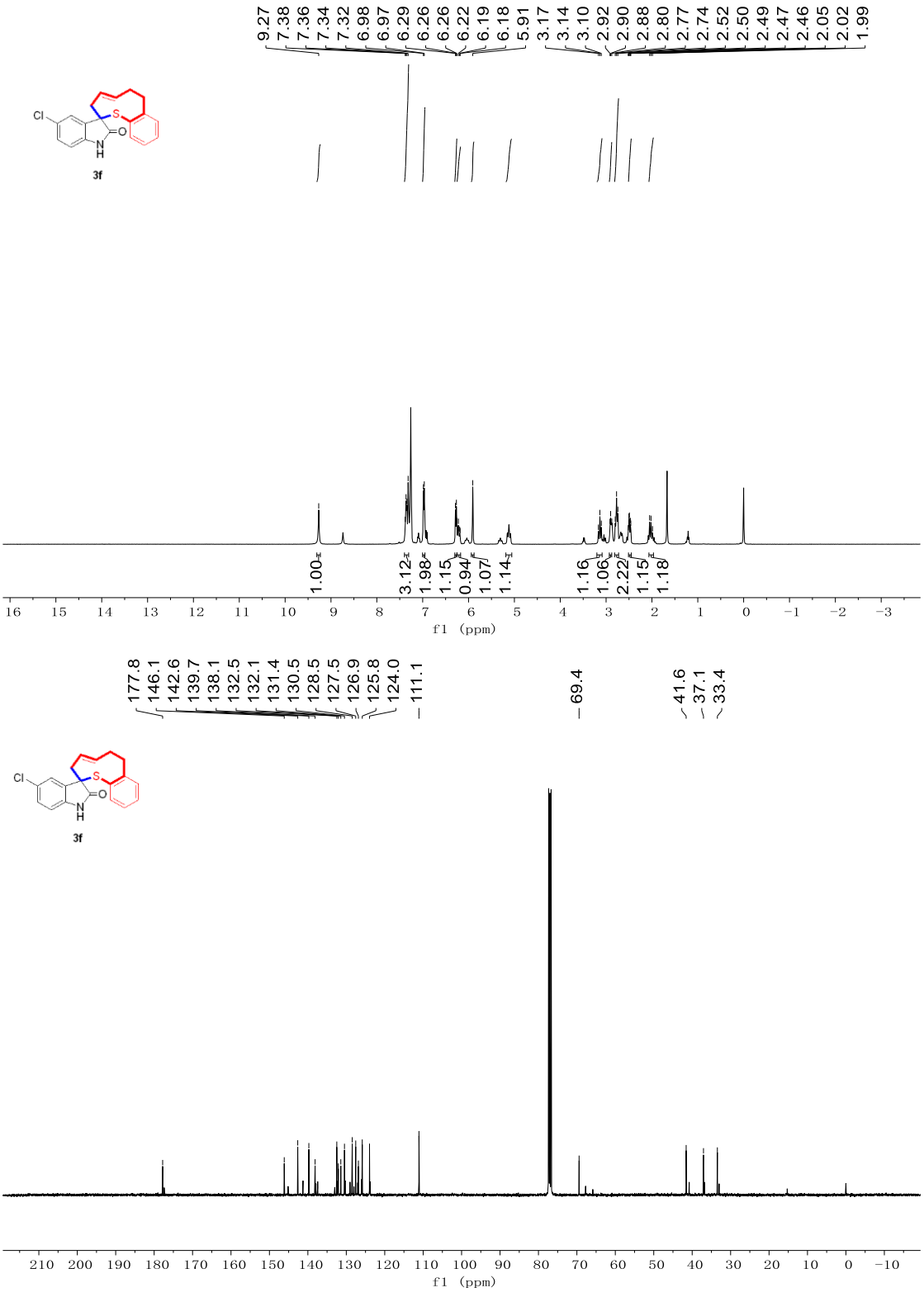
10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210
f1 (ppm)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6.18
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3.17
3.14
3.10
2.92
2.90
2.88
2.80
2.77
2.74
2.52
2.50
2.49
2.47
2.46
2.05
2.02
1.99
Cl
S
O
N
H
3f
1.00
3.12
1.98
1.15
0.94
1.07
1.14
1.16
1.06
2.22
1.15
1.18
f1 (ppm)
177.8
146.1
142.6
139.7
138.1
132.5
132.1
131.4
130.5
128.5
127.5
126.9
125.8
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69.4
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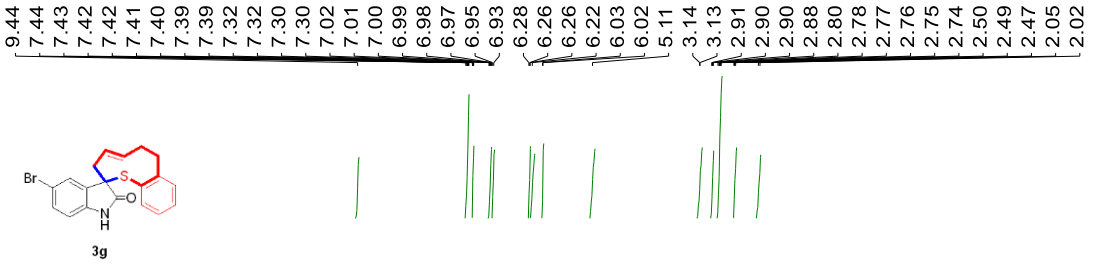
37.1
33.4
Cl
S
O
N
H
3f
f1 (ppm)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6.98
6.97
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6.26
6.26
6.22
6.03
6.02
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3.13
2.91
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2.77
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2.49
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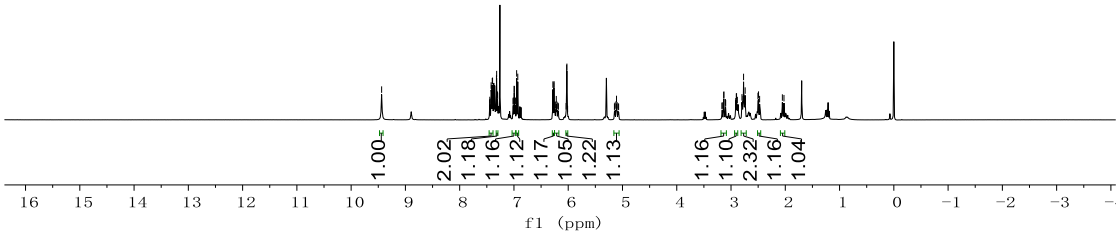
2.02
Br
S
O
N
H

3g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1.17
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1.22
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1.10
2.32
1.16
1.04
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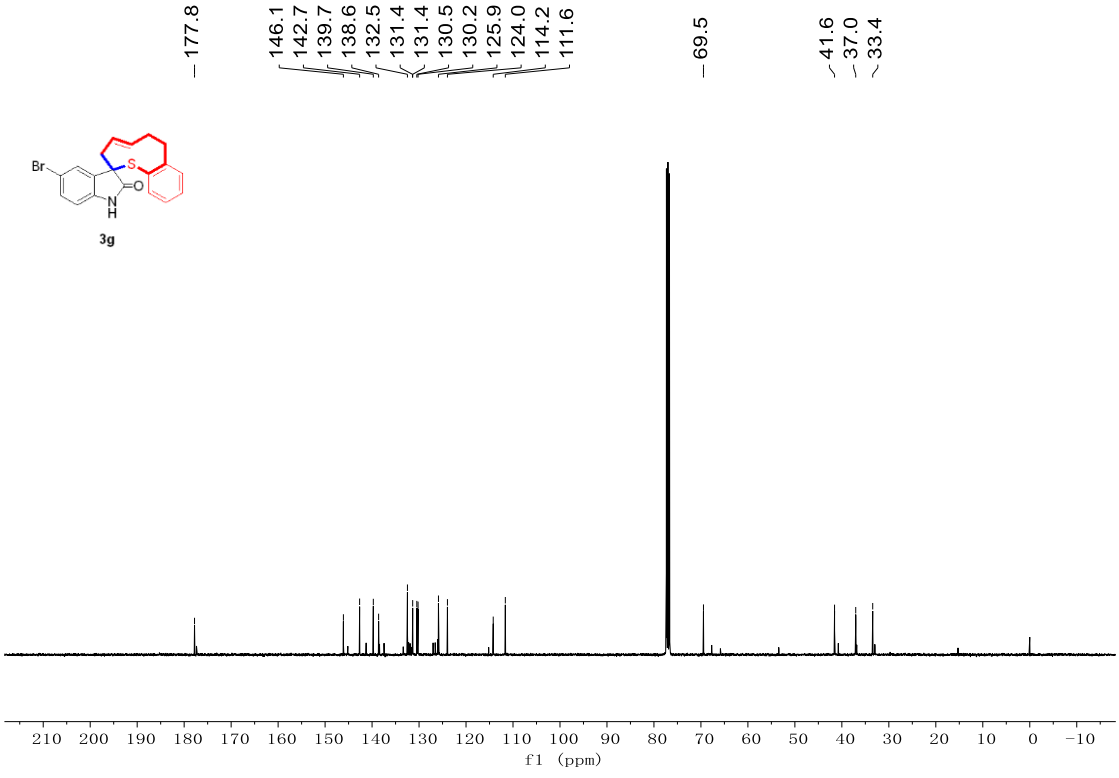
f1 (ppm)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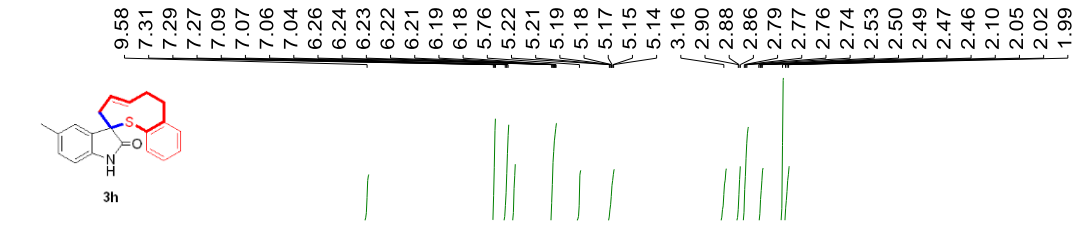
139.7
138.6
132.5
131.4
131.4
130.5
130.2
125.9
124.0
114.2
111.6
69.5
41.6
37.0
33.4
Br
S
O
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

3g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6.19
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5.21
5.19
5.18
5.17
5.15
5.14
3.16
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2.86
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2.49
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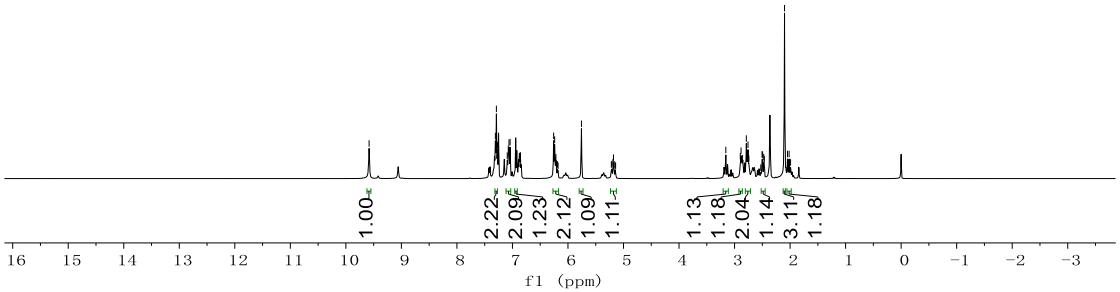
2.10
2.05
2.02
1.99

3h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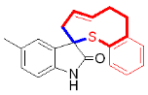
1.23
2.12
1.09
1.11
1.13
1.18
2.04
1.14
3.11
1.18
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


