Supporting Information

Rhodium-catalyzed direct C-H bond alkynylation of aryl sulfonamides with bromoalkynes

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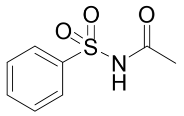
Contents

1) General Information

All reactions were carried out under air atmosphere in oven-dried glassware with magnetic stirring, unless otherwise specified. All other reagents and solvents were purchased from Energy Chemical or J&K Chemical Company and used without any further purification. TLC information was recorded on GF-254 (Qingdao Haiyang Chemical Co., Ltd. P. R. China) plates. Purification of reaction products was carried out by flash chromatography using Silica gel (200-300 mesh, Qingdao Haiyang Chemical Co. Ltd. P. R. China). All products were recorded using Bruker Avance-400 instruments, calibrated to TMS (^{1}H NMR spectra) and $CDCl_3$ (^{13}C NMR spectra) as the internal reference (0.00 ppm for 1H NMR spectra and 100.00 ppm for ^{13}C NMR spectra). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Melting points were measured uncorrected.

2) Synthetic methods of starting materials[1]

To a mixture of aryl sulfonamide (2.0 mmol) and anhydride (3.0 mmol), 3 mol % of anhydrous $ZnCl_2$ was added and the reaction stirred at room temperature for 1-12 h. After completion of the reaction (monitored by TLC), then poured into a mixture of EtOAc (15.0 mL) and H_2O (15.0 mL). The layers were separated and the aqueous was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and evaporated *in vacuo*. The crude compound was purified by column chromatography (hexanes and ethyl acetate) to afford the corresponding N-acylated product **1**.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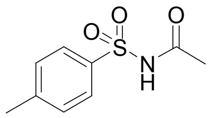
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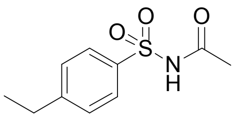
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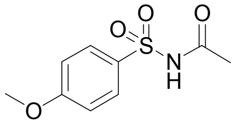
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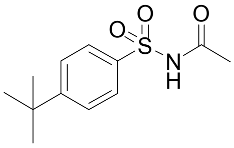
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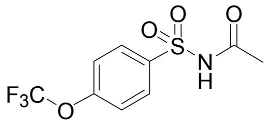
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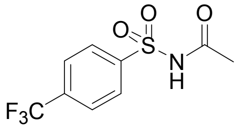
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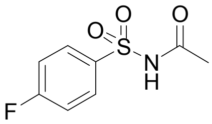
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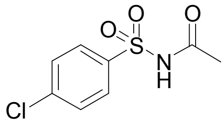
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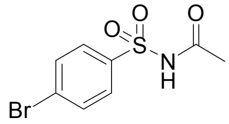
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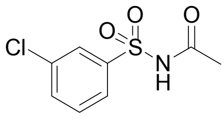
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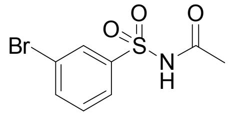
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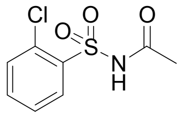
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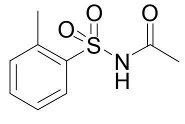
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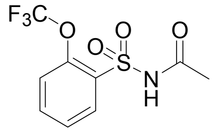
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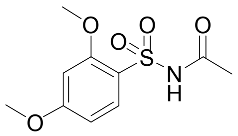
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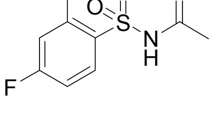
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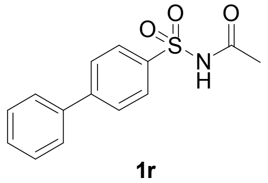
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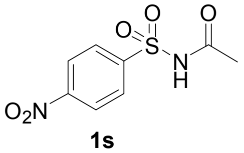
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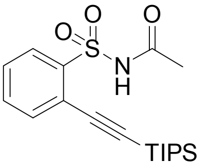
3) Rhodium-catalyzed direct C-H bond alkynylation

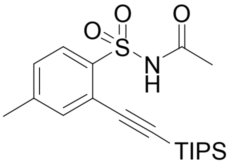
A mixture of N-acylated aryl sulfonamide **1** (0.20 mmol), (triisopropylsilyl)ethynyl bromide **2** (57 mg, 0.22 mmol), $[Cp^*RhCl_2]_2$ (3.5 mg, 0.004 mmol, 2 mol %), Ag_2CO_3 (55 mg, 0.2 mmol, 1equiv), LiOAc (4.1 mg, 0.004 mmol, 20 mol %), and DCE (1 mL) were charged into a reaction tube. The reaction mixture was stirred at 100 °C for 12 h. After the mixture cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/EtOAc to afford the desired product **3** or **4**.

4) Characterization Data for products 3 and 4

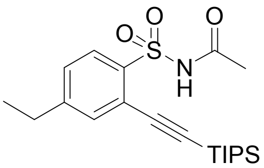


3a

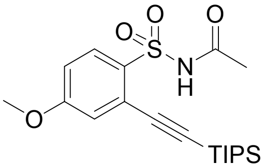
N-Acetyl-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (**3a**) White solid, isolated yield 83% (63 mg); mp: 119-120 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.15 (d, 1H, *J* = 8.0 Hz), 8.08 (s, 1H), 7.68 (d, *J* = 8.0 Hz,1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.55-7.48 (m, 1H), 2.08 (s, 2H), 1.32-1.10 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.69, 139.80, 135.67, 133.23, 129.97, 128.52, 121.57, 102.51, 101.92, 23.28, 18.67, 11.37. HRMS (ESI) m/z calcd for $C_{19}H_{30}NO_3SSi$ $(M+H)^+$ 380.1716, found 380.1713.



3b **N-Acetyl-4-methyl-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide** (**3b**) White solid, isolated yield 82% (65 mg); mp: 113-114 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.03 (d, *J* = 8.0 Hz,1H), 7.47 (s, 1H), 7.30-7.26 (m, 1H), 2.41 (s, 3H), 2.07 (s, 3H), 1.26-1.15 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.72, 144.38, 135.14, 130.13, 129.26, 121.40, 102.64, 104.22, 101.14, 23.27, 21.25, 18.69, 11.38. HRMS (ESI) m/z calcd for $C_{20}H_{32}NO_3SSi$ $(M+H)^+$ 394.1897, found 394.1895.

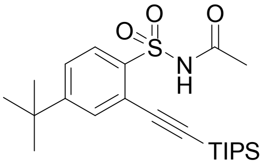


3c **N-Acetyl-4-ethyl-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide** (**3c**) White solid, isolated yield 85% (69 mg); mp: 86-87 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$): 8.07 (s, 1H), δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 2.70 (q, 2H), 2.17 (s, 3H), 1.28-1.15 (m, 24H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.77, 150.42, 137.13, 135.11, 130.21, 128.10, 121.48, 102.73, 101.04, 28.55, 23.28, 18.69, 14.83, 11.39. HRMS (ESI) m/z calcd for $C_{21}H_{34}NO_3SSi$ $(M+H)^+$ 408.2047, found 408.2019.



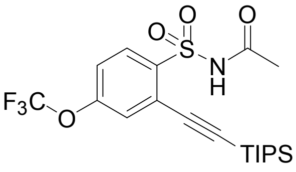
3d

N-Acetyl-4-methoxy-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (**3d**) White solid, isolated yield 78% (64 mg); mp: 85-87 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07 (d, *J* = 8.0 Hz, 1H), 8.03 (s, 1H), 7.13 (s, 1H), 6.97-6.94 (m, 1H), 3.88 (s, 3H), 2.07 (s, 3H), 1.26-1.14 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.32, 163.08, 132.52, 131.50, 123.36, 121.19, 113.48, 102.26, 101.33, 55.84, 23.25, 18.67, 11.37. HRMS (ESI) m/z calcd for $C_{21}H_{34}NO_3SSi$ $(M+H)^+$ 410.1843, found 410.1842.



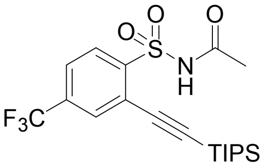
3e

N-Acetyl-4-tert-butyl-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (**3e**) White solid, isolated yield 76% (66 mg); mp: 85-87 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06 (s, 1H), 8.04 (s, 1H), 7.63 (s, 1H), 7.51-7.48 (m, 1H), 2.09 (s, 3H), 1.34 (s, 9H), 1.26-1.18 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.78, 157.25, 136.94, 132.68, 129.98, 125.82, 121.20, 103.01, 100.79, 35.11, 30.86, 23.31, 18.69, 11.42. HRMS (ESI) m/z calcd for $C_{23}H_{38}NO_3SSi$ $(M+H)^+$ 436.2342, found 436.2346.



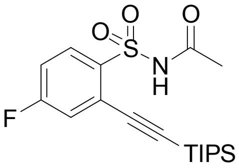
3f

N-Acetyl-4-trifluoromethoxy-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (**3f**) White solid, isolated yield 73% (68 mg); mp: 114-115 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.21 (d, *J* = 8.0 Hz, 1H), 8.05 (s, 1H), 7.44 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 2.09 (s, 3H), 1.32-1.09 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.39, 152.35, 137.81, 132.61, 126.91, 123.94, 119.94, 101.11, 100.99, 23.38, 18.64., 11.33. HRMS (ESI) m/z calcd for $C_{20}H_{29}F_3NO_4SSi$ $(M+H)^+$ 464.1539, found 464.1534.



3g

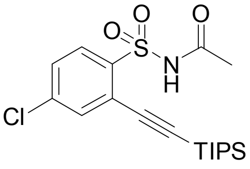
N-Acetyl-4-trifluoromethyl-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (**3g**) White solid, isolated yield 71% (64 mg); mp: 86-88 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.30 (d, *J* = 8.0 Hz, 1H), 8.14 (s, 1H), 7.86 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 2.09 (s, 3H), 1.27-1.15 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.39, 142.77, 135.22 (q, *J* = 34 Hz), 132.28 (d, *J* = 4 Hz), 131.04, 125.18 (d, *J* = 4 Hz), 124.01, 122.59, 121.29, 104.48, 101.09, 29.68, 23.38, 18.65, 11.33. HRMS (ESI) m/z calcd for $C_{20}H_{29}F_3NO3SSi$ $(M+H)^+$ 448.1590, found 448.1587.



3h

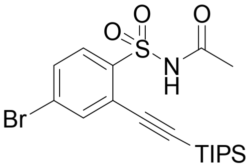
N-Acetyl-4-fluoro-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (**3g**) White solid, isolated yield 67% (53 mg); mp: 138-139 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.19-8.15 (m, 1H), 8.05 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 2.08 (s, 3H), 1.34-1.16 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.48, 166.19, 163.63, 135.84, 133.20 (d, *J* = 10 Hz),124.24, 122.52 (d, *J* = 24 Hz),115.55 (d, *J* = 24 Hz), 103.57, 101.20, 23.32, 18.64, 11.33. HRMS (ESI) m/z calcd for $C_{19}H_{29}FNO_3SSi$

(M+H)$^+$ 398.1622, found 398.1620.

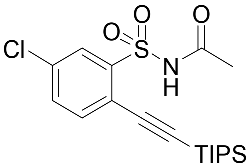


3i

N-Acetyl-4-chloro-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (3i) White solid, isolated yield 64% (53 mg); mp: 122-123 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.08 (s, 1H), 8.06 (s, 1H), 7.62 (s, 1H), 7.48-7.45 (m, 1H), 2.08 (s, 3H), 1.26-1.00 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.48, 139.88, 138.10, 135.20, 128.77, 123.18, 103.63, 101.15, 23.33, 18.66, 11.33. HRMS (ESI) m/z calcd for $C_{19}H_{29}ClNO_3SSi$ (M+H)$^+$ 414.1327, found 414.1329.

