Supporting Information

Rhodium(III)-Catalyzed *Ortho* Halogenations of *N*-Acylsulfoximines and Synthetic Applications toward Functionalized Sulfoximine Derivatives

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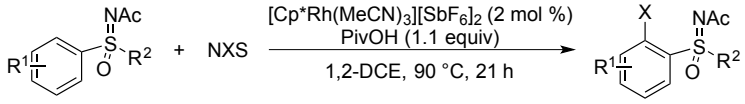
1 General information

Unless otherwise noted, material were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Substituted sulfoximines **1**,[1] $[Cp^*RhCl_2]_2$, $[Cp^*Rh(MeCN)_3][BF_4]_2$ and $[Cp^*Rh(MeCN)_3][SbF_6]_2$[2] were synthesized according to literature procedures. Reactions were monitored by thin layer chromatography (TLC) with aluminium sheets silica gel 60 F_{254} from Merck, and flash column chromatography purifications were performed using silica gel 60 (63-200 μm) from Merck.

^{1}H NMR spectra, ^{13}C NMR spectra and ^{19}F NMR spectra were recorded on Agilent VNMRS 400 or 600. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. Solvent for NMR is $CDCl_3$ unless the otherwise noted. High resolution mass spectra (HRMS) were measured on a Thermo Scientific LTQ Orbitrap XL with positive ion mode.

2 General procedure and characterization data of products

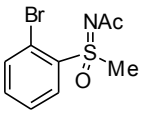
2.1 Procedure for the synthesis of 3 and 4



1 **2** X = Br, I **3** or **4**

To a screw-capped test tube were added in air sulfoximine **1** (0.30 mmol), NXS (0.33-0.60 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5.0 mg, 0.006 mmol), PivOH (33.7 mg, 0.33 mmol) and 1,2-DCE (3.0 mL). The mixture was stirred at 90 ^{o}C for 21 h. The mixture was then cooled to room temperature, diluted with EtOAc (10 mL), and washed with aqueous $Na_2S_2O_3$ (20 mL, saturated). The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The product was purified by flash chromatography on silica gel.

***N*-Acetyl-*S*-(2-bromophenyl)-*S*-methyl sulfoximine (3a)**



Following general procedure using NBS (80.1 mg, 0.45 mmol), **3a** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 85% yield (70.4 mg).

Melting point: 96 – 98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 3.38 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.5, 137.7, 135.6, 134.6, 131.8, 128.4, 119.1, 41.6, 26.2.

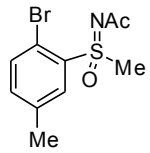
MS (CI): *m*/*z* = 278 (62), 276 ([M+H]$^+$, 100), 262 (4), 261 (5), 260 (6), 259 (4), 234 (13), 232 (14), 196

(5).

IR (ATR): ν = 3016, 2924, 2852, 1631, 1568, 1364, 1202, 1099, 753 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_9H_{10}BrNO_2S+Na]^+$: 297.9508. Found: 297.9510.

_N_-Acetyl-_S_-(2-bromo-5-methylphenyl)-_S_-methyl sulfoximine (3b)



Following general procedure using NBS (58.7 mg, 0.33 mmol), **3b** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 70% yield (60.9 mg).

Melting point: 118 – 120 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.01 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 3.36 (s, 3H), 2.35 (s, 3H), 2.05 (s, 3H).

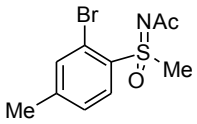
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.6, 139.1, 137.2, 135.4, 132.2, 115.5, 41.6, 26.2, 20.9.

MS (CI): *m/z* = 292 (92), 290 ($[M+H]^+$, 100), 275 (6), 274 (5), 248 (8), 246 (7).

IR (ATR): ν = 3009, 2923, 2857, 1636, 1366, 1202, 1100, 820, 767, 684 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{12}BrNO_2S+Na]^+$: 311.9664. Found: 311.9667.

_N_-Acetyl-_S_-(2-bromo-4-methylphenyl)-_S_-methyl sulfoximine (3c)



Following general procedure using NBS (80.1 mg, 0.45 mmol), **3c** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 80% yield (69.6 mg).

Melting point: 108 – 111 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.06 (d, *J* = 8.4 Hz, 1H), 7.51 (s, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 3.36 (s, 3H), 2.34 (s, 3H), 2.04 (s, 3H).

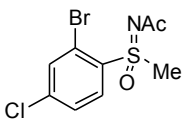
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.4, 146.0, 136.1, 134.5, 131.7, 129.1, 118.8, 41.7, 26.2, 21.0.

MS (CI): *m/z* = 292 (71), 290 ($[M+H]^+$, 100), 275 (7), 274 (8), 248 (30), 246 (15).

IR (ATR): ν = 3084, 2926, 1638, 1588, 1363, 1208, 1106, 820, 769, 666 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{12}BrNO_2S+H]^+$: 289.9845. Found: 289.9853.

_N_-Acetyl-_S_-(2-bromo-4-chlorophenyl)-_S_-methyl sulfoximine (3d)



Following general procedure using NBS (80.1 mg, 0.45 mmol), **3d** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 80% yield (74.5 mg).

Melting point: 150 – 151 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 3.35 (s, 3H), 2.04 (s, 3H).

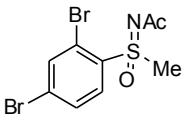
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.4, 140.6, 136.4, 135.2, 132.9, 128.7, 119.6, 41.6, 26.1.

MS (CI): *m/z* = 312 (76), 310 ($[M+H]^+$, 100), 296 (30), 295 (18), 294 (24), 293 (18), 274 (15), 268 (20), 266 (33).

IR (ATR): ν = 3091, 2923, 2856, 1634, 1559, 1361, 1212, 1099, 823, 792, 666 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_9H_9BrClNO_2S+H]^+$: 309.9299. Found: 309.9294.

_N_-Acetyl-_S_-(2,4-dibromophenyl)-_S_-methyl sulfoximine (3e)



Following general procedure using NBS (80.1 mg, 0.45 mmol), **3e** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 85% yield (90.5 mg).

Melting point: 165 – 169 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (d, *J* = 8.4 Hz, 1H), 7.86 (s, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 3.34 (s, 3H), 2.04 (s, 3H).

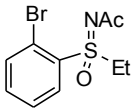
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.4, 137.9, 137.0, 133.0, 131.7, 128.9, 119.7, 41.5, 26.1.

MS (CI): *m/z* = 354 ($[M+H]^+$, 100), 338 (22), 337 (23), 322 (26), 310 (24), 274 (16).

IR (ATR): ν = 3090, 2923, 2857, 1628, 1552, 1359, 1214, 1089, 823, 777 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_9H_9Br_2NO_2S+H]^+$: 353.8794. Found: 353.8788.

_N_-Acetyl-_S_-(2-bromophenyl)-_S_-ethyl sulfoximine (3f)



Following general procedure using NBS (80.1 mg, 0.45 mmol), **3f** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 86% yield (74.8 mg).

Melting point: 137 – 139 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.17 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 3.62 – 3.56 (m, 2H), 2.05 (s, 3H), 1.18 (t, *J* = 7.4 Hz, 3H).

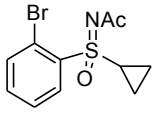
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.4, 135.6, 135.5, 134.4, 133.1, 128.3, 119.0, 47.3, 26.1, 6.2.

MS (CI): *m/z* = 292 (51), 290 ($[M+H]^+$, 100), 260 (9), 248 (14), 246 (29), 244 (16).

IR (ATR): ν = 3069, 2924, 1636, 1566, 1424, 1367, 1098, 735 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{12}BrNO_2S+Na]^+$: 311.9664. Found: 311.9657.

_N_-Acetyl-_S_-(2-bromophenyl)-_S_-cyclopropyl sulfoximine (3g)



Following general procedure using NBS (80.1 mg, 0.45 mmol), **3g** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 92% yield (83.4 mg).

Melting point: 164 – 165 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 3.24 – 3.18 (m, 1H), 2.06 (s, 3H), 1.68 – 1.61 (m, 1H), 1.26 – 1.18 (m, 1H), 0.91 – 0.82 (m, 2H).

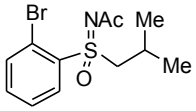
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.3, 138.3, 135.5, 134.0, 131.9, 128.2, 118.6, 29.9, 26.1, 5.9, 4.7.

MS (CI): *m/z* = 302 ($[M+H]^+$, 100), 262 (16), 260 (16), 258 (31), 246 (18), 244 (13).

IR (ATR): ν = 3059, 2924, 1631, 1568, 1422, 1366, 1204, 718 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{11}H_{12}BrNO_2S+H]^+$: 301.9845. Found: 301.9838.

_N_-Acetyl-_S_-(2-bromophenyl)-_S_-isobutyl sulfoximine (3h)



Following general procedure using NBS (80.1 mg, 0.45 mmol), **3h** was obtained as a yellow oil with pentane/EtOAc (3/1) used as eluent in 71% yield (67.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 3.54 – 3.40 (m, 2H), 2.21 – 2.11 (m, 1H), 2.03 (s, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H).

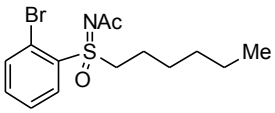
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.3, 137.2, 135.6, 134.3, 132.6, 128.4, 119.0, 60.2, 26.2, 23.8, 22.6, 22.5.

MS (CI): *m/z* = 320 (56), 318 ($[M+H]^+$, 84), 276 (74), 274 (21), 262 (6), 260 (4), 246 (3), 244 (2).

IR (ATR): ν = 3064, 2965, 1637, 1568, 1429, 1362, 1097, 754 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{12}H_{16}BrNO_2S+H]^+$: 318.0158. Found: 318.0154.

_N_-Acetyl-_S_-(2-bromophenyl)-_S_-hexyl sulfoximine (3i)



Following general procedure using NBS (80.1 mg, 0.45 mmol), **3i** was obtained as a yellow oil with pentane/EtOAc (3/1) used as eluent in 75% yield (77.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 3.61 – 3.48 (m, 2H), 2.04 (s, 3H), 1.80 – 1.70 (m, 1H), 1.47 – 1.37 (m, 1H), 1.43 – 1.25 (m, 2H), 1.19 – 1.15 (m, 4H), 0.78 (t, *J* = 6.8 Hz, 3H).

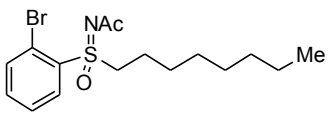
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.4, 136.3, 135.6, 134.4, 132.9, 128.3, 118.9, 52.6, 31.0, 27.6, 26.2, 22.2, 21.4, 13.8.

MS (CI): *m/z* = 348 (77), 346 ($[M+H]^+$, 61), 304 (5), 302 (3), 266 (10).

IR (ATR): ν = 3075, 2931, 2863, 1643, 1570, 1438, 1360, 1099, 758 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{14}H_{20}BrNO_2S+Na]^+$: 368.0290. Found: 368.0281.

_N_-Acetyl-_S_-(2-bromophenyl)-_S_-octyl sulfoximine (3j)



Following general procedure using NBS (80.1 mg, 0.45 mmol), **3j** was obtained as a yellow oil with pentane/EtOAc (3/1) used as eluent in 70% yield (78.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.17 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 3.60 – 3.49 (m, 2H), 2.04 (s, 3H), 1.78 – 1.71 (m, 1H), 1.45 – 1.37 (m, 1H), 1.32 – 1.25 (m, 2H), 1.20 – 1.15 (m, 8H), 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.4, 136.3, 135.6, 134.4, 132.9, 128.3, 119.0, 52.6, 31.6, 28.8,

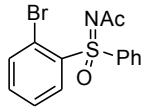
28.0, 26.2, 22.5, 21.5, 14.0.

MS (CI): *m/z* = 376 (81), 374 ([M+H]$^+$, 100), 330 (2), 294 (3), 203 (3).

IR (ATR): ν = 3078, 2026, 2858, 1644, 1570, 1442, 1360, 1100, 758 (cm^{-1}).

HRMS *m/z*: Calcd for [$C_{16}H_{24}BrNO_2S$+H]$^+$: 374.0784. Found: 374.0778.

_N_-Acetyl-_S_-(2-bromophenyl)-_S_-phenyl sulfoximine (3k)



Following general procedure using NBS (80.1 mg, 0.45 mmol), **3k** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 80% yield (81.2 mg).

mono:di = 6:1 (determined by ^{1}H NMR of the crude mixture), only mono-substituted product was isolated.

Melting point: 117 – 120 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.47 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.55 – 7.51 (m, 3H), 7.44 (t, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 2.17 (s, 3H).

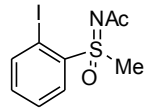
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.3, 138.3, 137.3, 135.7, 134.3, 133.6, 132.3, 128.9, 128.9, 128.2, 119.8, 26.6.

MS (CI): *m/z* = 338 ([M+H]$^+$, 100), 294 (15), 260 (12), 203 (12), 201 (13).

IR (ATR): ν = 3084, 2922, 2854, 1644, 1569, 1363, 1215, 1092, 760, 686 (cm^{-1}).

HRMS *m/z*: Calcd for [$C_{14}H_{12}BrNO_2S$+H]$^+$: 337.9845. Found: 337.9836.

_N_-Acetyl-_S_-(2-iodophenyl)-_S_-methyl sulfoximine (4a)



Following general procedure using NIS (101.3 mg, 0.45 mmol), **4a** was obtained as a light yellow solid with pentane/EtOAc (3/1) used as eluent in 76% yield (73.7 mg).

Melting point: 119 – 121 °C.

^{1}H NMR (400 MHz, CDCl3) δ (ppm) 8.23 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 3.38 (s, 3H), 2.08 (s, 3H).

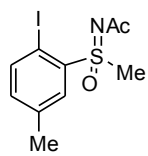
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.5, 143.0, 140.6, 134.2, 131.1, 129.2, 91.3, 41.0, 26.2.

MS (CI): *m/z* = 324 ([M+H]$^+$, 100), 308 (5), 307 (2), 280 (9), 196 (12).

IR (ATR): ν = 3083, 2922, 2856, 1634, 1564, 1362, 1209, 1092, 752 (cm^{-1}).

HRMS *m/z*: Calcd for [$C_9H_{10}INO_2S$+Na]$^+$: 345.9369. Found: 345.9369.

_N_-Acetyl-_S_-(2-iodo-5-methylphenyl)-_S_-methyl sulfoximine (4b)



Following general procedure using NIS (135.0 mg, 0.60 mmol), **4b** was obtained as a light yellow solid with pentane/EtOAc (3/1) used as eluent in 88% yield (89.0 mg).

Melting point: 140 – 142 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.05 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8

Hz, 1H), 3.36 (s, 3H), 2.34 (s, 3H), 2.08 (s, 3H).

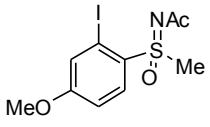
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.6, 142.8, 140.2, 140.0, 135.3, 131.8, 87.0, 41.1, 26.3, 21.0.

MS (CI): *m/z* = 338 ($[M+H]^+$, 100), 322 (3), 321 (1), 294 (6), 210 (6).

IR (ATR): ν = 3073, 2920, 1630, 1362, 1200, 1094, 814, 770, 680 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{12}INO_2S+Na]^+$: 359.9526. Found: 359.9536.

_N_-Acetyl-_S_-(2-iodo-4-methoxylphenyl)-_S_-methyl sulfoximine (4c)



Following general procedure using NIS (101.3 mg, 0.45 mmol), **4c** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 79% yield (83.7 mg).

Melting point: 114 – 116 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (d, *J* = 8.8 Hz, 1H), 7.54 (s, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 3.79 (s, 3H), 2.07 (s, 3H).

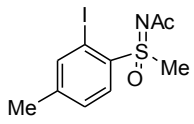
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.5, 163.0, 132.6, 131.7, 128.8, 113.9, 92.3, 55.9, 41.7, 26.4.

MS (CI): *m/z* = 354 ($[M+H]^+$, 100), 338 (3), 310 (1), 295 (1), 226 (6).

IR (ATR): ν = 3019, 2922, 2852, 1636, 1575, 1363, 1204, 1099, 825, 759 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{12}INO_3S+H]^+$: 353.9655. Found: 353.9648.

_N_-Acetyl-_S_-(2-iodo-4-methylphenyl)-_S_-methyl sulfoximine (4d)



Following general procedure using NIS (101.3 mg, 0.45 mmol), **4d** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 82% yield (82.9 mg).

Melting point: 146 – 148 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 8.2 Hz, 1H), 7.87 (s, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 3.36 (s, 3H), 2.31 (s, 3H), 2.08 (s, 3H).

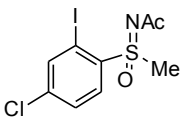
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.6, 145.6, 143.5, 137.5, 131.1, 129.9, 91.3, 41.2, 26.3, 20.7.

MS (CI): *m/z* = 338 ($[M+H]^+$, 100), 322 (6), 234 (1), 210 (4).

IR (ATR): ν = 2923, 2859, 1639, 1582, 1362, 1203, 1097, 820, 768, 661 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{10}H_{12}INO_2S+H]^+$: 337.9706. Found: 337.9705.

_N_-Acetyl-_S_-(4-chloro-2-iodophenyl)-_S_-methyl sulfoximine (4e)



Following general procedure using NIS (101.3 mg, 0.45 mmol), **4e** was obtained as a light yellow solid with pentane/EtOAc (3/1) used as eluent in 75% yield (80.5 mg).

Melting point: 164 – 166 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.15 (d, *J* = 8.8 Hz, 1H), 8.03 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 3.35 (s, 3H), 2.07 (s, 3H).

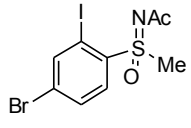
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.5, 142.3, 140.1, 139.4, 132.1, 129.4, 91.7, 41.0, 26.2.

MS (CI): *m/z* = 358 ([M+H]$^+$, 26), 314 (5), 269 (3), 230 (100).

IR (ATR): ν = 3089, 2922, 2854, 1636, 1551, 1360, 1209, 1088, 823, 782, 689 (cm^{-1}).

HRMS *m/z*: Calcd for [$C_9H_9ClINO_2S$+Na]$^+$: 379.8979. Found: 379.8978.

_N_-Acetyl-_S_-(4-bromo-2-iodophenyl)-_S_-methyl sulfoximine (4f)



Following general procedure using NIS (101.3 mg, 0.45 mmol), **4f** was obtained as a light yellow solid with pentane/EtOAc (3/1) used as eluent in 76% yield (91.7 mg).

Melting point: 166 – 167 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.19 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 3.35 (s, 3H), 2.07 (s, 3H).

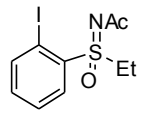
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.5, 144.9, 139.9, 132.4, 132.3, 128.7, 92.0, 41.0, 26.2.

MS (CI): *m/z* = 404 (79), 402 ([M+H]$^+$, 37), 386 (5), 385 (3), 344 (3), 274 (3).

IR (ATR): ν = 3085, 2924, 2857, 1632, 1545, 1357, 1213, 1078, 823, 774 (cm^{-1}).

HRMS *m/z*: Calcd for [$C_9H_9BrINO_2S$+H]$^+$: 401.8655. Found: 401.8651.

_N_-Acetyl-_S_-ethyl-_S_-(2-iodophenyl) sulfoximine (4g)



Following general procedure using NIS (135.0 mg, 0.60 mmol), **4g** was obtained as a light yellow solid with pentane/EtOAc (3/1) used as eluent in 67% yield (67.8 mg).

Melting point: 152 – 153 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 8.4 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 3.63 – 3.57 (m, 2H), 2.08 (s, 3H), 1.17 (t, *J* = 7.4 Hz, 3H).

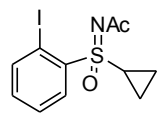
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.5, 143.1, 138.6, 134.2, 132.6, 129.1, 91.1, 46.6, 26.2, 6.3.

MS (CI): *m/z* = 338 ([M+H]$^+$, 100), 321 (3), 308 (1), 294 (6), 210 (10).

IR (ATR): ν = 3065, 2926, 2859, 1636, 1563, 1438, 1362, 1200, 1090, 765 (cm^{-1}).

HRMS *m/z*: Calcd for [$C_{10}H_{12}INO_2S$+Na]$^+$: 359.9526. Found: 359.9523.

_N_-Acetyl-_S_-cyclopropyl-_S_-(2-iodophenyl) sulfoximine (4h)



Following general procedure using NIS (101.3 mg, 0.45 mmol), **4h** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 70% yield (73.3 mg).

Melting point: 190 – 193 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.06 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 3.33 – 3.28 (m, 1H), 2.09 (s, 3H), 1.69 – 1.64 (m, 1H), 1.27 – 1.22 (m, 1H), 0.92 – 0.83 (m, 2H).

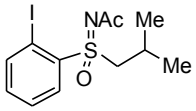
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.3, 142.9, 141.5, 133.8, 131.4, 129.0, 90.6, 29.3, 26.2, 6.1, 4.8.

MS (CI): *m/z* = 350 ([M+H]$^+$, 100), 333 (3), 308 (14), 306 (2), 251 (3), 222 (13).

IR (ATR): ν = 3065, 2923, 2854, 1632, 1564, 1441, 1359, 1209, 1083, 757 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{11}H_{12}INO_2S+Na]^+$: 371.9526. Found: 371.9521.

_N_-Acetyl-_S_-(2-iodophenyl)-_S_-isobutyl sulfoximine (4i)



Following general procedure using NIS (135.0 mg, 0.60 mmol), **4i** was obtained as a yellow oil with pentane/EtOAc (3/1) used as eluent in 60% yield (65.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.23 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 3.48 (dd, *J* = 6.3, 3.7 Hz, 2H), 2.20 – 2.10 (m, 1H), 2.06 (s, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H).

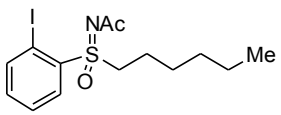
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.4, 143.0, 140.2, 134.0, 132.1, 129.2, 91.4, 59.6, 26.3, 23.9, 22.6, 22.56.

MS (CI): *m/z* = 366 ([M+H]$^+$, 100), 308 (1), 292 (5), 238 (5).

IR (ATR): ν = 3072, 2959, 1637, 1434, 1361, 1093, 755 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{12}H_{16}INO_2S+Na]^+$: 387.9839. Found: 387.9829.

_N_-Acetyl-_S_-hexyl-_S_-(2-iodophenyl) sulfoximine (4j)



Following general procedure using NIS (101.3 mg, 0.45 mmol), **4j** was obtained as a brown oil with pentane/EtOAc (3/1) used as eluent in 60% yield (70.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.19 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 3.56 (t, *J* = 8.1 Hz, 2H), 2.07 (s, 3H), 1.78 – 1.71 (m, 1H), 1.42 – 1.35 (m, 1H), 1.34 – 1.24 (m, 2H), 1.19 – 1.16 (m, 4H), 0.78 (t, *J* = 6.9 Hz, 3H).

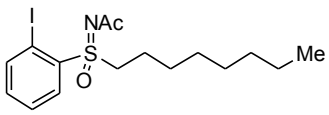
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.5, 143.0, 139.2, 134.1, 132.3, 129.1, 91.2, 51.9, 31.0, 27.7, 26.2, 22.2, 21.5, 13.8.

MS (CI): *m/z* = 394 ([M+H]$^+$, 78), 350 (2), 308 (6), 266 (63), 251 (5).

IR (ATR): ν = 3072, 2929, 2862, 1640, 1566, 1439, 1360, 1094, 757 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{14}H_{20}INO_2S+Na]^+$: 416.0152. Found: 416.0150.

_N_-Acetyl-_S_-(2-iodphenyl)-_S_-octyl sulfoximine (4k)



Following general procedure NIS (135.0 mg, 0.60 mmol), **4k** was obtained as a yellow oil with pentane/EtOAc (3/1) used as eluent in 72% yield (91.0 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.20 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.7 Hz,

1H), 7.20 (t, *J* = 9.0 Hz, 1H), 3.56 (t, *J* = 6.0 Hz, 2H), 2.08 (s, 3H), 1.80 – 1.70 (m, 1H), 1.43 – 1.35 (m, 1H), 1.35 – 1.25 (m, 2H), 1.21 – 1.15 (m, 8H), 0.79 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.5, 143.0, 139.3, 134.1, 132.4, 129.1, 91.2, 51.9, 31.6, 28.8, 28.0, 26.3, 22.5, 21.5, 14.0.

MS (CI): *m/z* = 422 ([M+H]$^+$, 29), 294 (5), 251 (2), 189 (1), 124 (3).

IR (ATR): ν = 3070, 2924, 2858, 1641, 1566, 1442, 1360, 1094, 756 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{24}INO_2S+H]^+$: 422.0645. Found: 422.0658.

_N_-Acetyl-_S_-(2-iodophenyl)-_S_-phenyl sulfoximine (4l)

Following general procedure using NIS (101.3 mg, 0.45 mmol), **4l** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 73% yield (84.3 mg).

mono:di = 12:1 (determined by ^{1}H NMR of the crude mixture), only mono-substituted product was isolated.

Melting point: 126 – 128 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.51 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.44 (t, *J* = 8.1 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 2.18 (s, 3H).

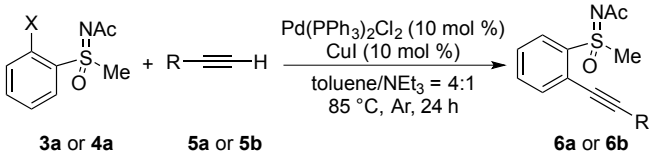
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.2, 143.2, 140.8, 136.9, 134.0, 133.5, 132.0, 129.2, 129.0, 128.9, 92.0, 26.7.

MS (CI): *m/z* = 386 ([M+H]$^+$, 69), 258 (12), 251 (1), 182 (2).

IR (ATR): ν = 3010, 2928, 1632, 1570, 1361, 1211, 1089, 750, 684 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{14}H_{12}INO_2S+Na]^+$: 407.9526. Found: 407.9525.

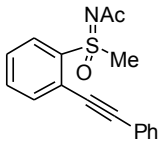
2.2 Procedure for the syntheses of 6a and 6b



3a or **4a** **5a** or **5b** **6a** or **6b**

To a screw-capped test tube were added under argon sulfoximine **3a** or **4a** (0.20 mmol), alkyne (0.40 mmol), $[Pd(PPh_3)_2Cl_2]$ (14.0 mg, 0.020 mmol), CuI (3.8 mg, 0.020 mmol) and toluene (4.0 mL). Then NEt_3 (1.0 mL) was added to the system. The mixture was stirred at 85 °C for 24 h and then cooled to room temperature. After dilution with DCM (10 mL) the mixture was filtered through a Celite pad and washed with DCM (3 x 20 mL). The filtrate was concentrated, and the product was purified by flash column chromatography on silica gel.

***N*-Acetyl- *S*-methyl-*S*-(2-(phenylethynyl)phenyl) sulfoximine (6a)**



Following general procedure using sulfoximine **3a** (55.2 mg, 0.20 mmol) and ethynylbenzene (**5a**, 40.8 mg, 0.40 mmol), **6a** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 58% yield (34.5 mg).

Following general procedure using sulfoximine **4a** (64.6 mg, 0.20 mmol) and ethynylbenzene (**5a**, 40.8 mg, 0.40 mmol), **6a** was obtained in 92% yield (54.8 mg).

Melting point: 127 – 129 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.15 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.59 – 7.46 (m, 4H), 7.35 – 7.32 (m, 3H), 3.46 (s, 3H), 2.00 (s, 3H).

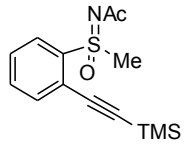
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.7, 139.0, 134.6, 133.0, 131.5, 129.6, 129.4, 128.8, 128.6, 121.9, 121.0, 98.8, 85.2, 41.7, 26.4.

MS (CI): *m/z* = 298 ($[M+H]^+$, 100), 282 (4), 281 (2), 254 (8), 253 (4), 221 (1).

IR (ATR): ν = 3018, 2927, 2080, 1635, 1490, 1360, 1209, 751, 690 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{15}NO_2S+Na]^+$: 320.0716. Found: 320.0711.

***N*-Acetyl-*S*-methyl-*S*-2-((trimethylsilyl)ethynyl)phenyl sulfoximine (6b)**



Following general procedure using sulfoximine **4a** (64.6 mg, 0.20 mmol) and ethynyltrimethylsilane (**5b,** 39.3 mg, 0.40 mmol), **6b** was obtained as a brown oil with pentane/EtOAc (5/1) used as eluent in 95% yield (55.9 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 9.1 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.54 – 7.45 (m, 2H), 3.47 (s, 3H), 2.03 (s, 3H), 0.22 (s, 9H).

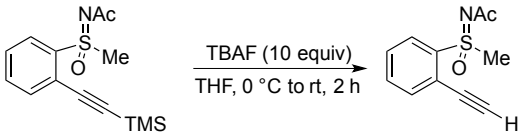
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.6, 139.5, 135.3, 132.9, 129.2, 129.0, 120.8, 105.4, 100.1, 41.2, 26.3, -0.6.

MS (CI): *m/z* = 294 ($[M+H]^+$, 100), 278 (36), 277 (32), 262 (8), 250 (57), 220 (2).

IR (ATR): ν = 3018, 2959, 2097, 1640, 1360, 1128, 761 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{14}H_{19}NO_2SSi+H]^+$: 294.0979. Found: 294.0973.

2.5 Procedure for the synthesis of 6c[5]

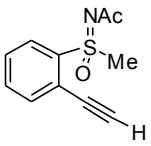


6b **6c**

To a solution of **6b** (58.7 mg, 0.20 mmol) in THF (30 mL) at 0 °C was added TBAF (2.0 mL, 2.0 mmol, 1 M in THF). The mixture was allowed to warm to room temperature, and stirred for 2 h. The crude mixture was diluted with Et_2O and the organic phase washed with aqueous NH_4Cl (20 mL, saturated),

followed by H_2O (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated in vacuo. The product was purified by flash chromatography on silica gel with pentane/EtOAc (2/1) as eluent to give the product **6c** (27.1 mg ,61% yield) as a yellow oil.

_N_-Acetyl-_S_-(2-(ethynyl)phenyl)-_S_-methyl sulfoximine (6c)



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 – 8.10 (m, 1H), 7.68 – 7.62 (m, 1H), 7.57 – 7.51 (m, 2H), 3.58 (s, 1H), 3.43 (s, 3H), 2.05 (s, 3H).

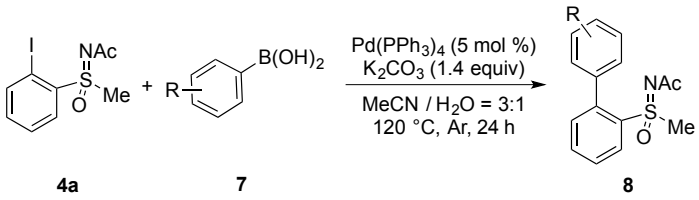
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.7, 139.9, 135.9, 133.0, 129.6, 129.5, 119.8, 86.9, 79.3, 41.8, 26.2.

MS (CI): *m/z* = 222 ($[M+H]^+$, 100), 206 (3), 205 (3), 178 (6).

IR (ATR): ν = 3015, 2927, 2104, 1634, 1363, 1216, 1126, 762 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{11}H_{11}NO_2S+Na]^+$: 244.0403. Found: 244.0409.

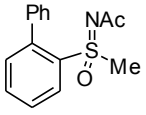
2.3 Procedure for the synthesis of 8[4]



4a **7** **8**

To a screw-capped test tube were added under argon *N*-acetyl-*S*-(2-iodophenyl)-*S*-methyl sulfoximine (**4a**, 129.3 mg, 0.40 mmol), boronic acid **7** (0.80 mmol), $Pd(PPh_3)_4$ (23.1 mg, 0.020 mmol), K_2CO_3 (77.4 mg, 0.56 mmol), MeCN (6.0 mL) and H_2O (2.0 mL). The mixture was stirred at 120 °C for 24 h. The mixture was then cooled to room temperature, diluted with EtOAc (10 mL), and washed with brine (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The product was purified by flash chromatography on silica gel.

_N_-Acetyl-_S_-([1,1'-biphenyl]-2-yl)-_S_-methyl sulfoximine (8a)



Following general procedure using phenylboronic acid (97.6 mg, 0.80 mmol), **8a** was obtained as a yellow syrup with pentane/EtOAc (2/1) used as eluent in 93% yield (101.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.40 – 7.33 (m, 3H), 7.33 – 7.26 (m, 3H), 2.89 (s, 3H), 1.91 (s, 3H).

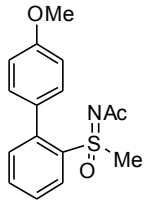
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.5, 140.8, 138.3, 137.0, 133.1, 132.9, 129.6, 129.0, 128.5, 128.3, 127.9, 43.3, 26.6.

MS (CI): *m/z* = 274 ($[M+H]^+$, 88), 258 (7), 257(5), 230 (8).

IR (ATR): ν = 3023, 2928, 1634, 1361, 1214, 1129, 760, 706 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{15}H_{15}NO_2S+H]^+$: 274.0896. Found: 274.0897.

_N_-Acetyl-_S_-(4'-methoxyl-[1,1'-biphenyl]-2-yl)-_S_-methyl sulfoximine (8b)



Following general procedure using (4-methoxyphenyl)boronic acid (121.6 mg, 0.80 mmol), **8b** was obtained as a white solid with pentane/EtOAc (7/3) used as eluent in 90% yield (109.1 mg).

Melting point: 88 – 90 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 10.0 Hz, 1H), 7.30 – 7.21 (m, 3H), 6.88 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 2.89 (s, 3H), 1.97 (s, 3H).

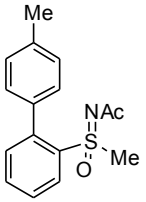
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.5, 159.7, 140.6, 137.3, 133.3, 133.1, 130.9, 130.3, 129.0, 128.0, 113.3, 55.3, 43.0, 26.7.