178.4
146.2
143.0
139.1
137.3
132.1
132.0
130.6
130.5
129.9
128.8
128.1
125.3
124.7
110.0
69.7
41.9
37.1
33.5
21.1



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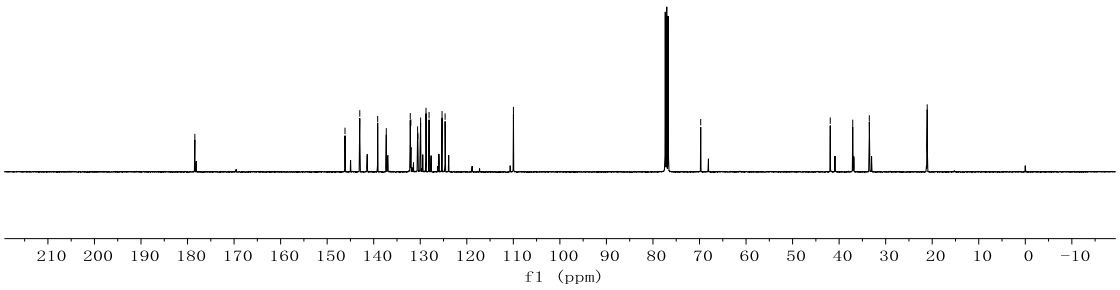
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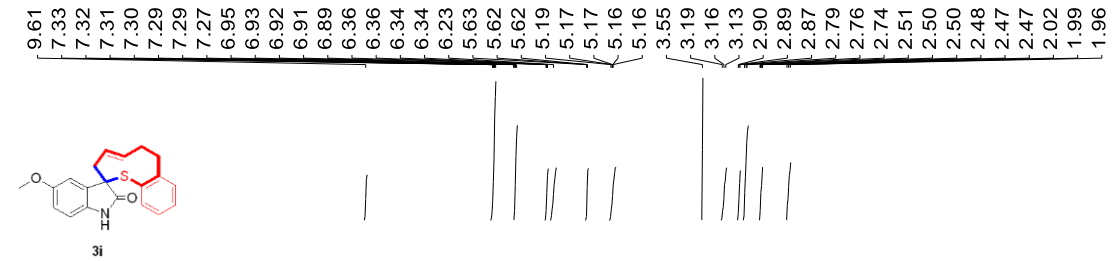
f1 (ppm)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6.23
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5.62
5.62
5.19
5.17
5.17
5.16
5.16
3.55
3.19
3.16
3.13
2.90
2.89
2.87
2.79
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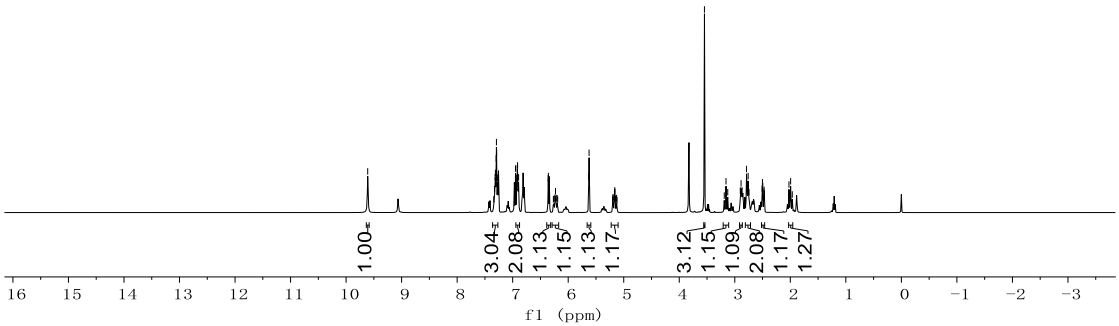
2.47
2.02
1.99
1.96

3i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1.17
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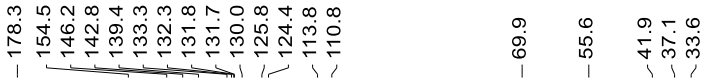
2.08
1.17
1.27
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)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113.8
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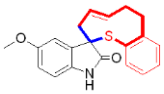
33.6



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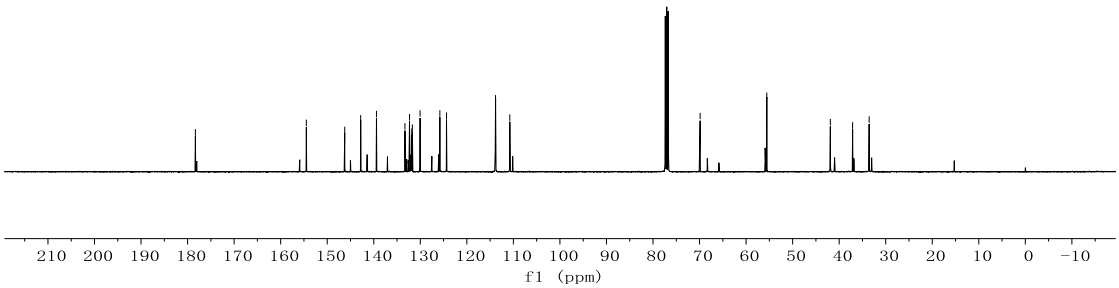
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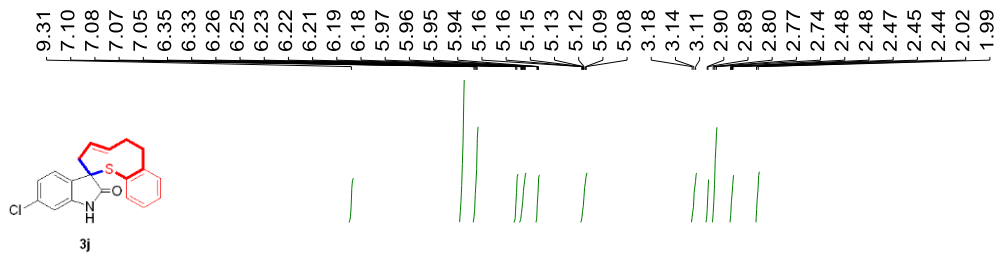
f1 (ppm)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6.18
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5.96
5.95
5.94
5.16
5.16
5.15
5.13
5.12
5.09
5.08
3.18
3.14
3.11
2.90
2.89
2.80
2.77
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2.48
2.47
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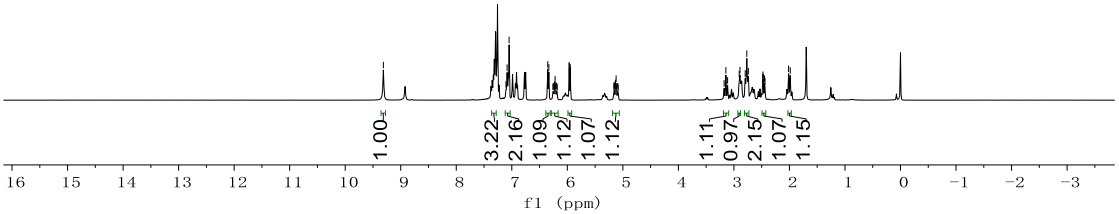
2.44
2.02
1.99
S
O
N
H
Cl

3j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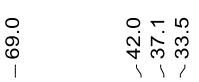
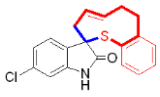
1.07
1.12
1.11
0.97
2.15
1.07
1.15
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


178.1
146.2
142.7
140.9
139.7
134.6
132.4
131.7
130.2
129.0
128.0
126.1
124.1
121.4
110.9

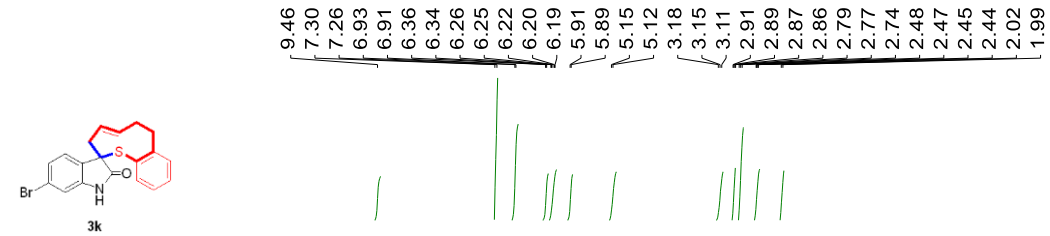

69.0

42.0
37.1
33.5


S
O
N
H
Cl

3j

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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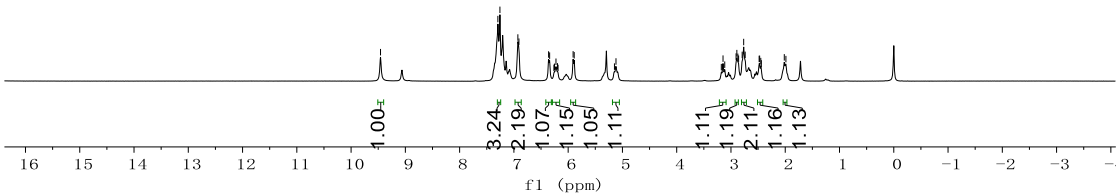
6.20
6.19
5.91
5.89
5.15
5.12
3.18
3.15
3.11
2.91
2.89
2.87
2.86
2.79
2.77
2.74
2.48
2.47
2.45
2.44
2.02
1.99
Br
S
O
N
H

3k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1.07
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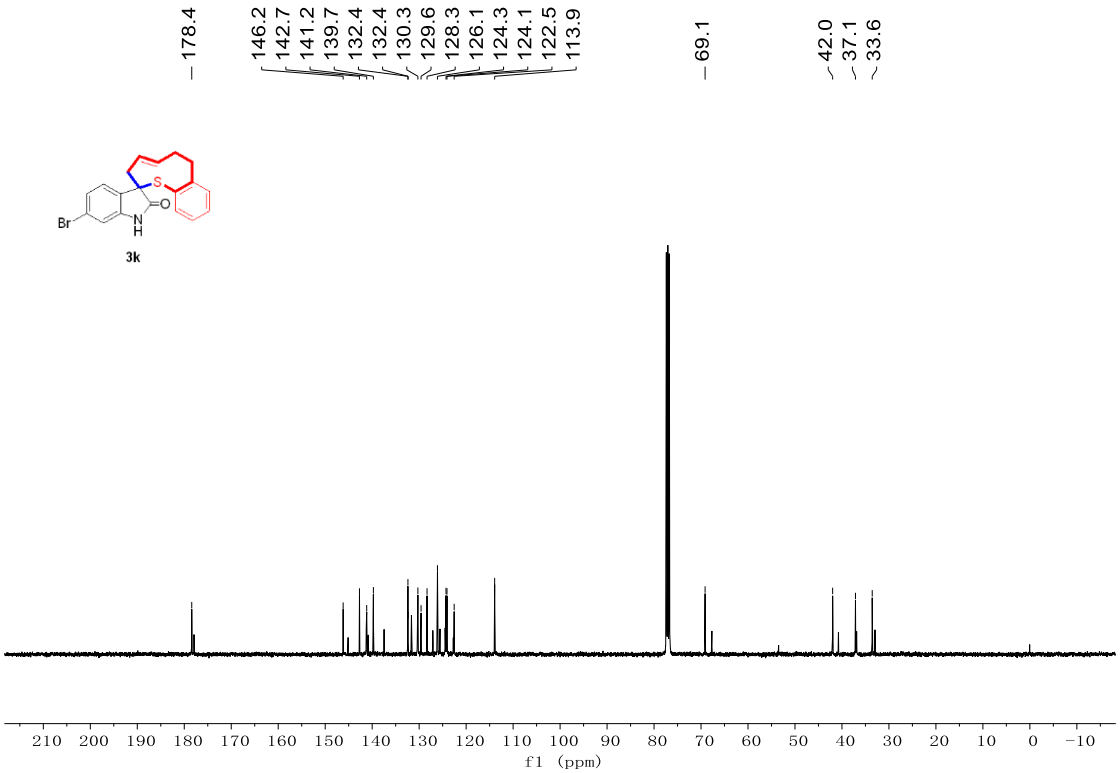
1.05
1.11
1.11
1.19
2.11
1.16
1.13
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)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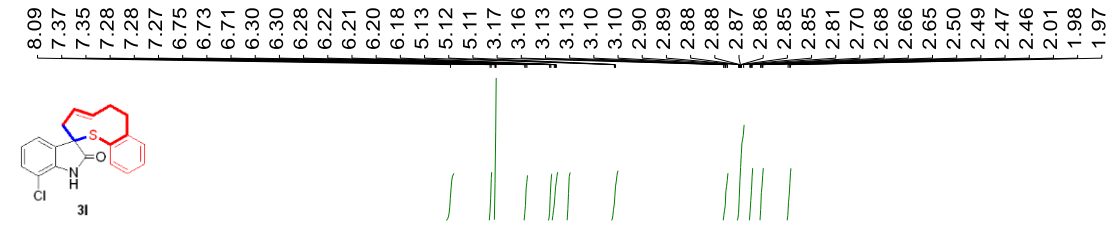
142.7
141.2
139.7
132.4
132.4
130.3
129.6
128.3
126.1
124.3
124.1
122.5
113.9
69.1
42.0
37.1
33.6
Br
S
O
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