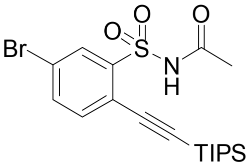


3j **N-Acetyl-4-bromo-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (3j)** White solid, isolated yield 67% (53 mg); mp: 118-119 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 2.08 (s, 3H), 1.26-1.16 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.46, 138.64, 138.05, 131.77, 131.56, 128.22,123.20, 103.71, 101.06, 23.35, 18.67, 11.31. HRMS (ESI) m/z calcd for $C_{19}H_{29}BrNO_3SSi$ (M+H)$^+$ 458.0822, found 458.0815.



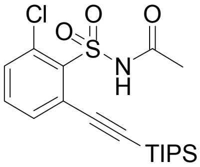
3k

N-Acetyl-5-chloro-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (3k) White solid, isolated yield 74% (61 mg); mp: 122-123 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.13 (s, 1H), 8.11 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 2.10 (s, 3H), 1.26-1.14 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.51, 141.13, 135.64, 134.87, 133.38, 130.11, 119.87, 103.16, 101.54, 23.38, 18.66, 11.34. HRMS (ESI) m/z calcd for $C_{19}H_{29}ClNO_3SSi$ (M+H)$^+$ 414.1327, found 414.1331.



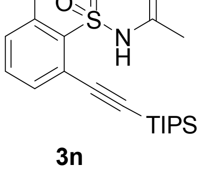
3l

N-Acetyl-5-bromo-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (3l)
White solid, isolated yield 77% (70 mg); mp: 121-122 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.20 (d, *J* = 8.0 Hz, 1H), 8.04 (s, 1H), 7.61 (q, *J* = 4.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 2.03 (s, 3H), 1.18-1.07 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.52, 141.10, 136.71, 136.34, 132.83, 122.58, 120.31, 103.35, 101.64, 23.38, 18.66, 11.33. HRMS (ESI) m/z calcd for $C_{19}H_{29}BrNO_3SSi$ (M+H)$^+$ 458.0822, found 458.0817.



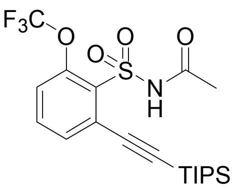
3m

N-Acetyl-2-chloro-6-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (3m)
White solid, isolated yield 63% (52 mg); mp: 143-144 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 4.0 Hz, 1H), 2.16 (s, 3H), 1.26-1.13 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.57, 135.95, 135.55, 133.95, 132.32, 125.31, 103.48, 102.60, 23.12, 18.63, 11.35. HRMS (ESI) m/z calcd for $C_{19}H_{29}ClNO_3SSi$ (M+H)$^+$ 414.1327, found 414.1330.



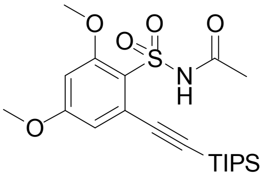
3n

N-Acetyl-2-methyl-6-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (3n)
White solid, isolated yield 77% (61 mg); mp: 80-81 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.39 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 2.76 (s, 3H), 2.08 (s, 3H), 1.26-1.17 (m, 21H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.20, 140.91, 138.46, 134.54, 133.41, 132.21, 123.12, 104.44, 101.37, 23.33, 22.66, 18.70, 11.42. HRMS (ESI) m/z calcd for $C_{20}H_{32}NO_3SSi$ (M+H)$^+$ 394.1897, found 394.1893.



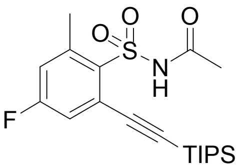
3o

N-Acetyl-2-trifluoromethoxy-6-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (**3o**) White solid, isolated yield 65% (60 mg); mp: 114-115 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 2.16 (s, 3H), 1.28-1.15 (m, 21H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.44, 147.50, 134.74, 133.73, 132.70, 125.73, 121.59, 118.93, 104.08, 101.93, 23.06, 18.60, 11.33. HRMS (ESI) m/z calcd for $C_{20}H_{29}F_3NO_4SSi$ $(M+H)^+$ 464.1539, found 464.1537.



3p

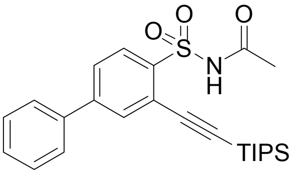
N-Acetyl-2,4-dimethoxy-6-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (**3p**) White solid, isolated yield 58% (51 mg); mp: 168-169 ^{o}C; ^{1}H NMR (400 MHz, CDCl3): δ 6.74 (s, 1H), 6.50 (s, 1H), 3.93 (s, 3H), 3.86 (s, 3H), 2.19 (s, 3H), 1.19-1.14 (m, 21H), ^{13}C NMR (100 MHz, CDCl3): δ 170.11, 163.60, 159.34, 126.54, 120.25, 112.79, 102.62, 101.13, 100.07, 56.83, 55.80, 22.84, 18.62, 11.36. HRMS (ESI) m/z calcd for $C_{21}H_{34}NO_5SSi$ $(M+H)^+$ 440.1928, found 440.1931.



3q

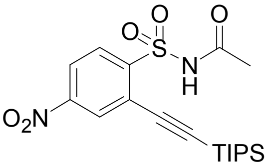
N-Acetyl-4-fluoro-2-methyl-6-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (**3q**) White solid, isolated yield 61% (50 mg); mp: 142-143 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 2.76 (s, 3H), 2.07 (s, 3H), 1.31-1.08 (m, 21H), ^{13}C NMR (100 MHz, CDCl3): δ 168.01, 164.70, 162.15, 144.75 (d, *J* = 10 Hz), 134.68, 123.02, 144.75 (q, *J* = 20 Hz), 103.09, 102.96, 23.36, 23.01, 18.67, 11.37. HRMS (ESI) m/z calcd for $C_{20}H_{31}FNO_3SSi$ $(M+H)^+$

412.1779, found 412.1782.



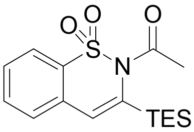
3r

3-[(Triisopropylsilanyl)-ethynyl]-biphenyl-4-sulfonic acid acetyl-amide (**3r**) White solid, isolated yield 64% (58 mg); mp: 142-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (t, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H,), 6.67 (d, *J* = 8.0 Hz, 1H), 7.60-7.42 (m, 5H), 2.11 (s, 3H), 1.26-1.16 (m, 21H), ^{13}C NMR (100 MHz, CDCl3): δ 167.72, 146.50, 138.29, 138.15, 134.17, 130.67, 129.14, 128.96, 127.36, 127.05, 121.99, 102.56, 101.76, 23.36, 18.71, 11.40. HRMS (ESI) m/z calcd for $C_{25}H_{34}NO_3SSi$ $(M+H)^+$ 456.2029, found 456.2027.



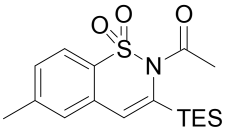
3s

N-Acetyl-4-nitro-2-[(triisopropylsilanyl)-ethynyl]-benzenesulfonamide (**3s**) White solid, isolated yield 63% (54 mg); mp: 116-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (t, *J* = 4.0 Hz, 1H), 8.39-8.31 (m, 1H), 8.30-8.14 (m, 1H), 2.10 (s, 3H), 1.22-1.18 (m, 21H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.32, 150.21, 144.59, 132.07, 130.11, 123.44, 122.98, 106.01, 100.43, 23.45, 18.67, 11.31. HRMS (ESI) m/z calcd for $C_{19}H_{29}N_2O_5SSi$ $(M+H)^+$ 425.1567, found 425.1564.



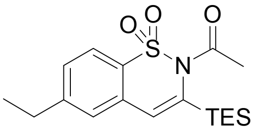
4a

1-(1,1-dioxido-3-triethylsilanyl-2H-benzo[e][1,2]thiazin-2-yl)ethanone (**4a**) White solid, isolated yield 79% (53 mg); mp: 147-148 °C;; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.49 (s, 1H), 7.27 (s, 1H), 2.71 (s, 3H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.91-0.86 (m, 6H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.51, 135.70, 134.09, 133.00, 131.78, 127.66, 127.54, 123.38, 117.33, 25.88, 25.85, 7.27, 3.90. HRMS (ESI) m/z calcd for $C_{16}H_{24}NO_3SSi$ $(M+H)^+$ 338.1247, found 338.1275.



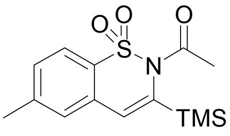
4b

1-(6-Methyl-1,1-dioxido-3-triethylsilanyl-2H-benzo[e][1,2]thiazin-2-yl)ethanone (**4b**) White solid, isolated yield 75% (53 mg); mp: 152-153 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.35 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 2.70 (s, 3H), 2.47 (s, 3H), 0.99 (t, *J* = 8.0 Hz, 9H), 0.91-0.86 (m, 6H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.51, 135.70, 134.09, 133.00, 127.66, 127.54, 123.38, 117.33, 25.88, 25.58, 7.27, 3.93. HRMS (ESI) m/z calcd for $C_{17}H_{26}NO_3SSi$ $(M+H)^+$ 352.1403, found 352.1406.



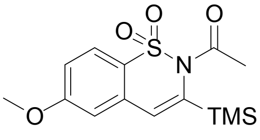
4c

1-(6-Ethyl-1,1-dioxido-3-triethylsilanyl-2H-benzo[e][1,2]thiazin-2-yl)ethanone (**4c**) White solid, isolated yield 74% (54 mg); mp: 137-138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.39 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 2.76 (q, *J* = 8.0 Hz, 2H), 2.70 (s, 3H), 1.28 (t, *J* = 8.0 Hz, 3H), 0.99 (t, *J* = 8.0 Hz, 9H), 0.91-0.85 (m, 6H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.56, 149.89, 135.80, 131.73, 131.51, 127.43, 126.78, 123.43, 117.19, 29.07, 25.85, 15.10, 7.31, 4.02. HRMS (ESI) m/z calcd for $C_{18}H_{28}NO_3SSi$ $(M+H)^+$ 366.1560, found 366.1564.



4d

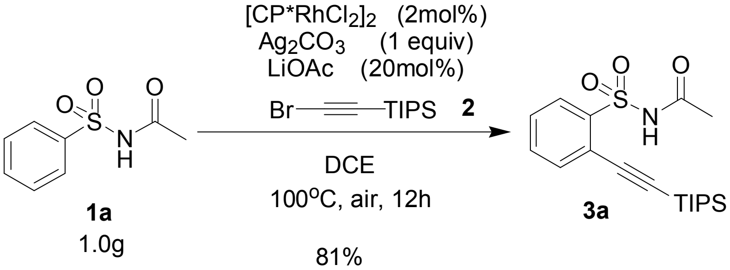
1-(6-Methyl-1,1-dioxo-3-trimethylsilanyl-2H-benzo[e][1,2]thiazin-2-yl)ethanone (**4d**) White solid, isolated yield 71% (44 mg); mp: 152-153 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.35 (s, 1H), 7.33 (s, 1H), 7.30 (s, 1H) , 2.71 (s, 3H), 2.47 (s, 3H), 0.38 (m, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.84, 144.03, 135.55, 131.53, 131.13, 128.69, 1228.37, 123.69, 119.90, 26.12, 22.19, 0.00, 7.31, 4.02. HRMS (ESI) m/z calcd for $C_{14}H_{20}NO_3SSi$ $(M+H)^+$ 310.0934, found 310.0931.