MS (CI): *m/z* = 304 ($[M+H]^+$, 100), 288 (6), 287 (3), 260 (6).

IR (ATR): ν = 3014, 2931, 2842, 1633, 1514, 1361, 829, 763 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{17}NO_3S+H]^+$: 304.1002. Found: 304.0999.

_N_-Acetyl-_S_-(4'-methyl-[1,1'-biphenyl]-2-yl)-_S_-methyl sulfoximine (8c)



Following general procedure using 4-tolylboronic acid (108.8 mg, 0.80 mmol), **8c** was obtained as a light yellow syrup with pentane/EtOAc (3/1) used as eluent in 95% yield (109.2 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.19 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 9.0 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.21 – 7.14 (m, 4H), 2.88 (s, 3H), 2.34 (s, 3H), 1.94 (s, 3H).

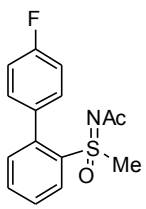
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.5, 140.8, 138.4, 137.1, 135.3, 133.0, 133.0, 129.5, 128.9, 128.6, 128.1, 43.1, 26.7, 21.2.

MS (CI): *m/z* = 288 ($[M+H]^+$, 81), 272 (2), 271 (1), 244 (8).

IR (ATR): ν = 3022, 2927, 1635, 1516, 1361, 1214, 1124, 822, 763 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{17}NO_2S+Na]^+$: 310.0872. Found: 310.0876.

_N_-Acetyl-_S_-(4'-fluoro-[1,1'-biphenyl]-2-yl)-_S_-methyl sulfoximine (8d)



Following general procedure using (4-fluorophenyl)boronic acid (112.0 mg, 0.80 mmol), **8d** was obtained as a light yellow syrup with pentane/EtOAc (3/1) used as eluent in 88% yield (102.3 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.19 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.30 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 8.7 Hz, 2H), 2.92 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.5, 162.7 (d, J_{C-F} = 247.5 Hz), 139.8, 137.2, 134.2 (d, J_{C-F} = 4.5 Hz), 133.2, 133.1, 131.4 (d, J_{C-F} = 7.5 Hz), 129.1, 128.5, 114.9 (d, J_{C-F} = 22.5 Hz), 43.4, 26.7.

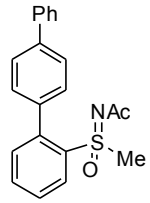
^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) –112.8.

MS (CI): *m/z* = 292 ([M+H]$^+$, 100), 276 (3), 275 (3), 272 (4), 248 (4).

IR (ATR): ν = 3022, 2929, 1634, 1511, 1362, 1214, 832, 764 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{15}H_{14}FNO_2S+Na]^+$: 314.0621. Found: 314.0614.

_N_-Acetyl-_S_-methyl-_S_-([1,1':4',1''-terphenyl]-2-yl) sulfoximine (8e)



Following general procedure using [1,1'-biphenyl]-4-ylboronic acid (158.4 mg, 0.80 mmol), **8e** was obtained as a white solid with pentane/EtOAc (2/1) used as eluent in 93% yield (130.4 mg).

Melting point: 132 – 134 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.49 (m, 6H), 7.40 – 7.35 (m, 4H), 7.31 – 7.27 (m, 2H), 2.93 (s, 3H), 1.92 (s, 3H).

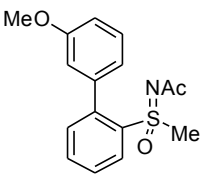
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.6, 141.2, 140.5, 140.0, 137.2, 137.0, 133.1, 133.0, 130.0, 129.0, 128.8, 128.3, 127.7, 127.0, 126.5, 43.4, 26.7.

MS (CI): *m/z* = 350 ([M+H]$^+$, 100), 334 (3), 333 (2), 307 (12), 272 (1).

IR (ATR): ν = 3029, 2927, 1634, 1361, 1214, 1127, 834, 754, 696 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{21}H_{19}NO_2S+Na]^+$: 372.1029. Found: 372.1026.

_N_-Acetyl-_S_-(3'-methoxyl-[1,1'-biphenyl]-2-yl)-_S_-methyl sulfoximine (8f)



Following general procedure using (3-methoxyphenyl)boronic acid (121.6 mg, 0.80 mmol), **8f** was obtained as a light yellow syrup with pentane/EtOAc (2/1) used as eluent in 92% yield (111.9 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.21 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.30 – 7.26 (m, 2H), 6.91 – 6.86 (m, 3H), 3.76 (s, 3H), 2.94 (s, 3H), 1.94 (s, 3H).

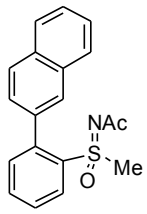
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.6, 159.0, 140.5, 139.6, 137.0, 133.1, 132.7, 129.0, 128.3, 121.9, 115.9, 113.7, 55.3, 43.3, 26.7.

MS (CI): *m/z* = 304 ([M+H]$^+$, 100), 288 (4), 183 (1), 152 (1).

IR (ATR): ν = 3013, 2934, 1631, 1461, 1360, 1211, 1031, 767, 707 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{16}H_{17}NO_3S+H]^+$: 304.1002. Found: 304.1002.

_N_-Acetyl-_S_-(2-(naphthalen-2-yl)phenyl)-_S_-methyl sulfoximine (8g)



Following general procedure using naphthalen-2-ylboronic acid (137.6 mg, 0.80 mmol), **8g** was obtained as a yellow syrup with pentane/EtOAc (3/1) used as eluent in 96% yield (124.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.24 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.77 (s, 1H), 7.76 – 7.74 (m, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.50 – 7.43 (m, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 2.87 (s, 3H), 1.89 (s, 3H).

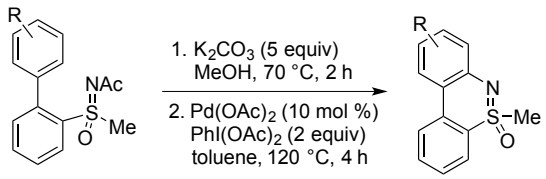
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.6, 140.7, 137.2, 135.6, 133.1, 133.06, 132.8, 132.4, 129.2, 128.8, 128.4, 128.0, 127.8, 127.5, 127.3, 126.82, 126.80, 43.3, 26.6.

MS (CI): *m/z* = 324 ([M+H]$^+$, 100), 308 (5), 281 (7), 203 (6).

IR (ATR): ν = 3054, 2926, 1635, 1480, 1359, 1211, 1076, 754 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{19}H_{17}NO_2S+H]^+$: 324.1053. Found: 324.1051.

2.4 Procedure for the synthesis of 9[5]

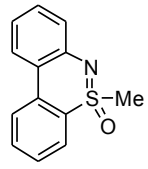


8 **9**

Sulfoximine **8** (0.30 mmol) and K_2CO_3 (1.5 mmol, 207.3 mg) were stirred in MeOH (15 mL) at 70 °C for 2 h. Upon the completion of the reaction as determined by TLC, the mixture was cooled to room temperature and the solvent was removed in vacuo.

To a solution of above mixture in toluene (3.0 mL) were added $Pd(OAc)_2$ (0.030 mmol, 6.7 mg) and $PhI(OAc)_2$ (0.60 mmol, 193.3 mg). The mixture was stirred at 120 °C for 4 h. Upon the completion of the reaction as determined by TLC, the mixture was cooled to room temperature and diluted with DCM (10 mL). The mixture was filtered through a Celite pad and washed with DCM (3 x 20 mL). The filtrate was concentrated, and the product was purified by flash column chromatography on silica gel.

5-Methyldibenzo[*c*,*e*][1,2]thiazine 5-oxide (9a)



Following general procedure using sulfoximine **8a** (82.0 mg, 0.30 mmol), **9a** was obtained as a light yellow solid with pentane/EtOAc (3/1) used as eluent in 96% yield (66.2 mg).

Melting point: 125 – 127 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* =8.0 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 3.45 (s, 3H).

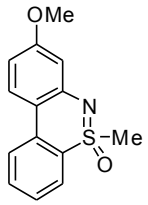
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 142.8, 134.0, 132.9, 130.7, 127.9, 124.84, 124.79, 123.9, 123.5, 120.8, 117.4, 44.7.

MS (CI): *m/z* = 230 ([M+H]$^+$, 100), 214 (5), 213 (3), 198 (5), 166 (3).

IR (ATR): ν = 3016, 2925, 2859, 1592, 1374, 1189, 740 (cm^{-1}).

HRMS *m/z*: Calcd for [$C_{13}H_{11}NOS$+Na]$^+$: 252.0454. Found: 252.0457.

8-Methoxy-5-methyldibenzo[*c*,*e*][1,2]thiazine 5-oxide (9b)



Following general procedure using sulfoximine **8b** (91.0 mg, 0.30 mmol), **9b** was obtained as a light yellow solid with pentane/EtOAc (3/1) used as eluent in 86% yield (67.1 mg).

Melting point: 149 – 151 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.02 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 6.68 (s, 1H), 6.61 (d, *J* = 8.9 Hz, 1H), 3.79 (s, 3H), 3.45 (s, 3H).

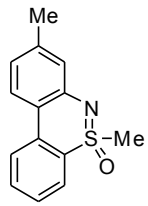
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 161.7, 144.5, 134.2, 133.0, 126.7, 124.8, 124,0, 123.3, 123.2, 110.7, 109.8, 107.1, 55.4, 44.8.

MS (CI): *m/z* = 260 ([M+H]$^+$, 100), 244 (3), 243 (2), 228 (4), 196 (2).

IR (ATR): ν = 2924, 2853, 1604, 1204, 1079, 841, 761 (cm^{-1}).

HRMS *m/z*: Calcd for [$C_{14}H_{13}NO_2S$+H]$^+$: 260.0740. Found: 260.0744.

5,8-Dimethyldibenzo[*c*,*e*][1,2]thiazine 5-oxide (9c)



Following general procedure using sulfoximine **8c** (86.2 mg, 0.30 mmol), **9c** was obtained as a white solid with pentane/EtOAc (3/1) used as eluent in 85% yield (62.2 mg).

Melting point: 157 – 159 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.07 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 3.43 (s, 3H), 2.30 (s, 3H).

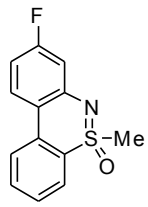
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 142.6, 141.1, 134.1, 132.8, 127.4, 124.9, 124.3, 123.9, 123.6, 123.3, 122.2, 114.8, 44.7, 21.4.

MS (CI): *m/z* = 244 ([M+H]$^+$, 100), 228 (5), 227 (3), 213 (2), 212 (6), 180 (3).

IR (ATR): ν = 3008, 2923, 2857, 1604, 1395, 1188, 1080, 794, 751 (cm^{-1}).

HRMS *m/z*: Calcd for [$C_{14}H_{13}NOS$+Na]$^+$: 266.0610. Found: 266.0616.

8-Fluoro-5-methyldibenzo[*c*,*e*][1,2]thiazine 5-oxide (9d)



Following general procedure using sulfoximine **8d** (87.4 mg, 0.30 mmol), **9d** was obtained as a light yellow solid with pentane/EtOAc (3/1) used as eluent in 92% yield (68.5 mg).

Melting point: 148 – 150 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.04 (d, *J* = 8.3 Hz, 1H), 7.90 (dd, *J* = 8.9, 6.2 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 10.3 Hz, 1H), 6.73 (t, *J* = 9.0 Hz, 1H), 3.45 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 164.2 (d, $J_{C\text{-}F}$ = 240.0 Hz), 144.8 (d, $J_{C\text{-}F}$ = 12.0 Hz), 133.6, 133.1, 127.7, 125.3, 125.2, 124.0, 123.7, 113.9 (d, $J_{C\text{-}F}$ = 3.0 Hz), 110.6 (d, $J_{C\text{-}F}$ = 22.5 Hz), 108.8 (d, $J_{C\text{-}F}$ = 22.5 Hz), 44.7.

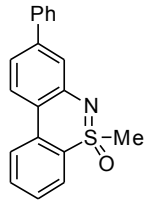
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) –110.3.

MS (CI): *m*/*z* = 248 ([M+H]$^+$, 100), 232 (4), 231 (3), 228 (10), 216 (4), 184 (2).

IR (ATR): ν = 3021, 2924, 2857, 1606, 1251, 1193, 1085, 796, 757 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{13}H_{10}FNOS+Na]^+$: 270.0359. Found: 270.0363.

5-Methyl-8-phenyldibenzo[*c*,*e*][1,2]thiazine 5-oxide (9e)



Following general procedure using sulfoximine **8e** (104.8 mg, 0.30 mmol), **79e** was obtained as a light yellow solid with pentane/EtOAc (3/1) used as eluent in 80% yield (73.2 mg).

Melting point: 163 – 165 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.44 (s, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.24 (m, 2H), 3.45 (s, 3H).

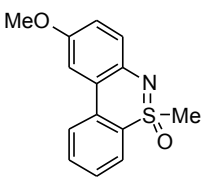
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.3, 143.1, 140.2, 133.8, 133.0, 128.8, 127.8, 127.6, 127.0, 124.6, 124.0, 123.9, 123.8, 122.9, 119.8, 116.4, 44.7.

MS (CI): *m*/*z* = 306 ([M+H]$^+$, 100), 290 (2), 289 (1), 274 (1), 242 (1).

IR (ATR): ν = 3019, 2925, 2858, 1600, 1387, 1187, 1079, 795, 745, 694 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{19}H_{15}NOS+Na]^+$: 328.0767. Found: 328.0765.

9-Methoxy-5-methyldibenzo[*c*,*e*][1,2]thiazine 5-oxide (9f)



Following general procedure using sulfoximine **8f** (91.0 mg, 0.30 mmol), **9f** was obtained as a brown solid with pentane/EtOAc (3/1) used as eluent in 41% yield (32.0 mg).

Melting point: 190 – 193 °C (decomposed).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.06 (d, *J* = 8.2 Hz, 1H), 7.82 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.54 – 7.48 (m, 1H), 7.42 (d, *J* = 2.9 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.95 (dd, *J* = 8.8, 2.9 Hz, 1H), 3.79 (s, 3H), 3.45 (s, 3H).

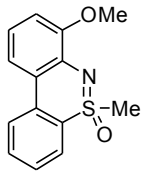
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 154.0, 136.5, 133.6, 132.7, 128.0, 125.7, 125.2, 124.0, 123.7, 118.0, 107.6, 55.8, 44.2.

MS (CI): *m/z* = 260 ([M+H]$^+$, 100), 244 (3), 243 (3), 228 (4), 197 (1).

IR (ATR): ν = 2923, 1598, 1478, 1281, 1180, 763 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{14}H_{13}NO_2S+Na]^+$: 282.0559. Found: 282.0567.

7-Methoxy-5-methyldibenzo[*c*,*e*][1,2]thiazine 5-oxide (9f')



Compound **9b'** was obtained as a brown solid with pentane/EtOAc (1/1) used as eluent in 42% yield (32.8 mg).

Melting point: 204 – 205 °C (decomposed).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.12 (d, *J* = 8.3 Hz, 1H), 7.83 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.67 – 7.64 (m , 1H), 7.58 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.53 – 7.48 (m, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 7.9, 1.0 Hz, 1H), 3.90 (s, 3H), 3.56 (s, 3H).

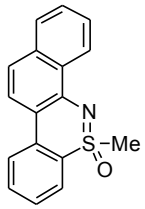
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 152.7, 133.8, 132.8, 132.7, 127.9, 124.9, 124.4, 123.6, 120.3, 118.2, 115.6, 111.2, 56.1, 44.4.

MS (CI): *m/z* = 260 ([M+H]$^+$, 100), 244 (1), 243 (1), 228 (2), 197 (1).

IR (ATR): ν = 3011, 2925, 1574, 1242, 1101, 730 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{14}H_{13}NO_2S+H]^+$: 260.0740. Found: 260.0743.

6-Methylbenzo[*e*]naphtho[1,2-*c*][1,2]thiazine 6-oxide (9g)



Following general procedure using sulfoximine **8g** (97.0 mg, 0.30 mmol), **9g** was obtained as a yellow solid with pentane/EtOAc (4/1) used as eluent in 60% yield (50.5 mg).

Melting point: 167 – 169 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.73 (dd, *J* = 5.2, 4.5 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.67 – 7.64 (m, 1H), 7.49 – 7.44 (m, 3H), 7.42 (d, *J* = 8.8 Hz, 1H), 3.52 (s, 3H).

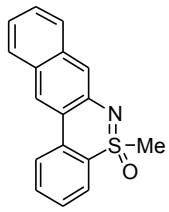
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 140.4, 134.6, 134.55, 132.9, 129.6, 127.4, 127.29, 127.28, 125.6, 125.1, 123.93, 123.89, 123.1, 120.7, 120.5, 111.6, 45.0.

MS (CI): *m/z* = 280 ([M+H]$^+$, 100), 264 (8), 248 (7), 203 (6), 108 (8).

IR (ATR): ν = 3018, 2926, 1594, 1511, 1367, 1240, 1183, 751 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{13}NOS+Na]^+$: 302.0610. Found: 302.0615.

5-Methylbenzo[*e*]naphtho[2,3-*c*][1,2]thiazine 5-oxide (9g')



Compound **9g'** was obtained as a yellow solid with pentane/EtOAc (2/1) used as eluent in 30% yield (25.3 mg).

Melting point: 203 – 204 °C (decomposed).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.45 (s, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.57 (s, 1H), 7.57 – 7.52 (m, 1H), 7.38 – 7.36 (m, 1H), 7.29 – 7.26 (m, 1H), 3.43 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 139.9, 135.2, 134.1, 133.1, 128.7, 128.3, 127.4, 127.0, 126.4, 124.7, 124.0, 124.0, 123.7, 120.1, 118.8, 44.5.

MS (CI): *m/z* = 280 ([M+H]$^+$, 100), 264 (1), 263 (2), 248 (2).

IR (ATR): ν = 3039, 2925, 1587, 1477, 1274, 1173, 741 (cm^{-1}).

HRMS *m/z*: Calcd for $[C_{17}H_{13}NOS+H]^+$: 280.0791. Found: 280.0796.

3 References

1. (a) Johnson, C. R.; Haake, M.; Schroeck, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 6594–6598. (b) García Mancheño, O.; Bistri, O.; Bolm, C. *Org. Lett.* **2007**, *9*, 3809–3811.

2. (a) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228–234. (b) White, C.; Thompson, S. J.; Maitlis, P. M. *J. C. S. Dalton*, **1977**, 165–172. (c) Smith, J. G.; Dibble, P. W.; Sandborn, R. E. *J. Org. Chem.* **1986**, *51*, 3762–3768.

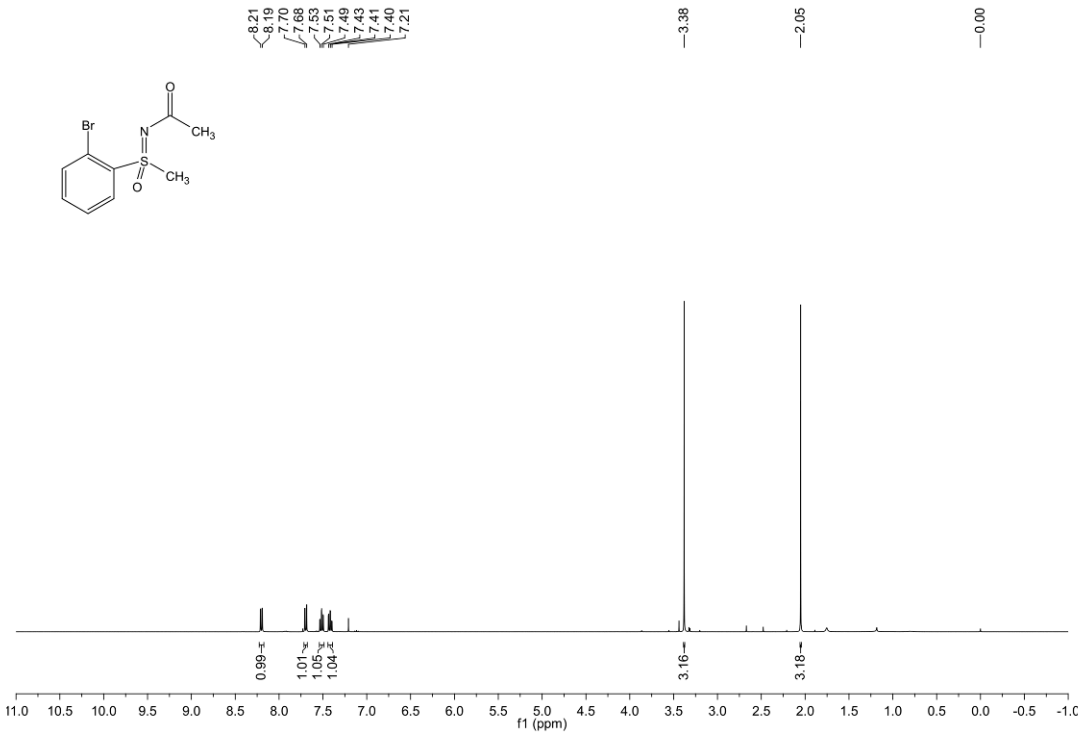
3. Fillion, E.; Zorzitto, A. K. *J. Am. Chem. Soc.* **2009**, *131*, 14608–14609.

4. Cho, G. Y.; Okamura, H.; Bolm, C. *J. Org. Chem.* **2005**, *70*, 2346–2349.

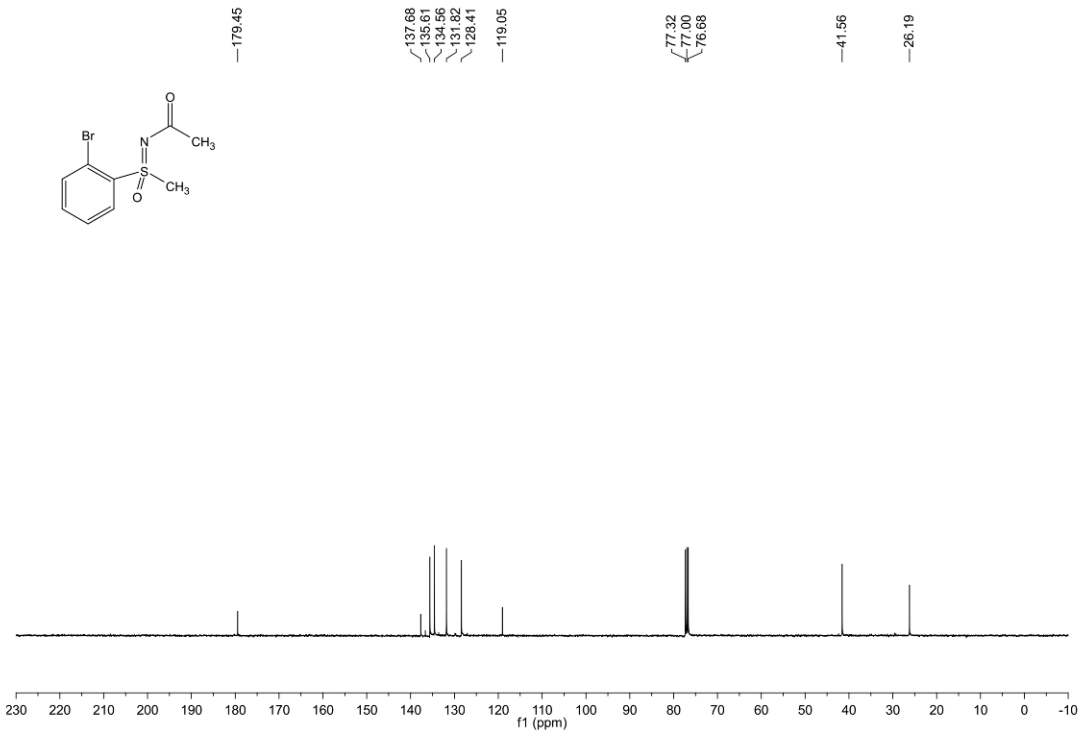
5. (a) Jordan-Hore, J. A.; Johansson, C. C. C.; Gulias, M.; Beck, E. M.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 16184–16186, and references therein. (b) Dong, W.; Parthasarathy, K.; Cheng, Y.; Pan, F.; C. Bolm, *Chem. - Eur. J.* **2014**, *20*, 15732–15736.

4 NMR Spectra

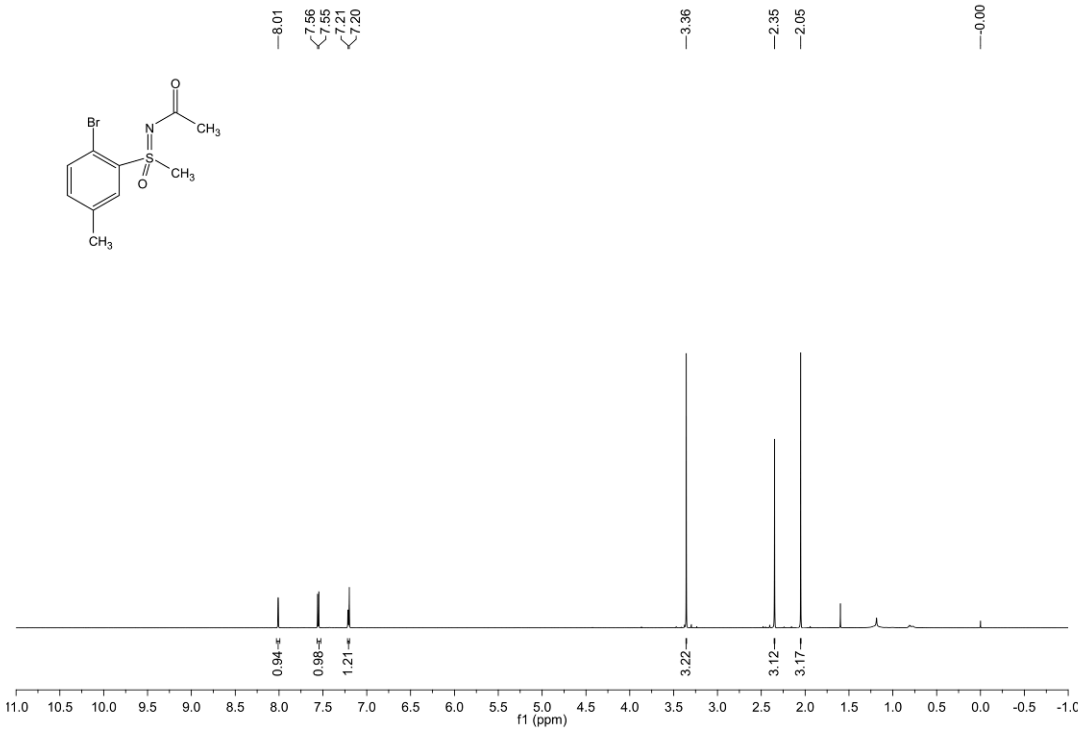
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3a



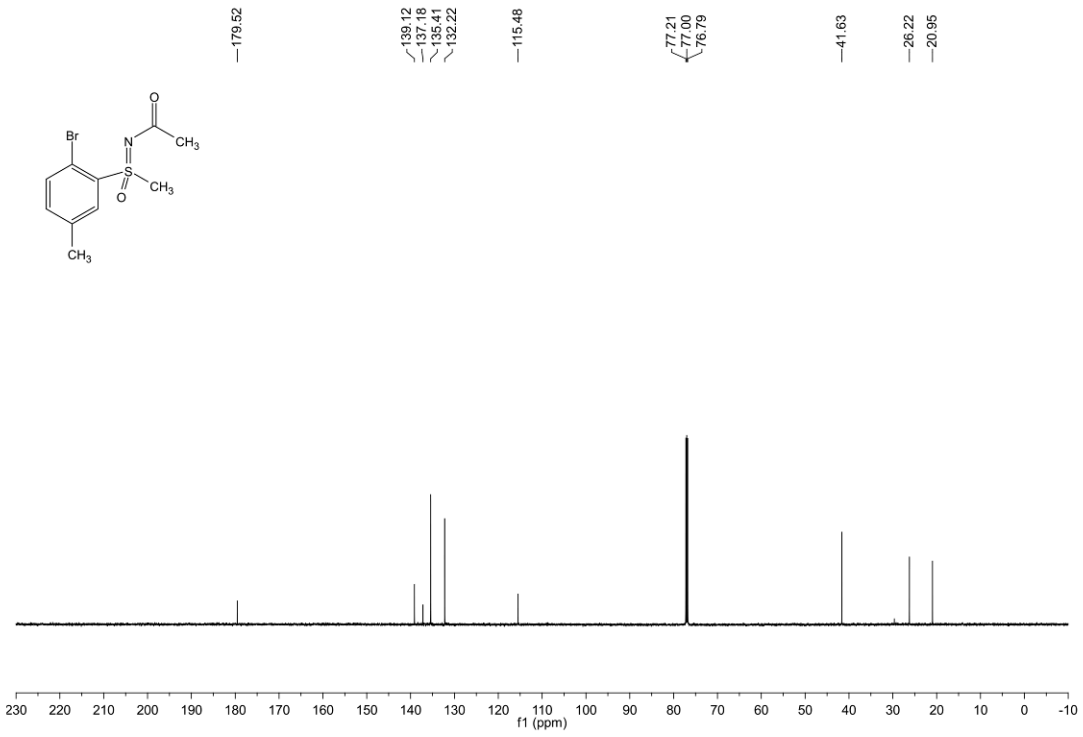
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3a



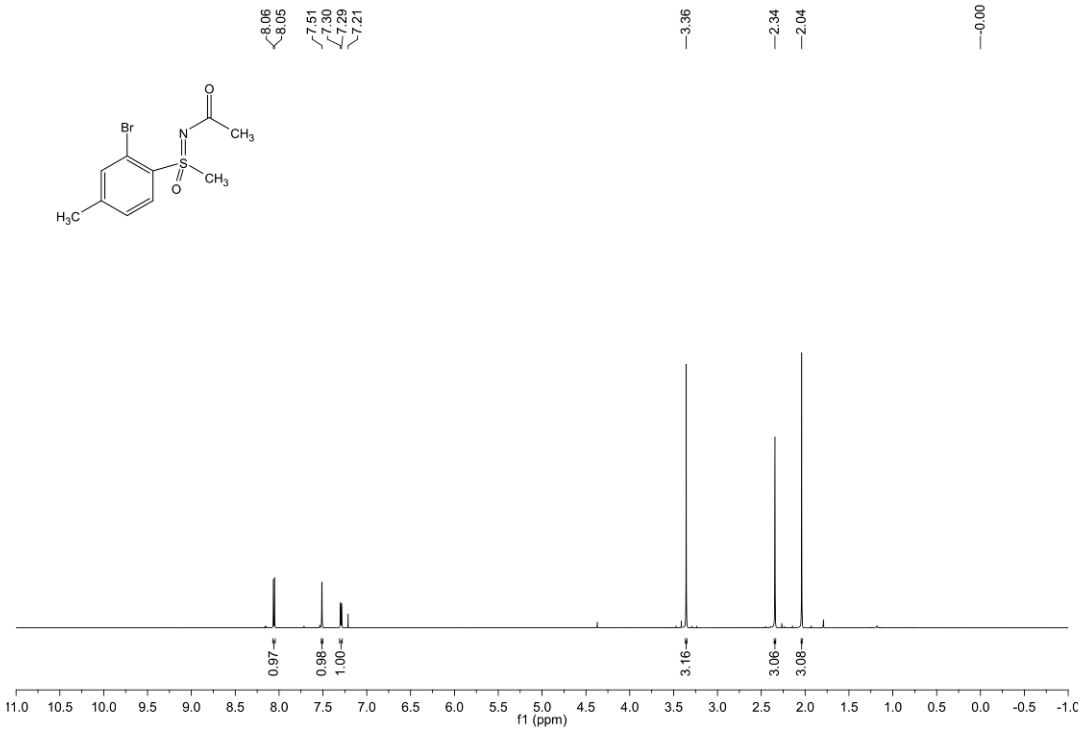
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3b



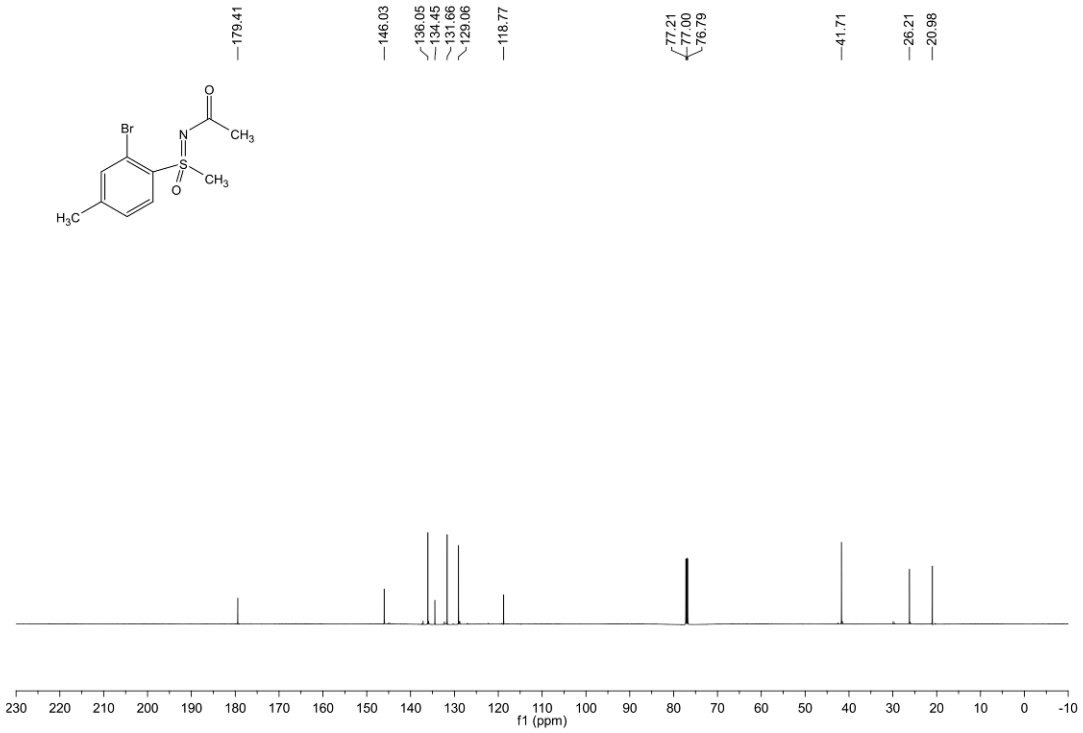
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 3b