3k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6.21
6.20
6.18
5.13
5.12
5.11
3.17
3.16
3.13
3.13
3.10
3.10
2.90
2.89
2.88
2.88
2.87
2.86
2.85
2.85
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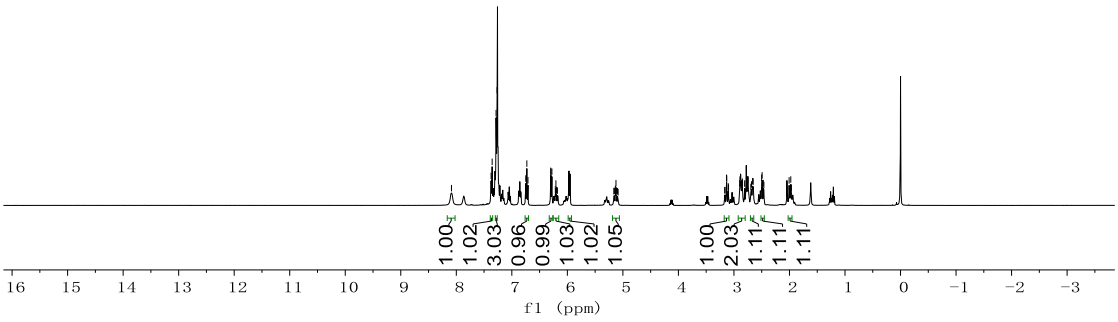
2.49
2.47
2.46
2.01
1.98
1.97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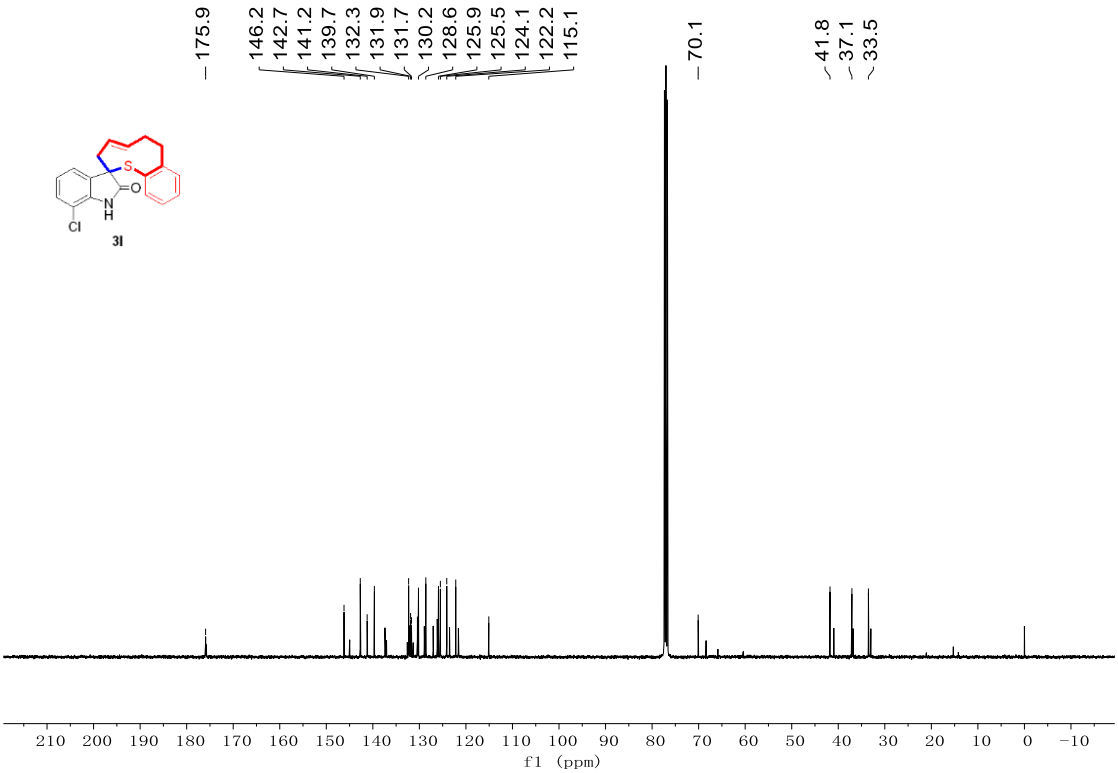
1.00
2.03
1.11
1.11
1.11
f1 (ppm)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132.3
131.9
131.7
130.2
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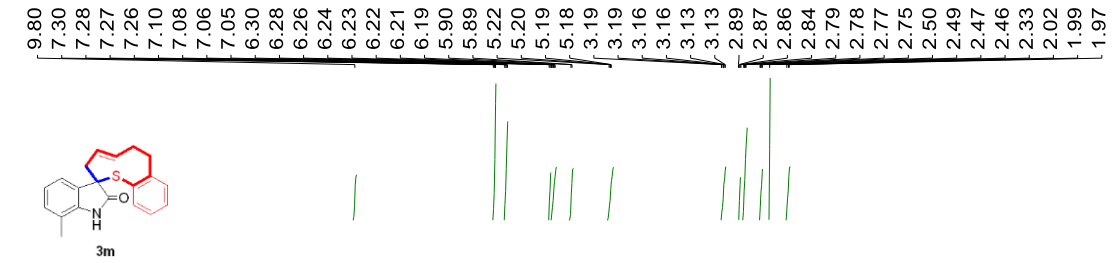
125.5
124.1
122.2
115.1
70.1
41.8
37.1
33.5
f1 (ppm)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6.24
6.23
6.22
6.21
6.19
5.90
5.89
5.22
5.20
5.19
5.18
3.19
3.19
3.16
3.16
3.13
3.13
2.89
2.87
2.86
2.84
2.79
2.78
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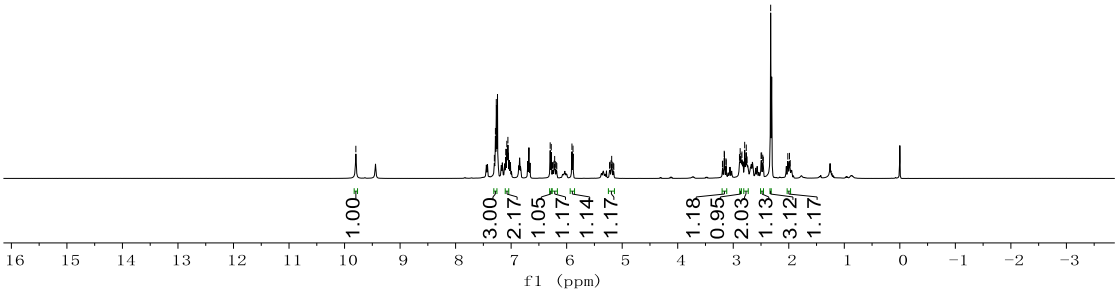
2.75
2.50
2.49
2.47
2.46
2.33
2.02
1.99
1.97

3m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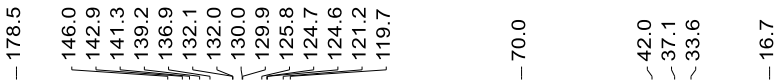
3.00
2.17
1.05
1.17
1.14
1.17
1.18
0.95
2.03
1.13
3.12
1.17
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)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132.0
130.0
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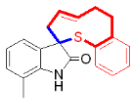
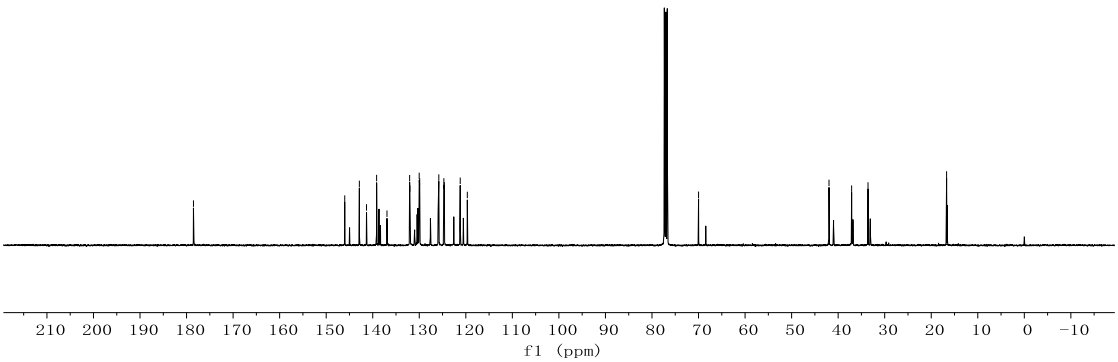
125.8
124.7
124.6
121.2
119.7
70.0
42.0
37.1
33.6
16.7