4e

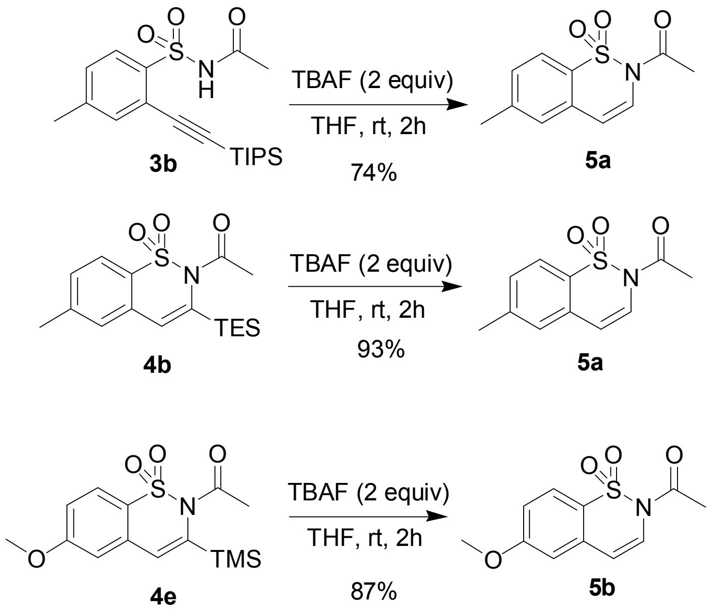
1-(6-Methoxy-1,1-dioxo-3-trimethylsilanyl-2H-benzo[e][1,2]thiazin-2-yl)ethanone e (**4e**) White solid, isolated yield 68% (43 mg); mp: 140-141 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.31 (s, 1H), 7.03-6.99 (m, 2H), 3.89 (s, 3H) , 2.71 (s, 3H), 0.39 (m, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.85, 163.24, 137.67, 131.70, 126.56, 125.88, 119.62, 113.45, 113.10, 55.97, 25.16, 0.00. HRMS (ESI) m/z calcd for $C_{14}H_{20}NO_4SSi$ $(M+H)^+$ 326.0833, found 326.0829.

5) Gram-scale reaction

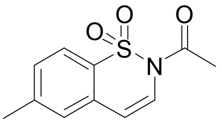


N-acylated aryl sulfonamide **1a** (1.0g, 5.0 mmol), (triisopropylsilyl)ethynyl bromide **2** (1.4g, 0.22 mmol), $[Cp^*RhCl_2]_2$ (88 mg, 0.02 mmol, 2 mol %), Ag_2CO_3 (1.375 g, 5 mmol, 1equiv), LiOAc (102.5 mg, 0.1 mmol, 20 mol %), and DCE (20 mL) were charged into a reaction tube. The reaction mixture was stirred at 100 °C for 12 h. After the mixture cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/EtOAc to afford the desired product **3a** (1.53g, 81%).

6) General procedure for desilylation of products of 3 and 4

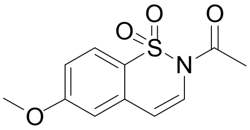


The compound **3** or **4** (0.2 mmol) in dry THF (4 mL) was added TBAF (1 mol/L in THF, 0.3 mL). The reaction mixture was stirred at room temperature for 2 h. Water was then added and the mixture was extracted with EtOAc. The organic layer was combined, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel chromatography to afford compound **5**.



5a

1-(6-Methyl-1,1-dioxo-2H-benzo[e][1,2]thiazin-2-yl)ethanone e (**5a**) White solid, isolated yield 74% (35 mg); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.36-7.31 (m, 2H), 7.21 (s, 1H) , 2.72 (s, 3H), 2.46 (m, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.36, 144.42, 132.43, 130.93, 129.13, 127.63, 125.79, 123.06, 110.57, 25.76, 21.65. HRMS (ESI) m/z calcd for $C_{11}H_{12}NO_3S$ $(M+H)^+$ 238.0539, found 238.0540.

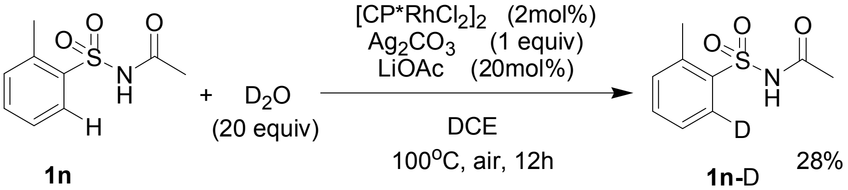


5b

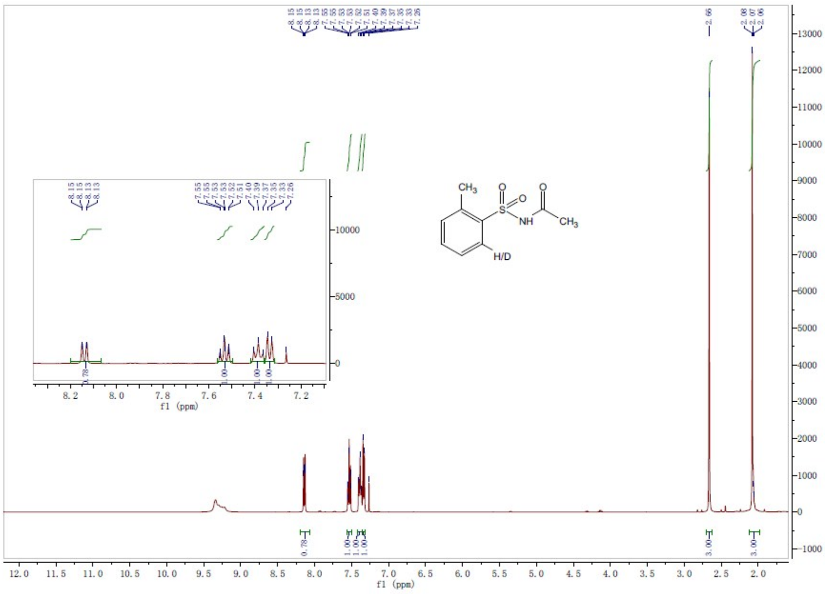
1-(6-Methoxy-1,1-dioxo-2H-benzo[e][1,2]thiazin-2-yl)ethanone (5b) White solid, isolated yield 87% (44 mg); 95-98 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 12.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.02 (q, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 4.0 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 2.72 (m, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.32, 163.37, 134.62, 126.29, 125.27, 114.68, 114.54, 111.20, 110.39, 55.81, 25.72. HRMS (ESI) m/z calcd for $C_{11}H_{12}NO_3S$ $(M+H)^+$ 238.0539, found 238.0540.

7) Mechanism study

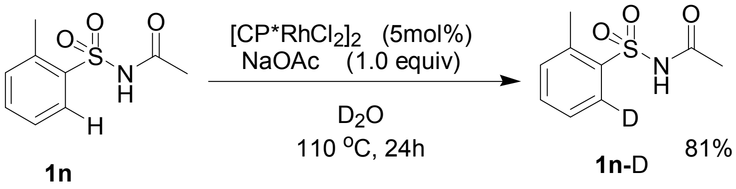
1. The H/D exchange experiments for the substrate 1n



A mixture of N-(o-tolylsulfonyl) acetamide **1n** (0.20 mmol), D_2O (72 μL, 4 mmol), $[Cp^*RhCl_2]_2$ (3.5 mg, 0.004 mmol, 2 mol %), Ag_2CO_3 (55 mg, 0.2 mmol, 1equiv), LiOAc (4.1 mg, 0.004 mmol, 20 mol %), and DCE (1 mL) were charged into a reaction tube. The reaction mixture was stirred at 100 °C for 12 h. After the mixture cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/EtOAc to afford the desired product **1n-D** (28%).



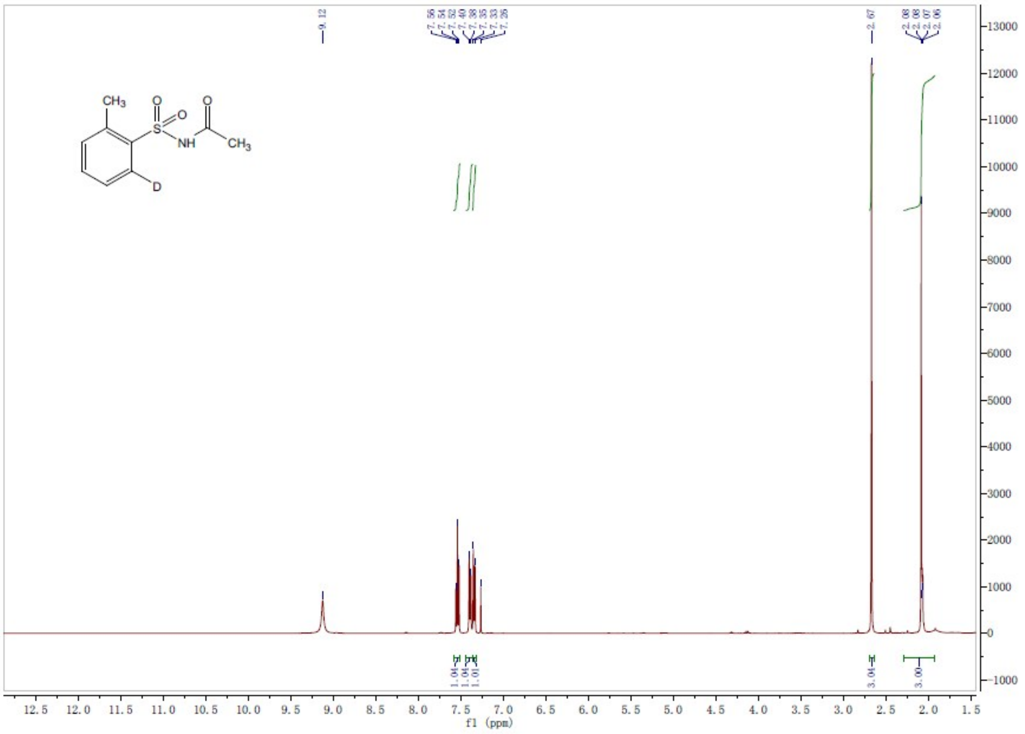
2. Kinetic isotope experiments

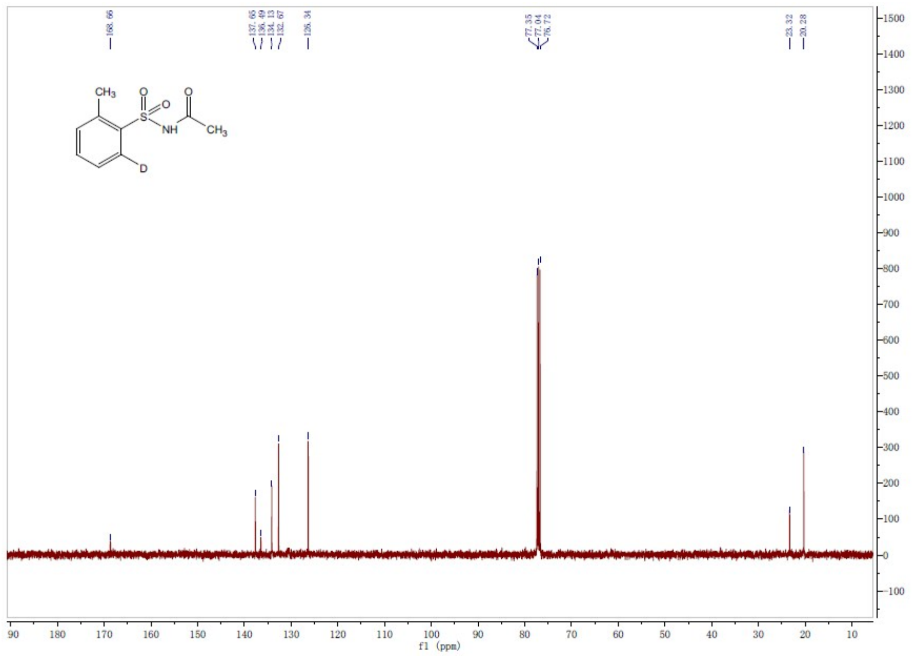


Preparation of N-((2-methylphenyl-6-d)slfonyl)acetamide (1n-D)[2]

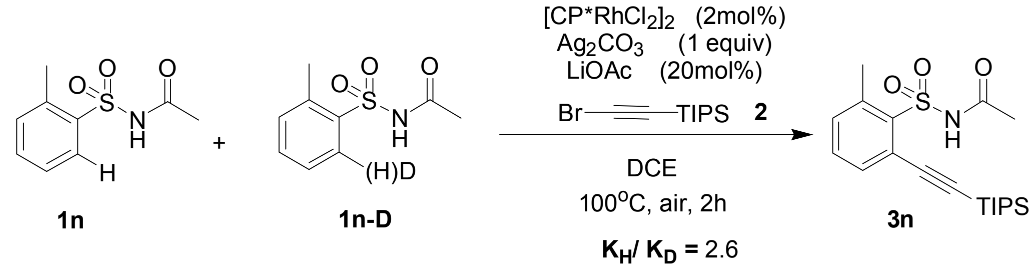
A mixture of 1 N-(o-tolylsulfonyl) acetamide **1n** (42.7 mg, 0.20 mmol), [Cp*$RhCl_2$]$_2$ (6.3 mg, 0.01 mmol), NaOAc (16.4 mg, 0.2 mmol), and D_2O (0.5 mL), were charged into a reaction tube. The reaction mixture was stirred at 110 °C for 24 h. After the mixture cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/EtOAc to afford the desired product **1n-D** as a white solid (36 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 2.67 (s, 3H), 2.07 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.66, 137.65, 136.49, 134.13, 132.67, 126.34, 23.32, 20.28.