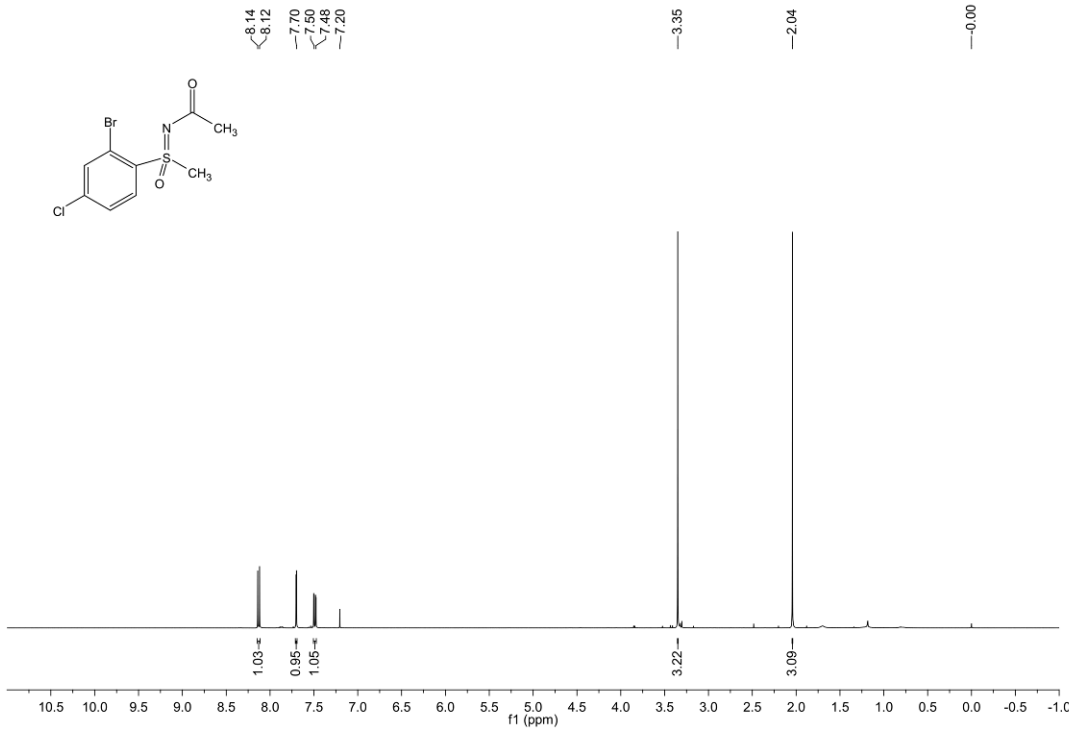
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3c



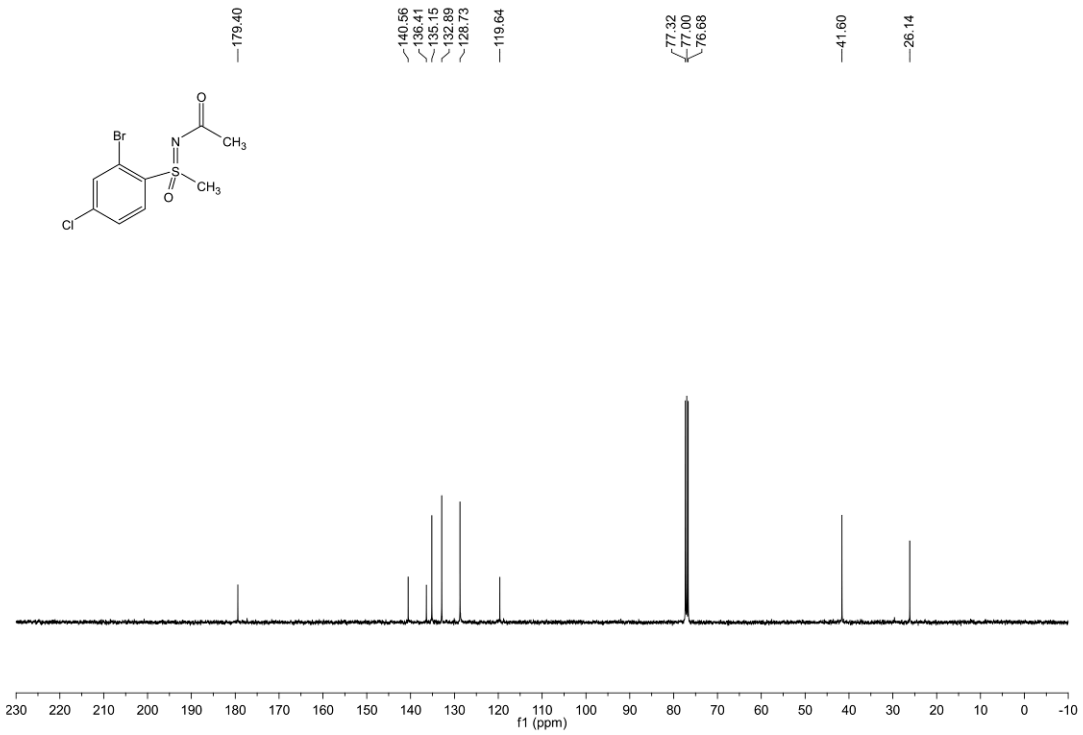
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 3c



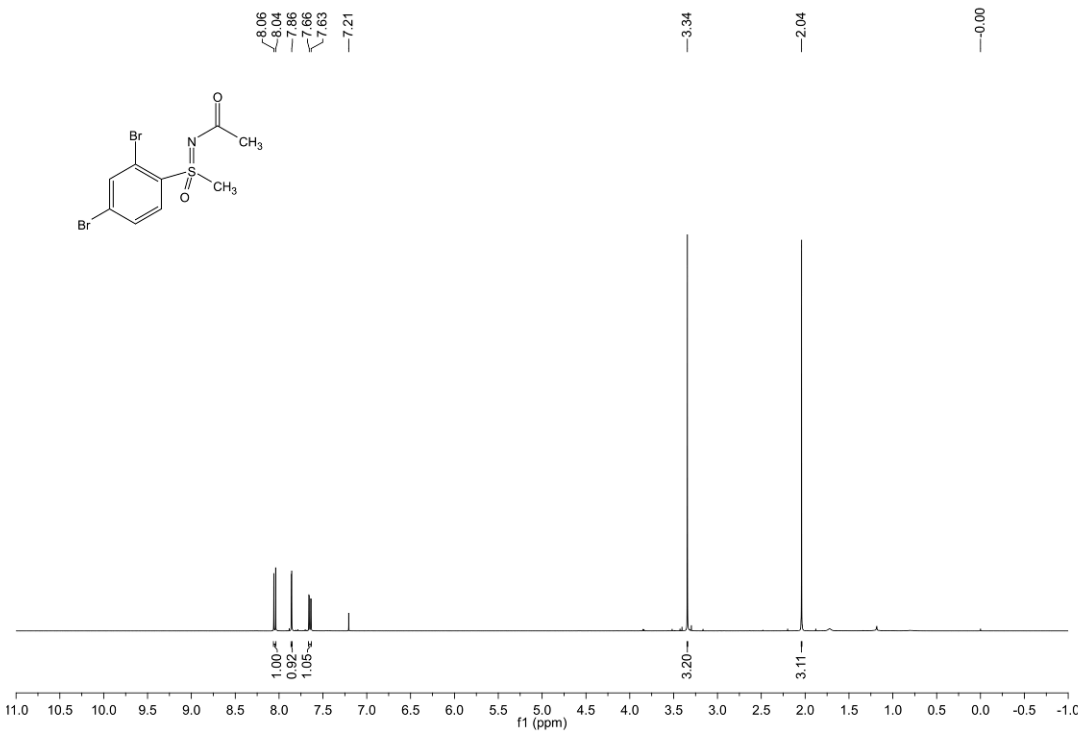
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3d



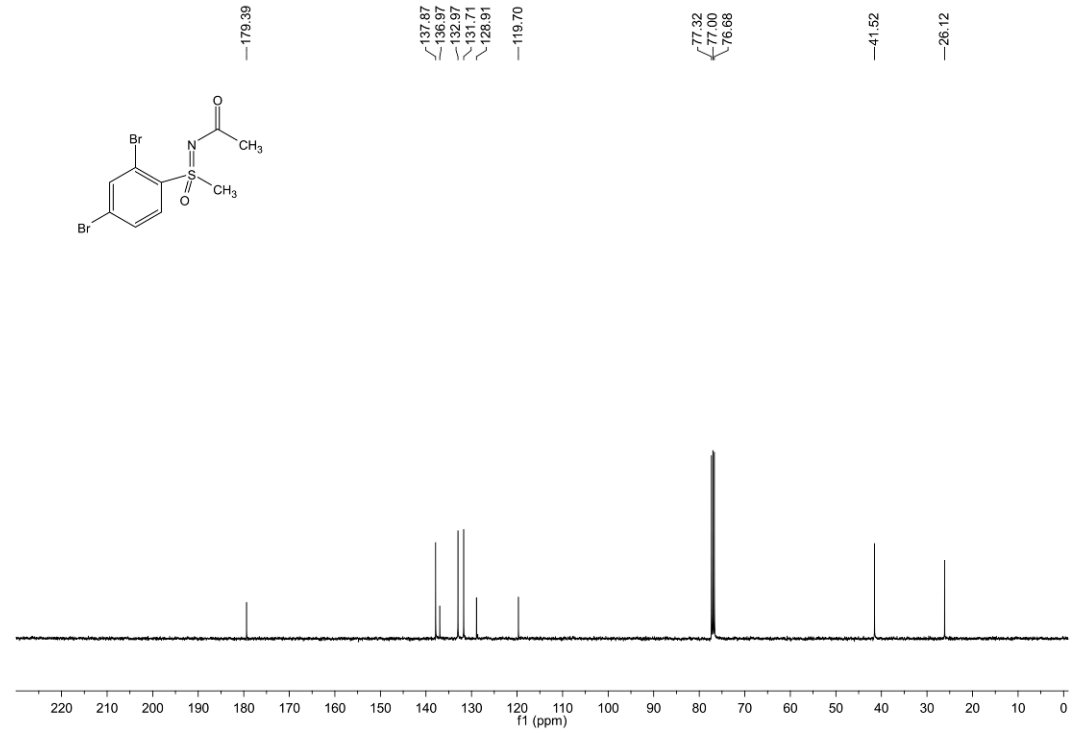
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3d



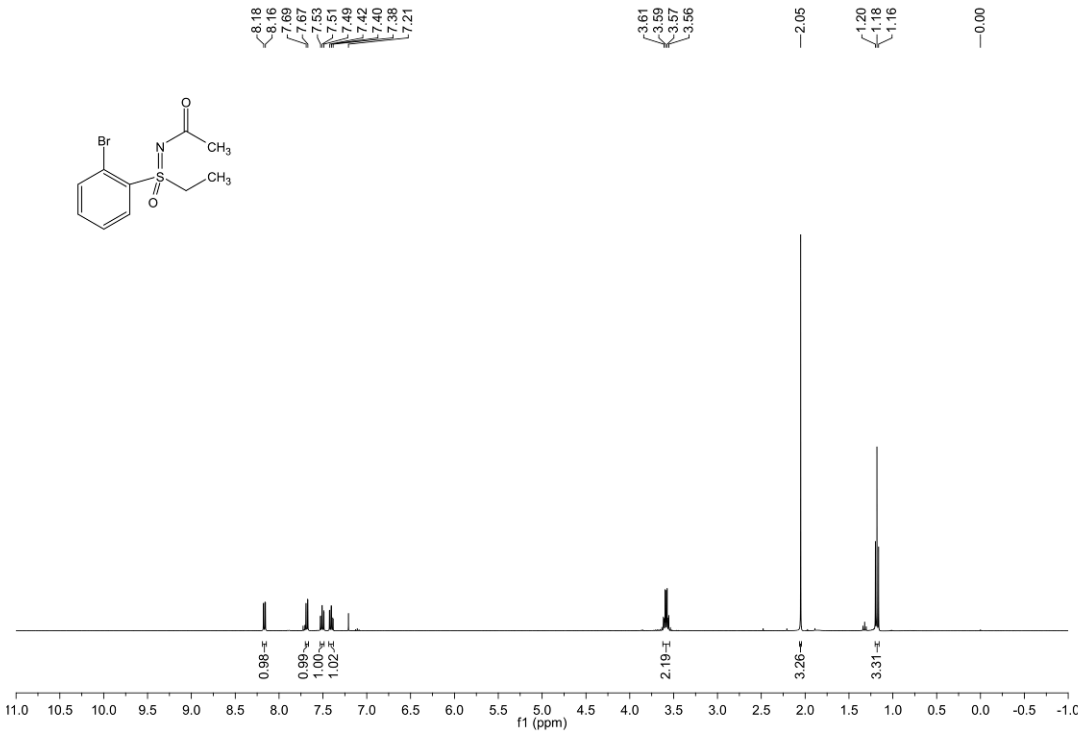
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3e



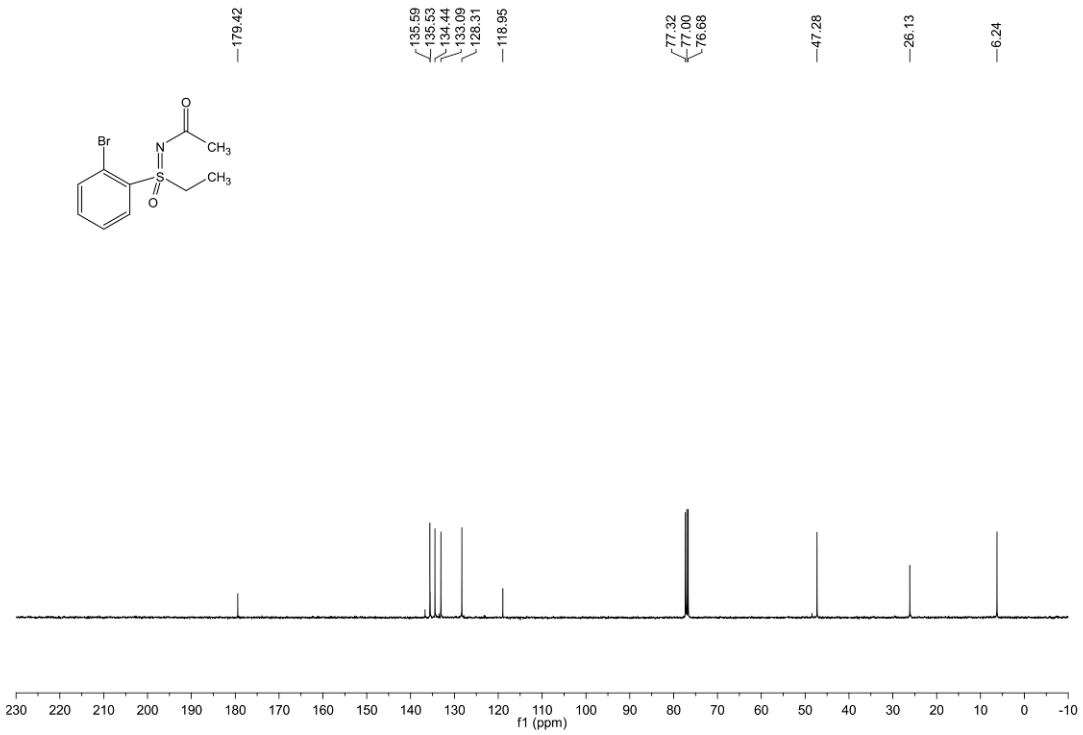
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3e



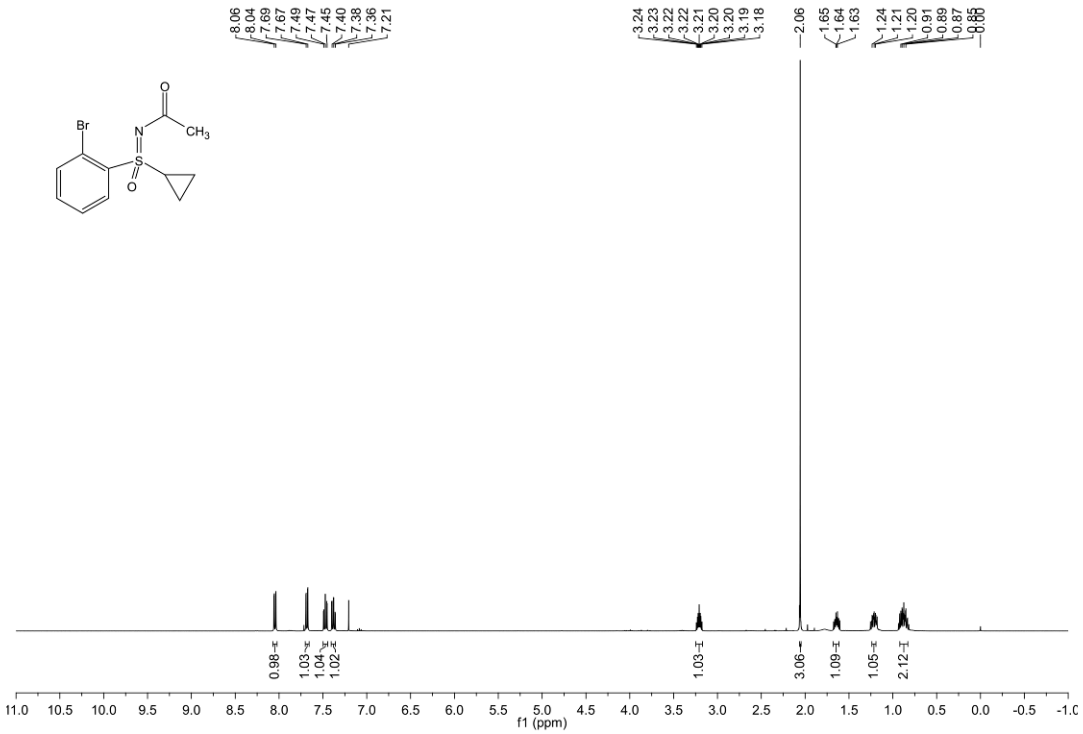
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3f



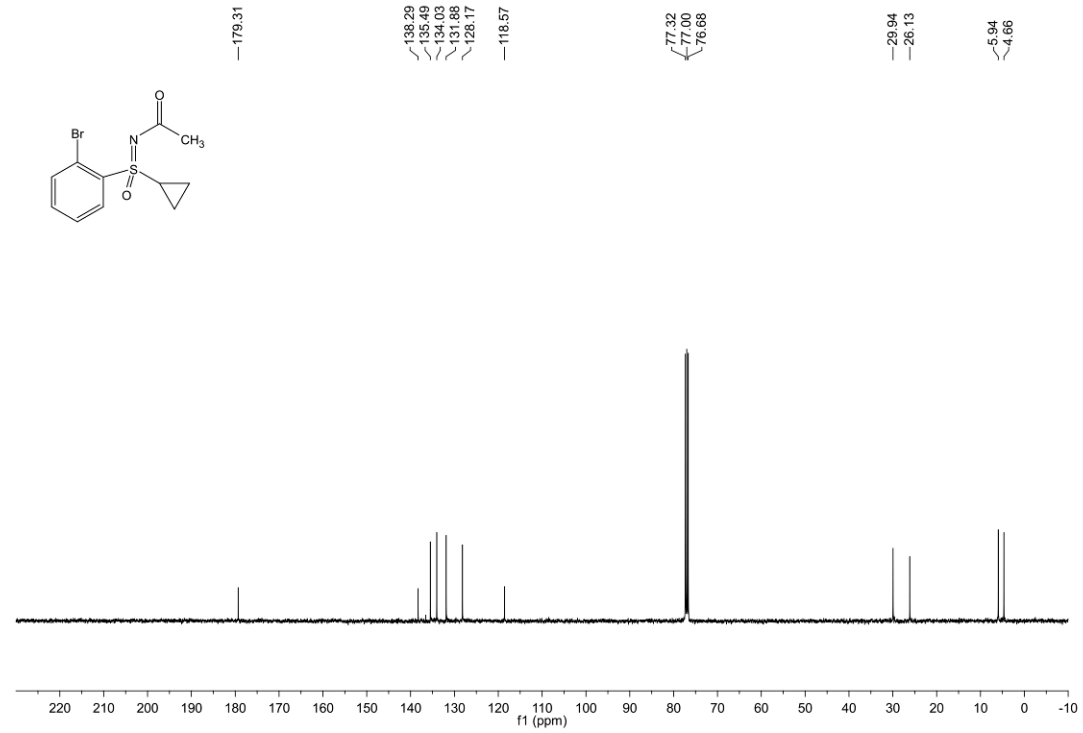
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3f



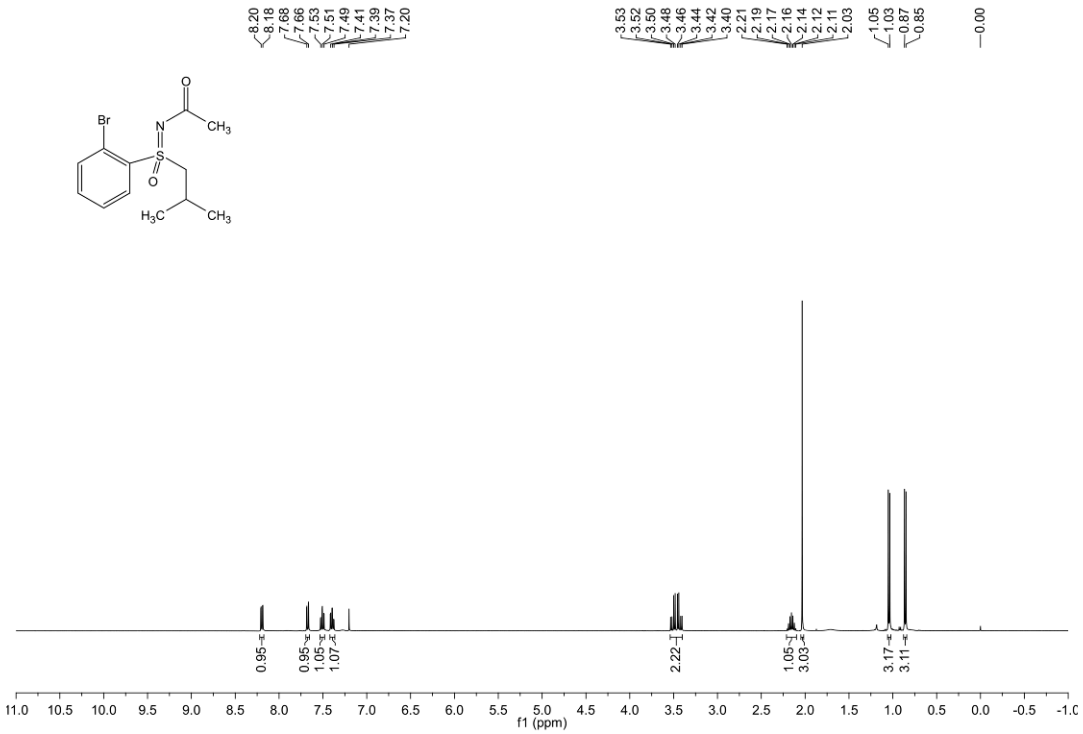
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3g



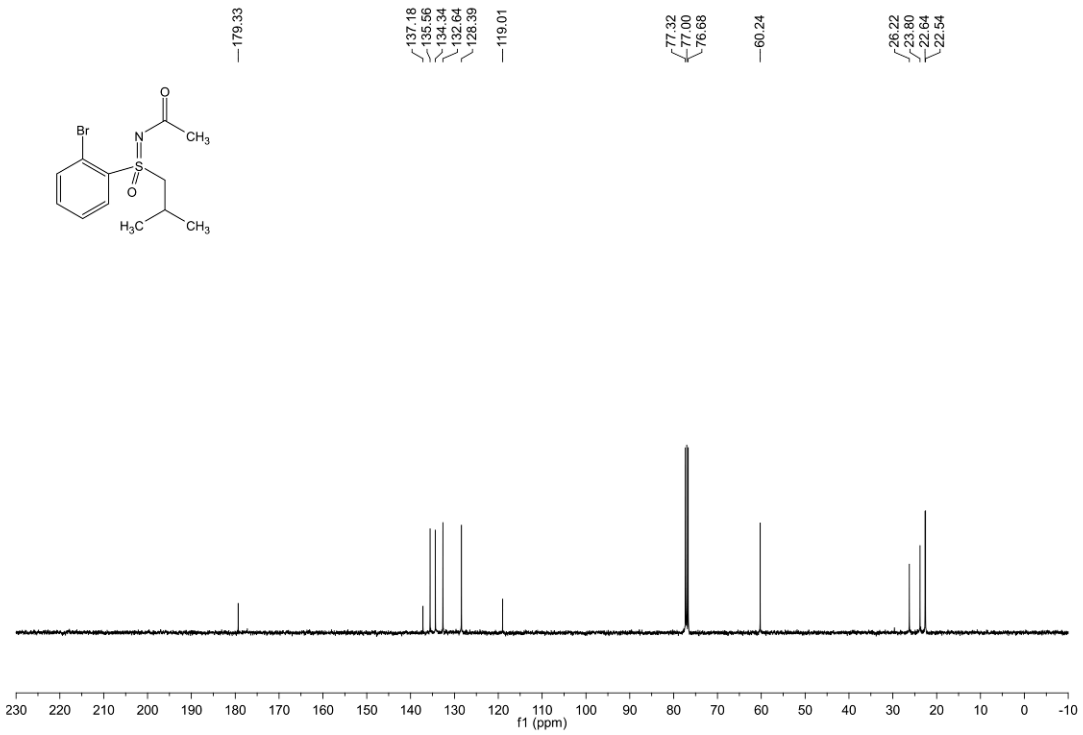
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3g



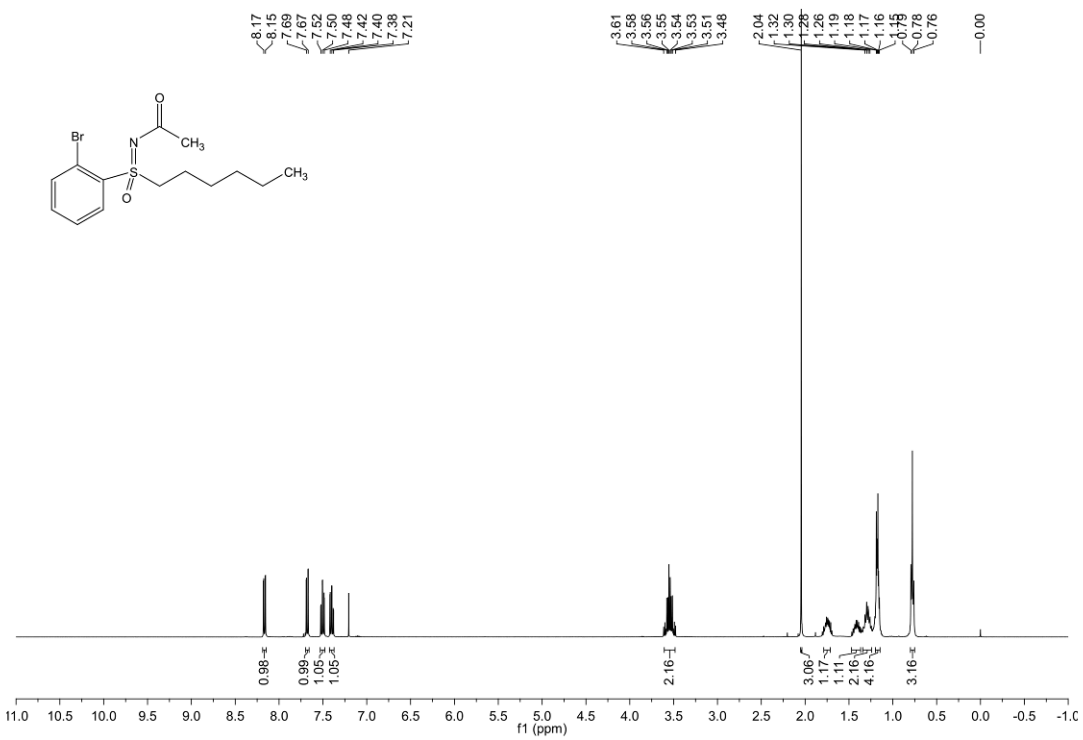
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3h



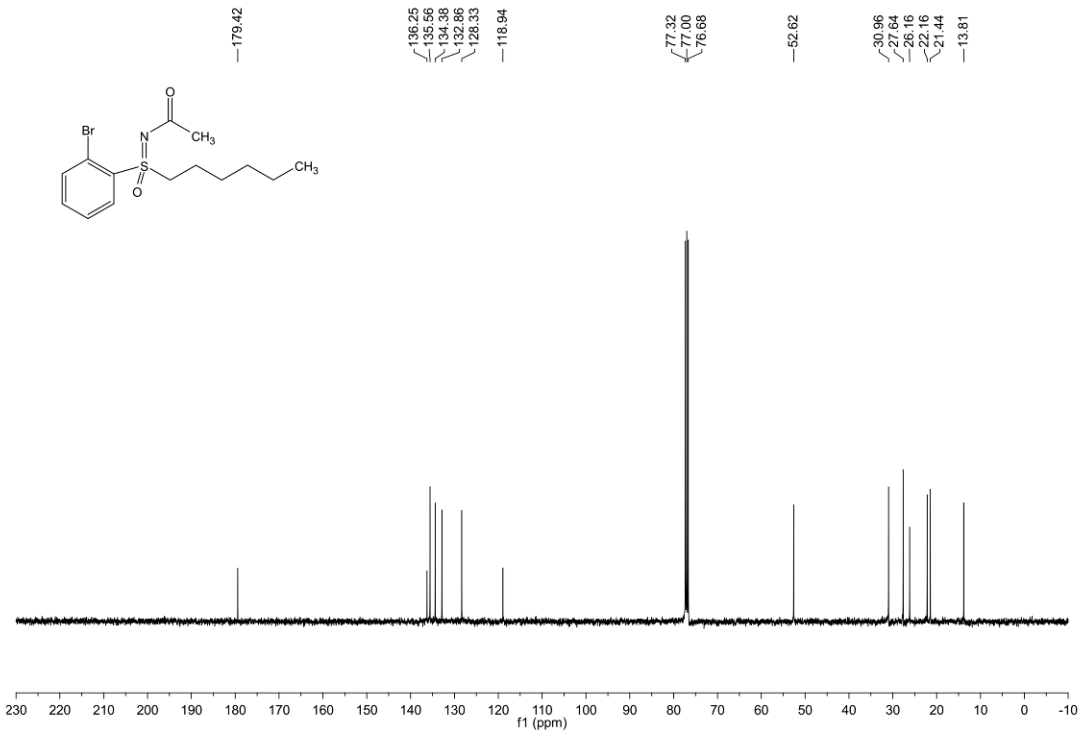
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3h



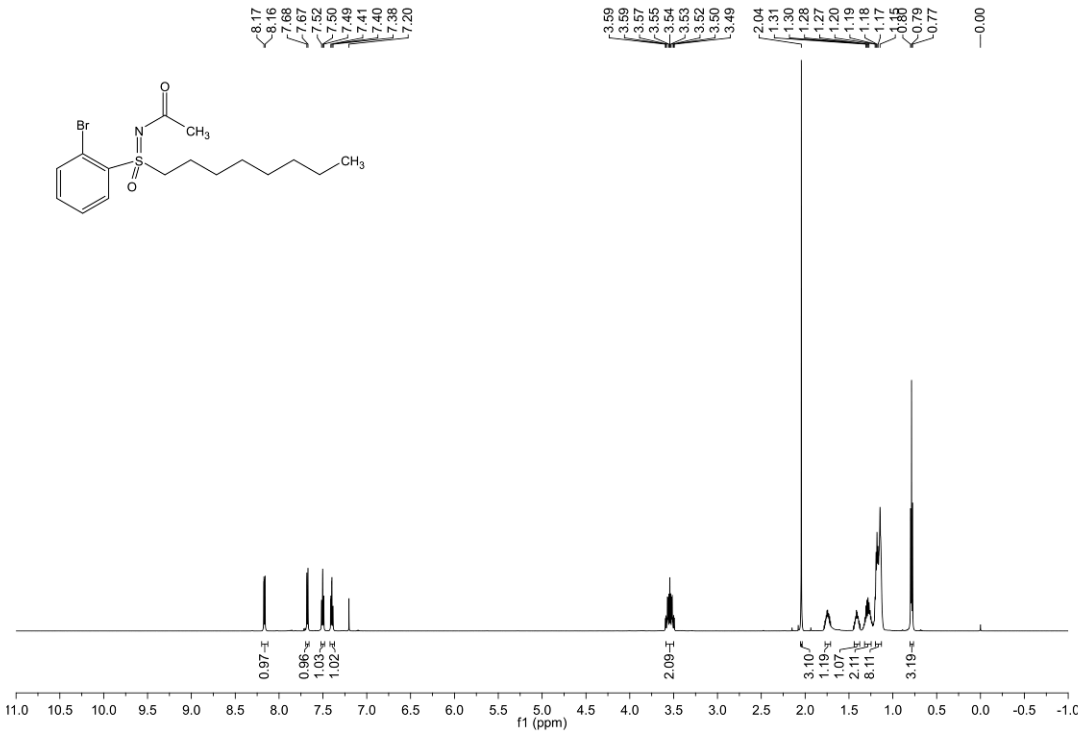
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3i