3m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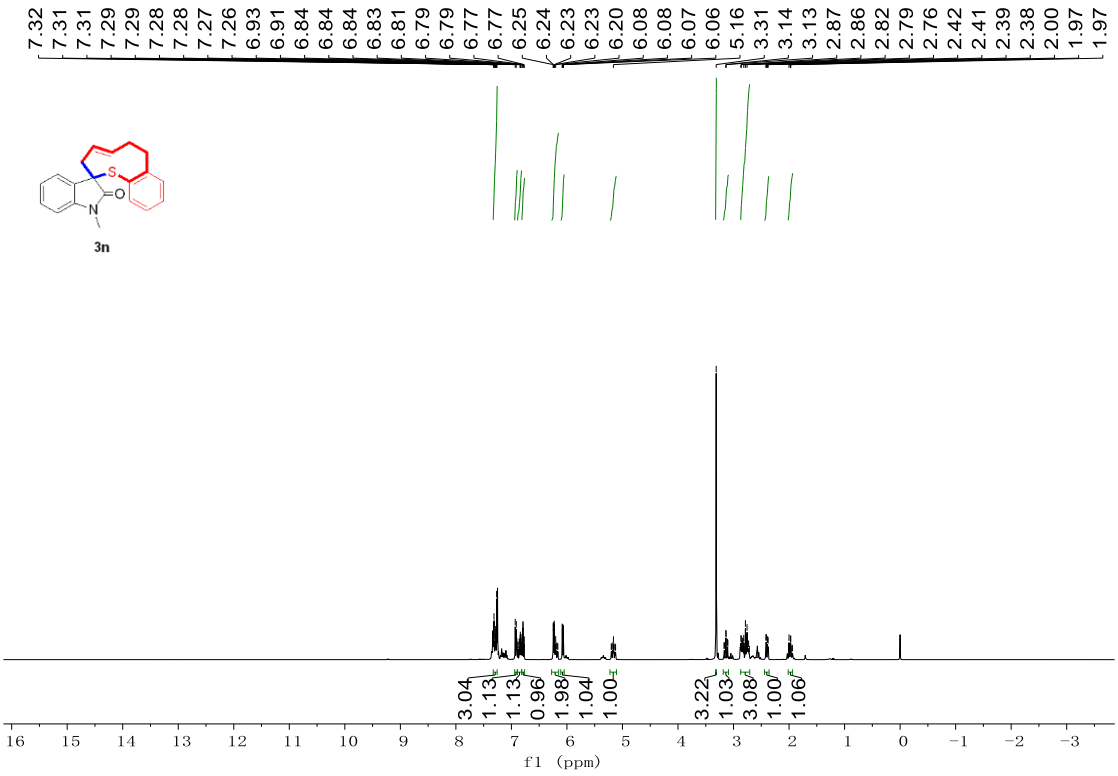
f1 (ppm)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6.84
6.83
6.81
6.79
6.79
6.77
6.25
6.24
6.23
6.23
6.20
6.08
6.08
6.07
6.06
5.16
3.31
3.14
3.13
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2.86
2.82
2.79
2.76
2.42
2.41
2.39
2.38
2.00
1.97
1.97
3n
3.04
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3.22
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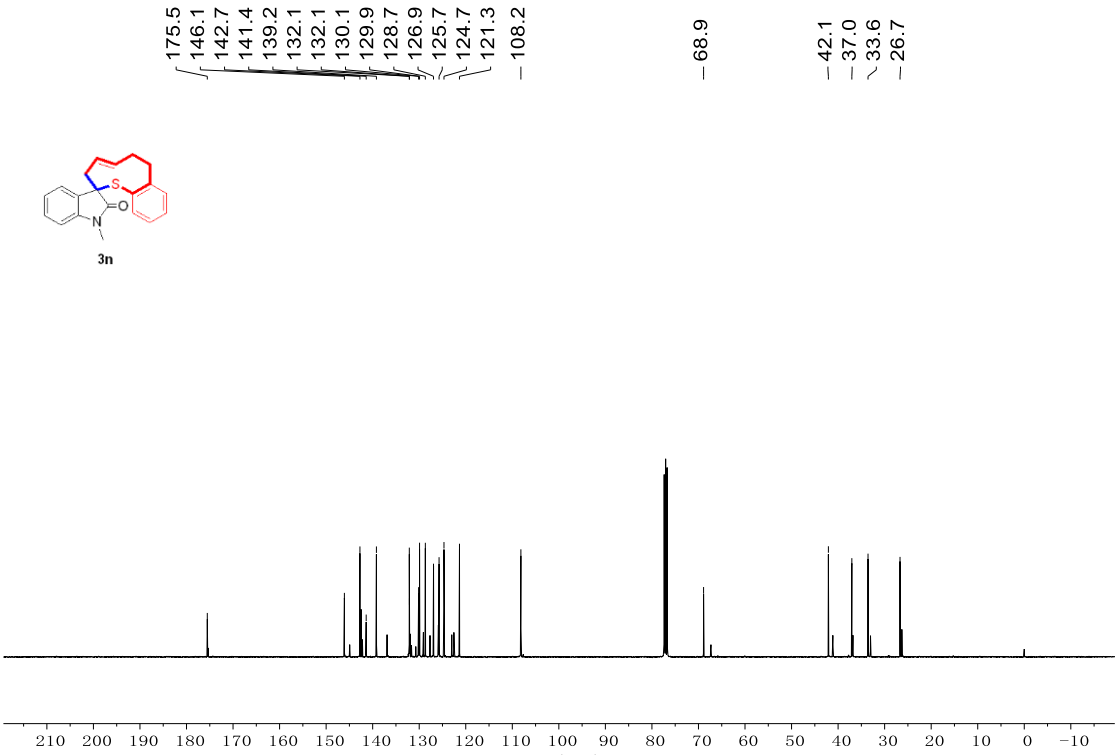
3.08
1.00
1.06
f1 (ppm)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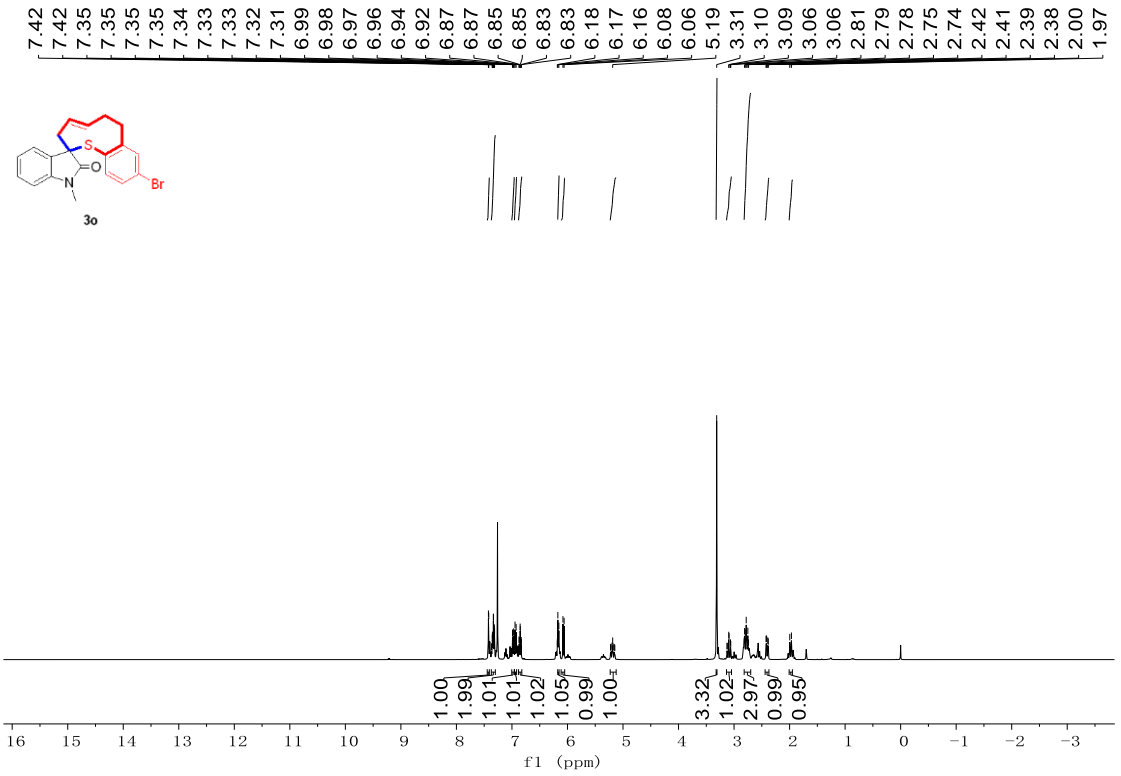
121.3
108.2
68.9
42.1
37.0
33.6
26.7
3n
f1 (ppm)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6.83
6.18
6.17
6.16
6.08
6.06
5.19
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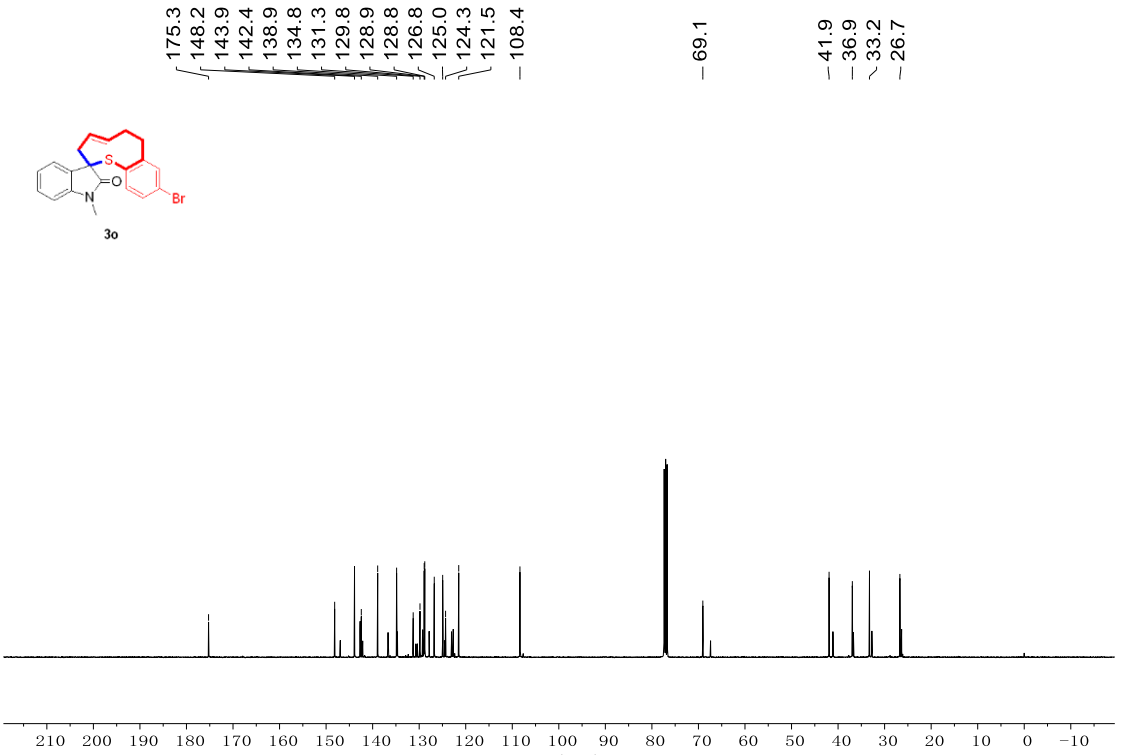
3.10
3.09
3.06
3.06
2.81
2.79
2.78
2.75
2.74
2.42
2.41
2.39
2.38
2.00
1.97
S
O
N
Br
3o
1.00
1.99
1.01
1.01
1.02
1.05
0.99
1.00
3.32
1.02
2.97
0.99
0.95
f1 (ppm)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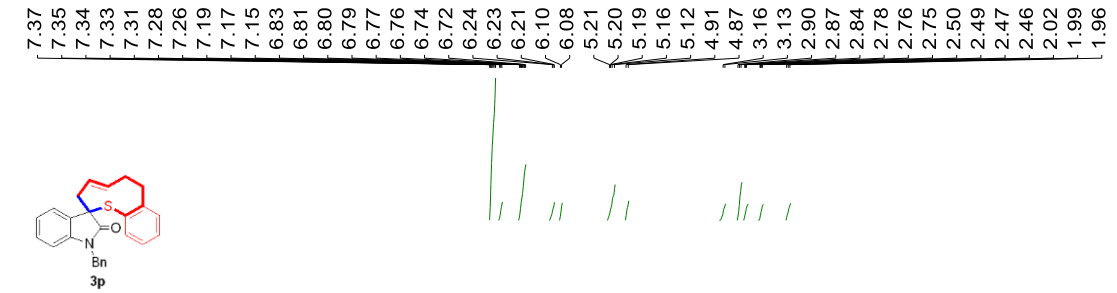
128.9
128.8
126.8
125.0
124.3
121.5
108.4
69.1
41.9
36.9
33.2
26.7
S
O
N
Br
3o
f1 (ppm)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5.19
5.16
5.12
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4.87
3.16
3.13
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2.87
2.84
2.78
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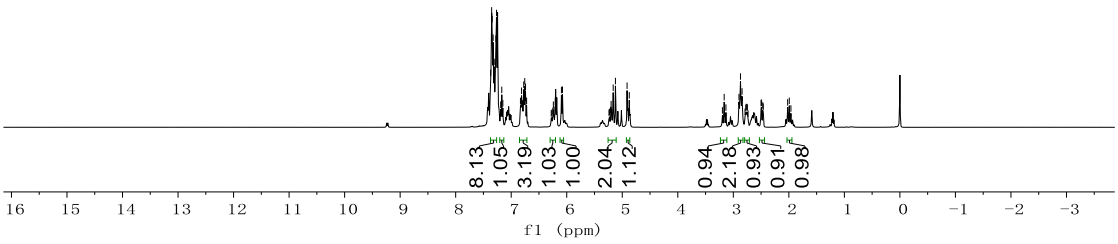
2.49
2.47
2.46
2.02
1.99
1.96
S
O
N
Bn