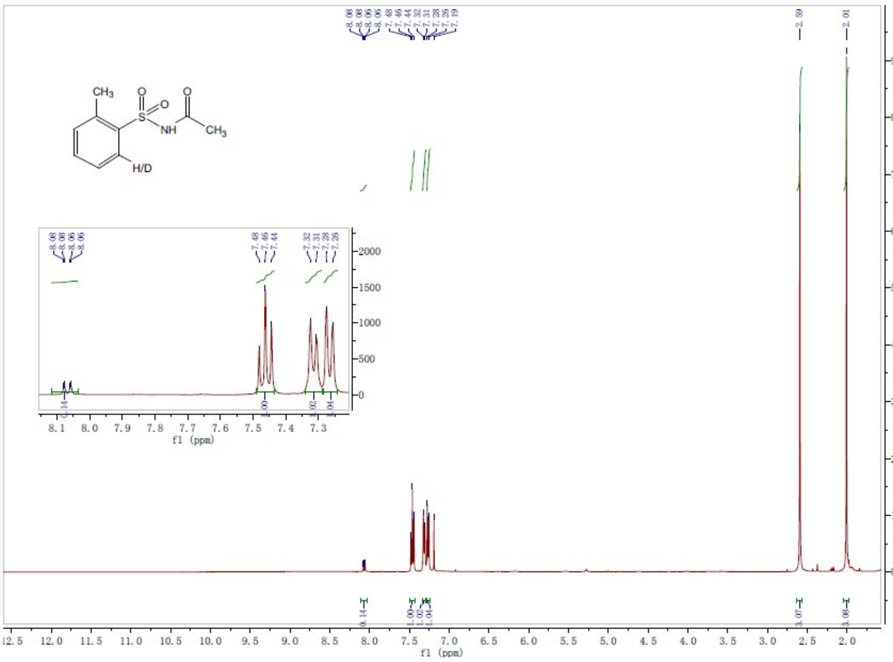




Intermolecular kinetic experiments



A mixture of N-(o-tolylsulfonyl) acetamide **1n** (0.10 mmol) and **1n-D** (0.10 mmol), (triisopropylsilyl)ethynyl bromide **2** (57 mg, 0.22 mmol), [Cp*RhCl$_2$]$_2$ (3.5 mg, 0.004 mmol, 2 mol %), Ag$_2$CO$_3$ (55 mg, 0.2 mmol, 1equiv), LiOAc (4.1 mg, 0.004 mmol, 20 mol %), and DCE (1 mL) were charged into a reaction tube. The reaction mixture was stirred at 100 °C for 2 h. After the mixture cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/EtOAc to afford a mixture of the intact substrates **1n and 1n-D**. The ratio of the intact substrates **1n** and **1n-D** was determined by ^{H}NMR, then, the Kinetic isotope effect (KIE = 2.6) was obtained.

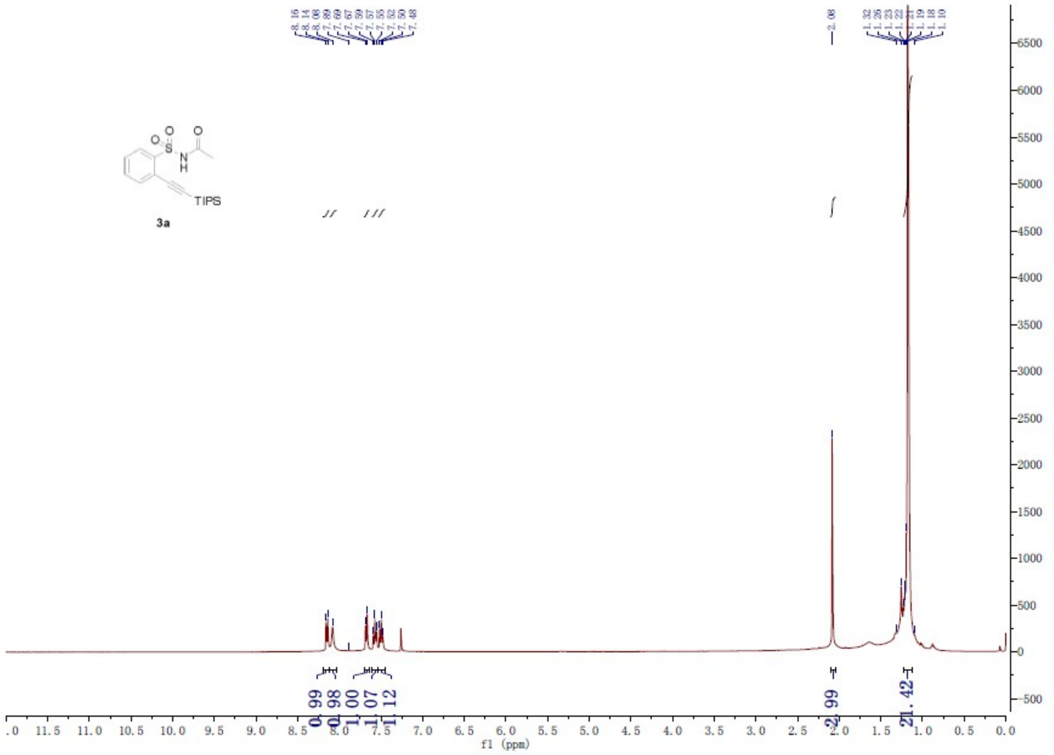


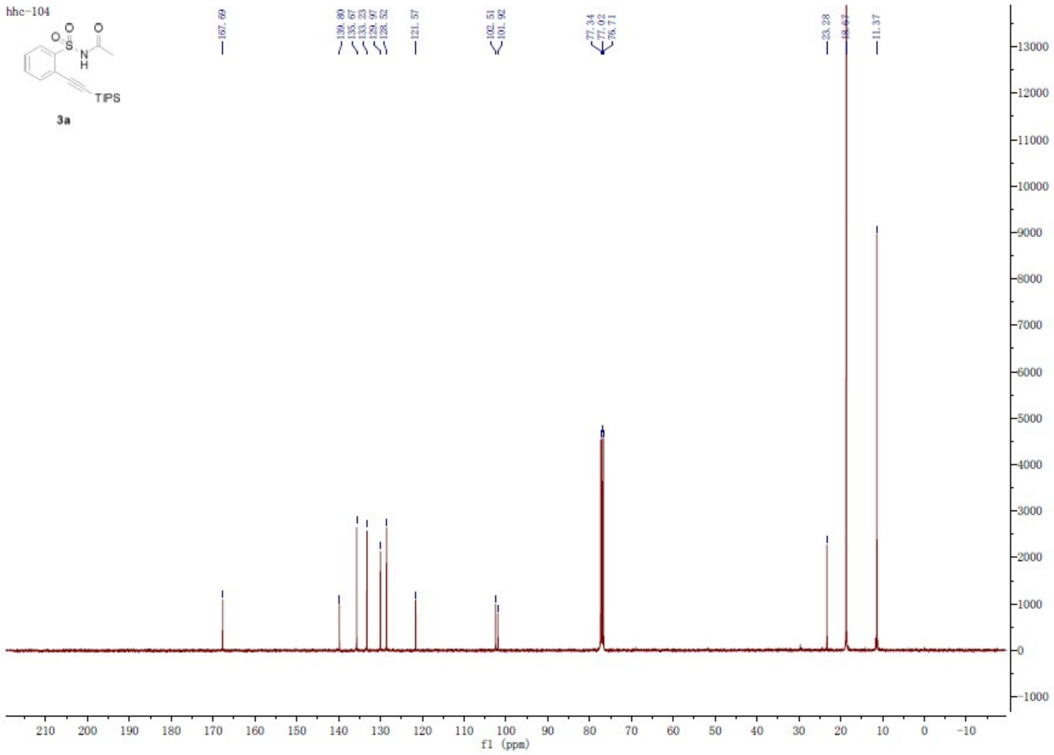
8) References

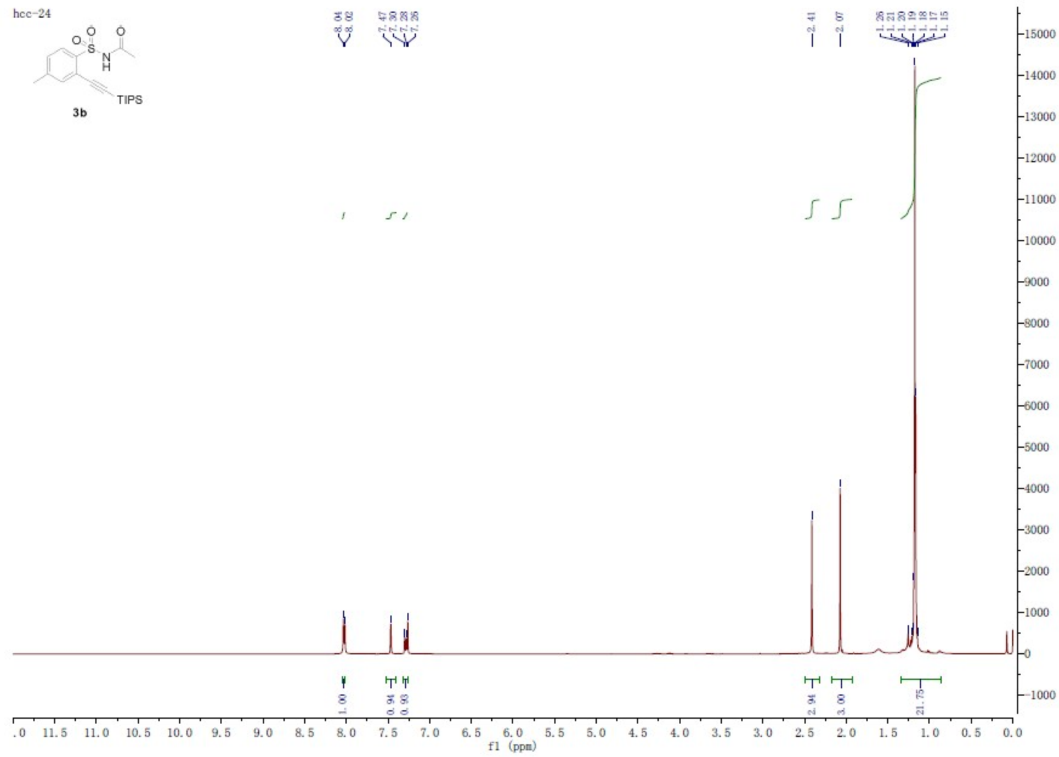
1 B. Mahipal, S. R. Yaragorla and C. R. Reddy, *Tetrahedron Lett.* 2007, **48**, 7528.