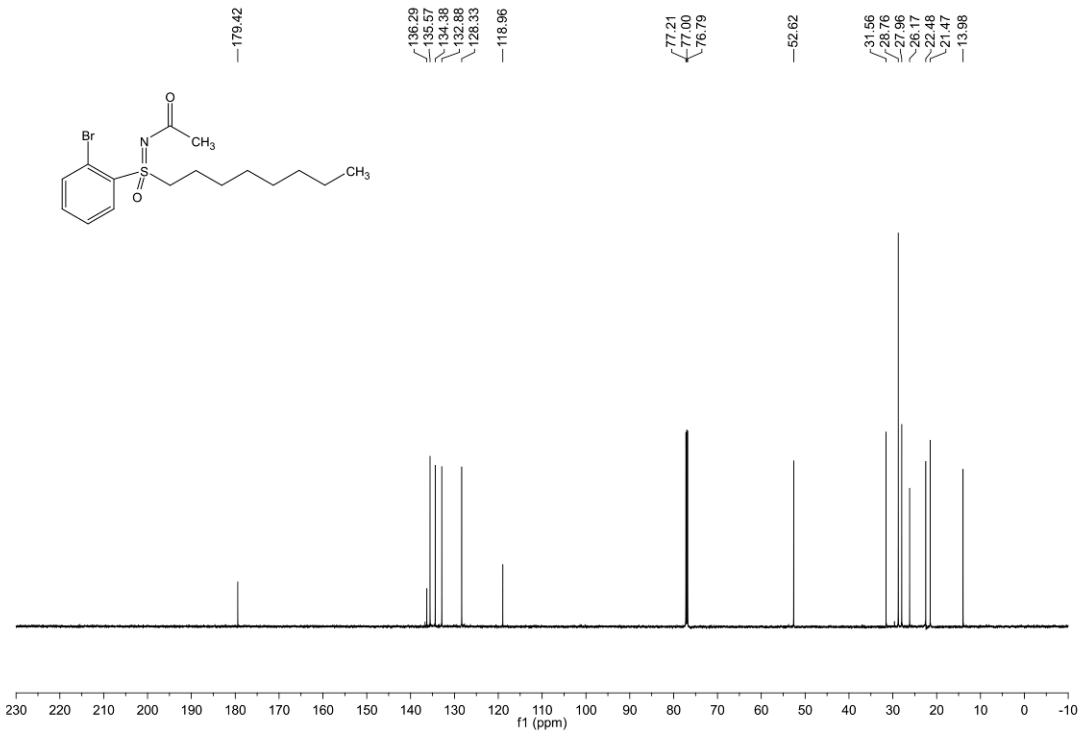
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3i



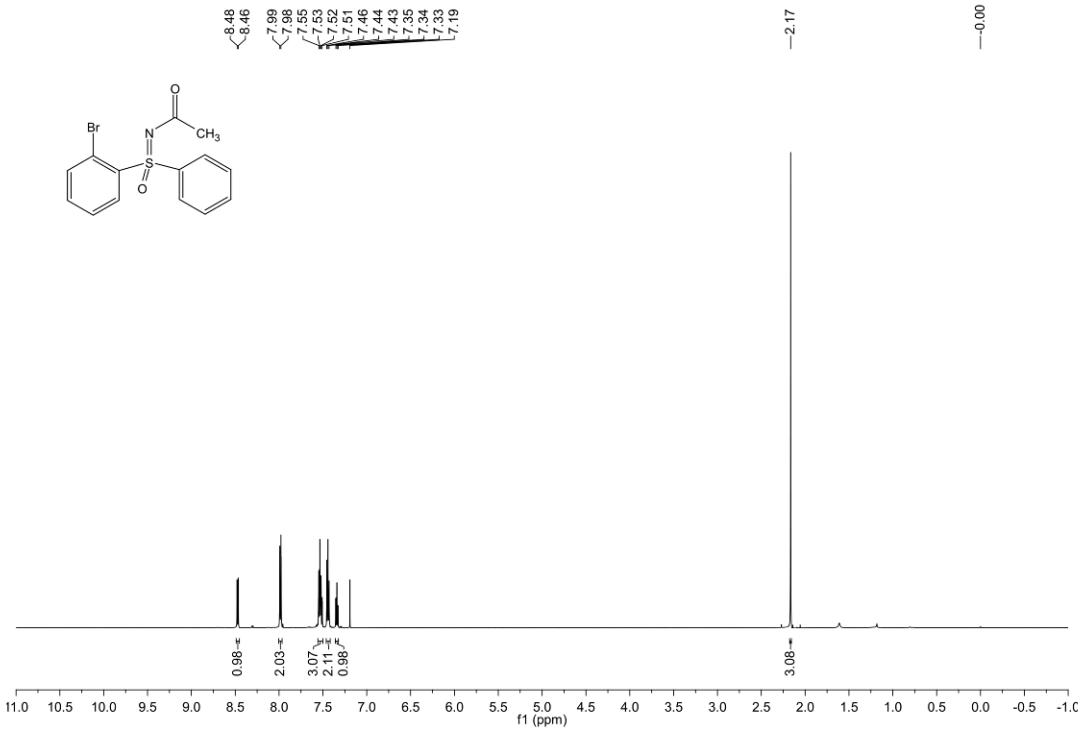
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3j



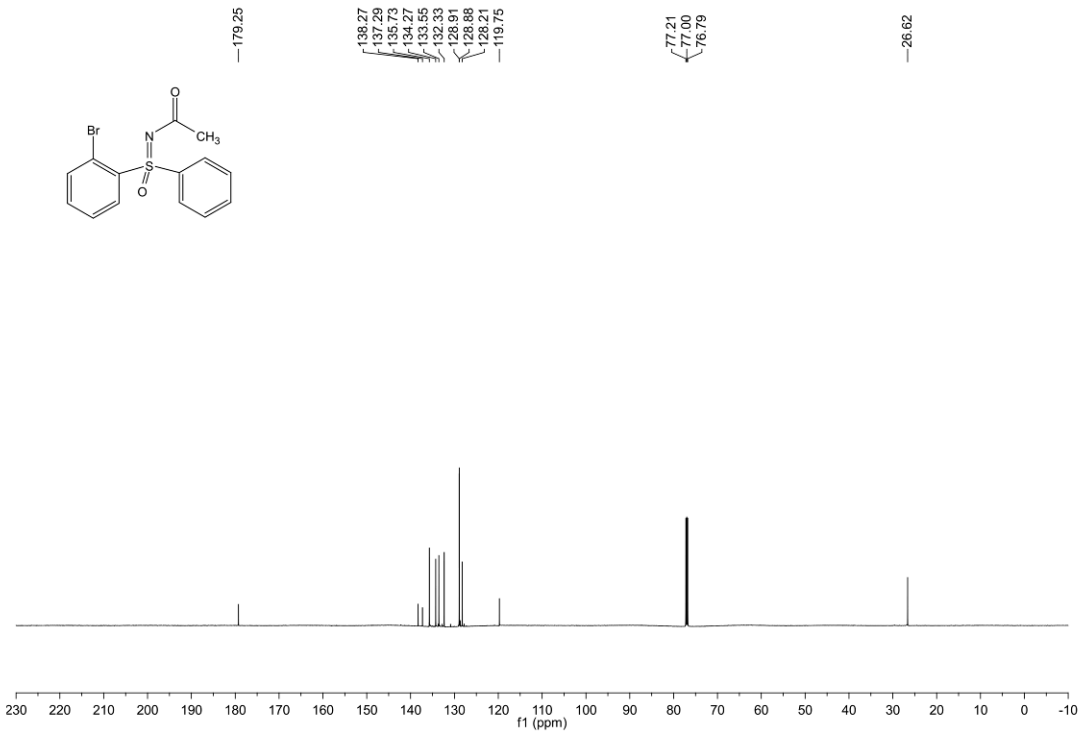
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 3j



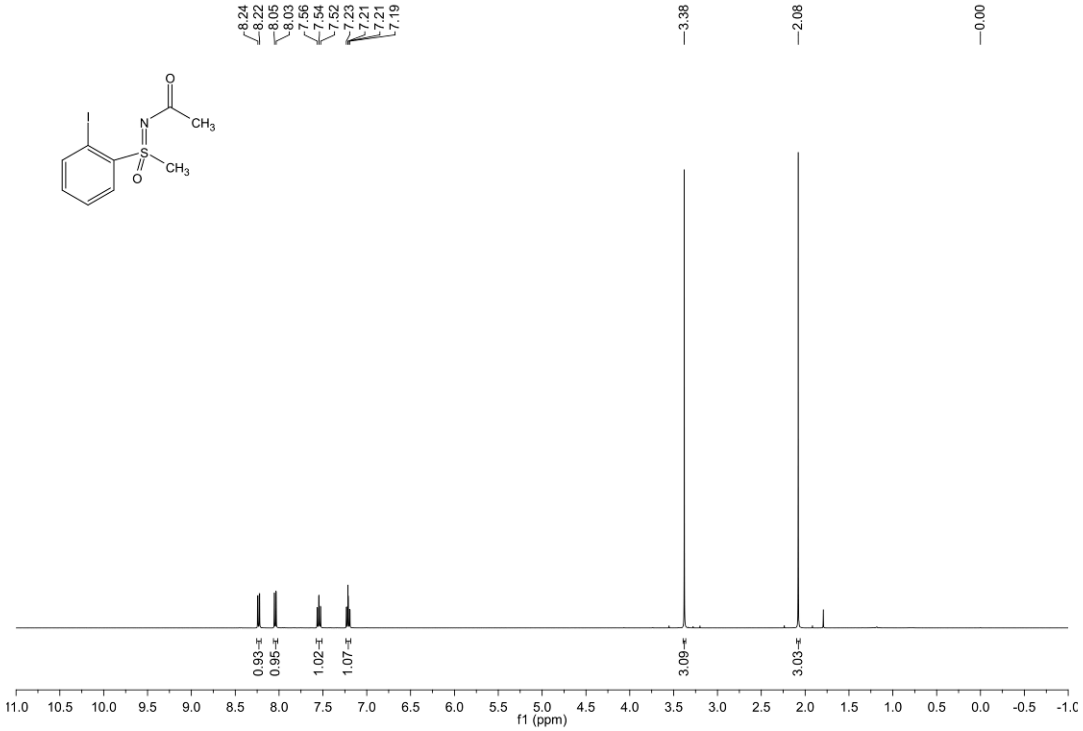
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3k



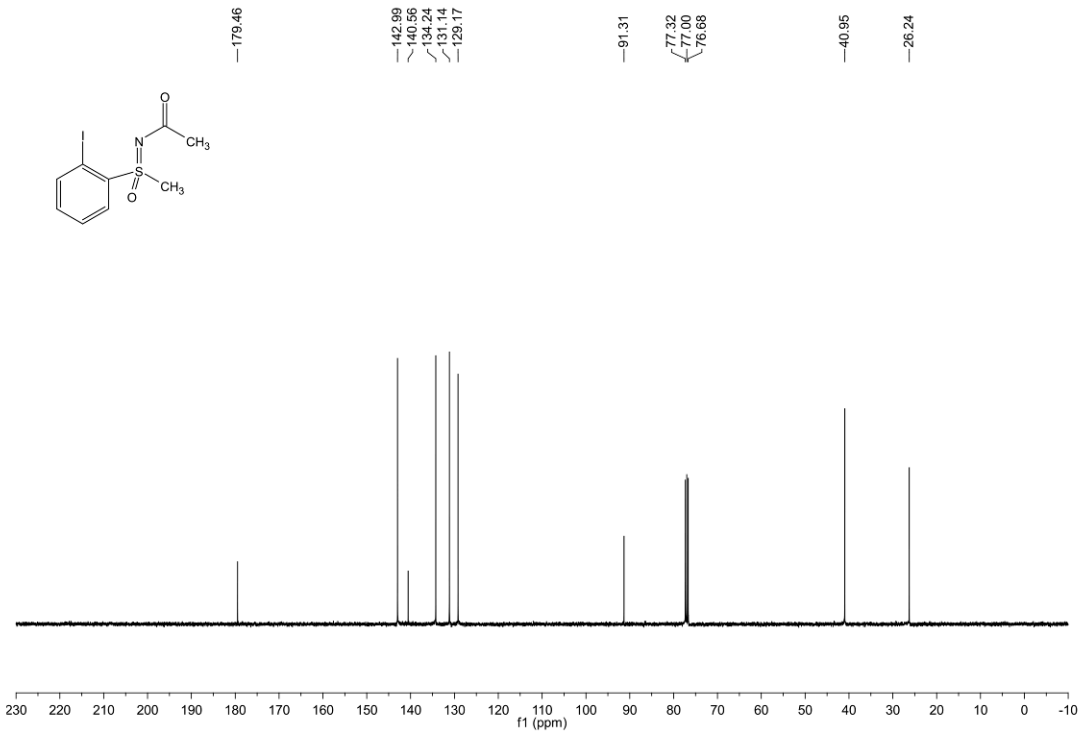
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 3k



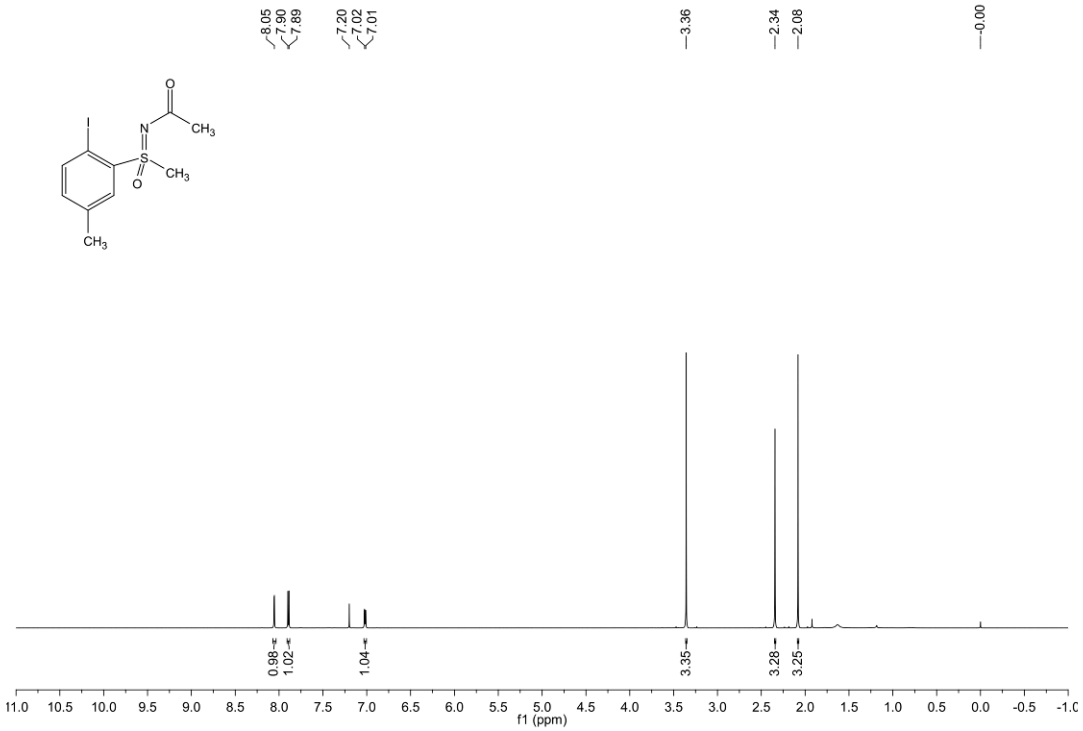
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4a



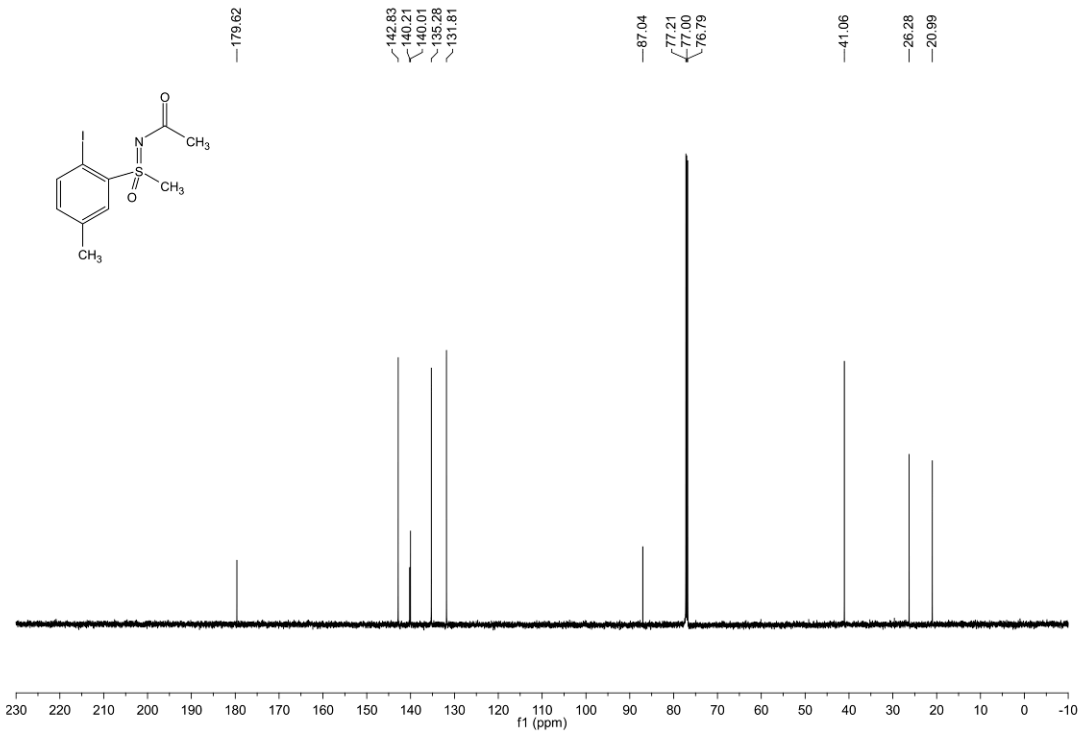
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4a



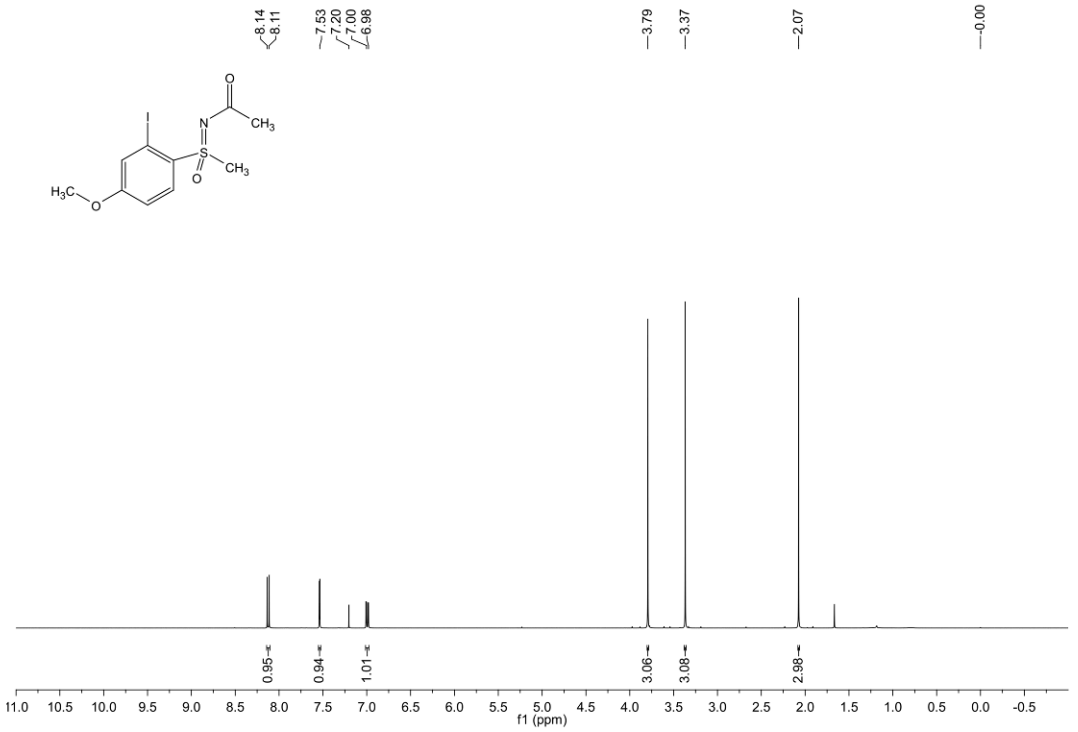
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4b



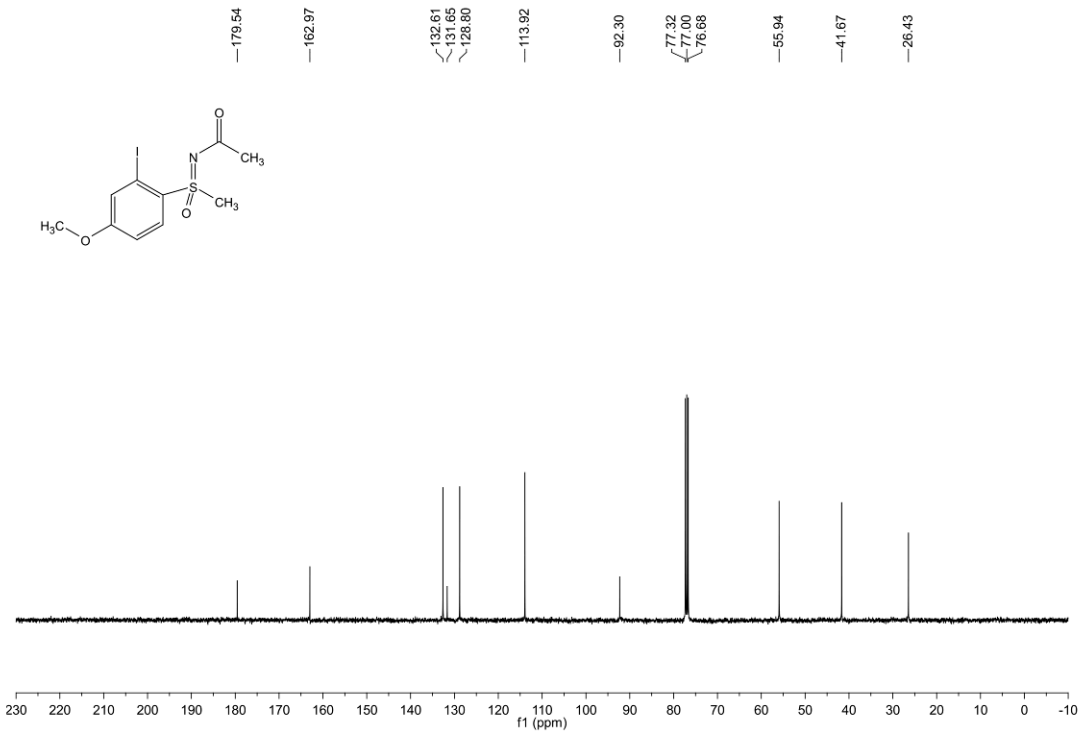
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 4b



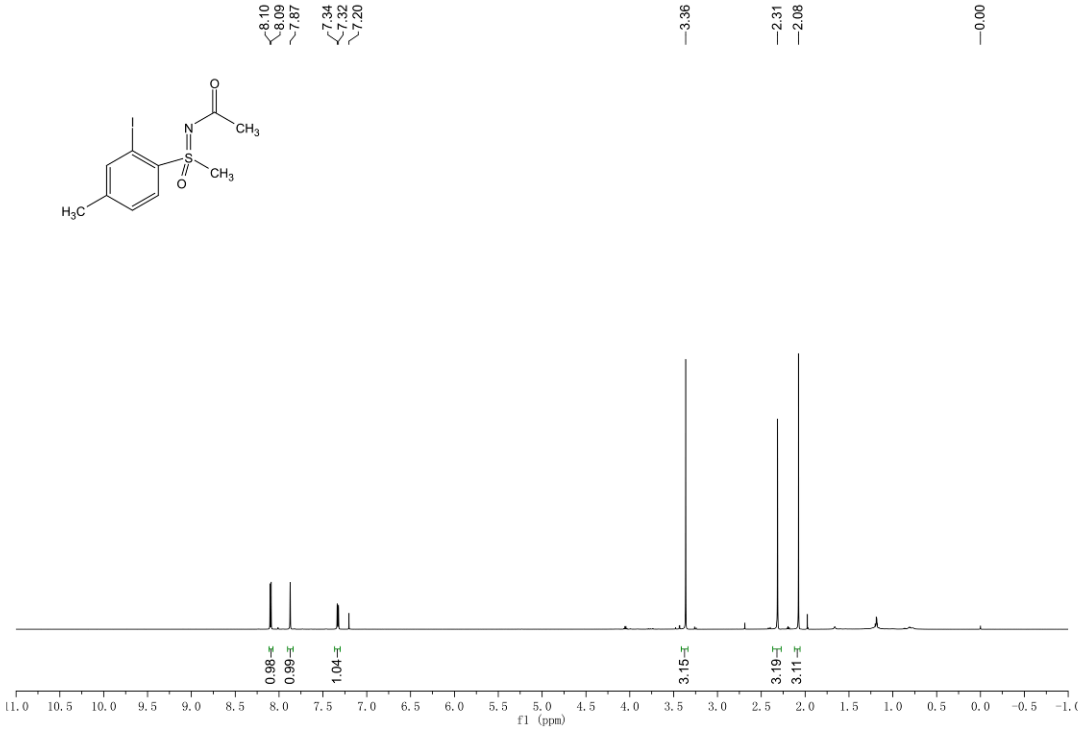
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4c



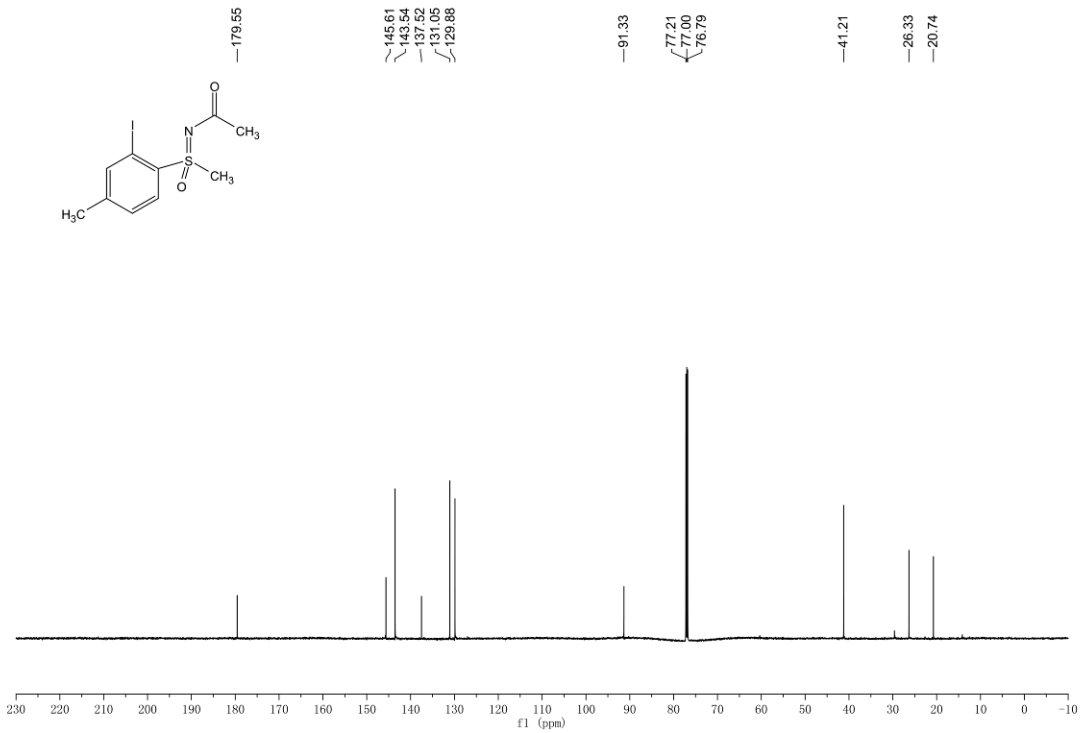
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4c



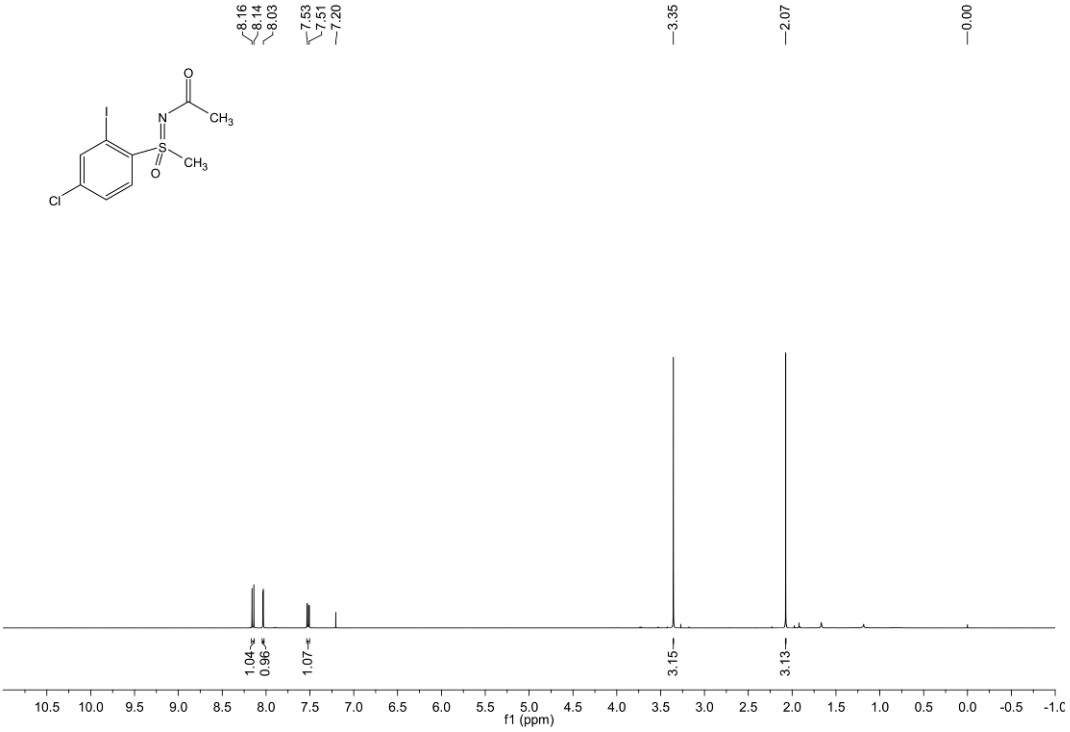
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4d



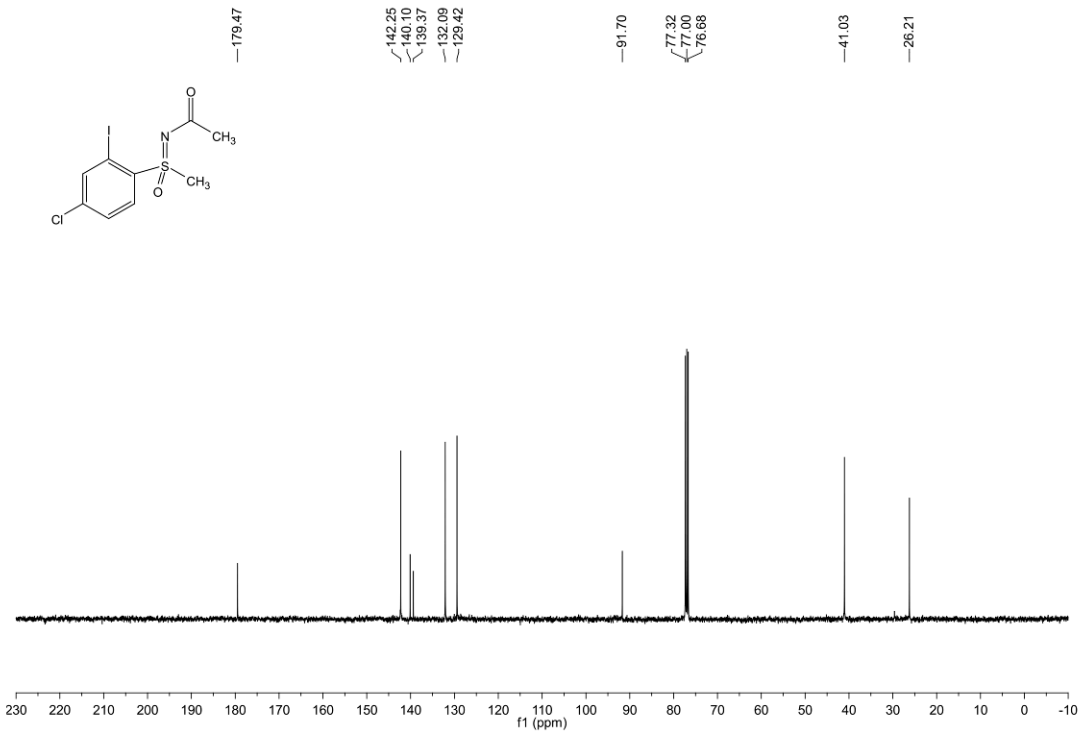
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 4d