3p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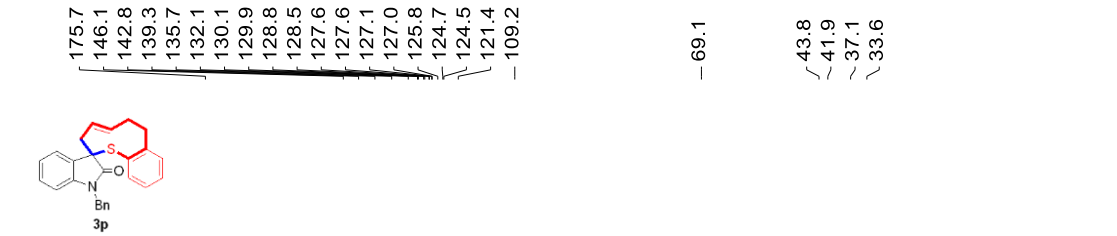
3.19
1.03
1.00
2.04
1.12
0.94
2.18
0.93
0.91
0.98
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)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130.1
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128.8
128.5
127.6
127.6
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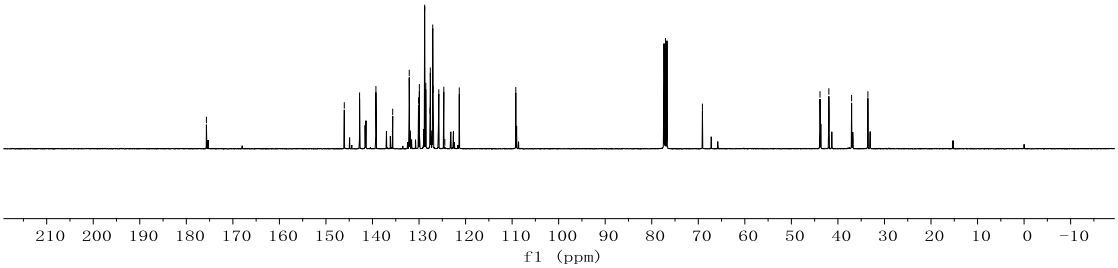
127.0
125.8
124.7
124.5
121.4
109.2
69.1
43.8
41.9
37.1
33.6

S
O
N
Bn

3p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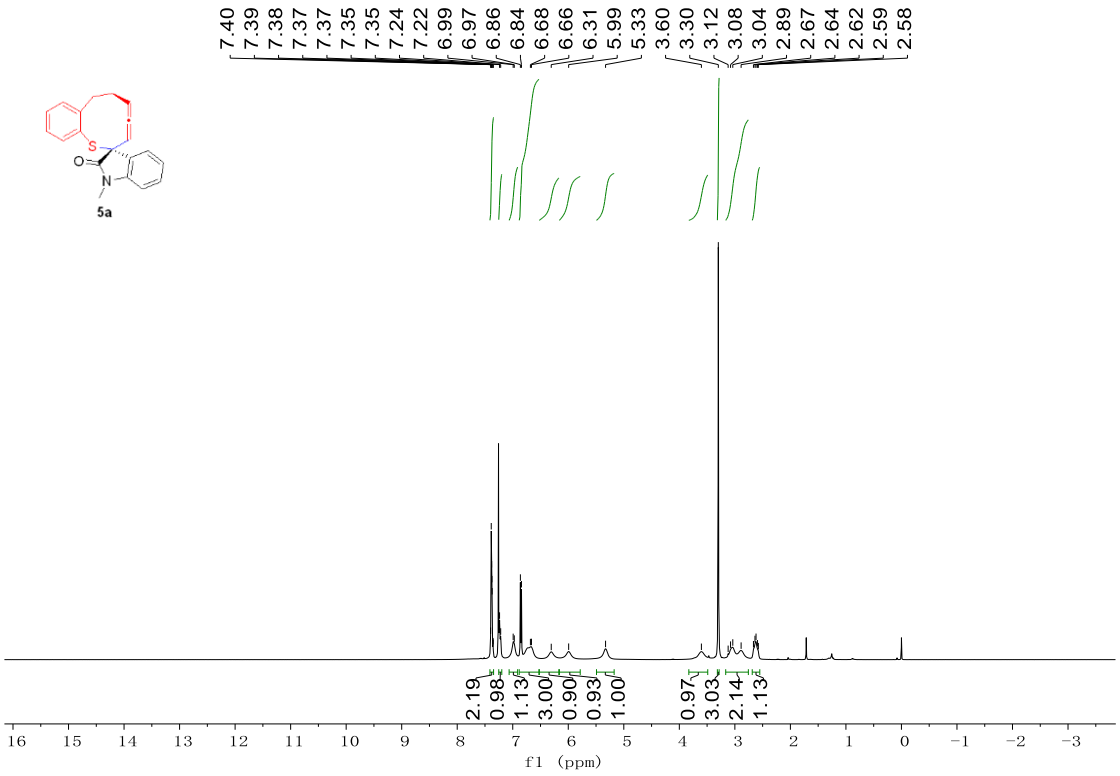
f1 (ppm)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6.84
6.68
6.66
6.31
5.99
5.33
3.60
3.30
3.12
3.08
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2.89
2.67
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2.58
5a
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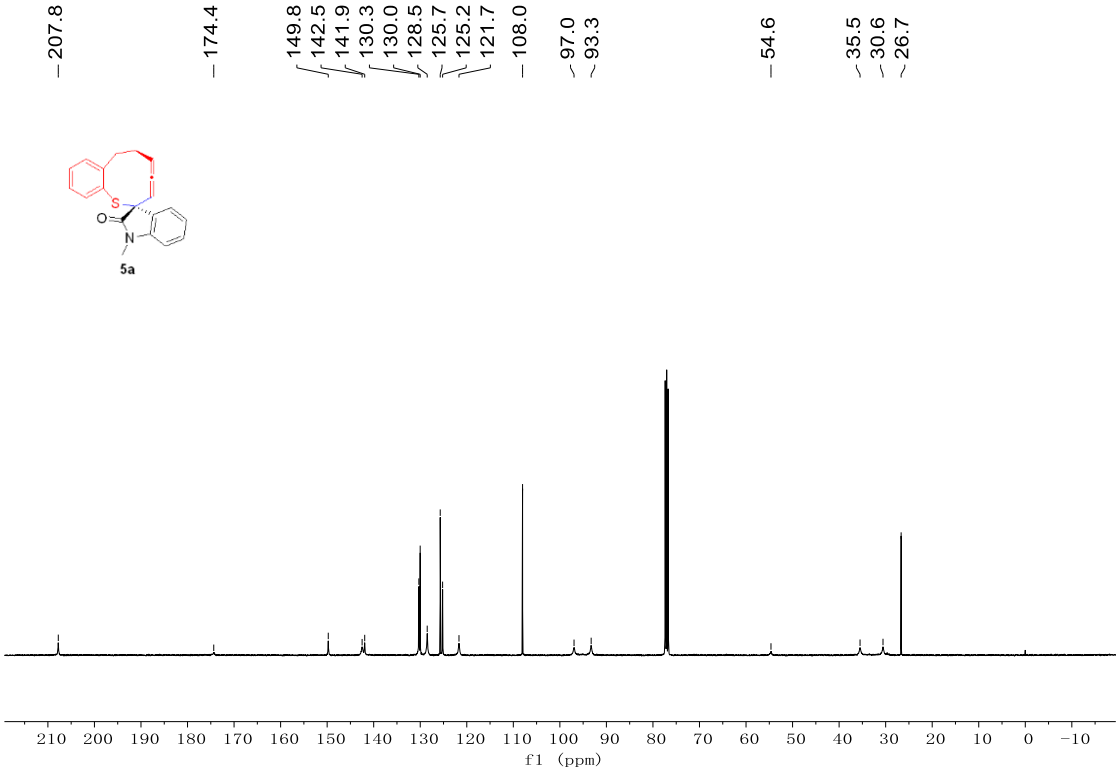
0.93
1.00
0.97
3.03
2.14
1.13
f1 (ppm)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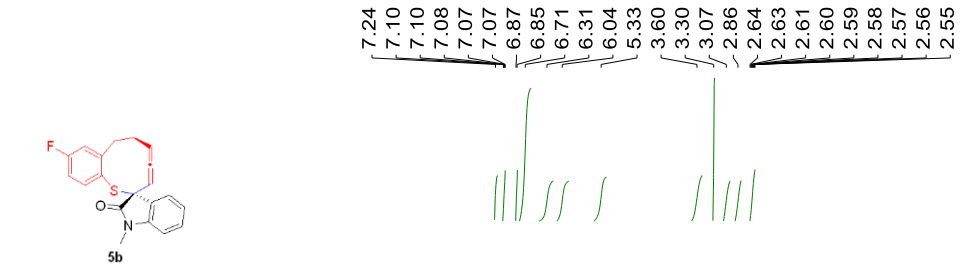
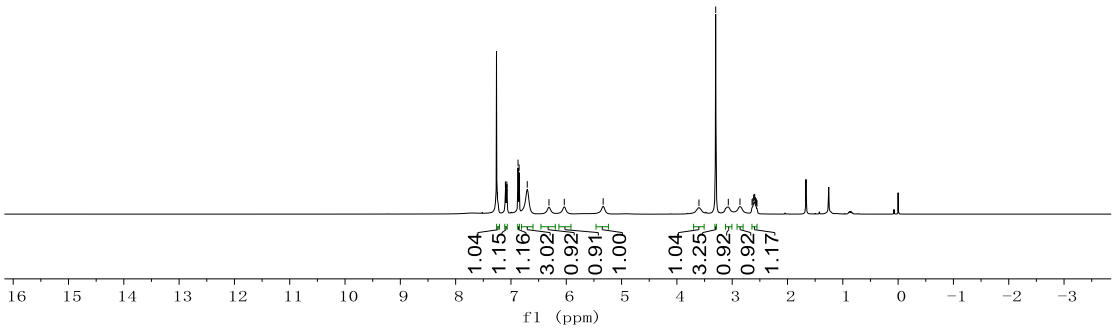
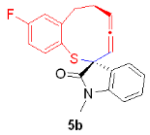
142.5
141.9
130.3
130.0
128.5
125.7
125.2
121.7
108.0
97.0
93.3
54.6
35.5
30.6
26.7
5a
f1 (ppm)


7.24
7.10
7.10
7.08
7.07
7.07
6.87
6.85
6.71
6.31
6.04
5.33
3.60
3.30
3.07
2.86
2.64
2.63
2.61
2.60
2.59
2.58
2.57
2.56
2.55