2. Y. Ran, Y. Yang, H. You and J. You, *ACS Catal.* 2018, **8**, 1796.

9) ^{1}H NMR and ^{13}C NMR Spectra of 3-5 Compounds



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2.07
1.26
1.21
1.20
1.19
1.18
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2.94
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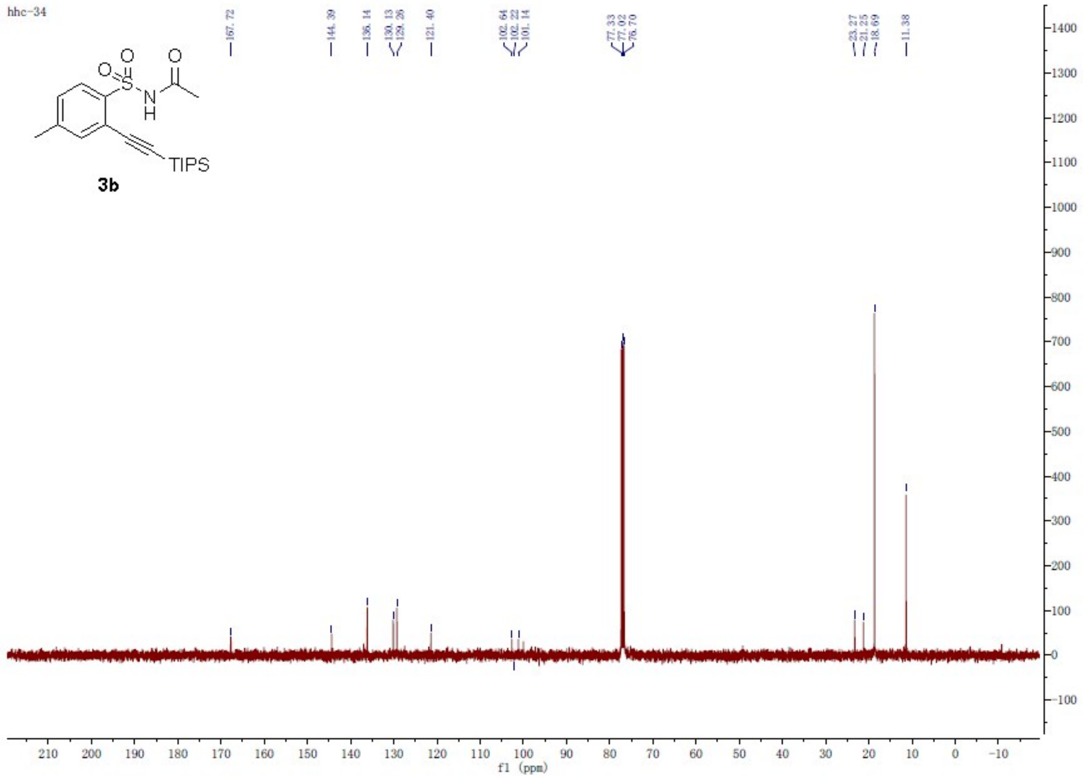
f1 (ppm)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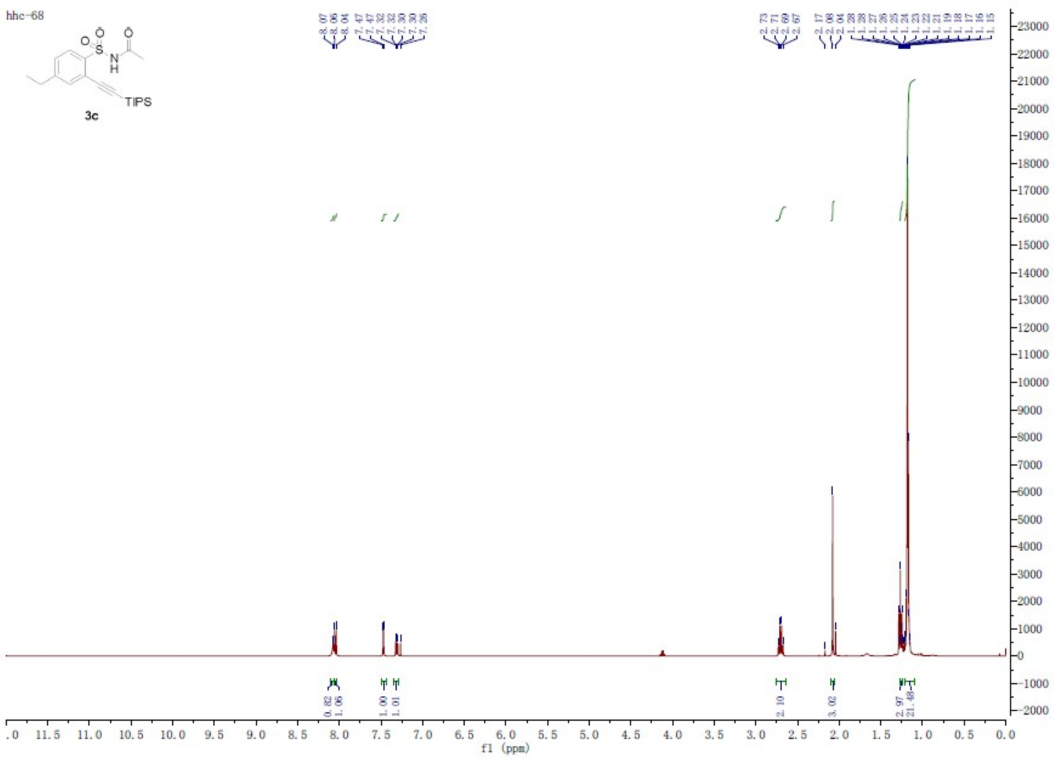
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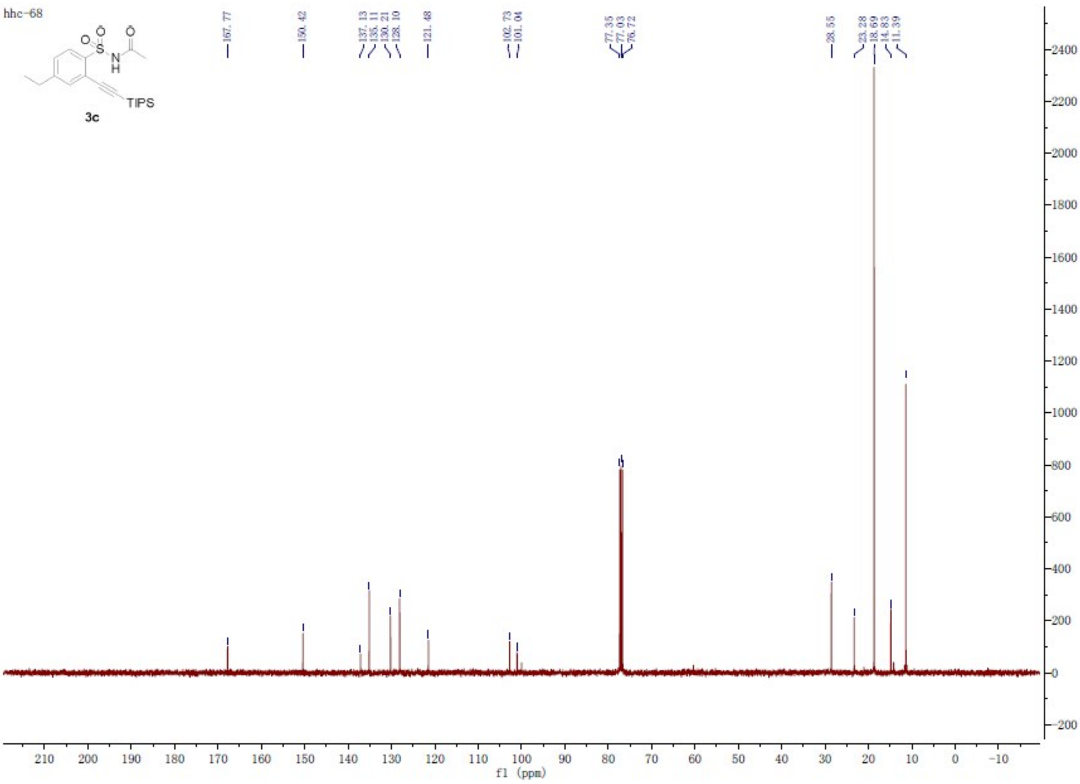
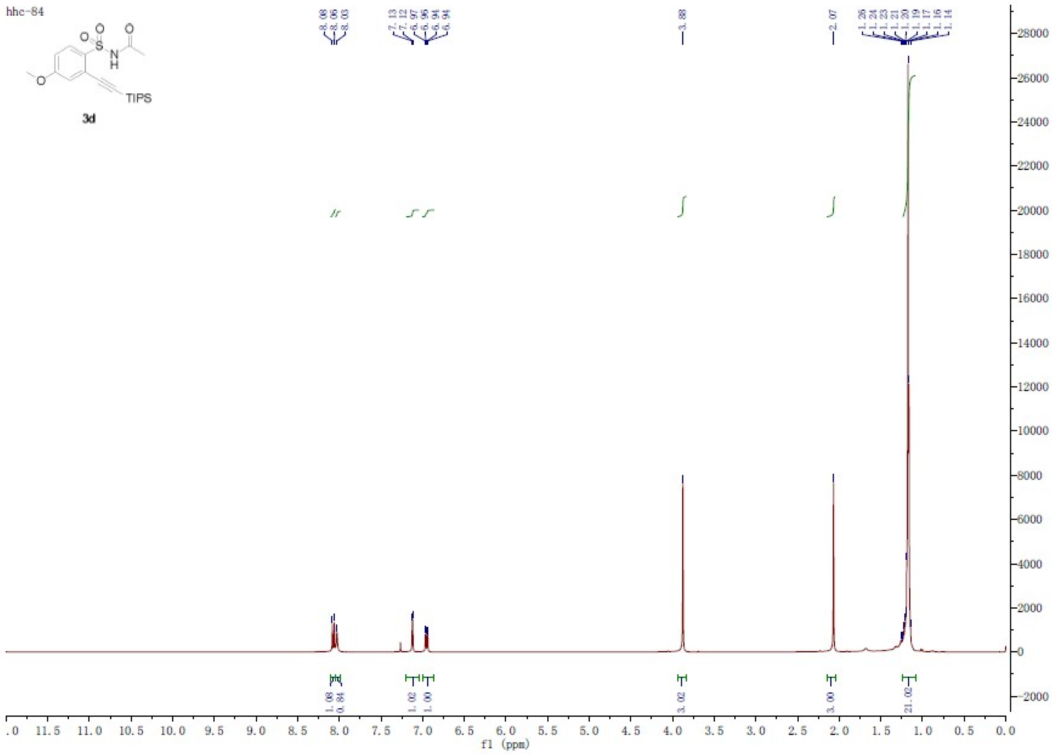
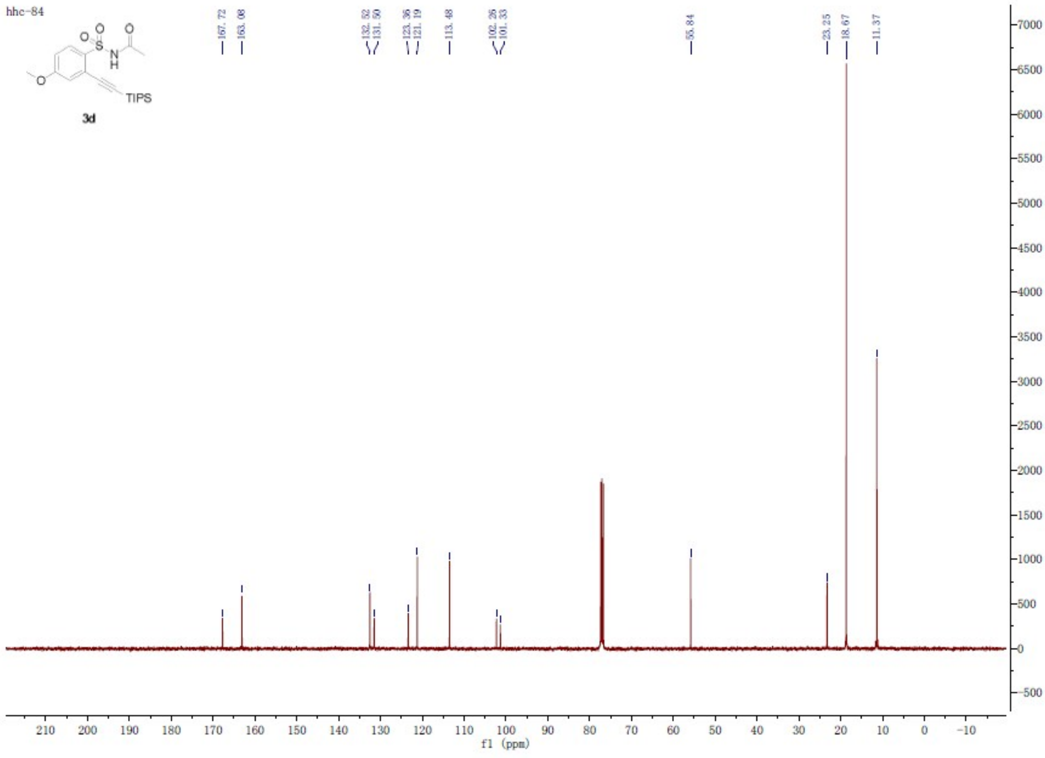
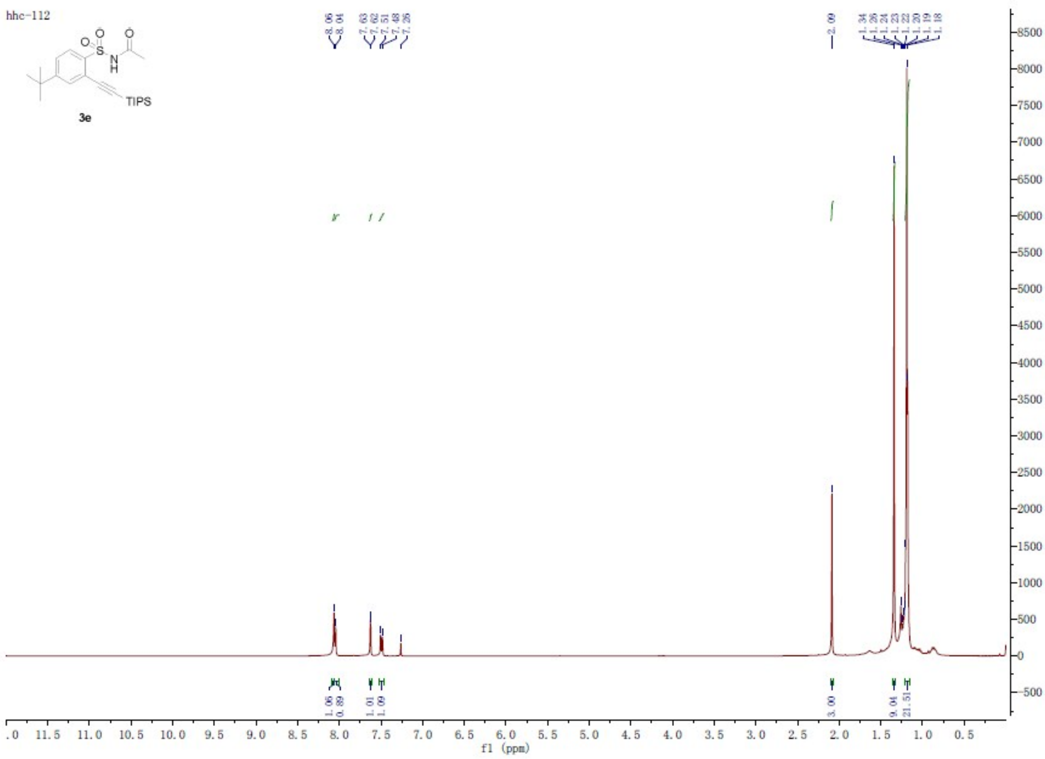
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