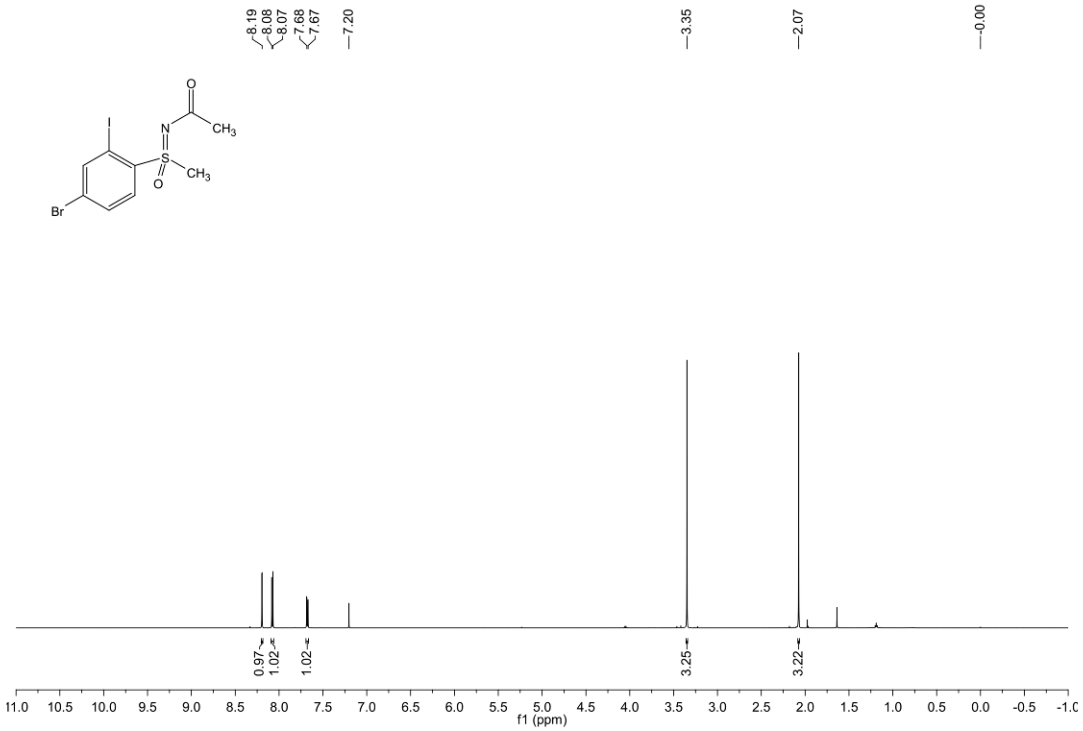
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4e



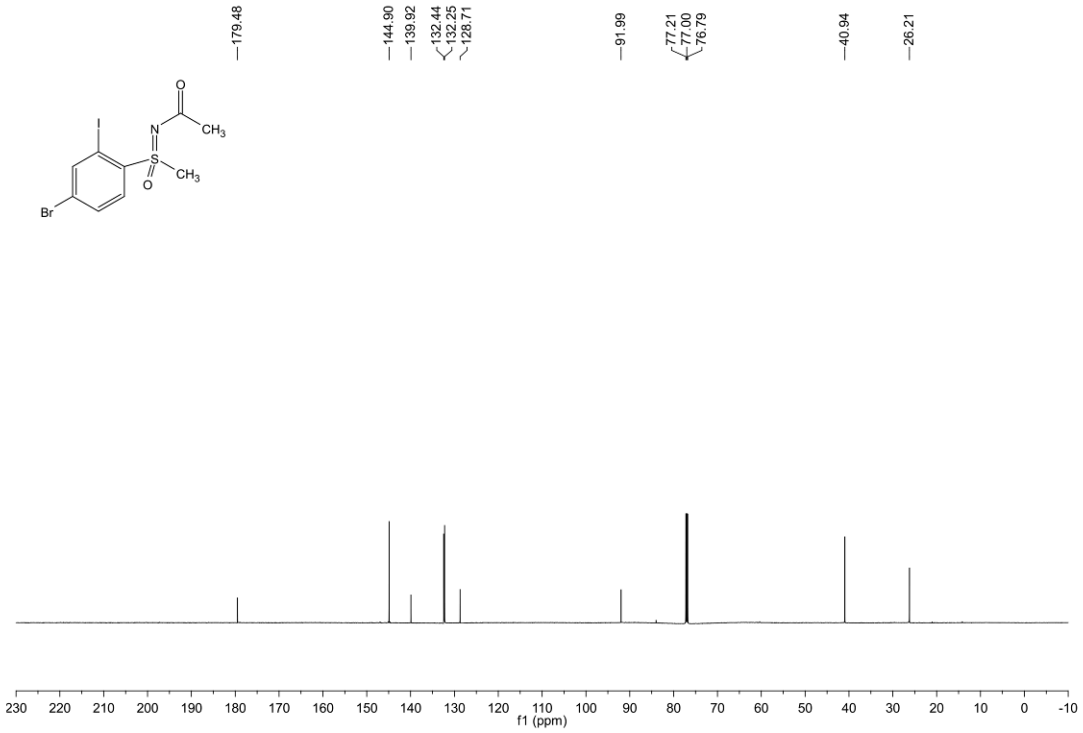
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4e



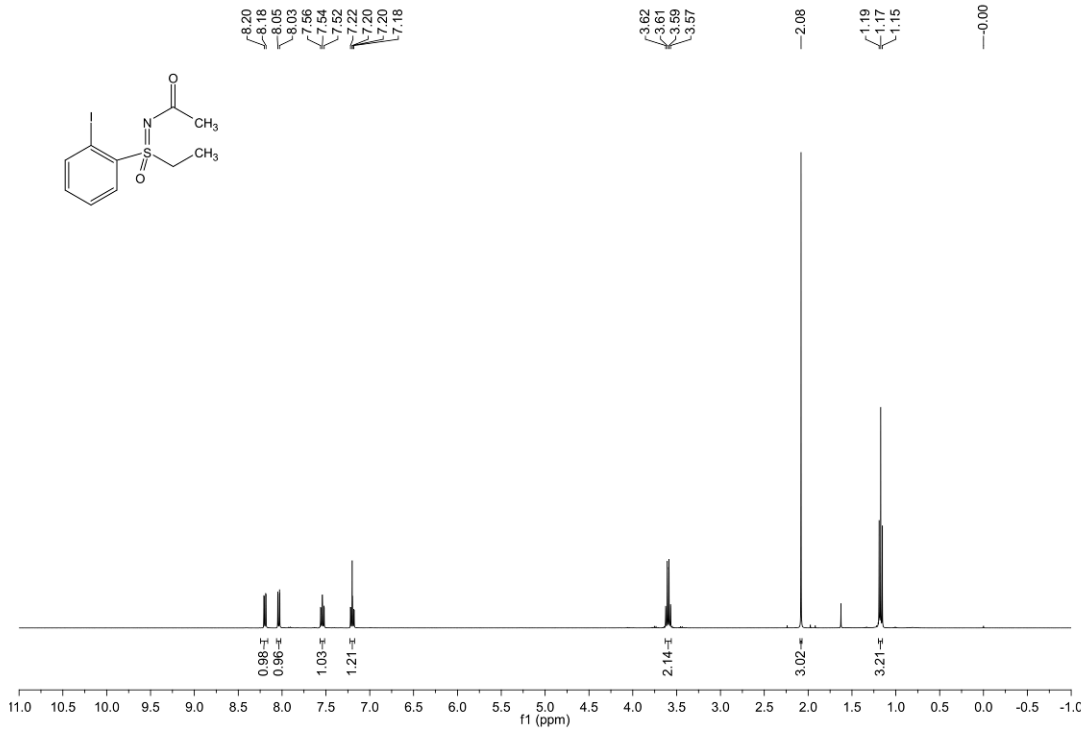
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4f



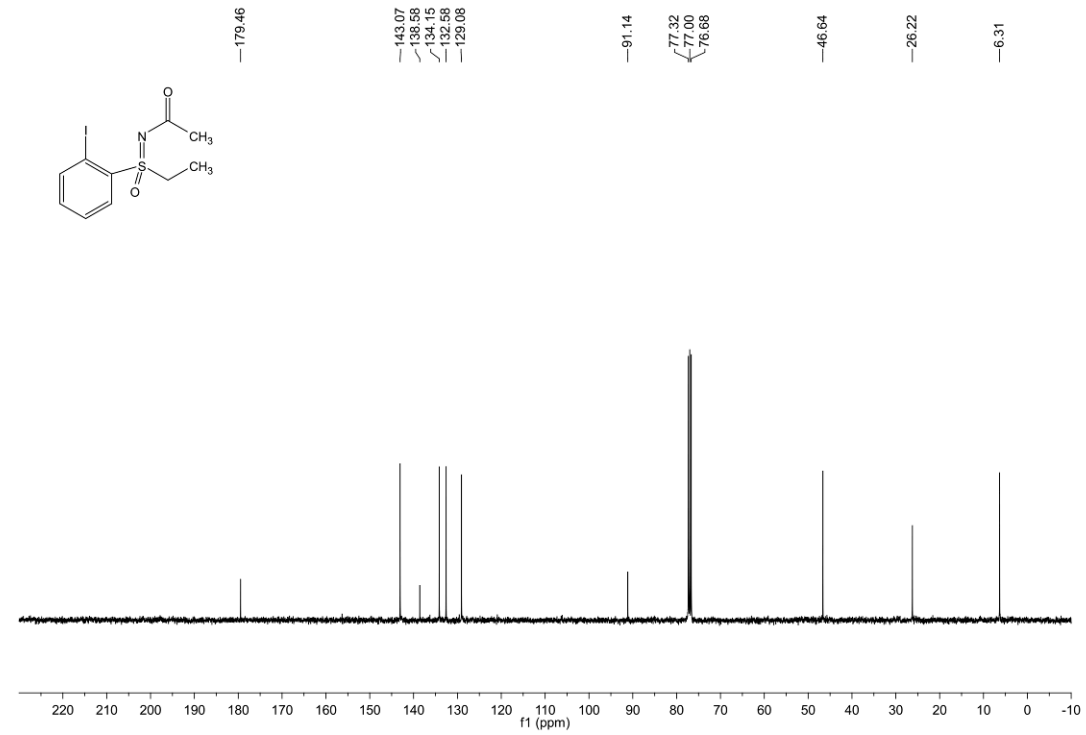
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 4f



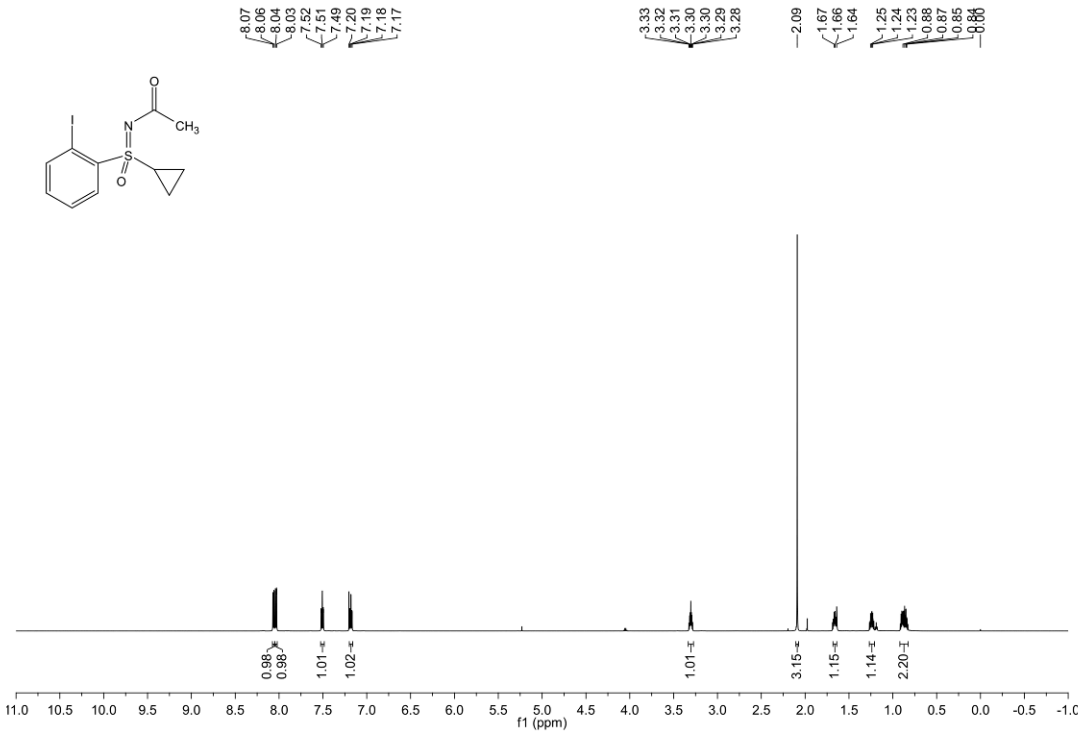
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4g



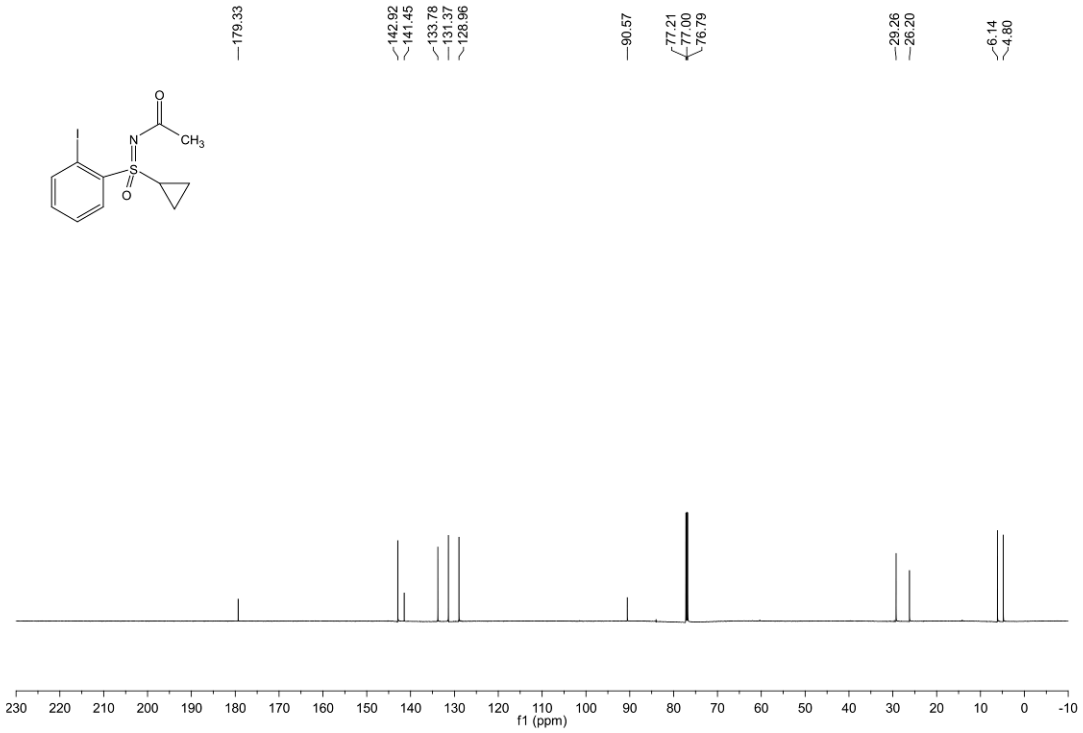
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4g



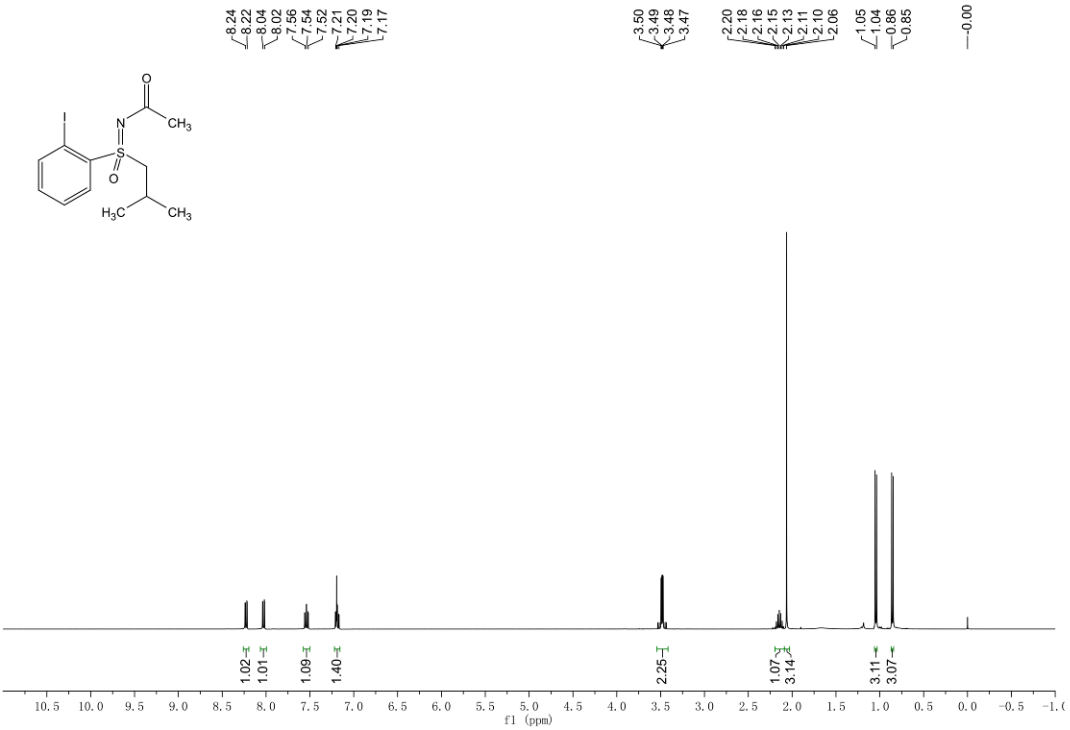
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4h



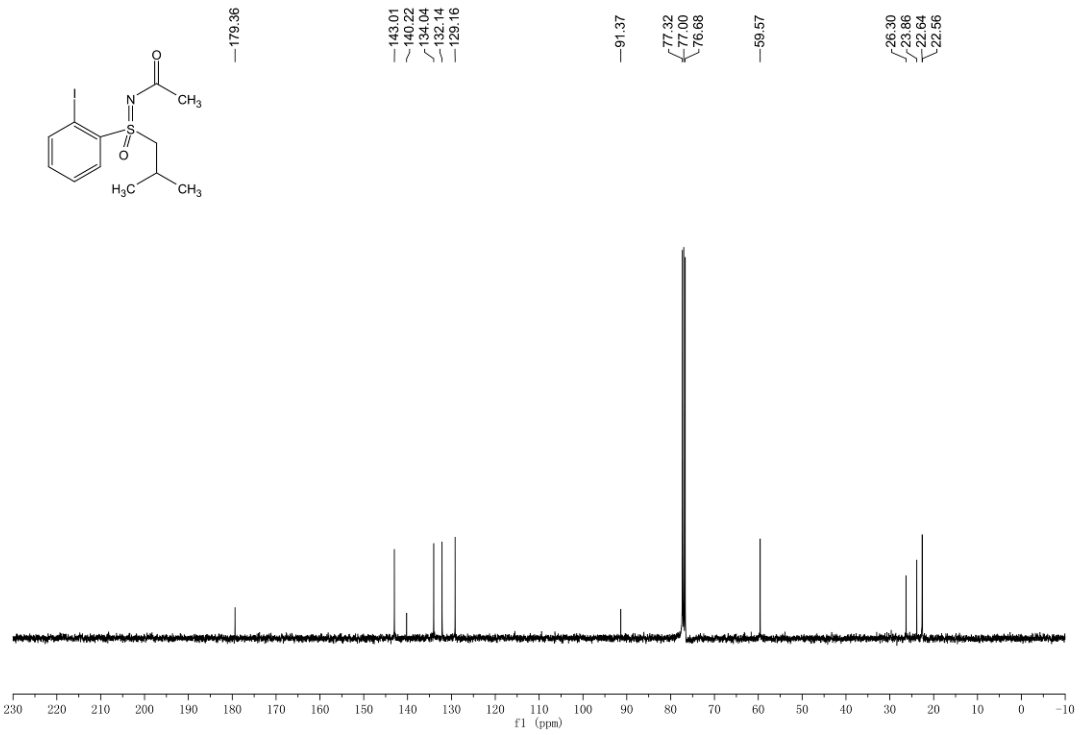
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 4h



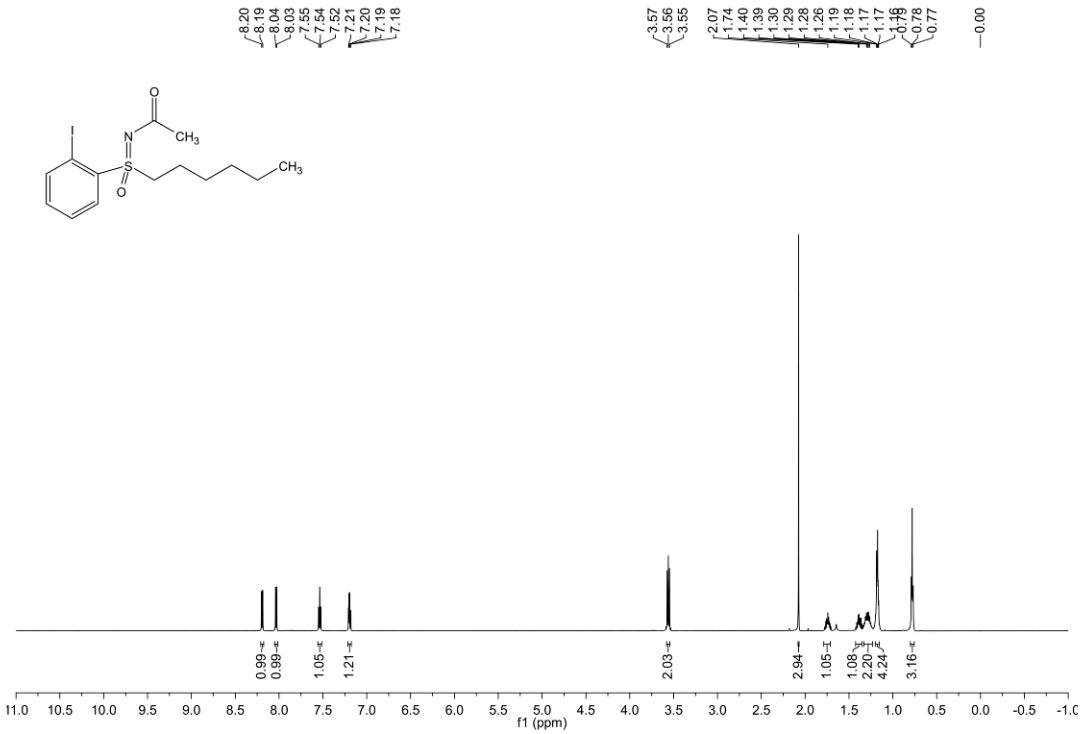
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4i



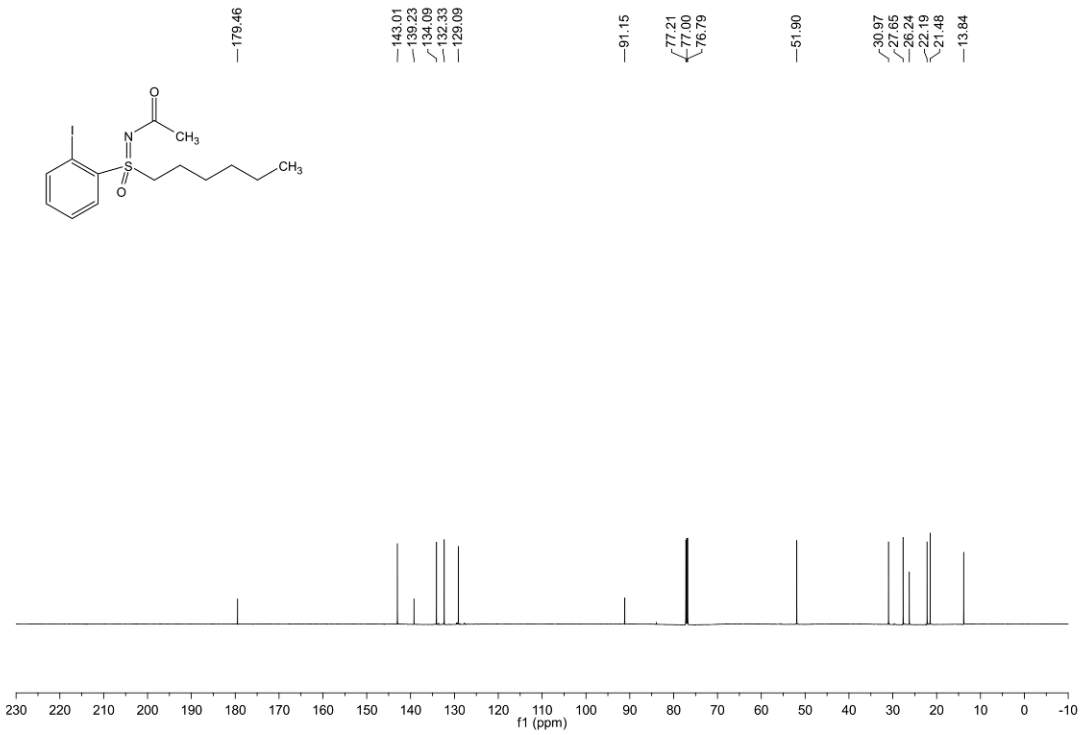
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4i



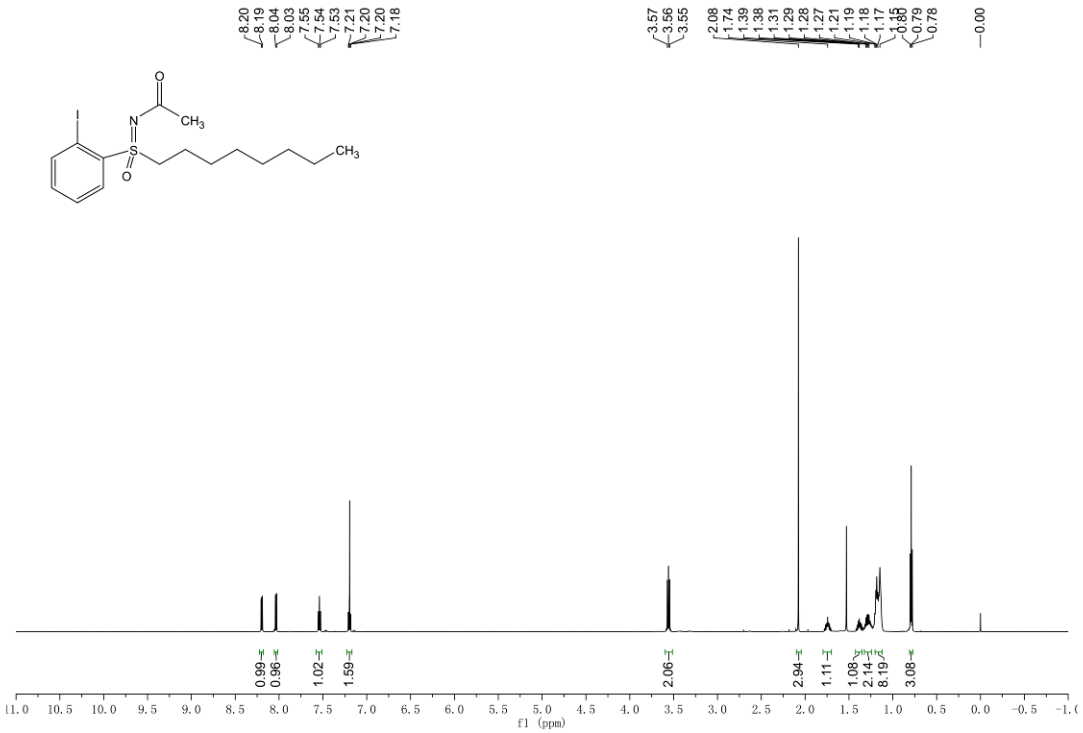
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4j



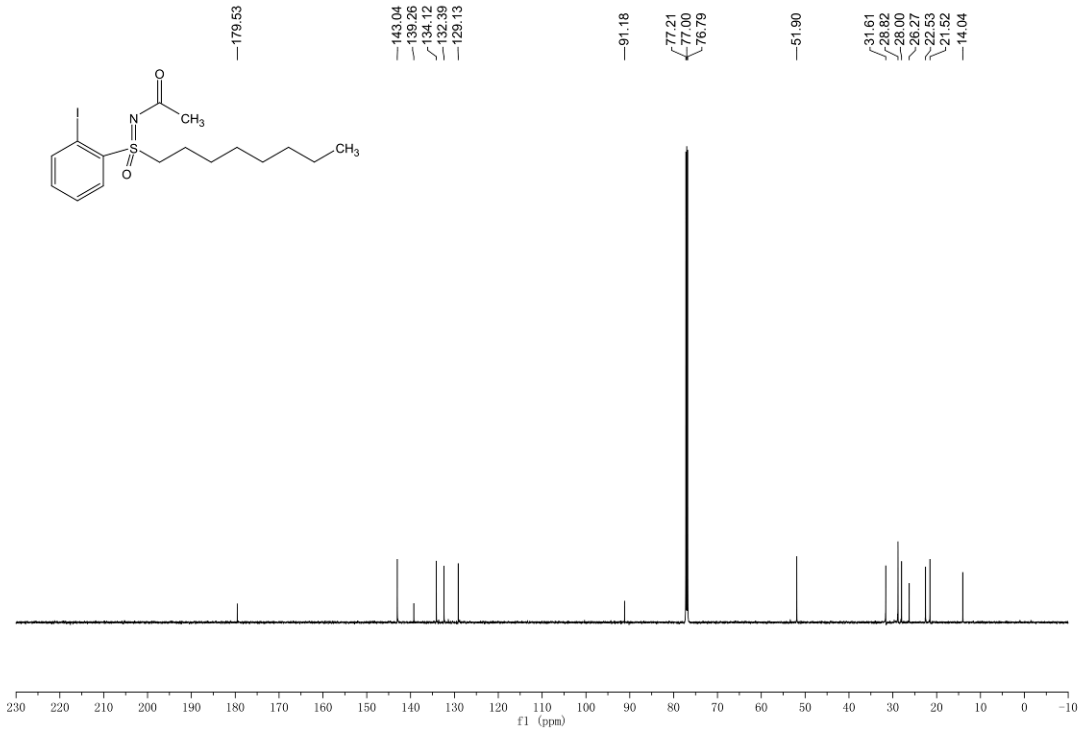
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 4j



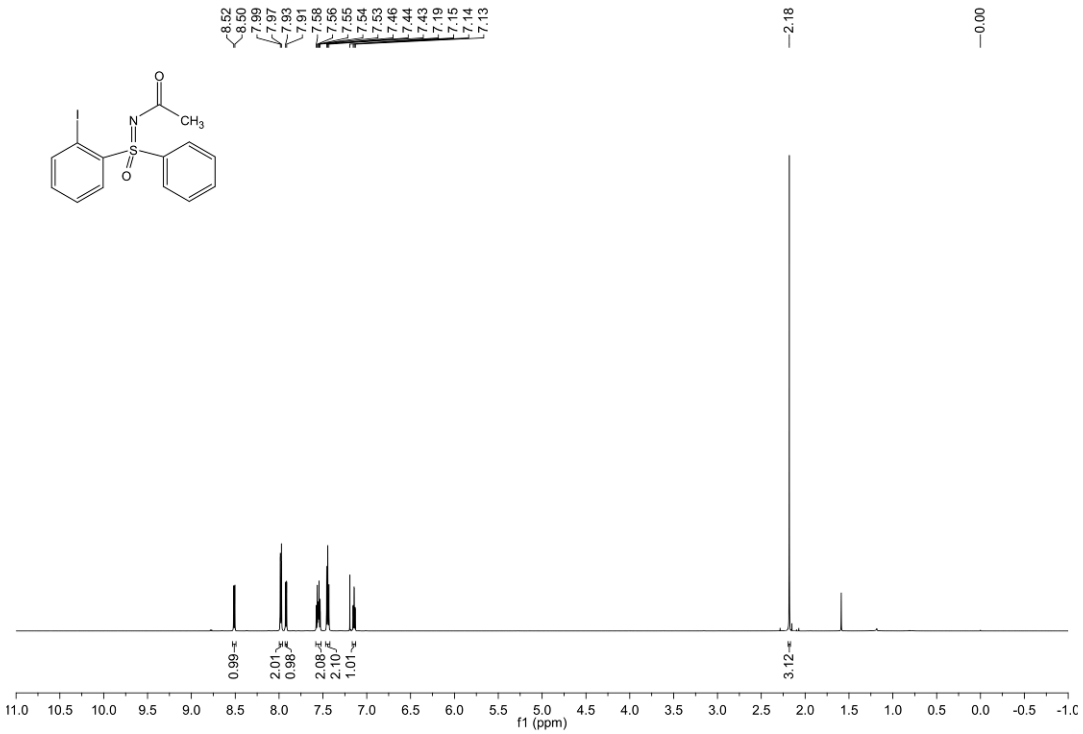
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4k