F
S
O
N

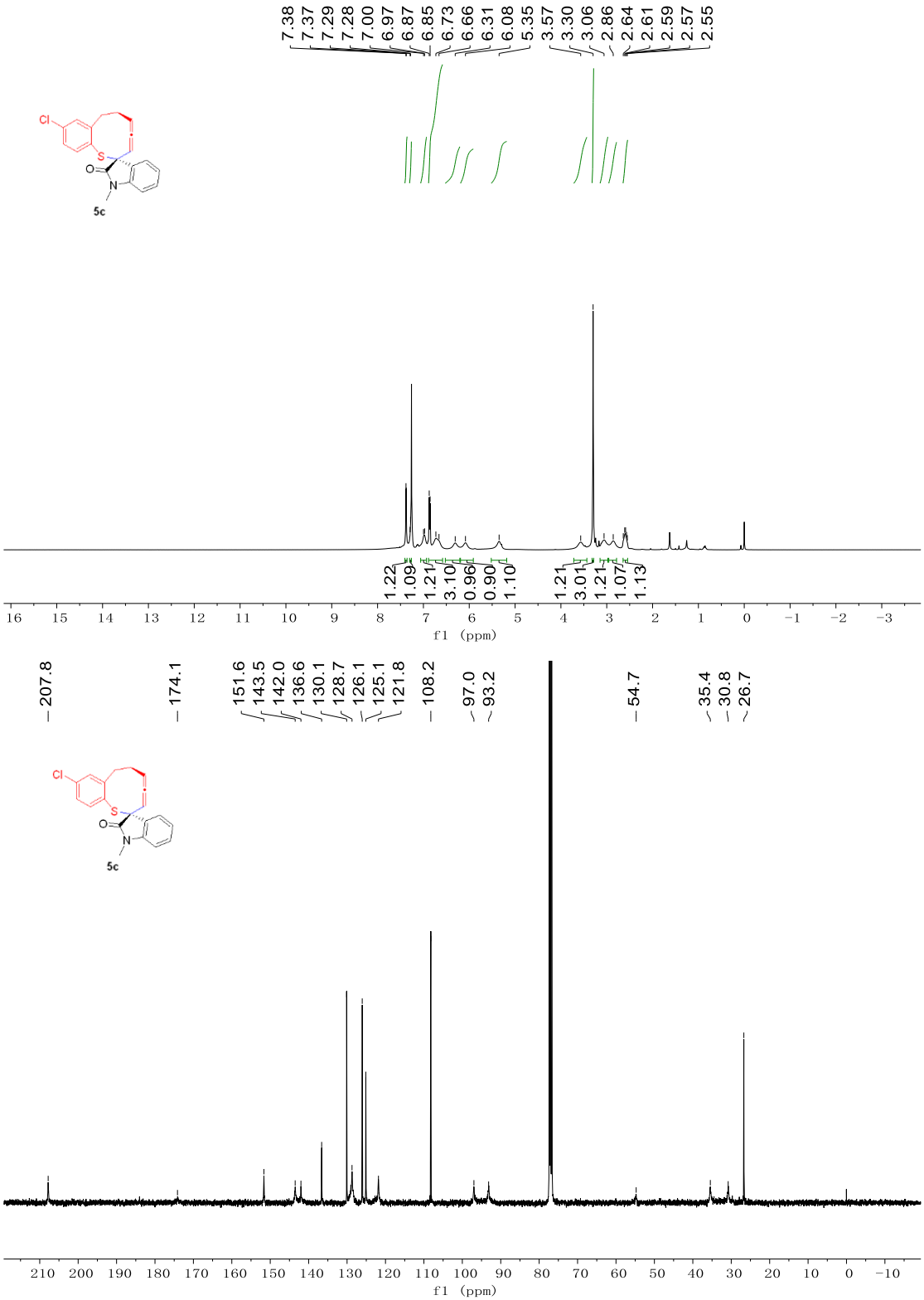
5b

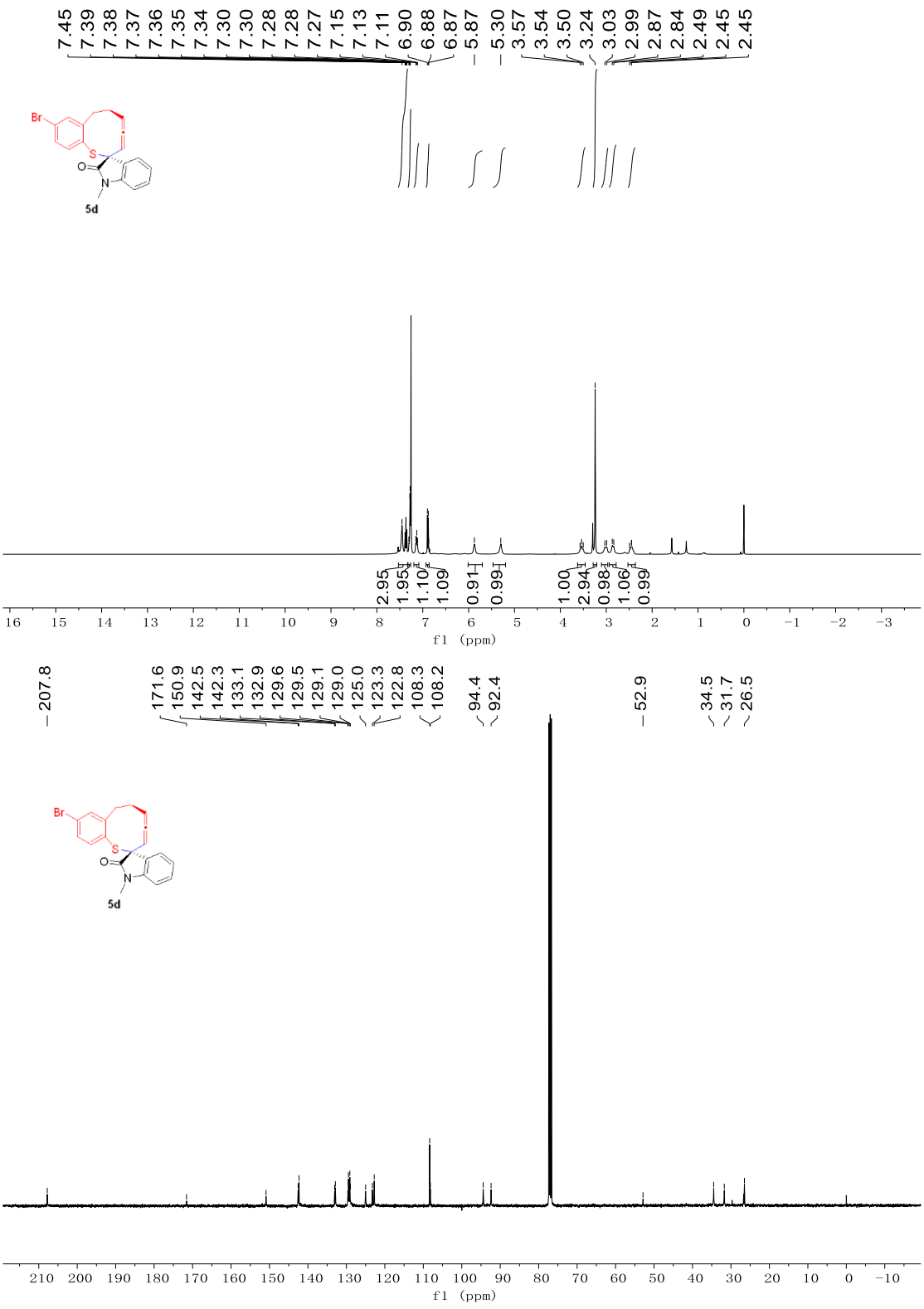

1.04
1.15
1.16
3.02
0.92
0.91
1.00
1.04
3.25
0.92
0.92
1.17
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

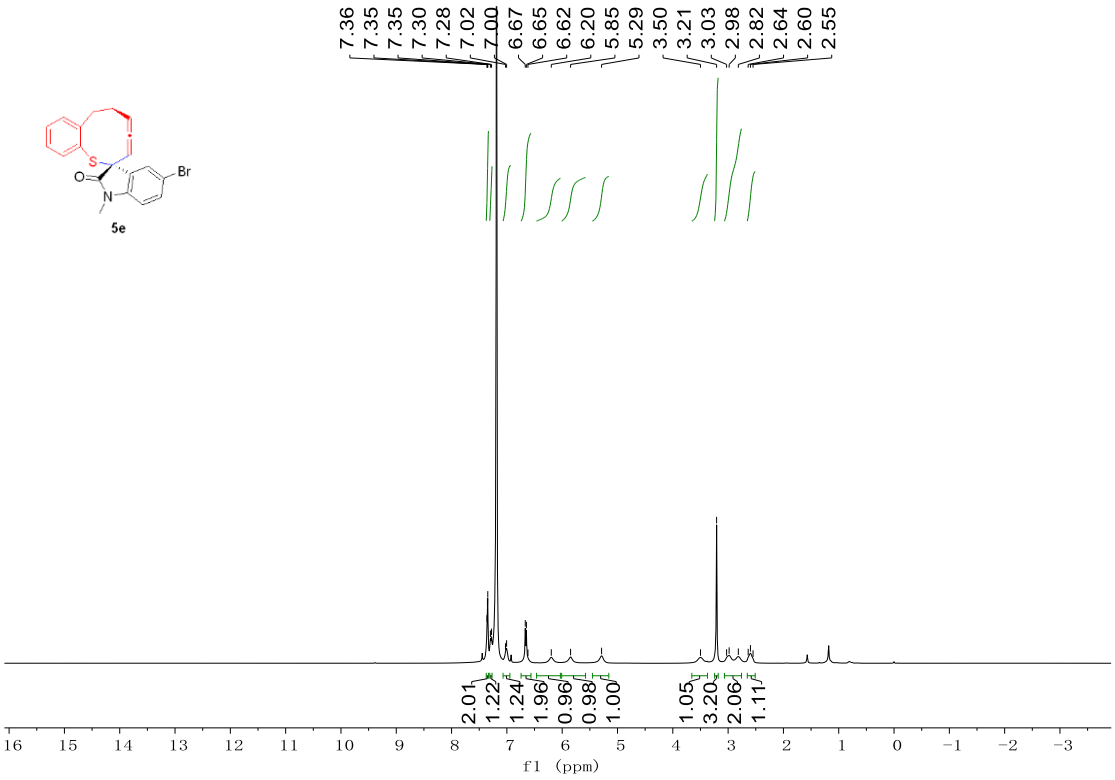

F
S
O
N

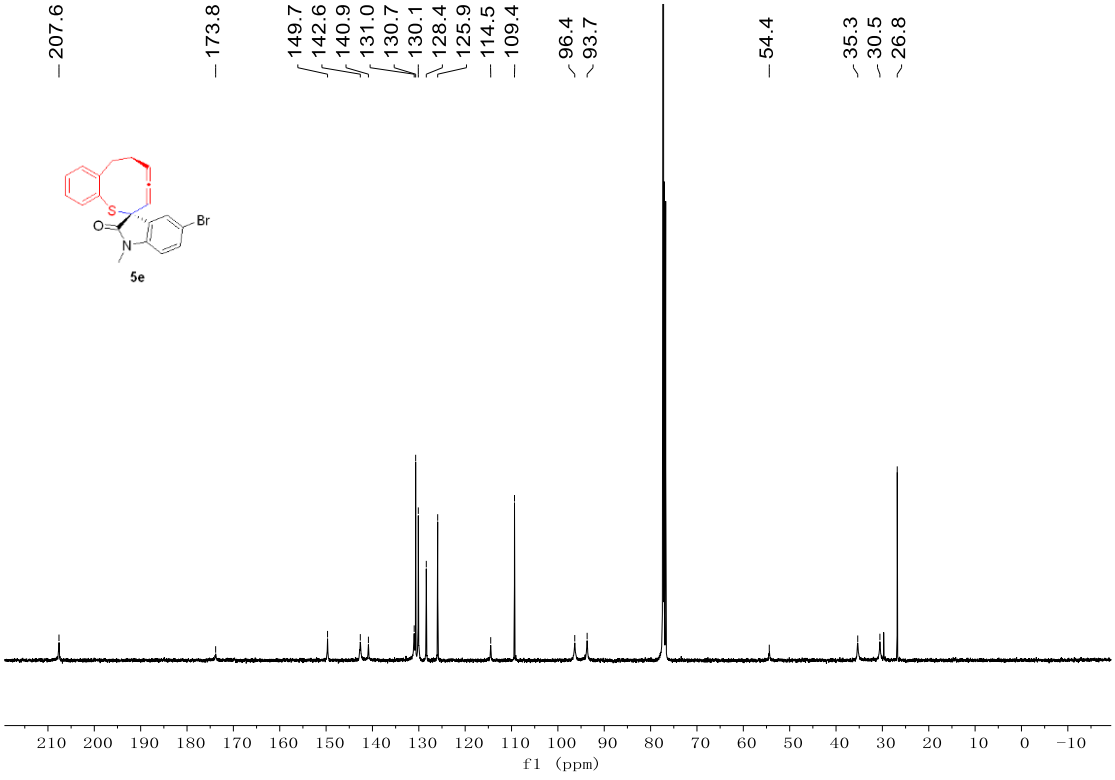
5b

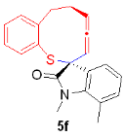
−109.85
0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)