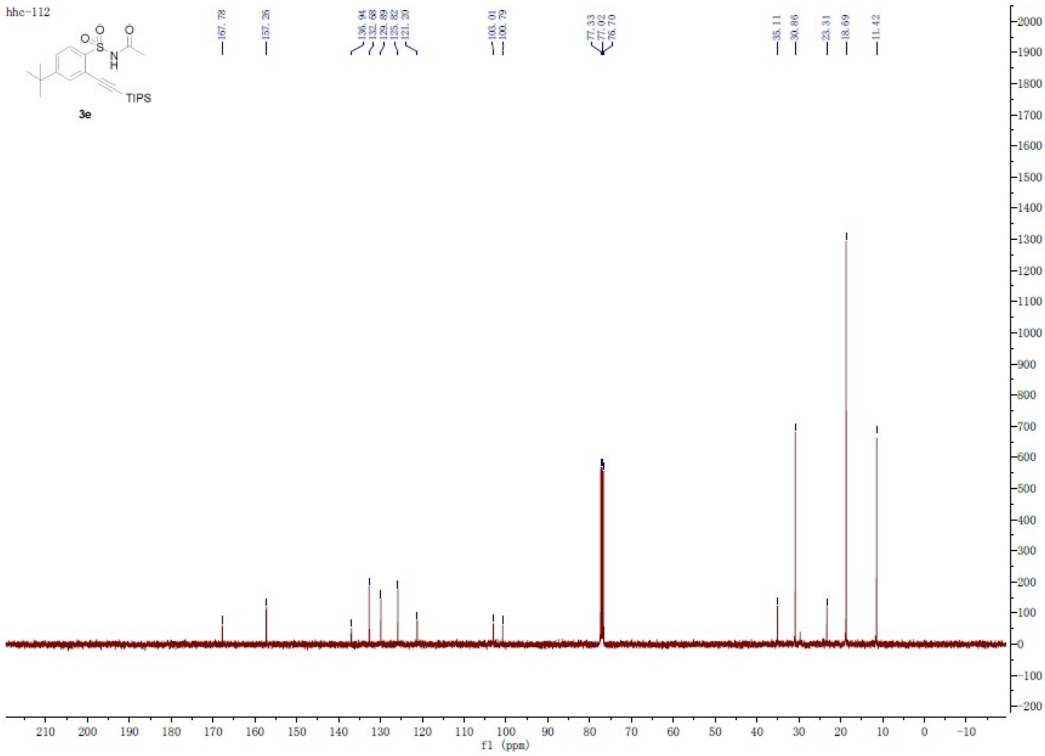

hhc-68
O S O
N
H
O
TIPS
3c
167.77
150.42
137.13
135.11
130.21
128.10
121.48
102.73
101.04
77.35
77.03
76.72
28.55
23.28
18.69
14.83
11.39
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


hhc-84
TIPS
3d
8.08
8.06
8.03
7.13
7.12
6.97
6.96
6.94
6.94
3.88
2.07
1.26
1.24
1.23
1.21
1.20
1.19
1.17
1.16
1.14
1.08
0.84
1.02
1.00
3.02
3.00
21.02
f1 (ppm)

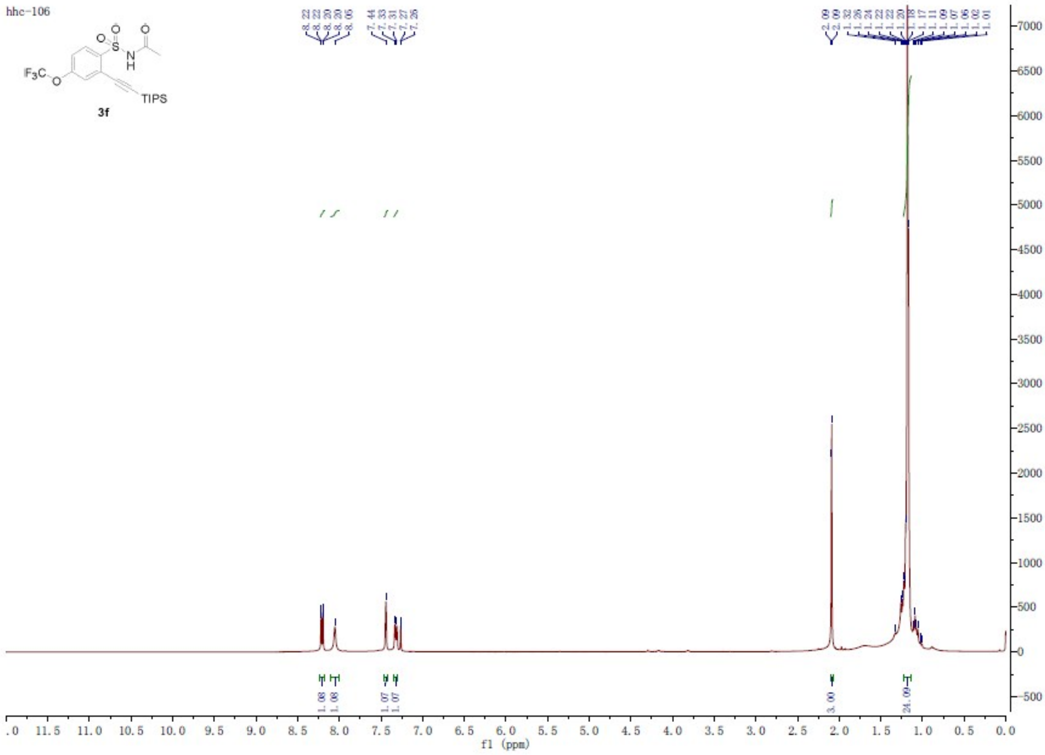

hhc-84
TIPS
3d
167.72
163.08
132.52
131.50
123.36
121.19
113.48
102.26
101.33
55.84
23.25
18.67
11.37
f1 (ppm)

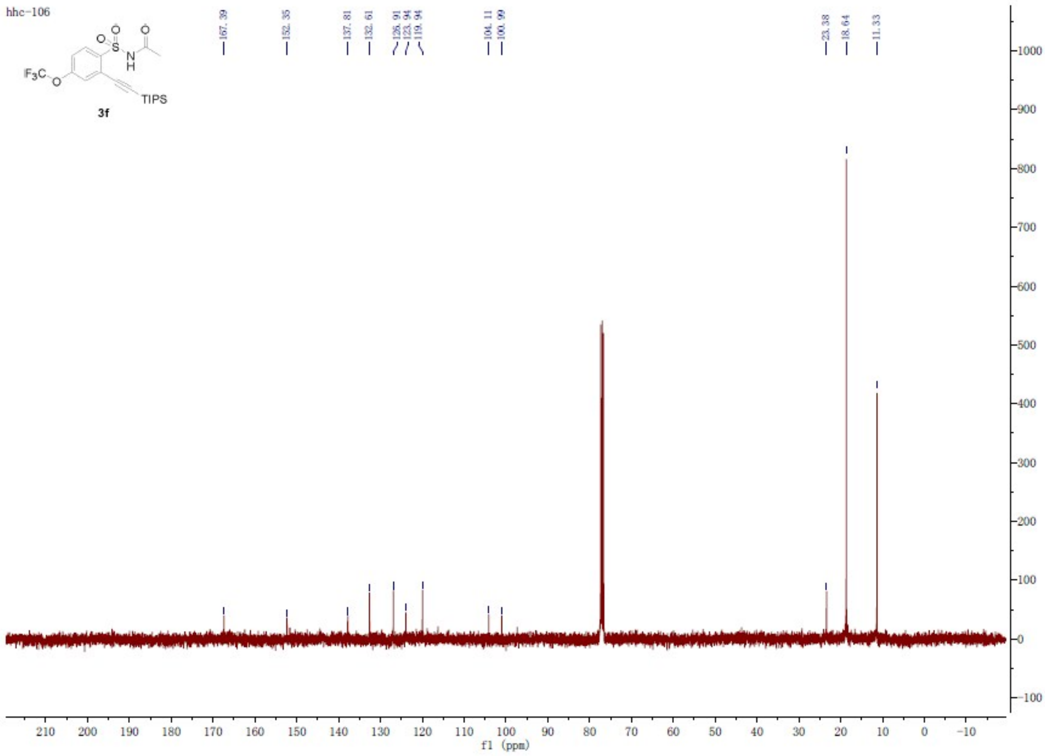

hhc-112
O
S
O
N
H
O
TIPS
8.06
8.04
7.63
7.62
7.51
7.48
7.26
2.09
1.34
1.26
1.24
1.23
1.22
1.20
1.19
1.18
1.06
0.89
1.01
1.09
3.00
9.04
21.51
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