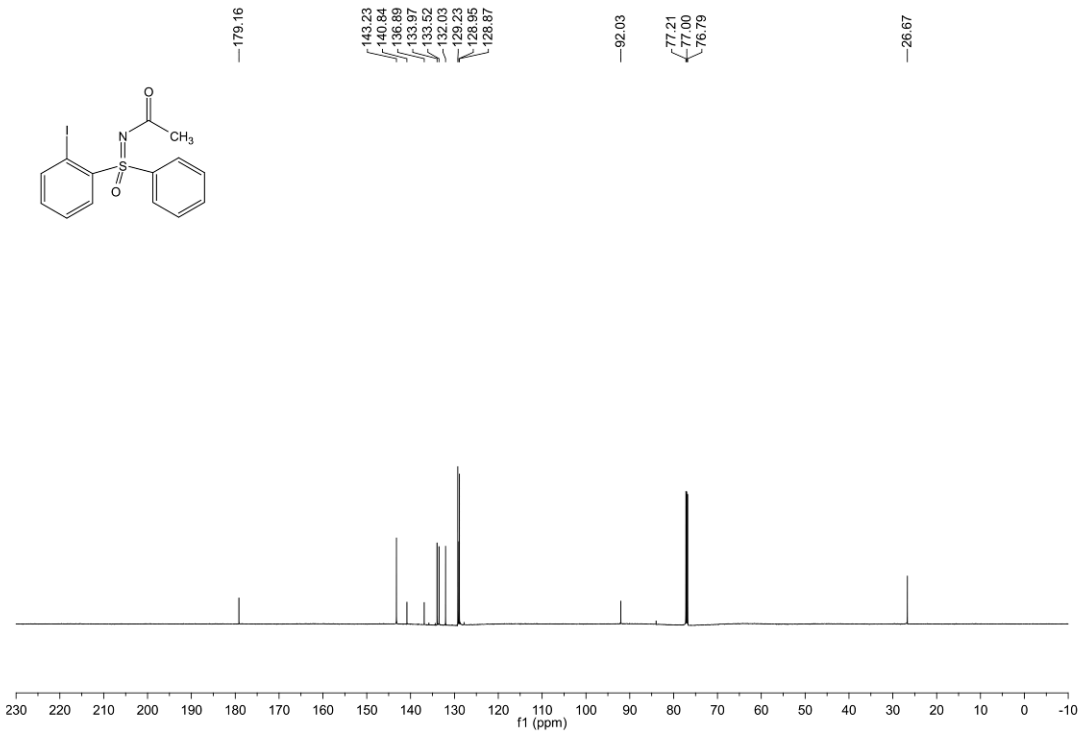
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 4k



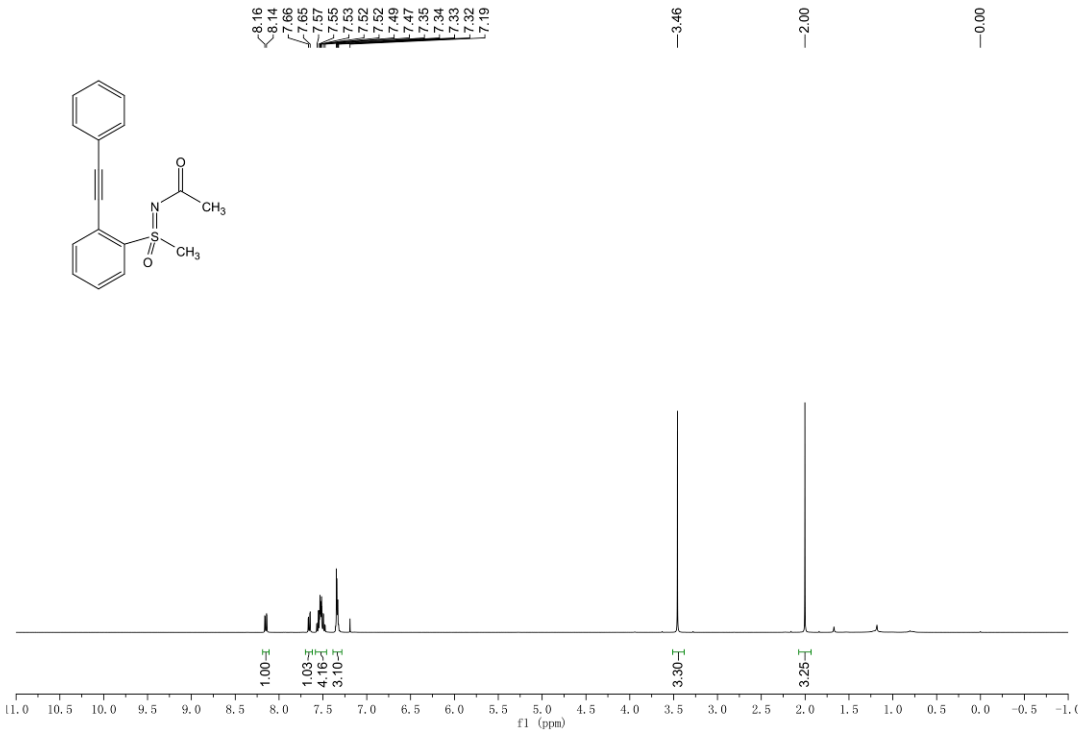
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4l



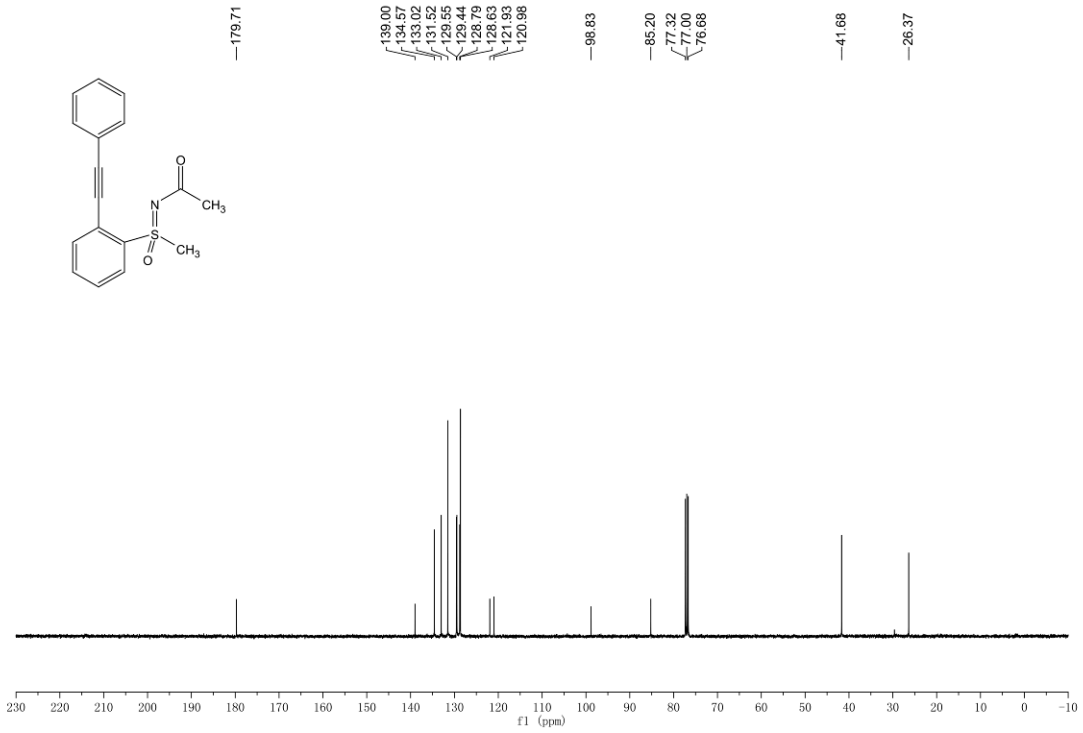
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 4l



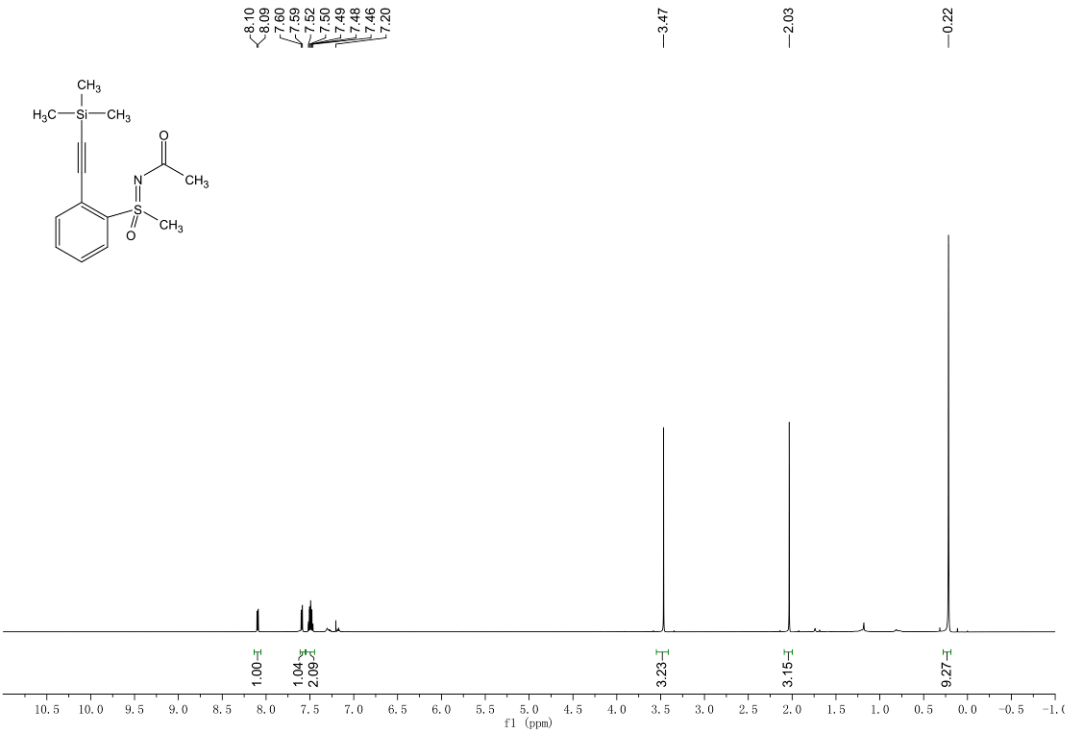
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6a



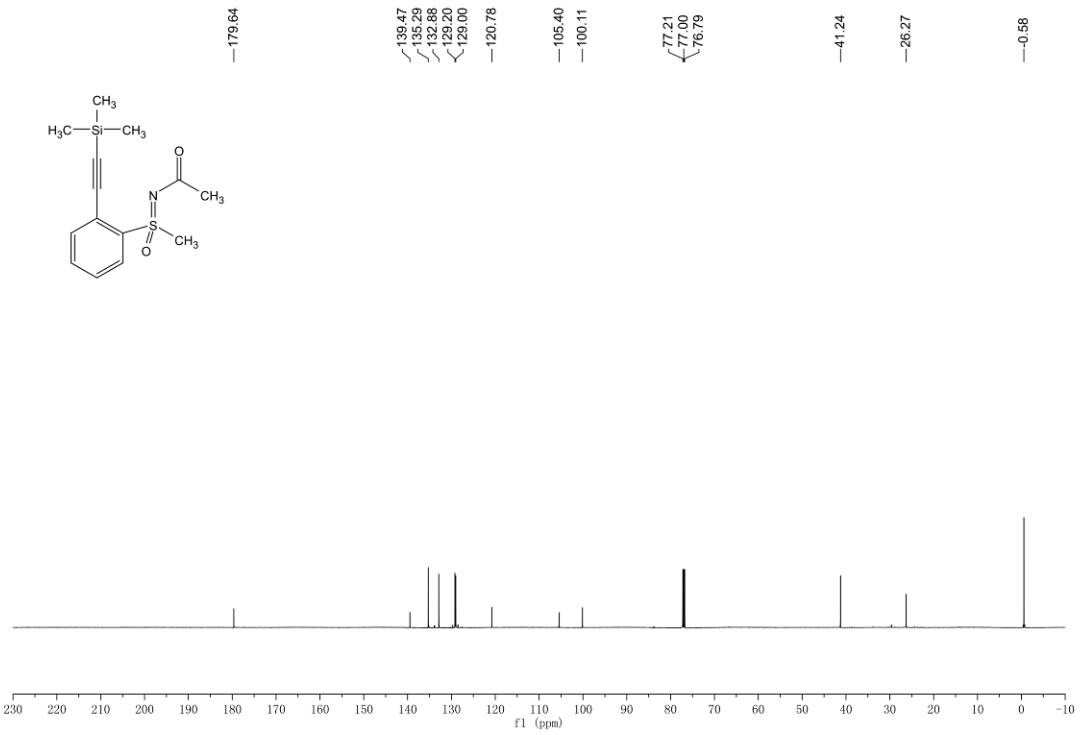
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 6a



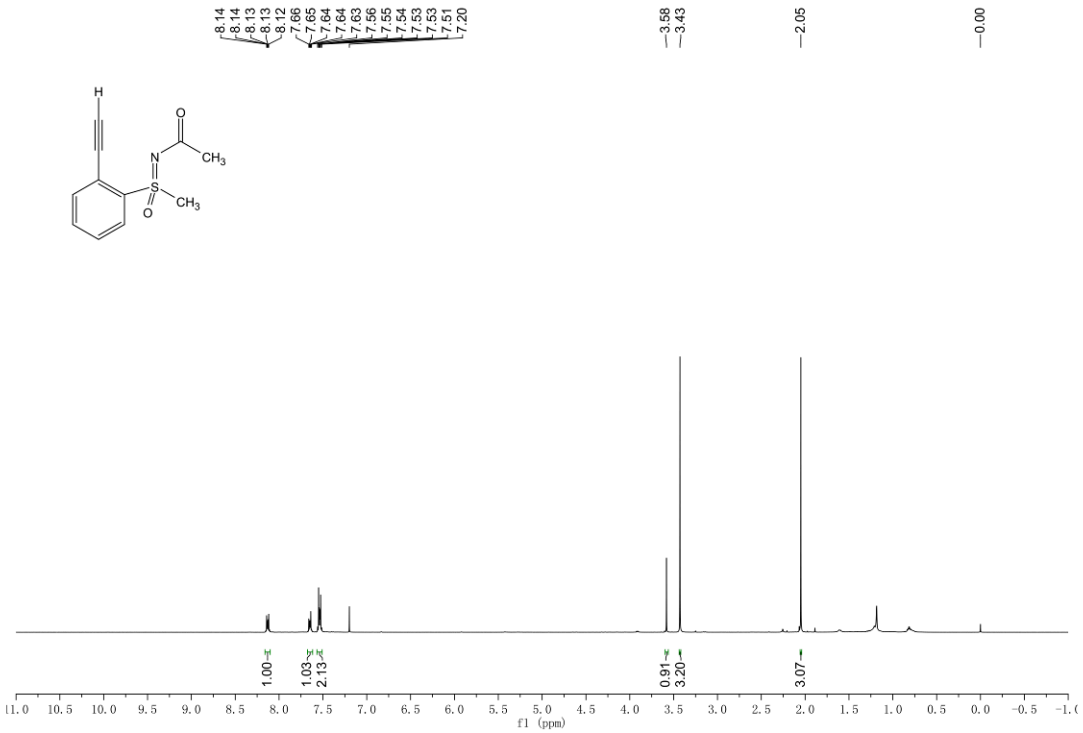
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 6b



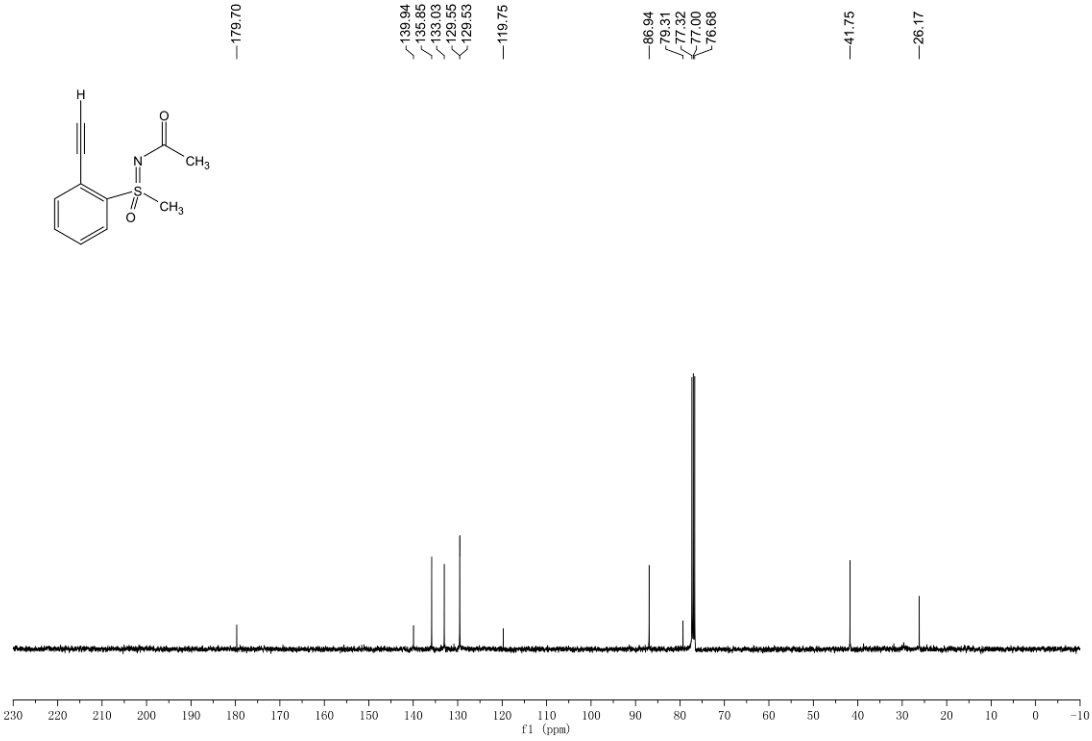
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 6b



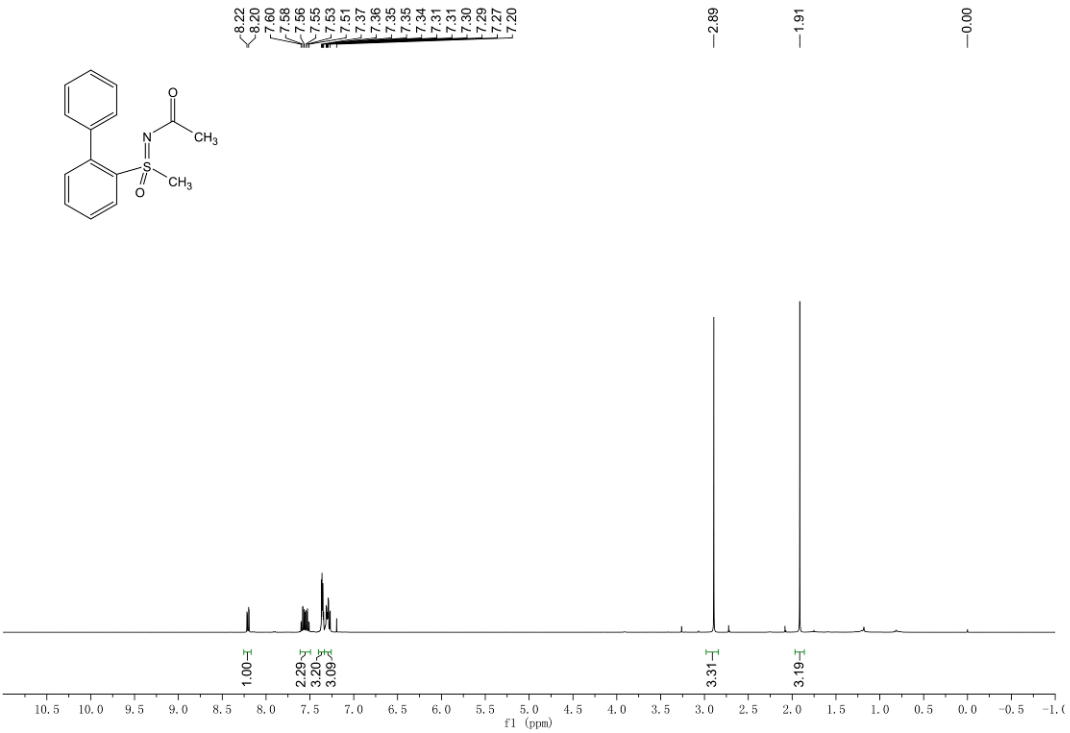
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6c



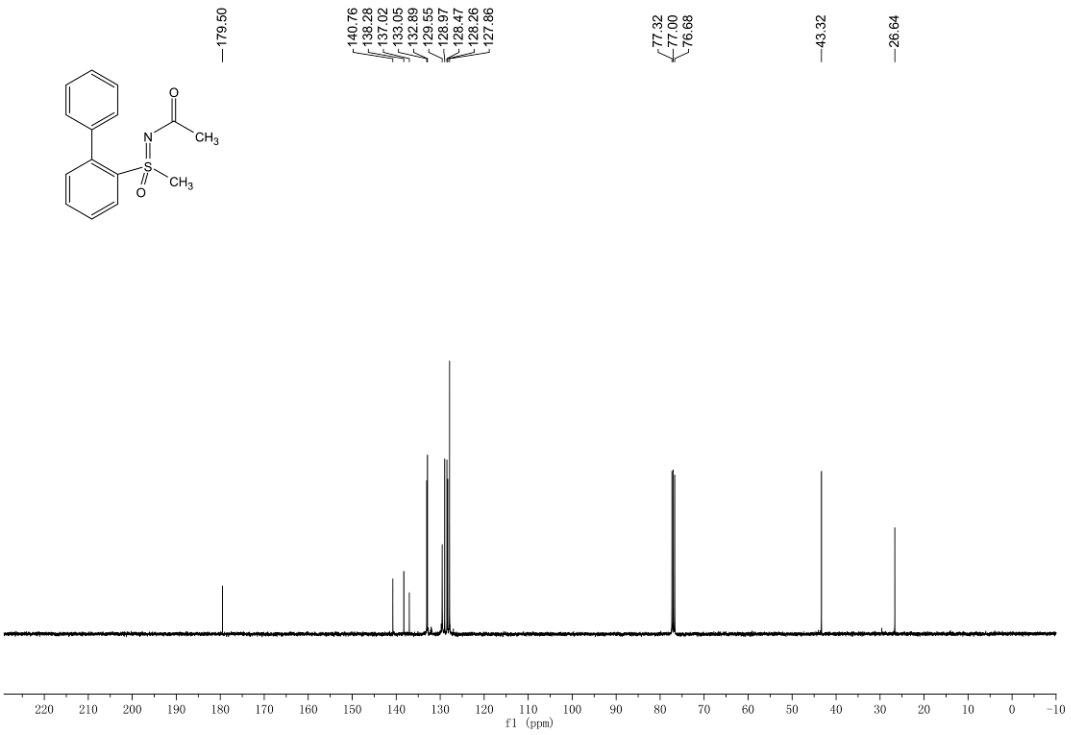
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 6c



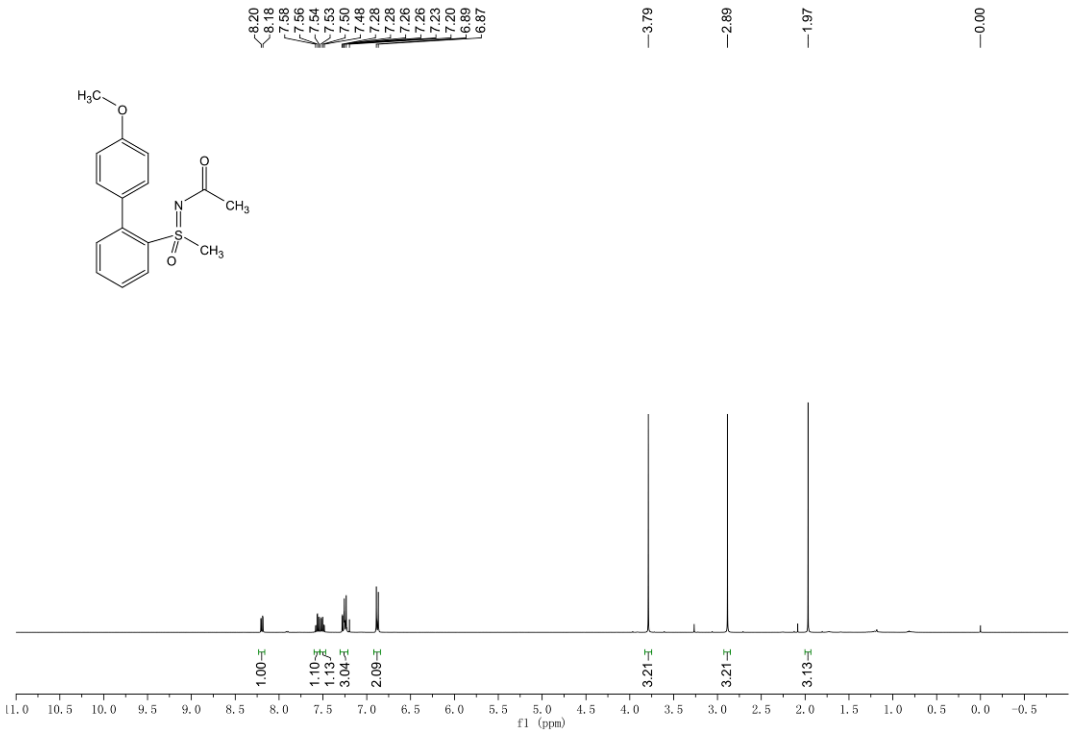
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 8a



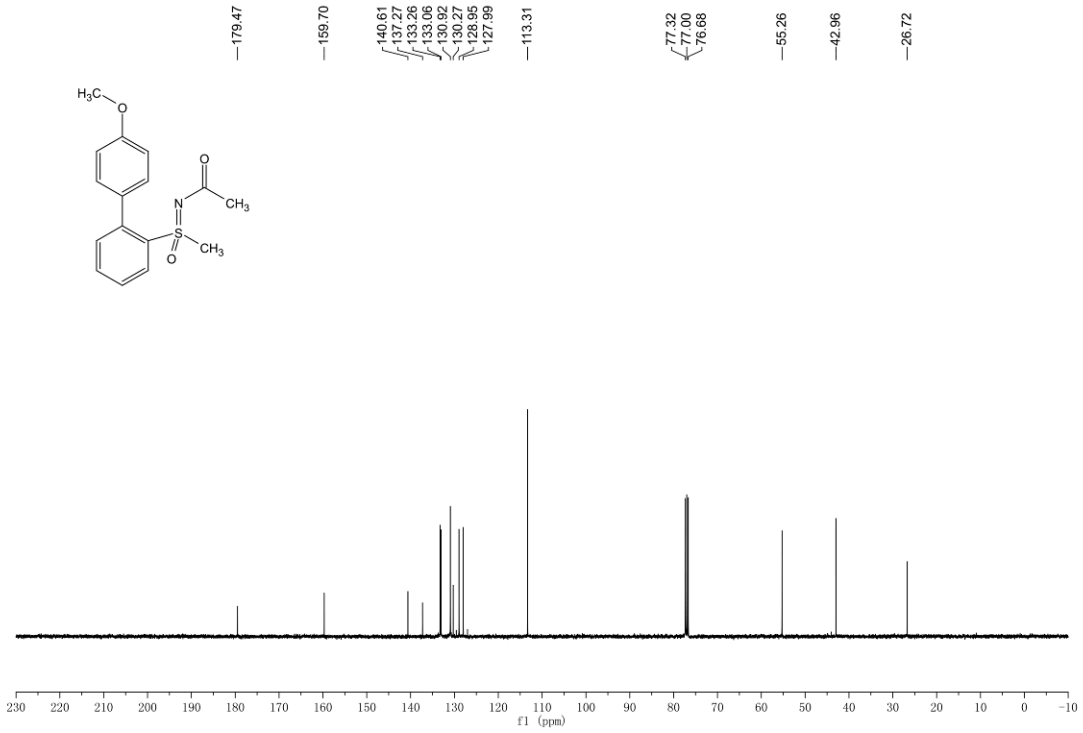
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 8a



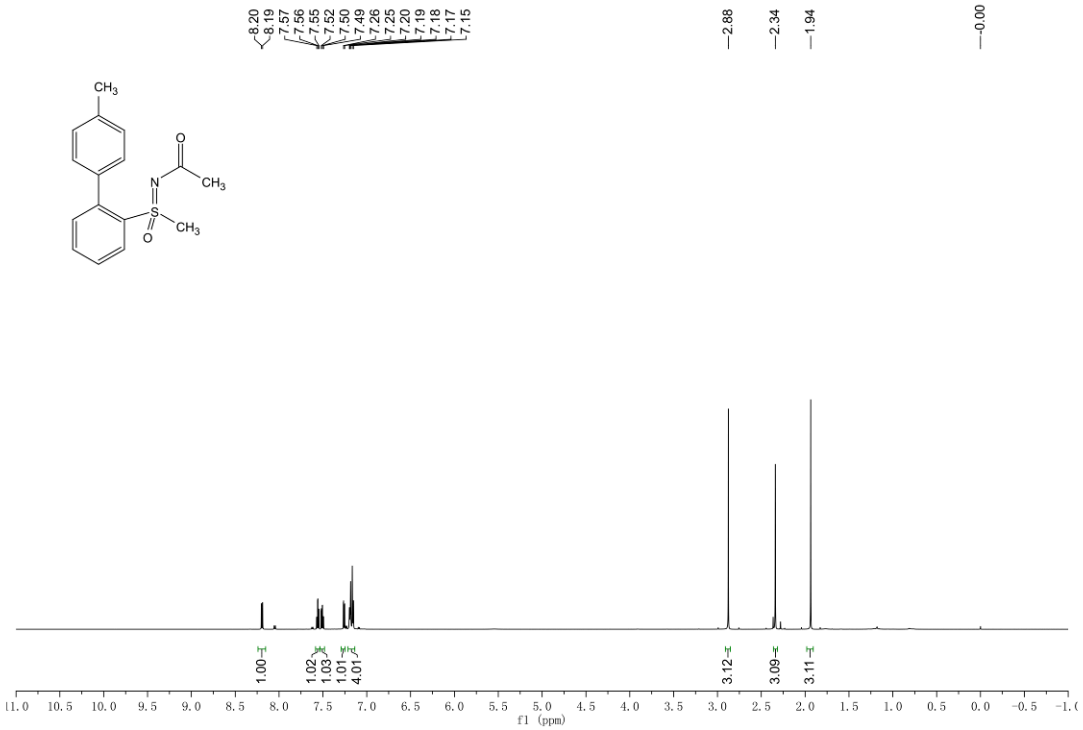
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 8b



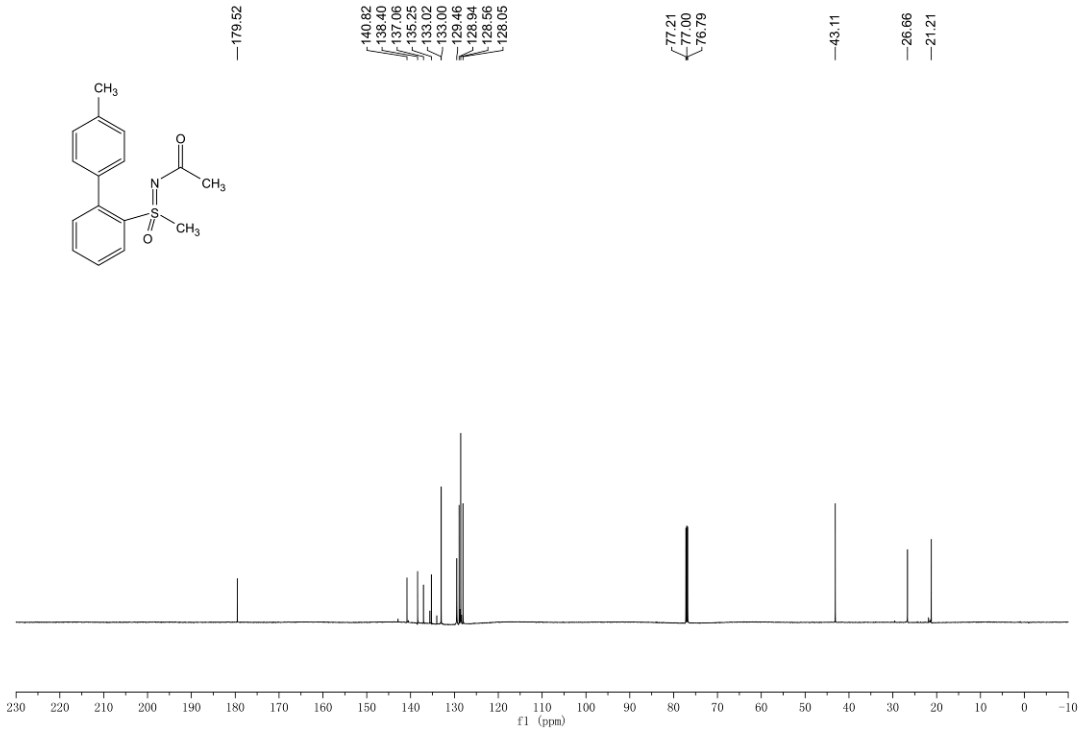
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 8b



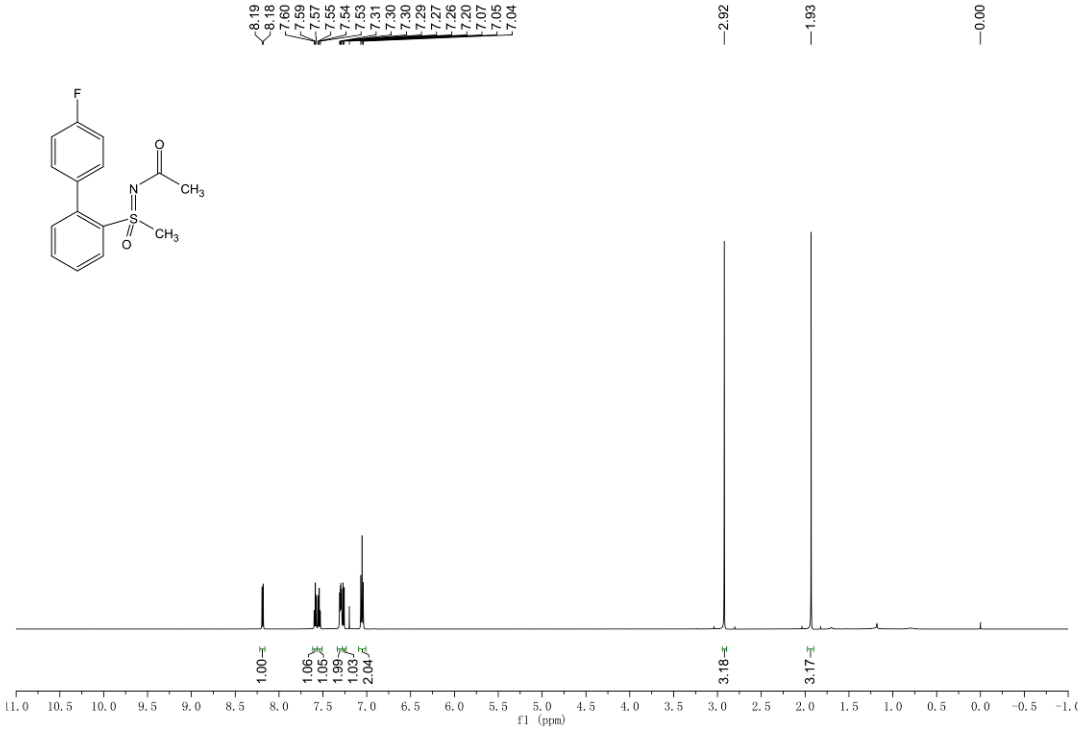
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 8c