7.38
7.37
7.29
7.28
7.00
6.97
6.87
6.85
6.73
6.66
6.31
6.08
5.35
3.57
3.30
3.06
2.86
2.64
2.61
2.59
2.57
2.55
Cl
S
O
N
5c
1.22
1.09
1.21
3.10
0.96
0.90
1.10
1.21
3.01
1.21
1.07
1.13
f1 (ppm)
207.8
174.1
151.6
143.5
142.0
136.6
130.1
128.7
126.1
125.1
121.8
108.2
97.0
93.2
54.7
35.4
30.8
26.7
f1 (ppm)

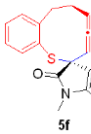

7.45
7.39
7.38
7.37
7.36
7.35
7.34
7.30
7.30
7.28
7.28
7.27
7.15
7.13
7.11
6.90
6.88
6.87
5.87
5.30
3.57
3.54
3.50
3.24
3.03
2.99
2.87
2.84
2.49
2.45
2.45
Br
S
O
N
5d
2.95
1.95
1.10
1.09
0.91
0.99
1.00
2.94
0.98
1.06
0.99
f1 (ppm)
207.8
171.6
150.9
142.5
142.3
133.1
132.9
129.6
129.5
129.1
129.0
125.0
123.3
122.8
108.3
108.2
94.4
92.4
52.9
34.5
31.7
26.5
Br
S
O
N
5d
f1 (ppm)


7.36
7.35
7.35
7.30
7.28
7.02
7.00
6.67
6.65
6.62
6.20
5.85
5.29
3.50
3.21
3.03
2.98
2.82
2.64
2.60
2.55
Br
5e
2.01
1.22
1.24
1.96
0.96
0.98
1.00
1.05
3.20
2.06
1.11
f1 (ppm)

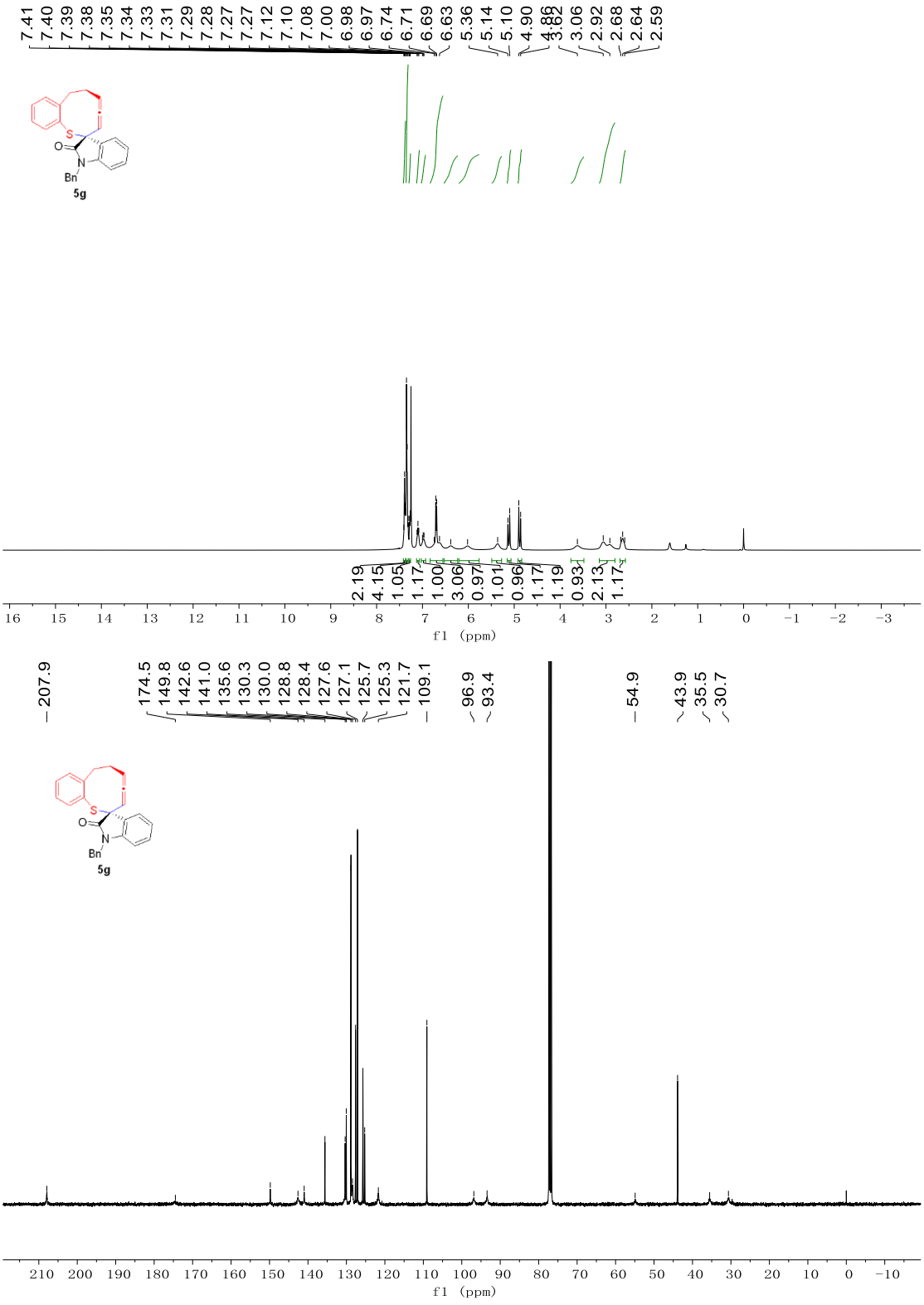

207.6
173.8
149.7
142.6
140.9
131.0
130.7
130.1
128.4
125.9
114.5
109.4
96.4
93.7
54.4
35.3
30.5
26.8
Br
5e
f1 (ppm)

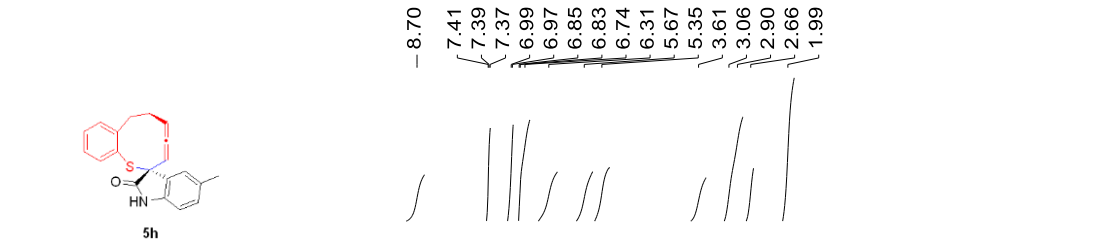

S
O
N
5f

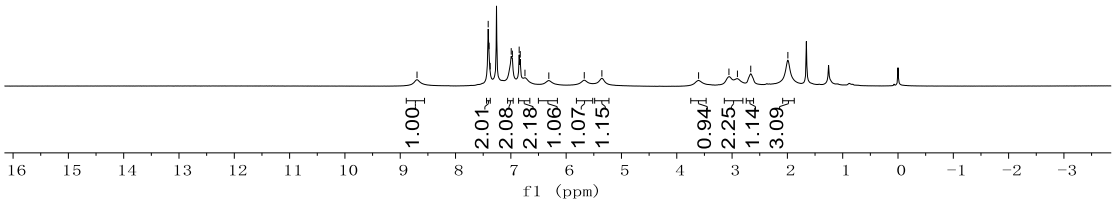
7.37
6.97
6.95
6.75
6.55
6.29
5.89
5.33
3.58
3.02
2.89
2.64
2.58
2.08
2.20
2.10
0.93
0.97
1.00
4.19
2.13
4.31
f1 (ppm)