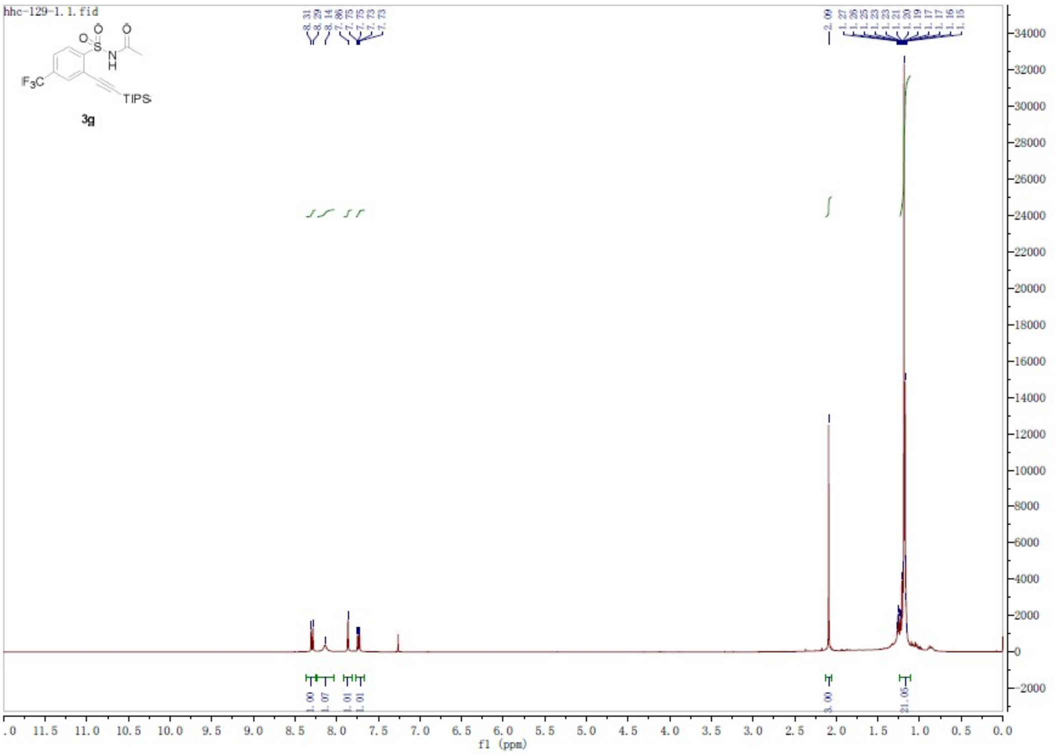
3e

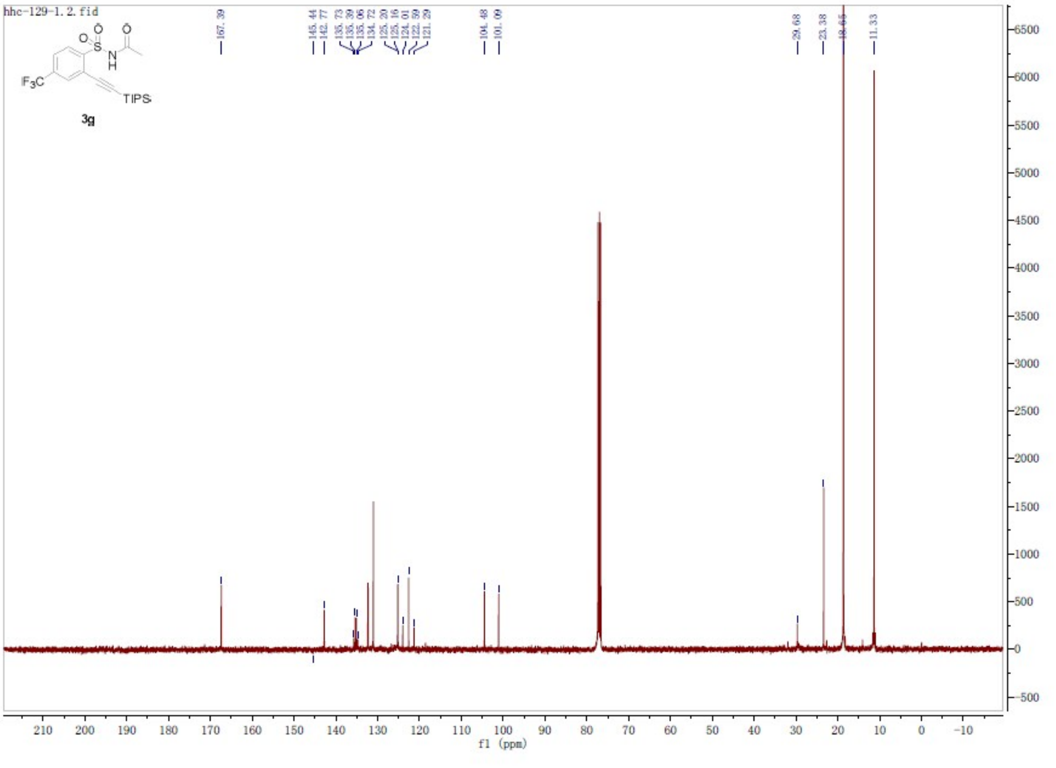

hhc-112
O
S
O
N
H
O
TIPS
167.78
157.26
136.94
132.68
129.89
125.82
121.20
103.01
100.79
77.33
77.02
76.70
35.11
30.86
23.31
18.69
11.42
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

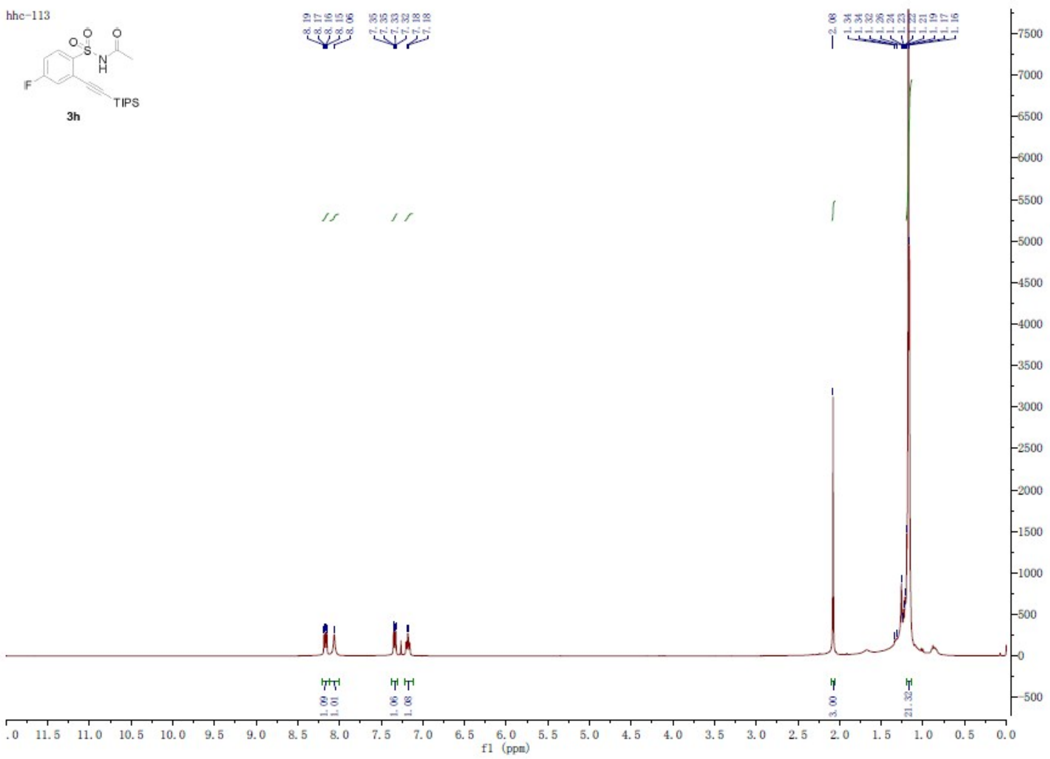
3e

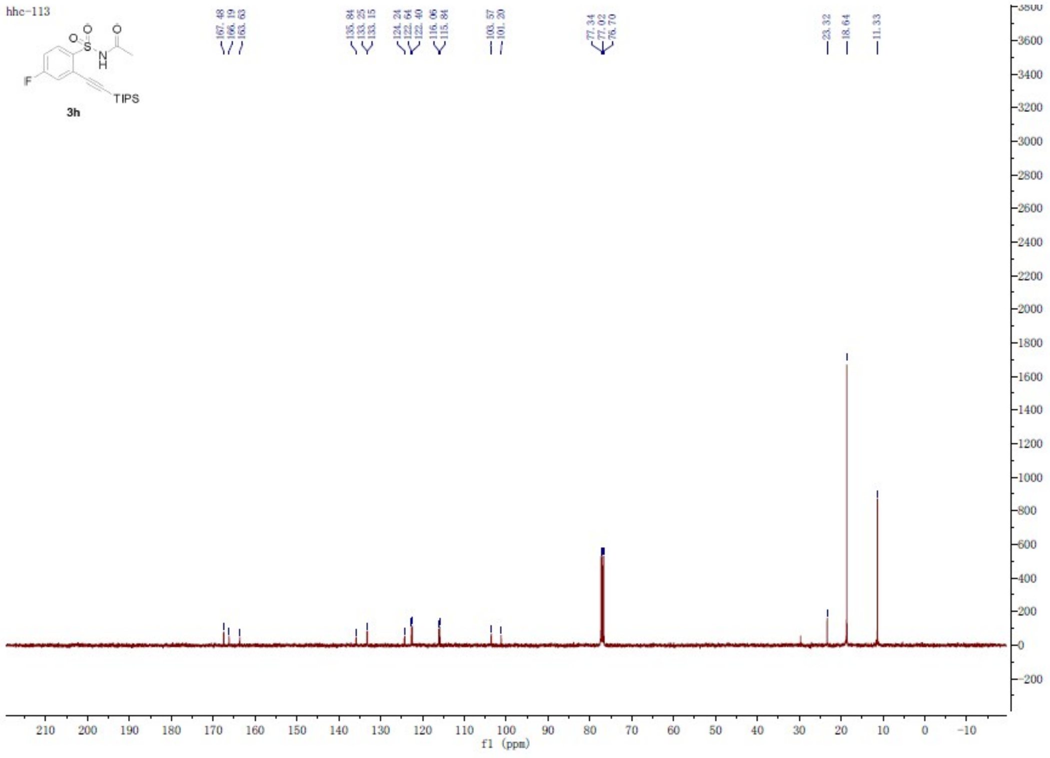

hhc-106
F$_3$C
O
S
O
O
N
H
O
TIPS
3f
8.22
8.22
8.20
8.20
8.05
7.44
7.33
7.31
7.27
7.26
2.09
2.09
1.32
1.26
1.24
1.22
1.22
1.20
1.18
1.17
1.11
1.09
1.07
1.06
1.02
1.01
1.08
1.08
1.07
1.07
3.00
24.09
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