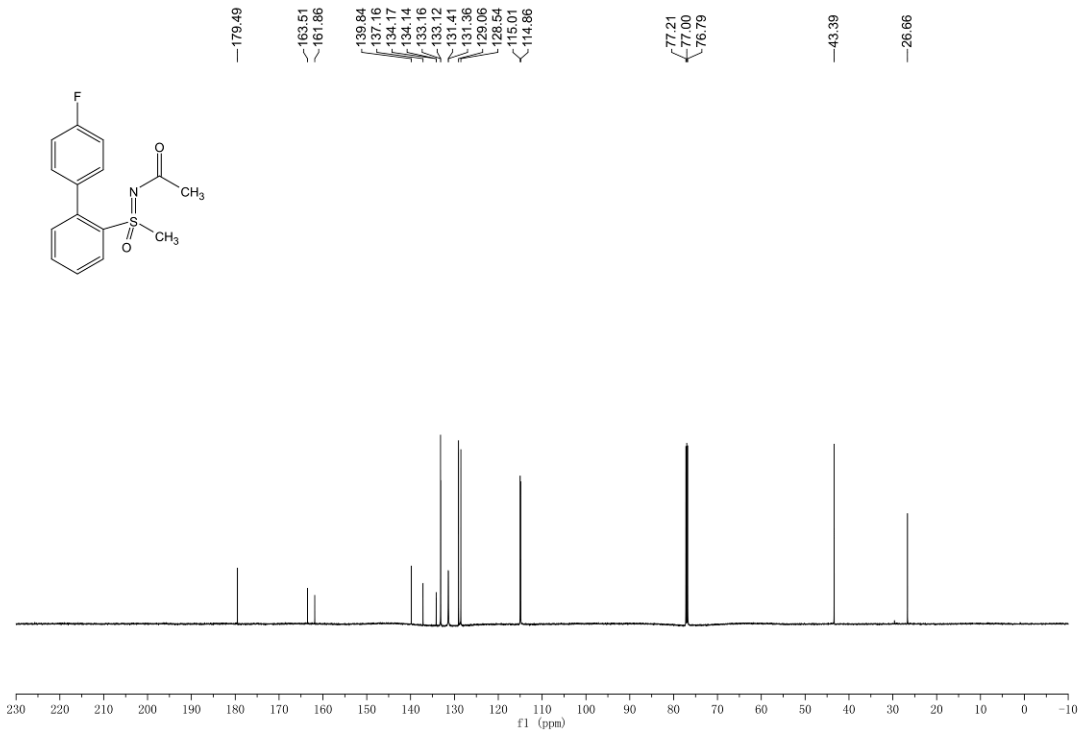
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 8c



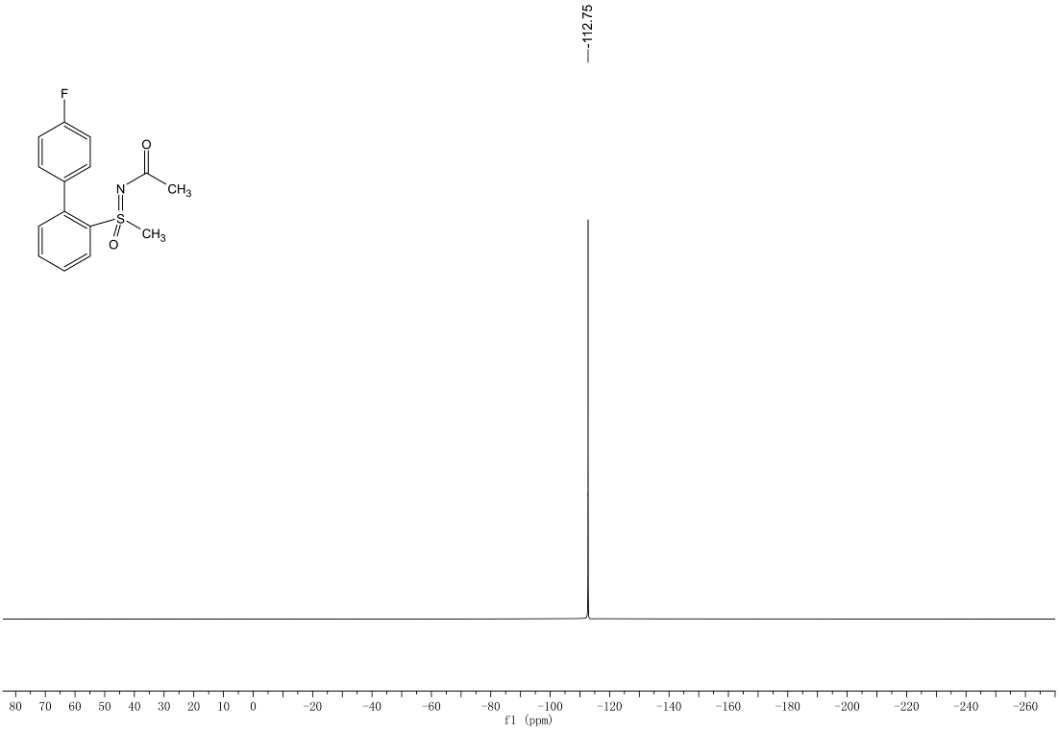
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 8d



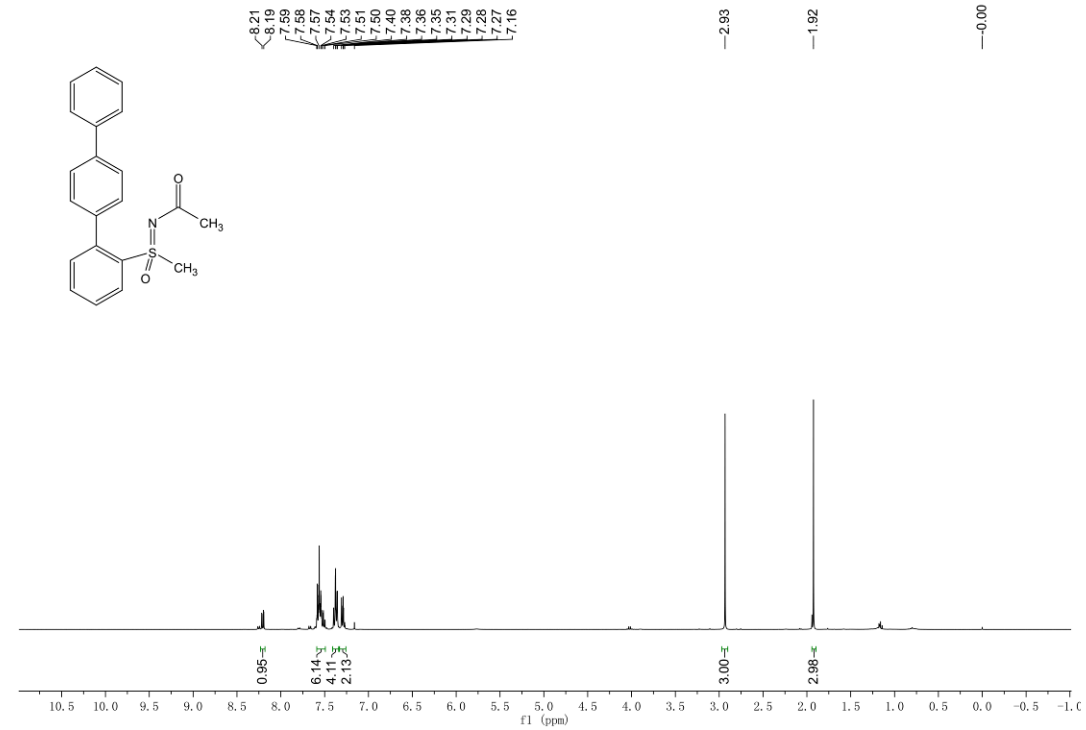
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 8d



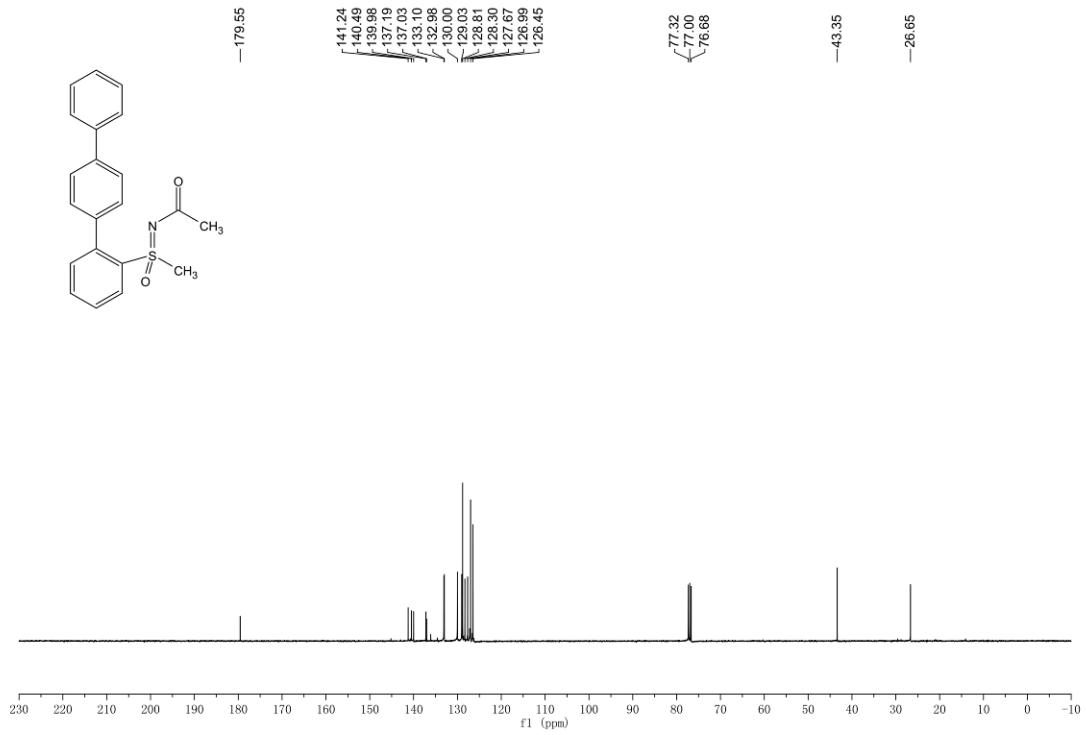
^{19}F NMR spectrum (282 MHz, $CDCl_3$) of 8d



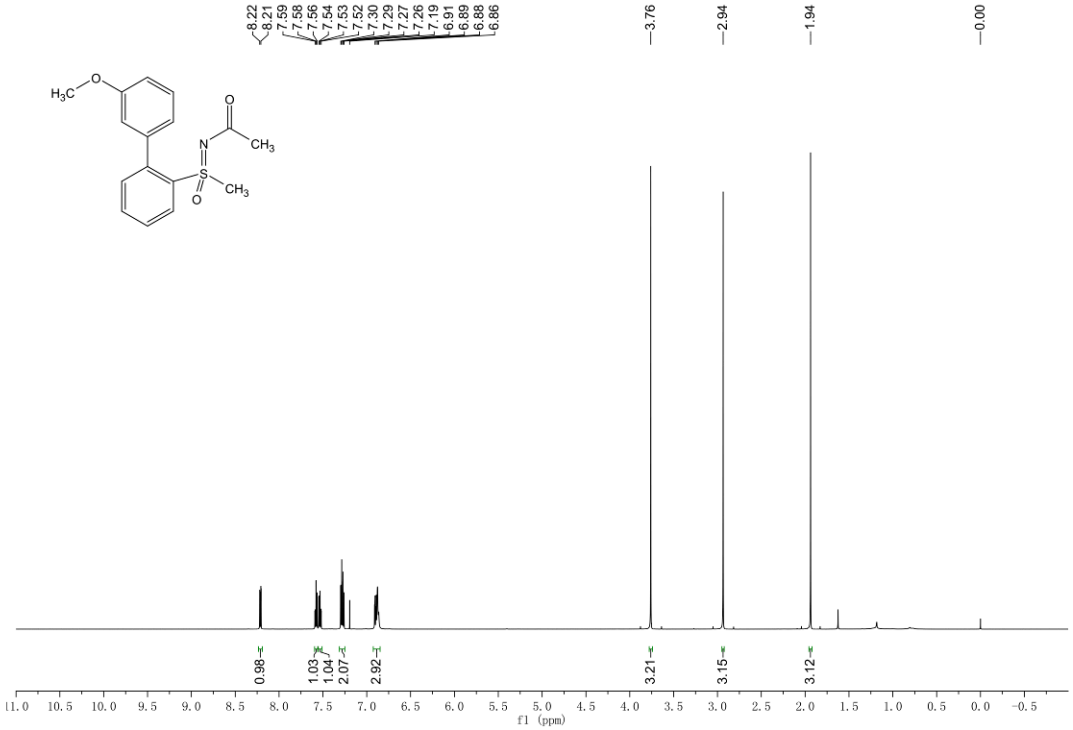
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 8e



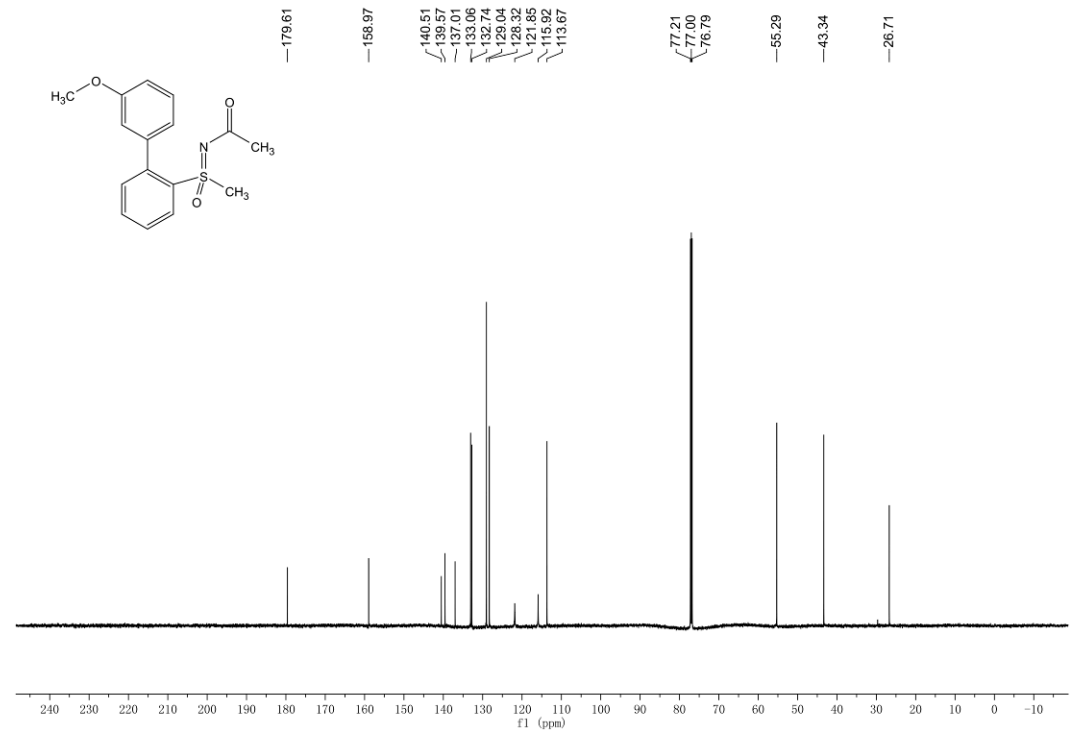
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 8e



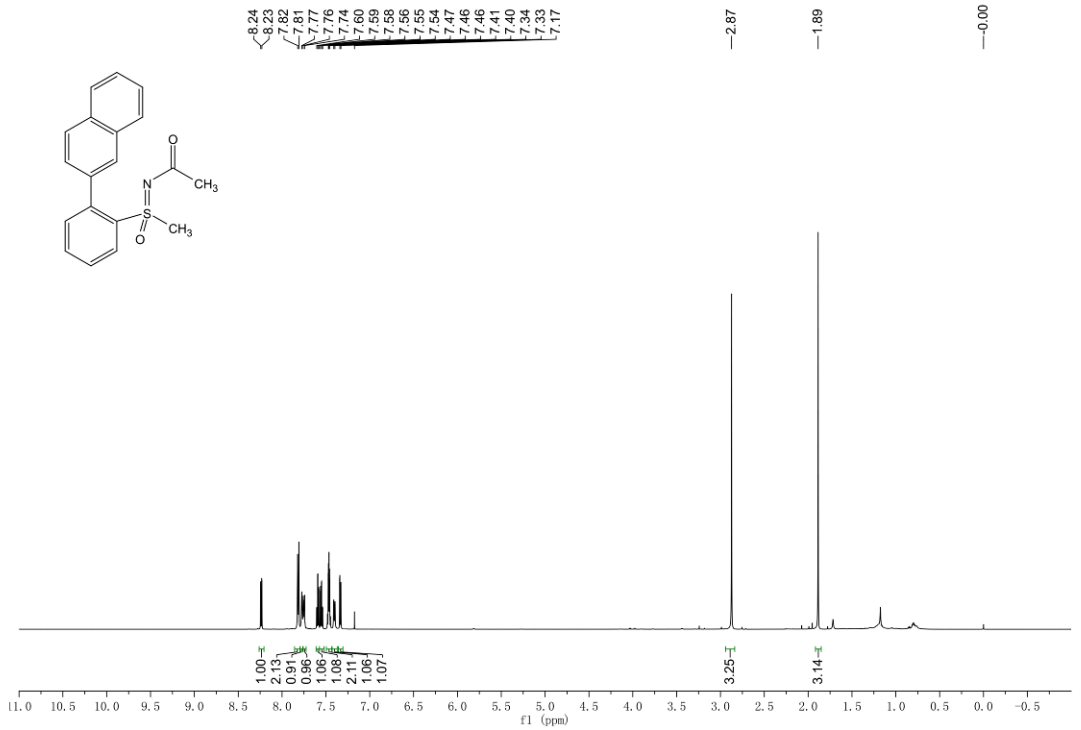
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 8f



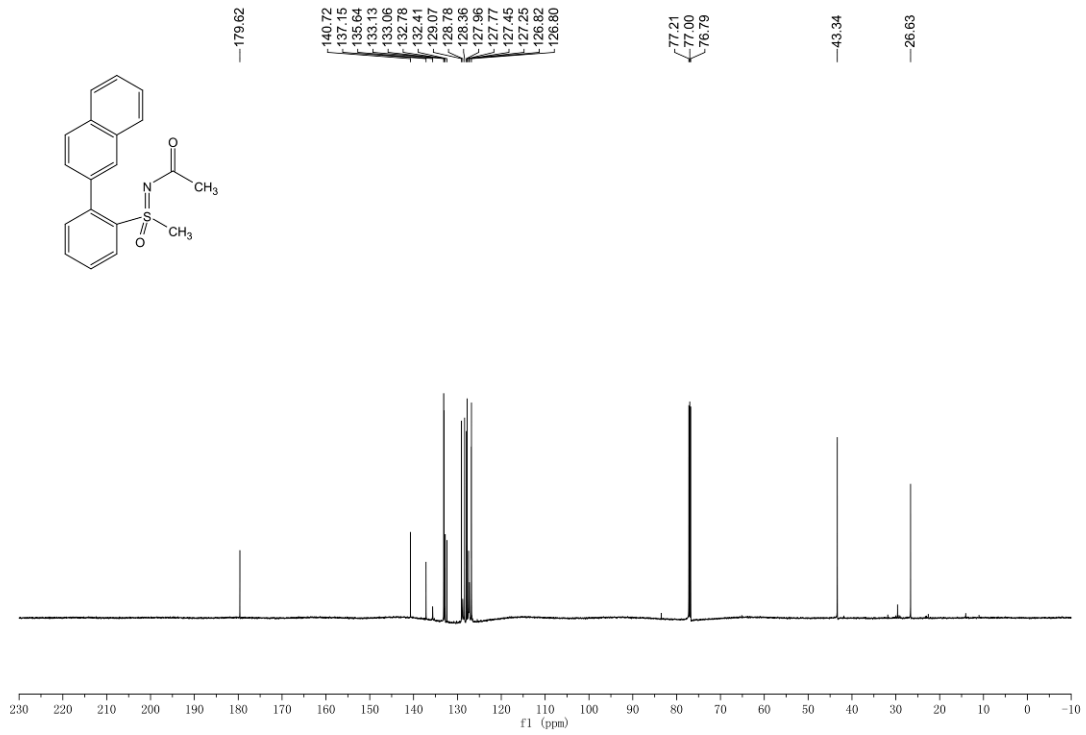
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 8f



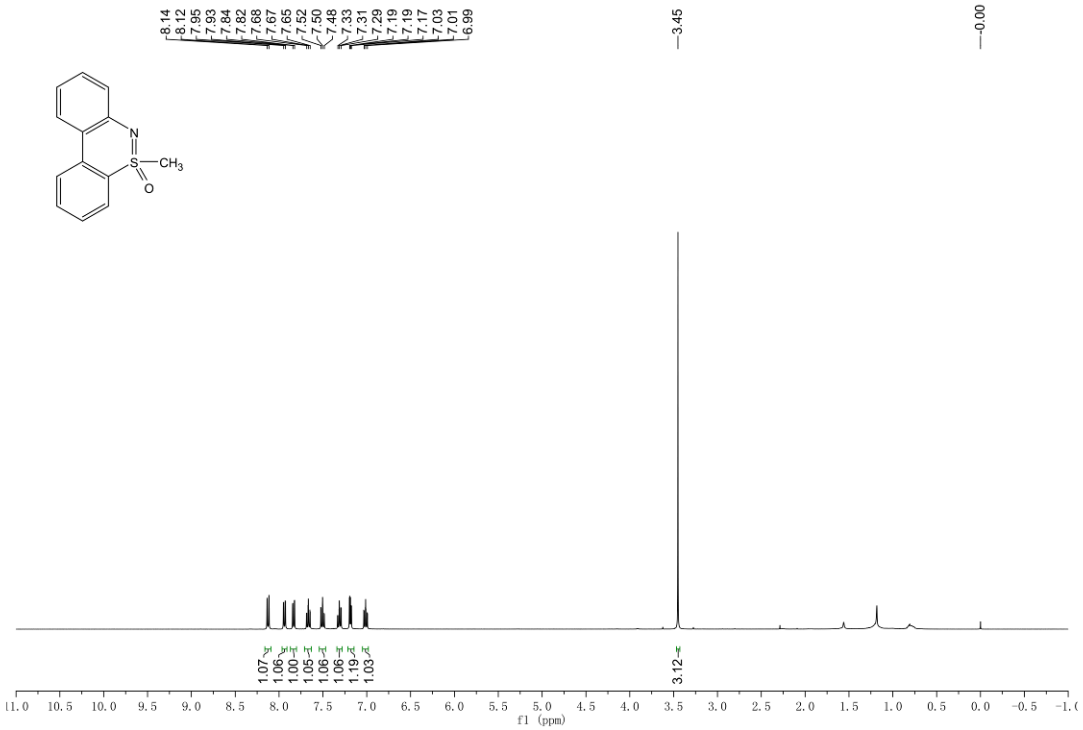
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 8g



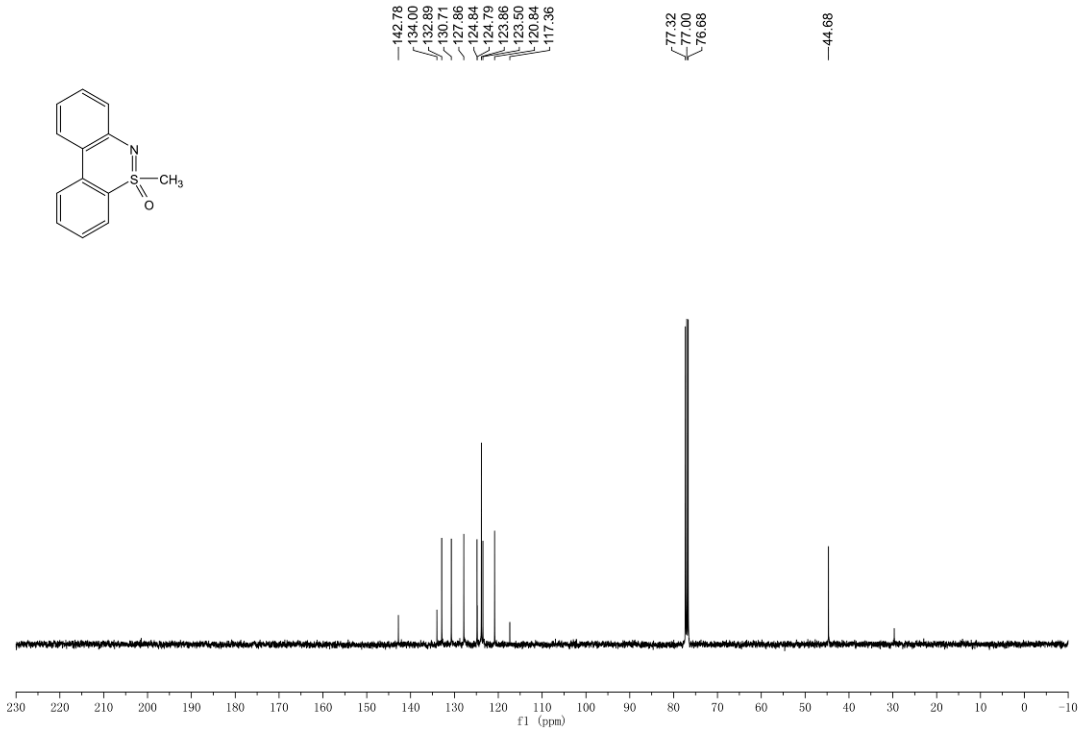
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 8g



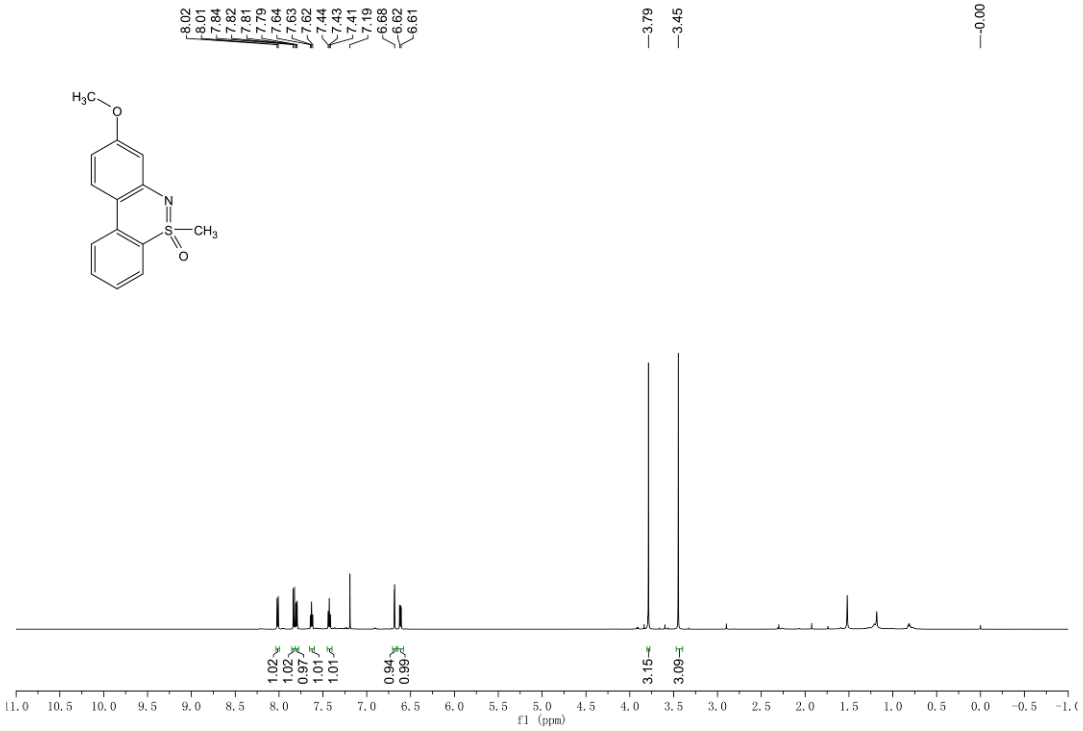
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 9a



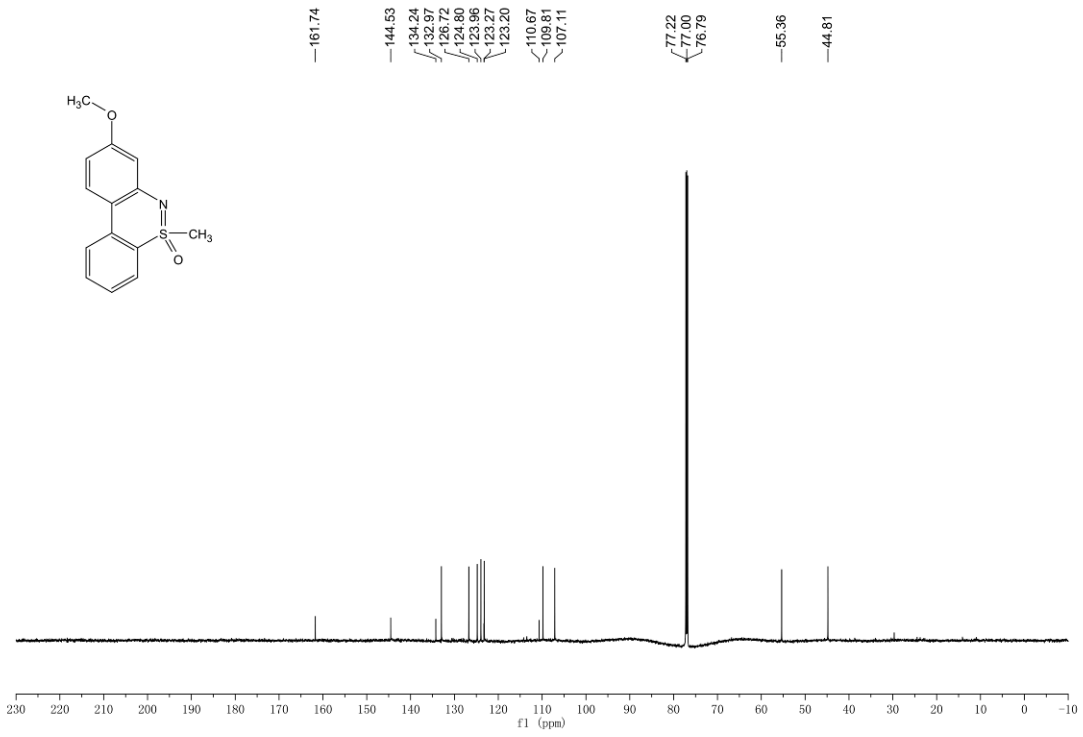
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 9a



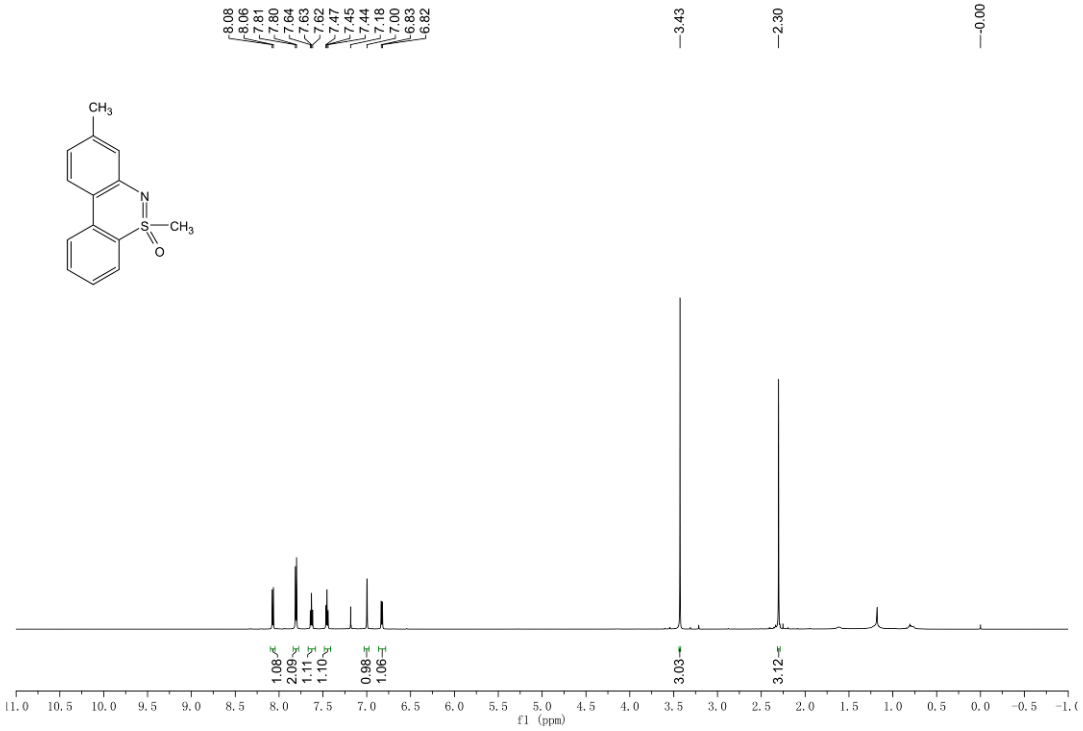
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 9b