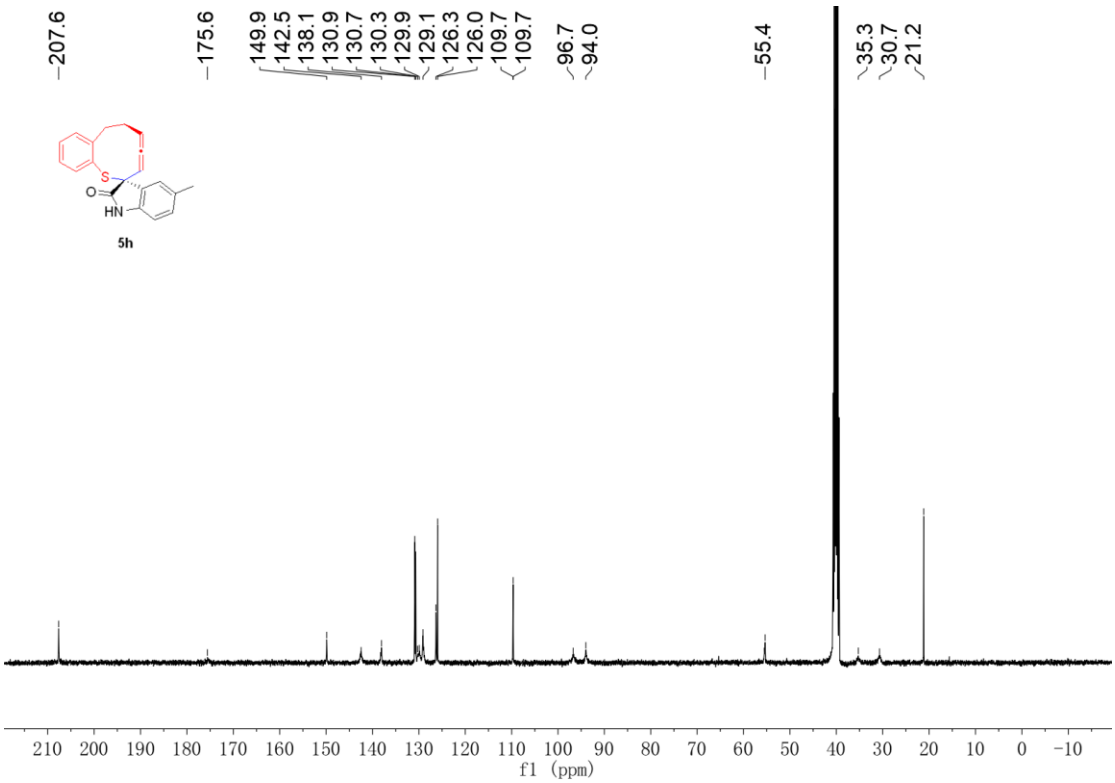

S
O
N
5f

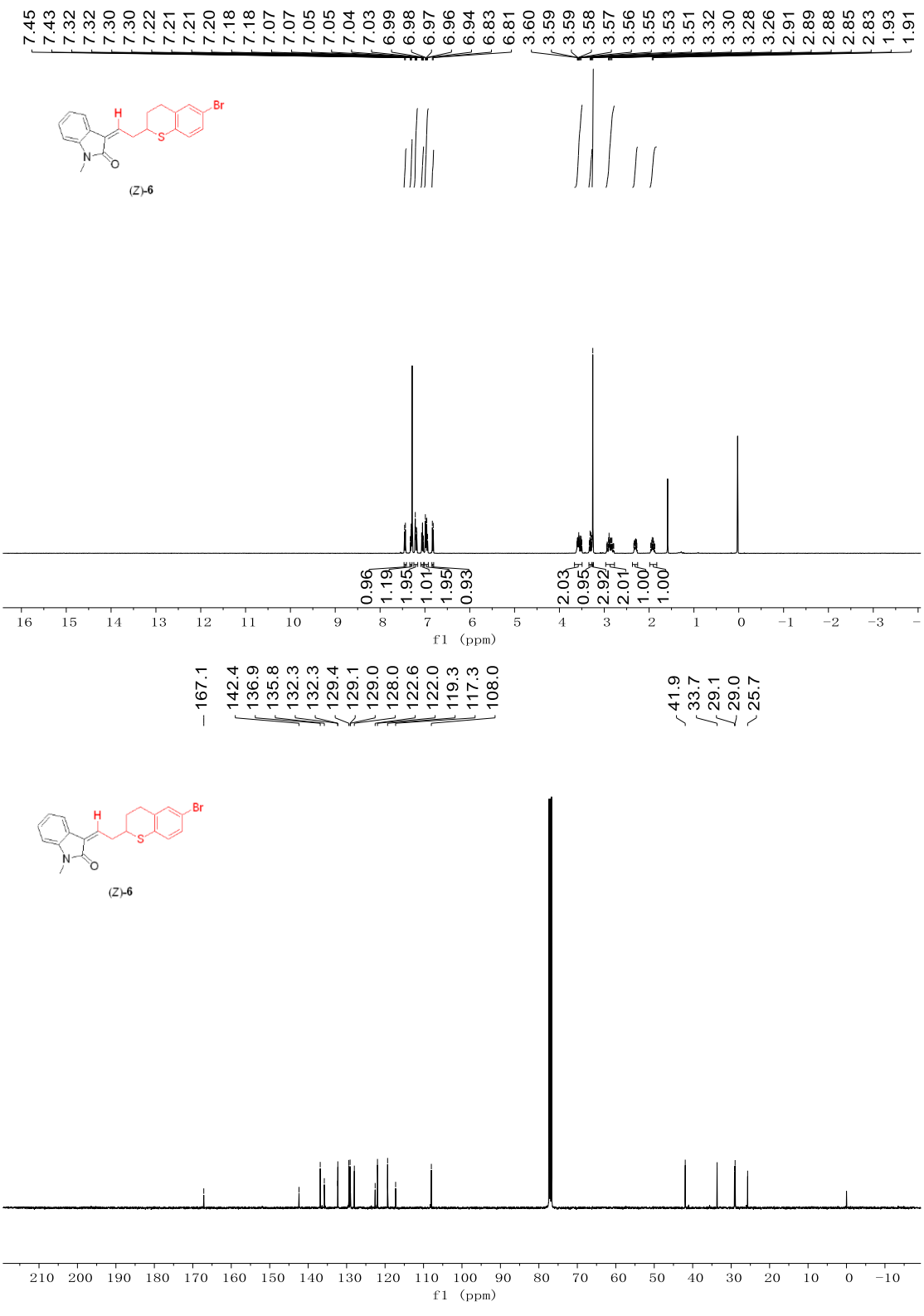
207.9
175.3
149.9
142.6
139.7
132.3
130.3
130.0
129.2
125.7
123.3
121.6
119.5
97.1
93.3
54.2
35.5
30.7
30.1
19.2
f1 (ppm)

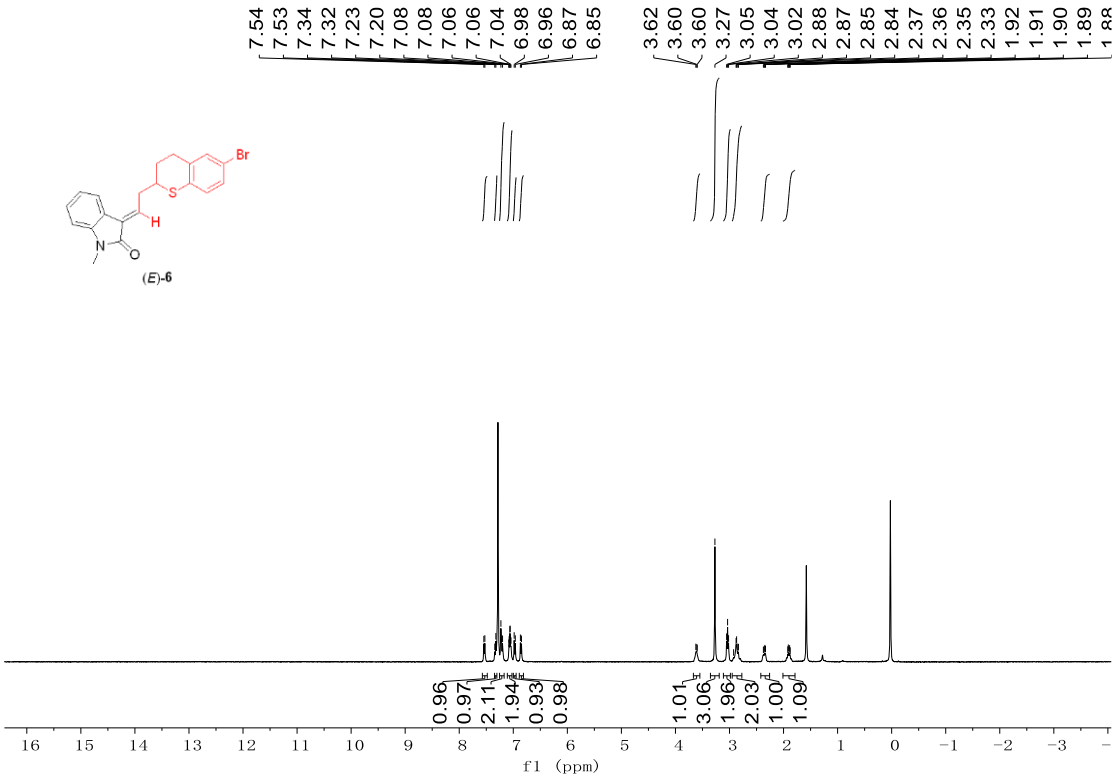

7.41
7.40
7.39
7.38
7.35
7.34
7.33
7.31
7.29
7.28
7.27
7.27
7.12
7.10
7.08
7.00
6.98
6.97
6.74
6.71
6.69
6.63
5.36
5.14
5.10
4.90
4.86
3.52
3.06
2.92
2.68
2.64
2.59
S
O
N
Bn
5g
2.19
4.15
1.05
1.17
1.00
3.06
0.97
1.01
0.96
1.17
1.19
0.93
2.13
1.17
f1 (ppm)
207.9
174.5
149.8
142.6
141.0
135.6
130.3
130.0
128.8
128.4
127.6
127.1
125.7
125.3
121.7
109.1
96.9
93.4
54.9
43.9
35.5
30.7
S
O
N
Bn
5g
f1 (ppm)

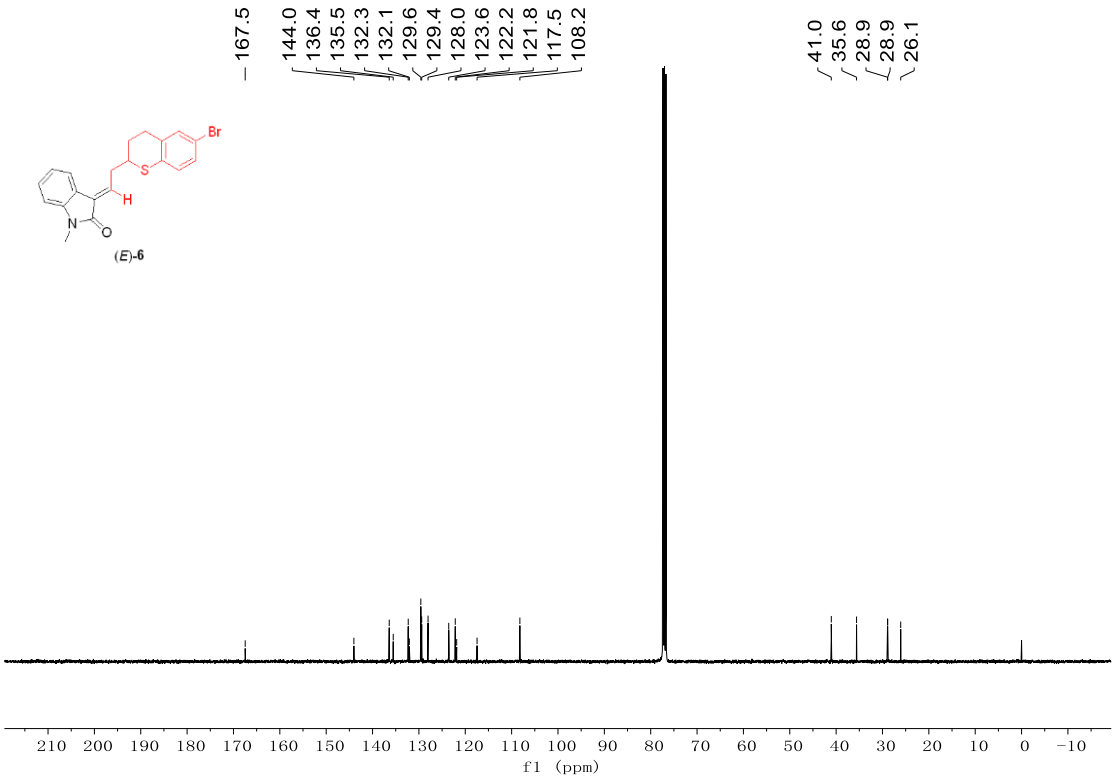

8.70
7.41
7.39
7.37
6.99
6.97
6.85
6.83
6.74
6.31
5.67
5.35
3.61
3.06
2.90
2.66
1.99
S
O
HN
5h


1.00
2.01
2.08
2.18
1.06
1.07
1.15
0.94
2.25
1.14
3.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


207.6
175.6
149.9
142.5
138.1
130.9
130.7
130.3
129.9
129.1
126.3
126.0
109.7
109.7
96.7
94.0
55.4
35.3
30.7
21.2
S
O
HN
5h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.45 7.43 7.32 7.32 7.30 7.30 7.22 7.21 7.21 7.20 7.18 7.18 7.07 7.07 7.05 7.05 7.04 7.03 6.99 6.98 6.97 6.96 6.94 6.83 6.81
3.60 3.59 3.59 3.58 3.57 3.56 3.55 3.53 3.51 3.32 3.30 3.28 3.26 2.91 2.89 2.88 2.85 2.83 1.93 1.91
H
Br
S
N
O
(Z)-6
0.96 1.19 1.95 1.01 1.95 0.93 2.03 0.95 2.92 2.01 1.00 1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)
167.1 142.4 136.9 135.8 132.3 132.3 129.4 129.1 129.0 128.0 122.6 122.0 119.3 117.3 108.0
41.9 33.7 29.1 29.0 25.7
H
Br
S
N
O
(Z)-6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.54
7.53
7.34
7.32
7.23
7.20
7.08
7.08
7.06
7.06
7.04
6.98
6.96
6.87
6.85
3.62
3.60
3.60
3.27
3.05
3.04
3.02
2.88
2.87
2.85
2.84
2.37
2.36
2.35
2.33
1.92
1.91
1.90
1.89
Br
S
H
N
O
(E)-6
0.96
0.97
2.11
1.94
0.93
0.98
1.01
3.06
1.96
2.03
1.00
1.09
f1 (ppm)


167.5
144.0
136.4
135.5
132.3
132.1
129.6
129.4
128.0
123.6
122.2
121.8
117.5
108.2
41.0
35.6
28.9
28.9
26.1
Br
S
H
N
O
(E)-6
f1 (ppm)