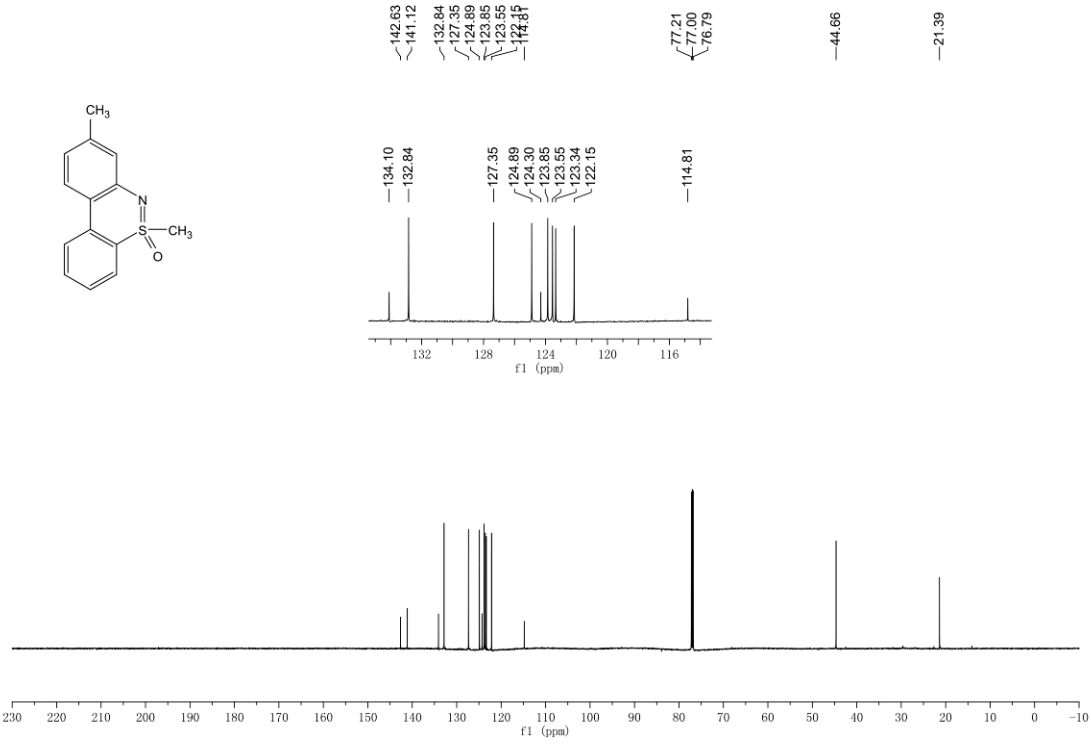
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 9b



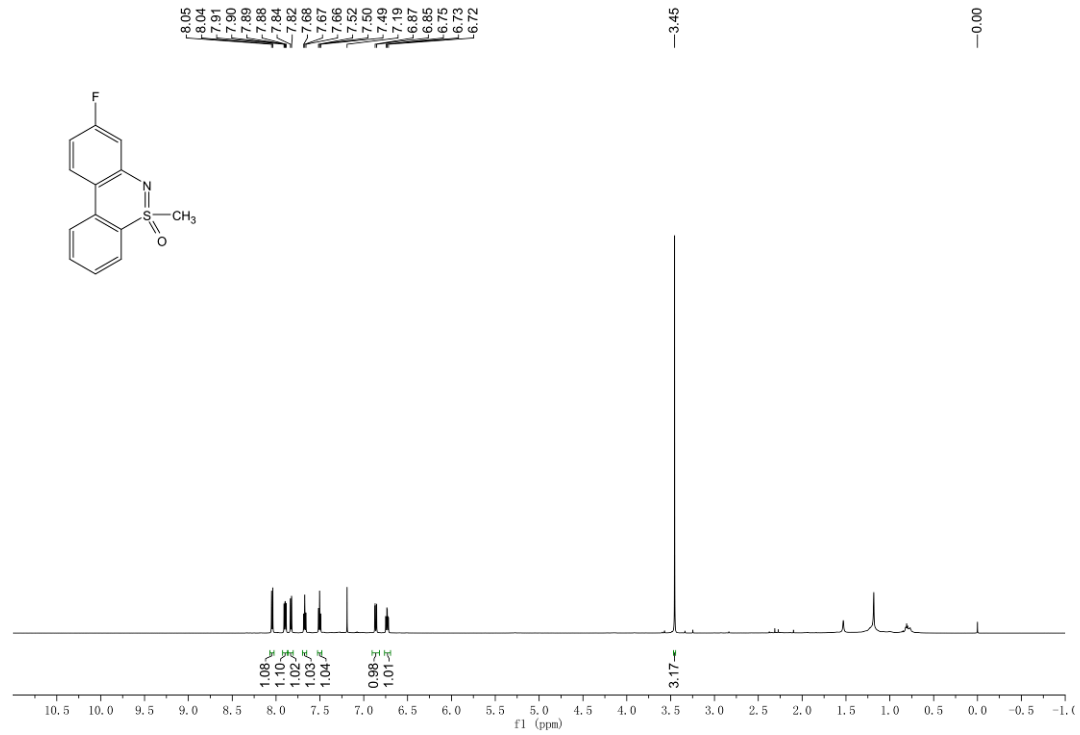
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 9c



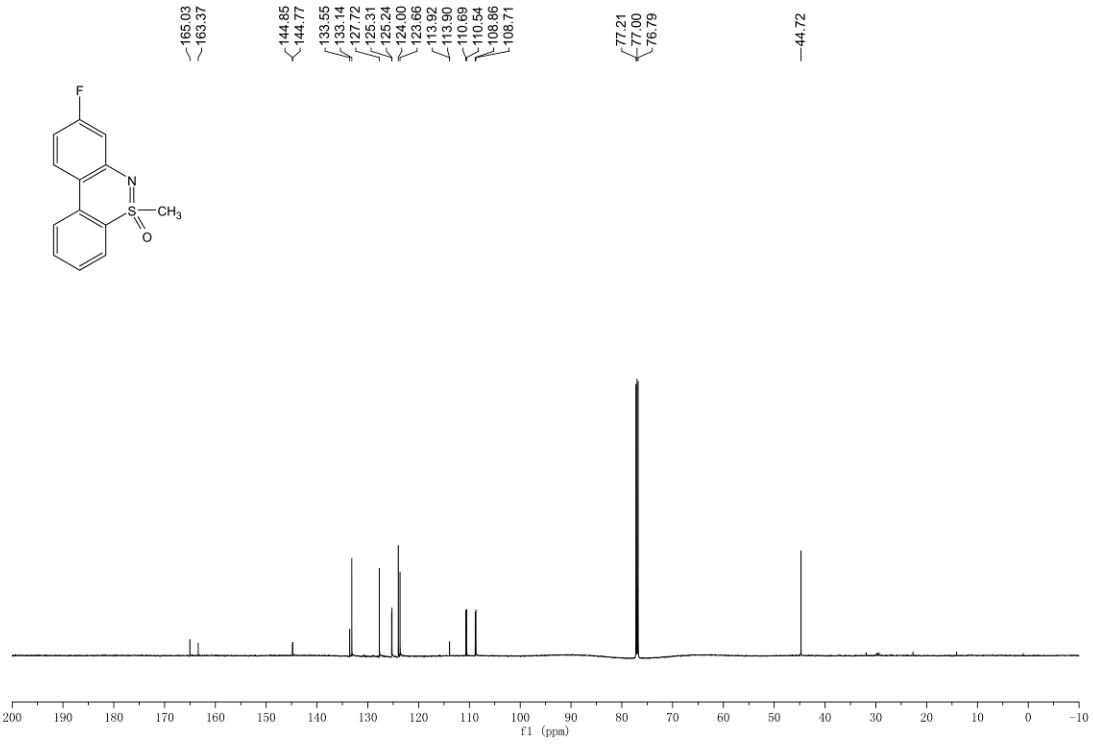
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 9c



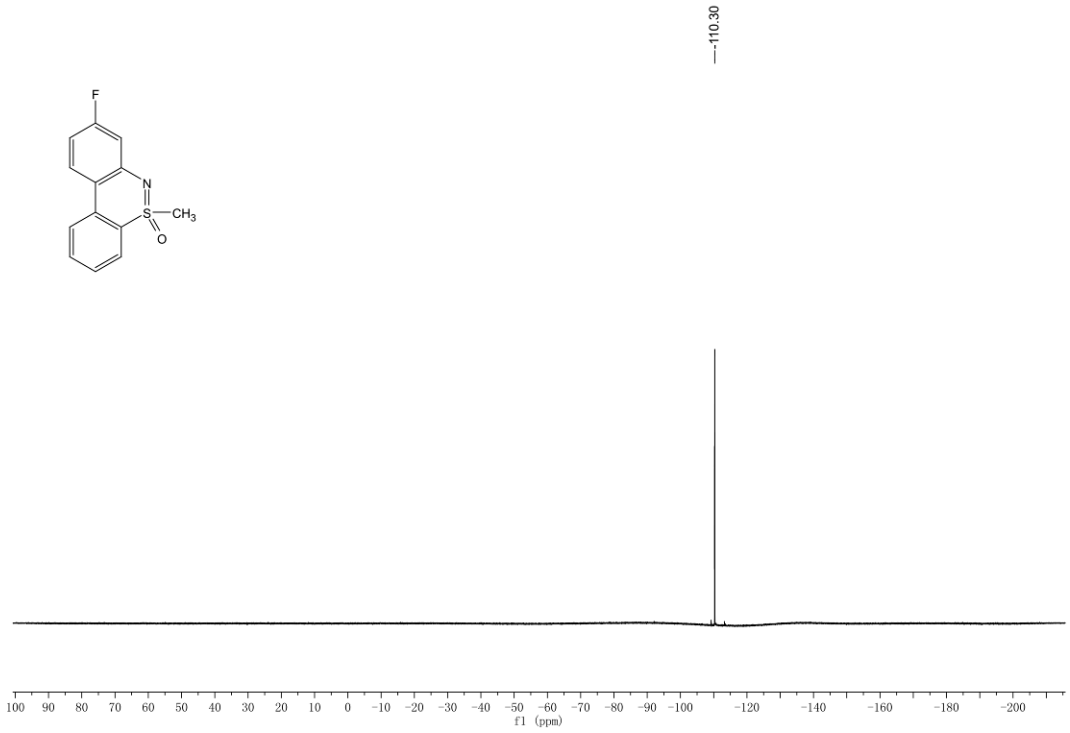
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 9d



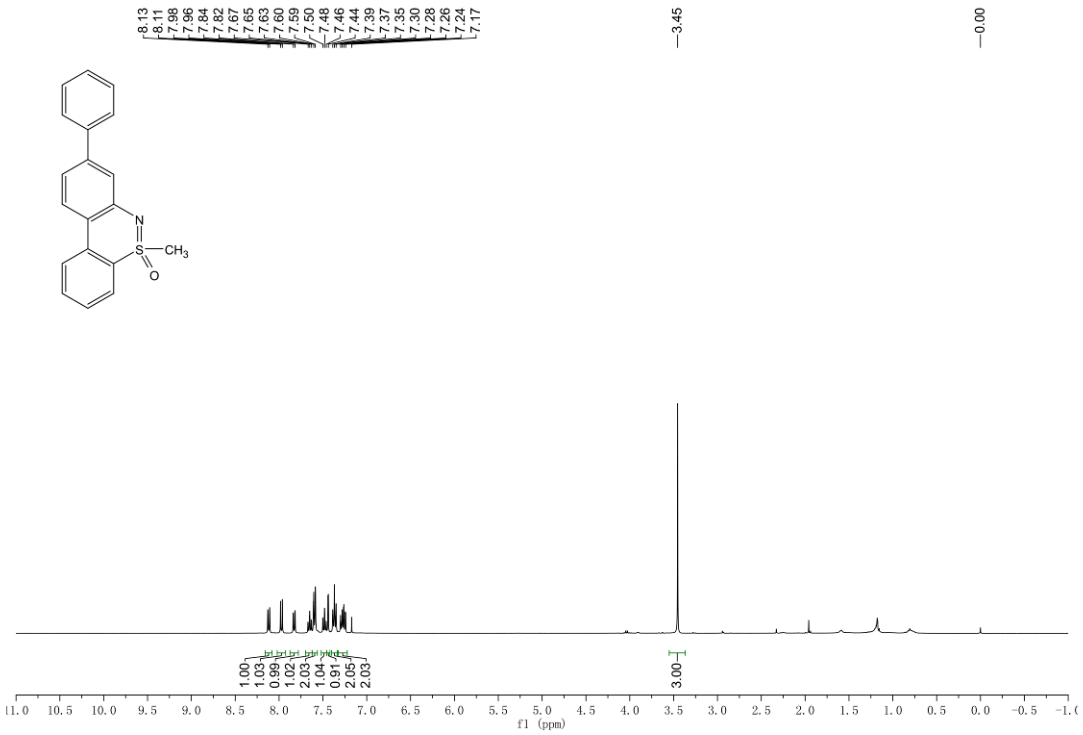
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 9d



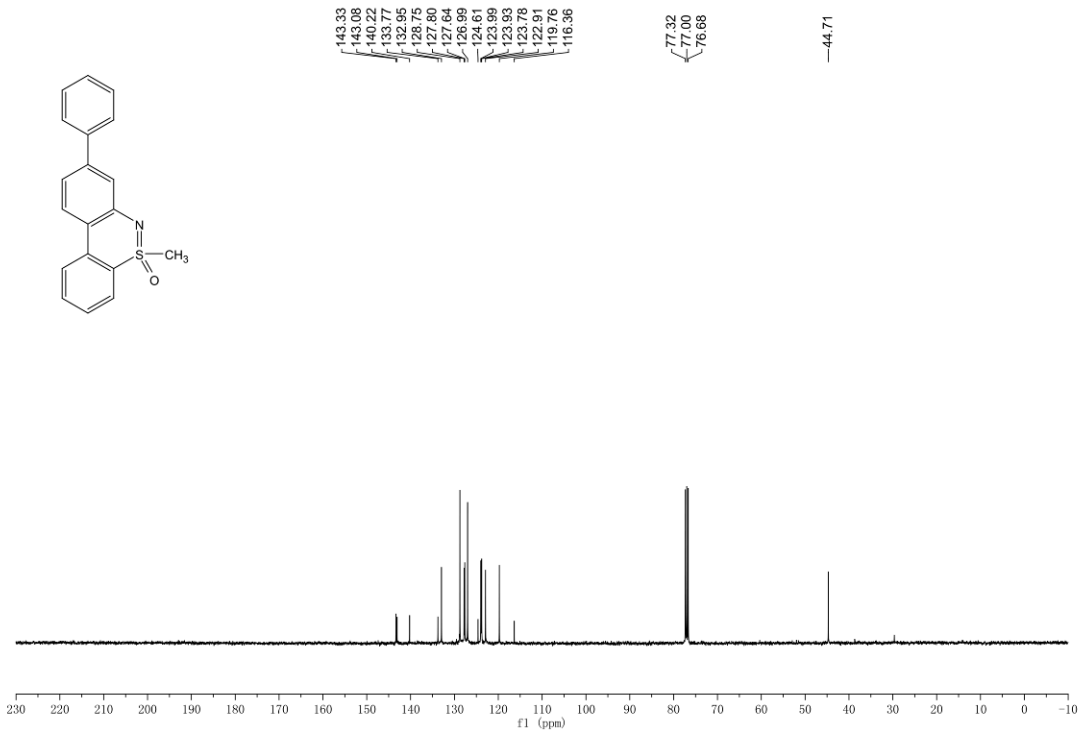
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 9d



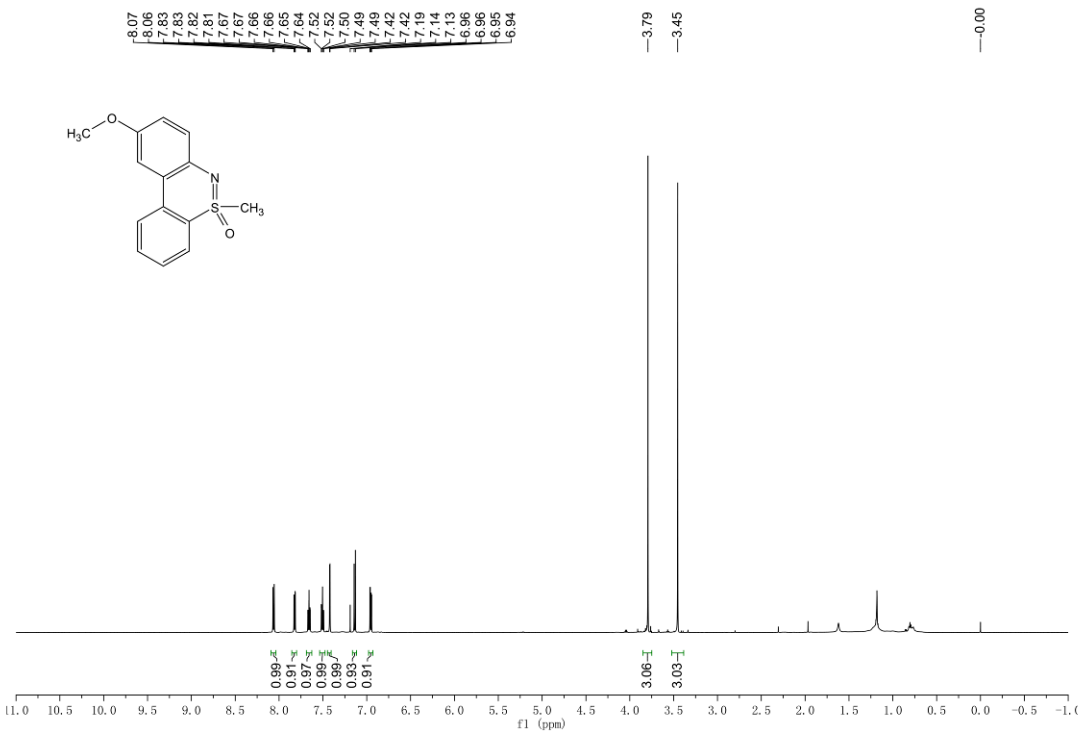
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 9e



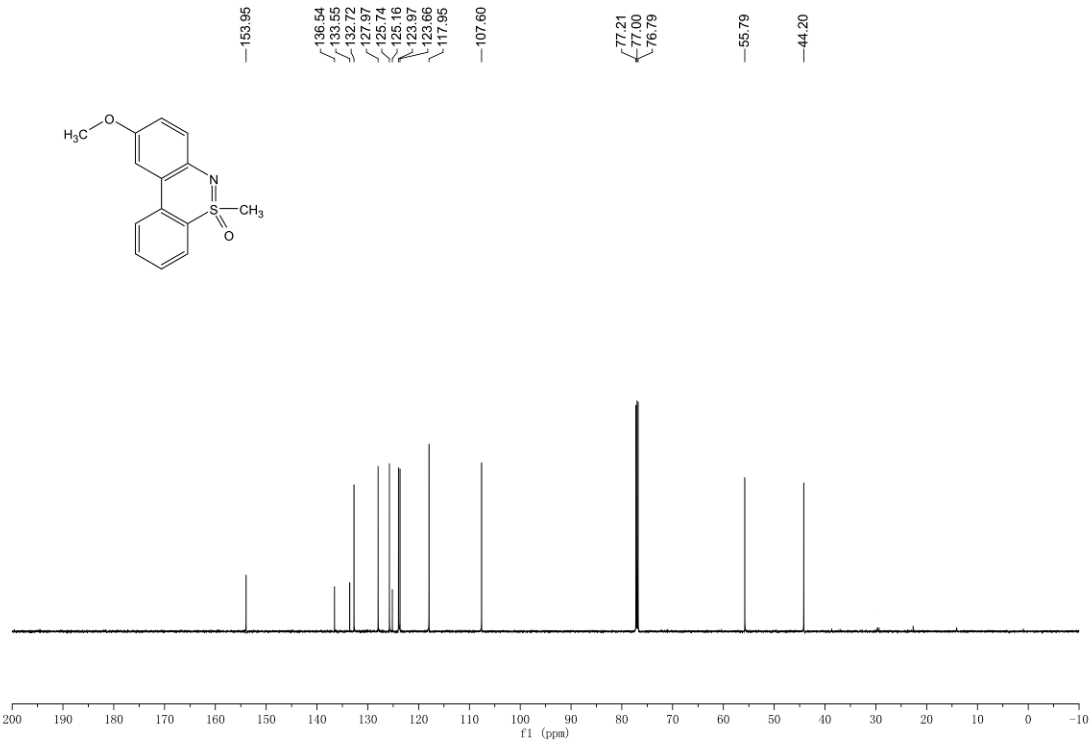
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 9e



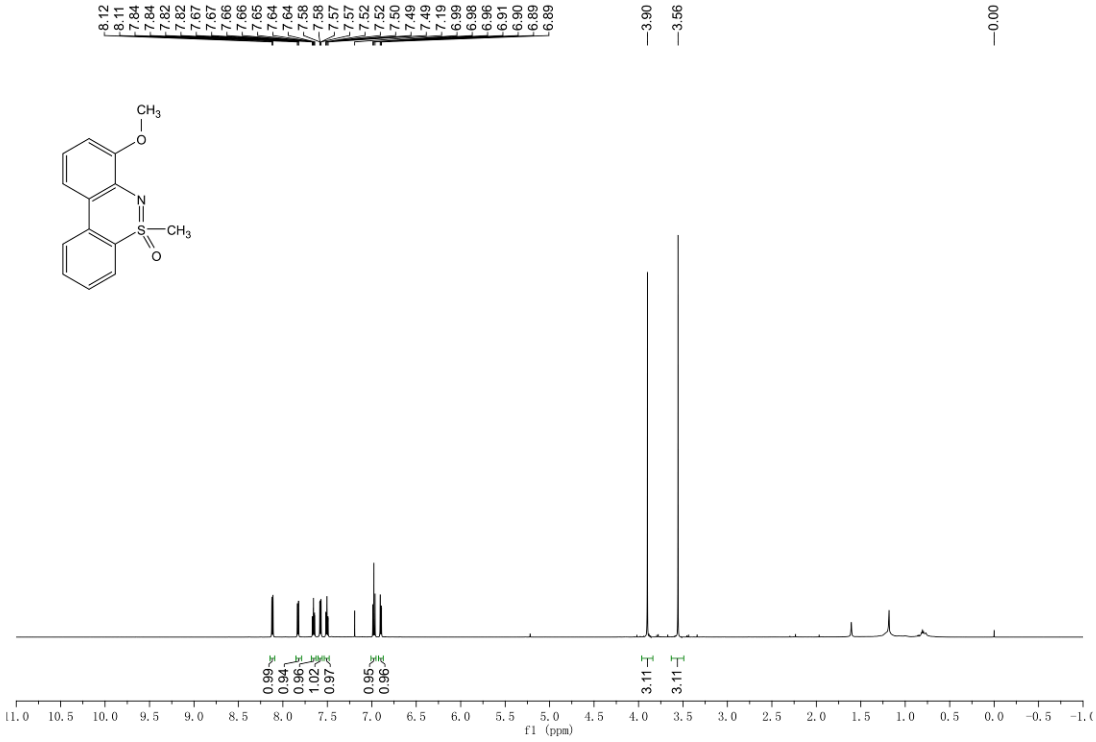
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 9f



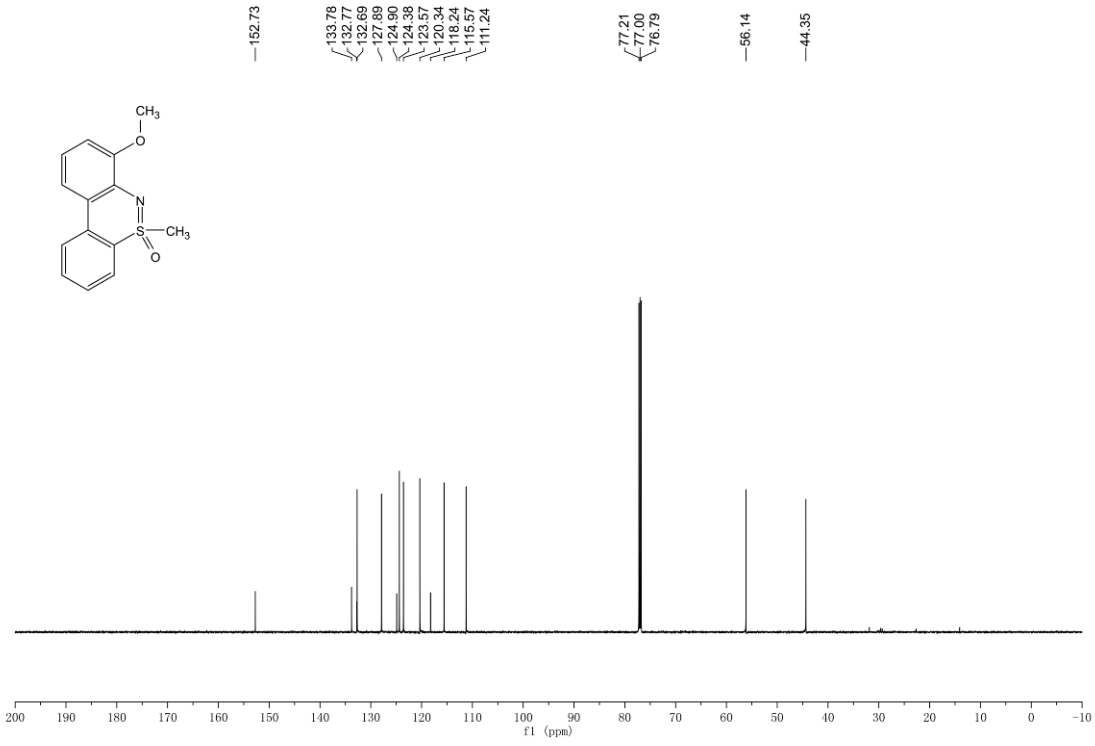
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 9f



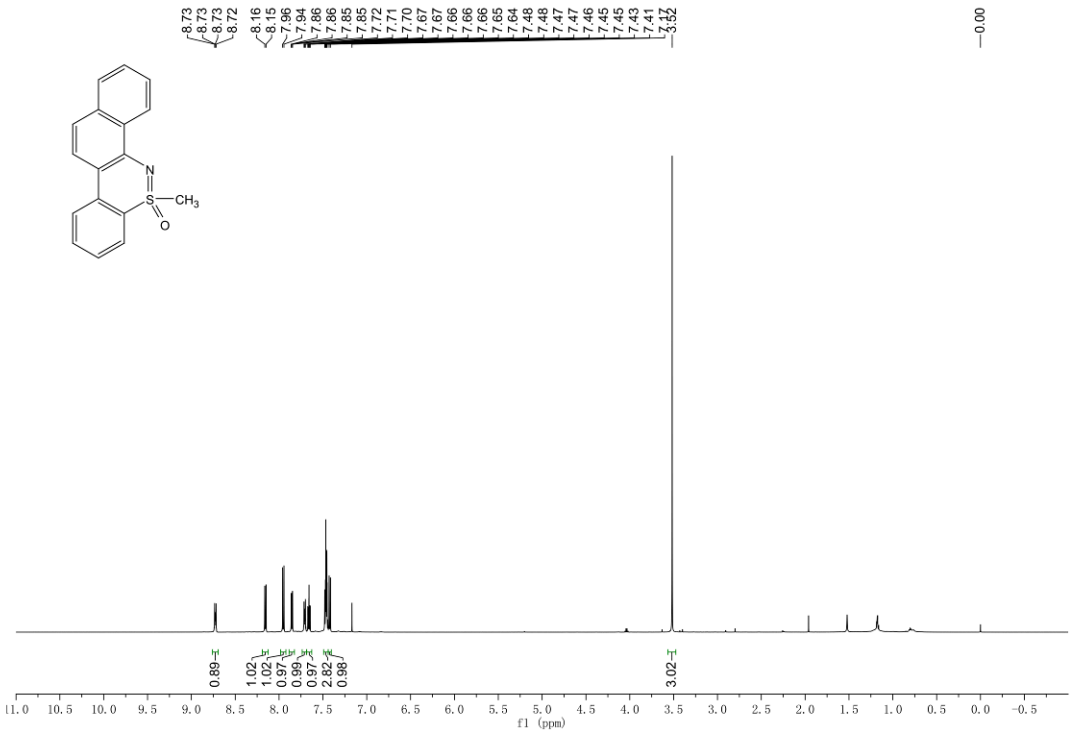
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 9f'



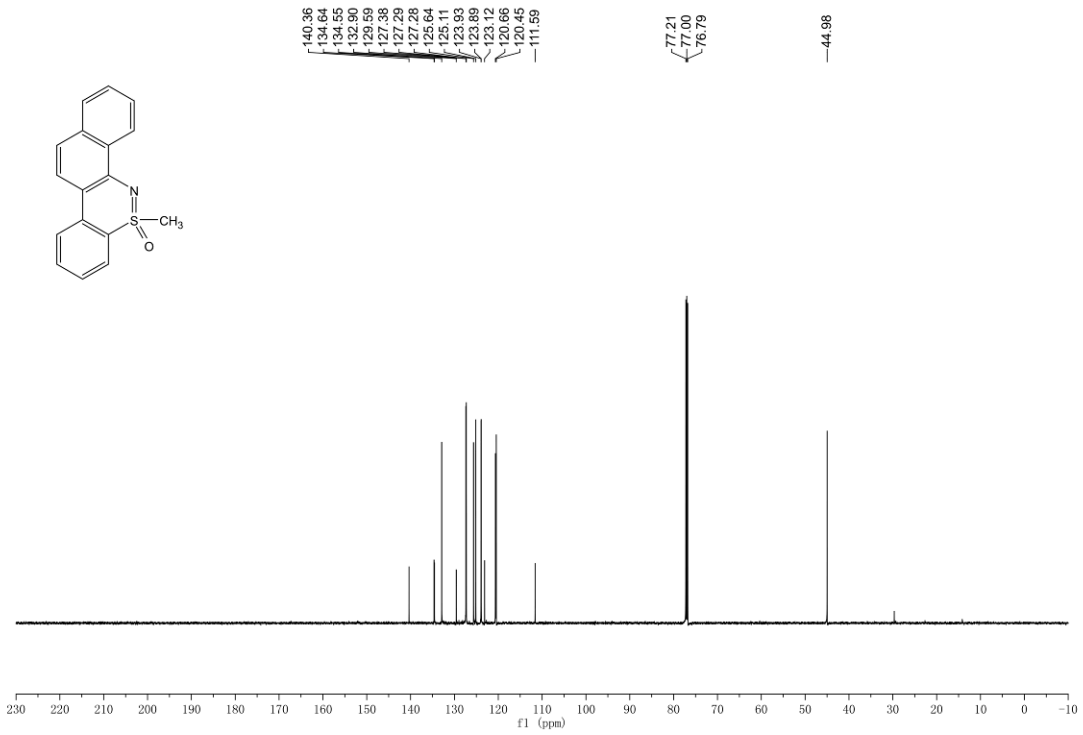
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 9f'



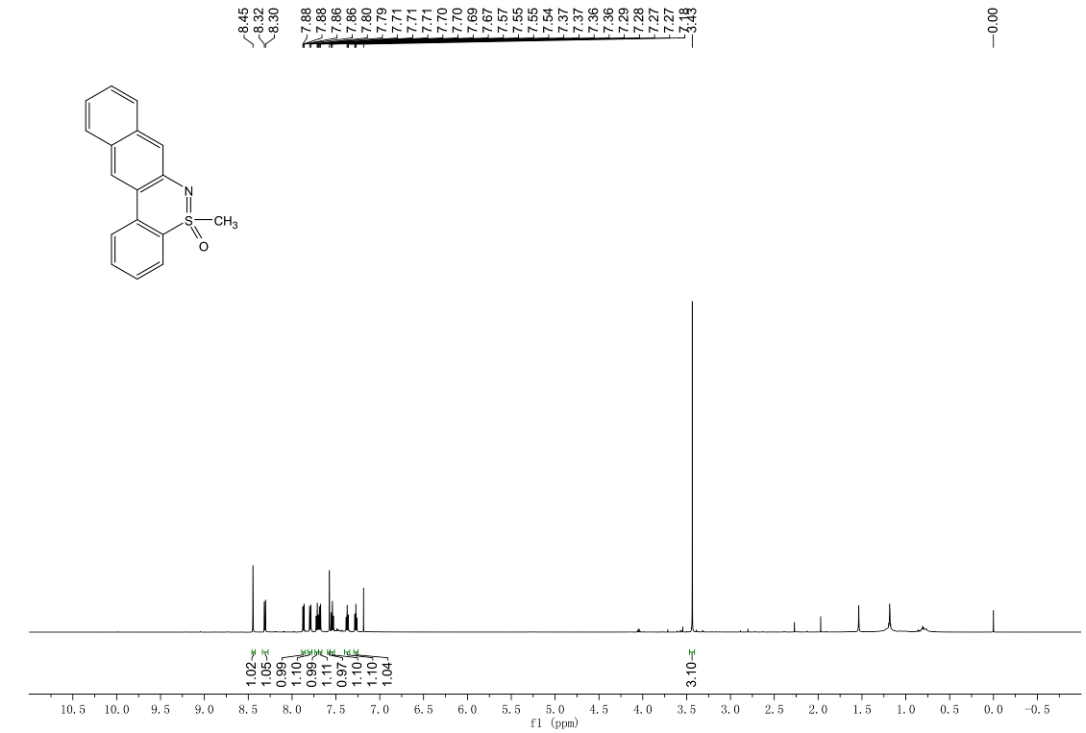
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 9g



^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 9g



^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 9g'



^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 9g'