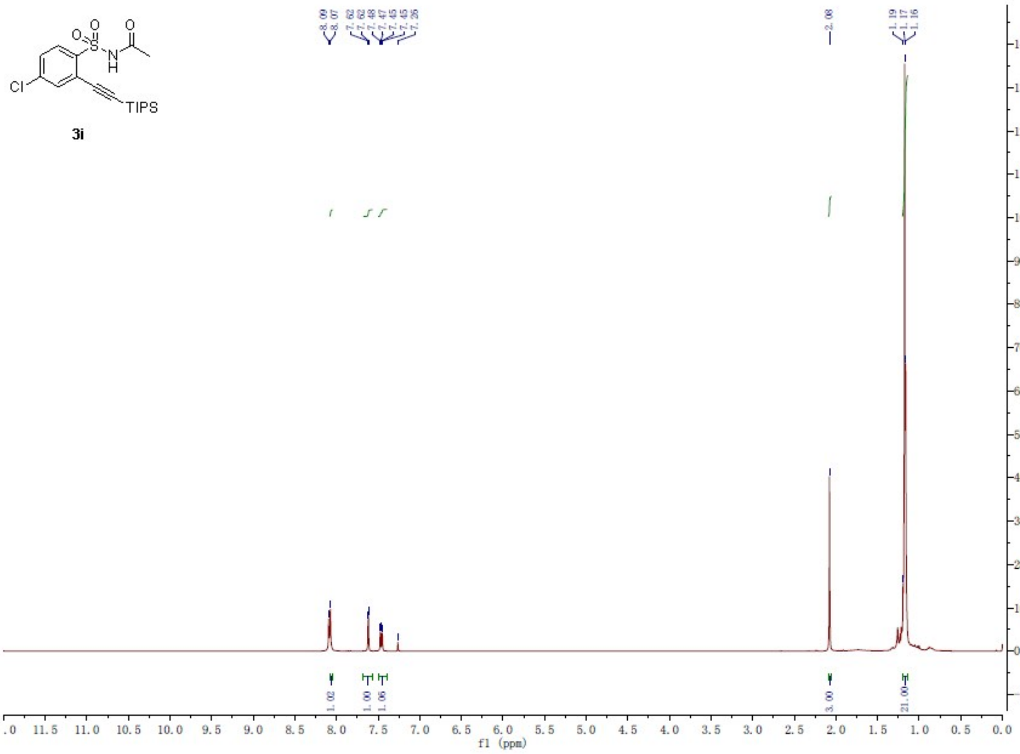

hhc-106
F$_3$C
O
S
O
O
N
H
O
TIPS
3f
167.39
152.35
137.81
132.61
126.91
123.94
119.94
104.11
100.99
23.38
18.64
11.33
1000
900
800
700
600
500
400
300
200
100
0
-100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

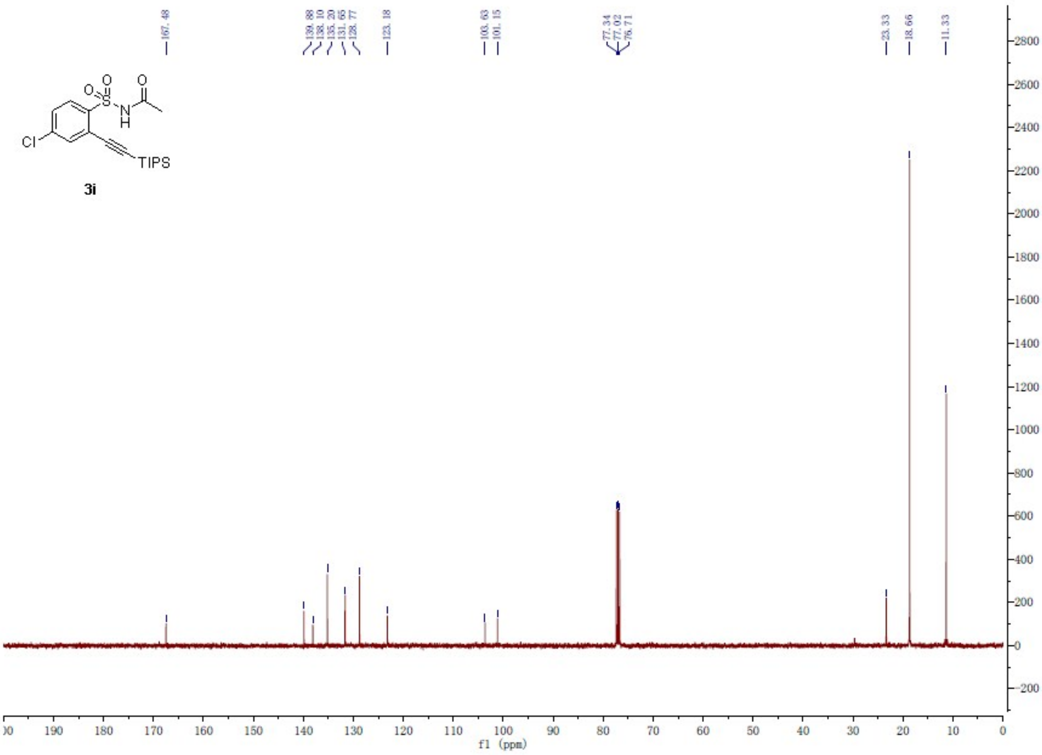

hhc-129-1.1.fid
F3C
TIPS
3g
8.31
8.29
8.14
7.86
7.75
7.75
7.73
7.73
2.09
1.27
1.26
1.25
1.23
1.23
1.21
1.20
1.19
1.17
1.17
1.16
1.15
1.00
1.07
1.01
1.01
3.00
21.05
f1 (ppm)

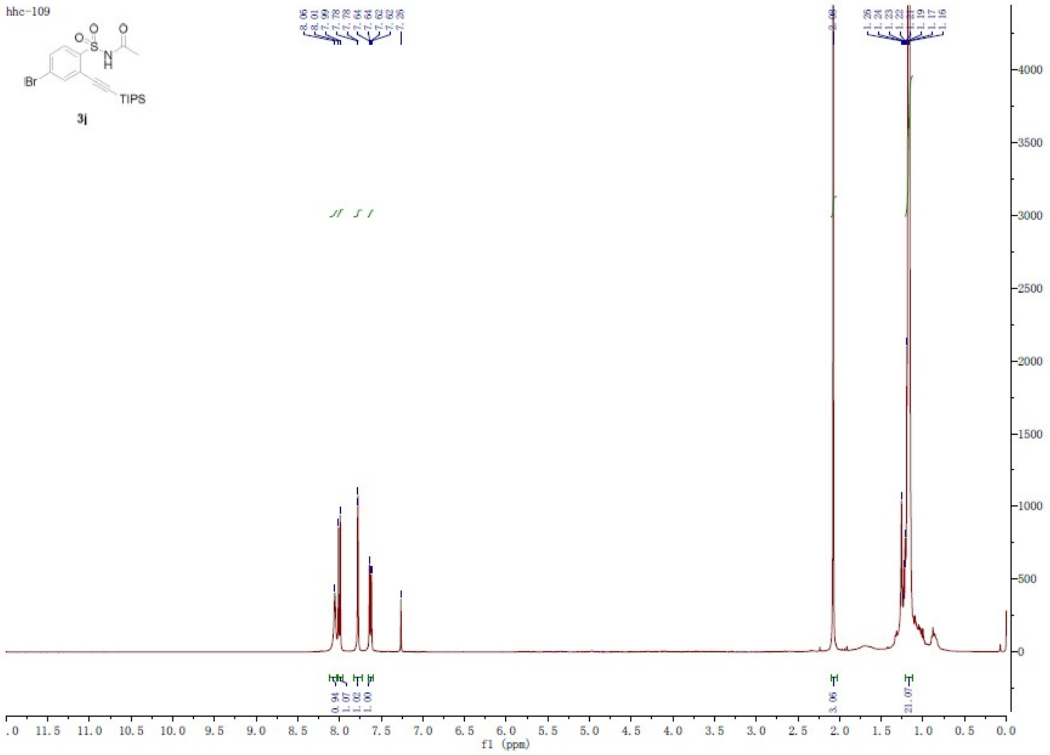

hhc-129-1.2.fid
F3C
TIPS
3g
167.39
145.44
142.77
135.73
135.39
135.06
134.72
125.20
125.16
124.01
122.59
121.29
104.48
101.09
29.68
23.38
18.65
11.33
f1 (ppm)

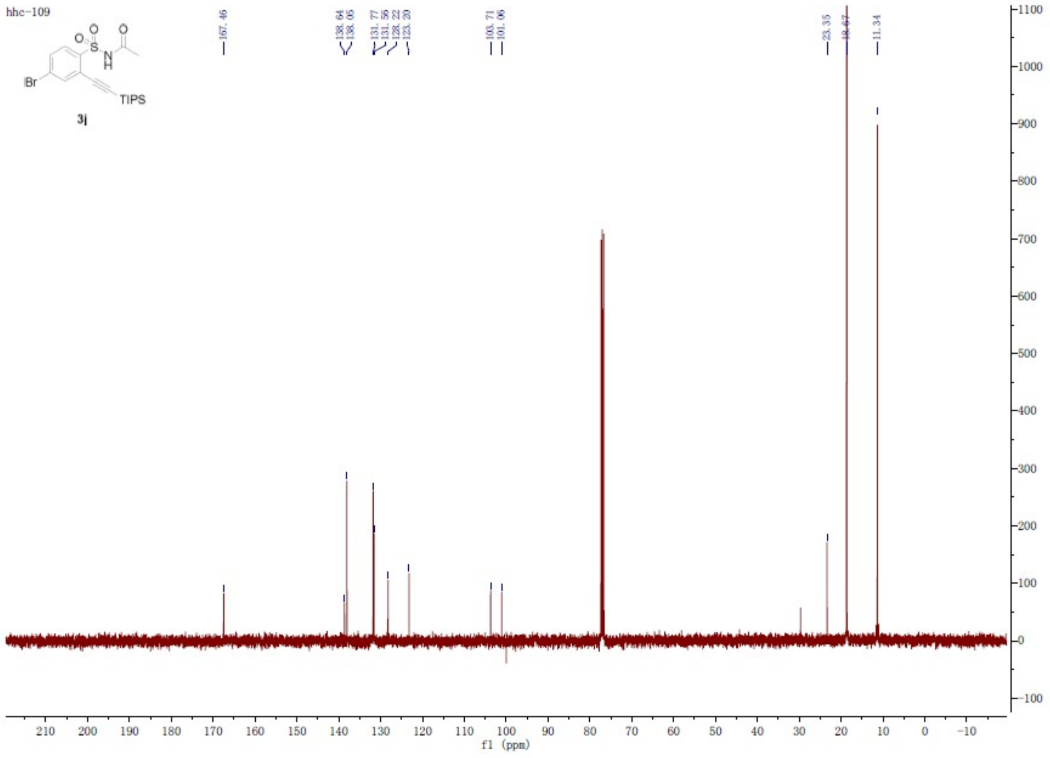

hhc-113
3h
F
TIPS
8.19 8.17 8.16 8.15 8.06
7.35 7.35 7.33 7.32 7.18 7.18
2.08
1.34 1.34 1.32 1.26 1.24 1.23 1.22 1.21 1.19 1.17 1.16
1.09 1.01 1.06 1.08 3.00 21.32
f1 (ppm)

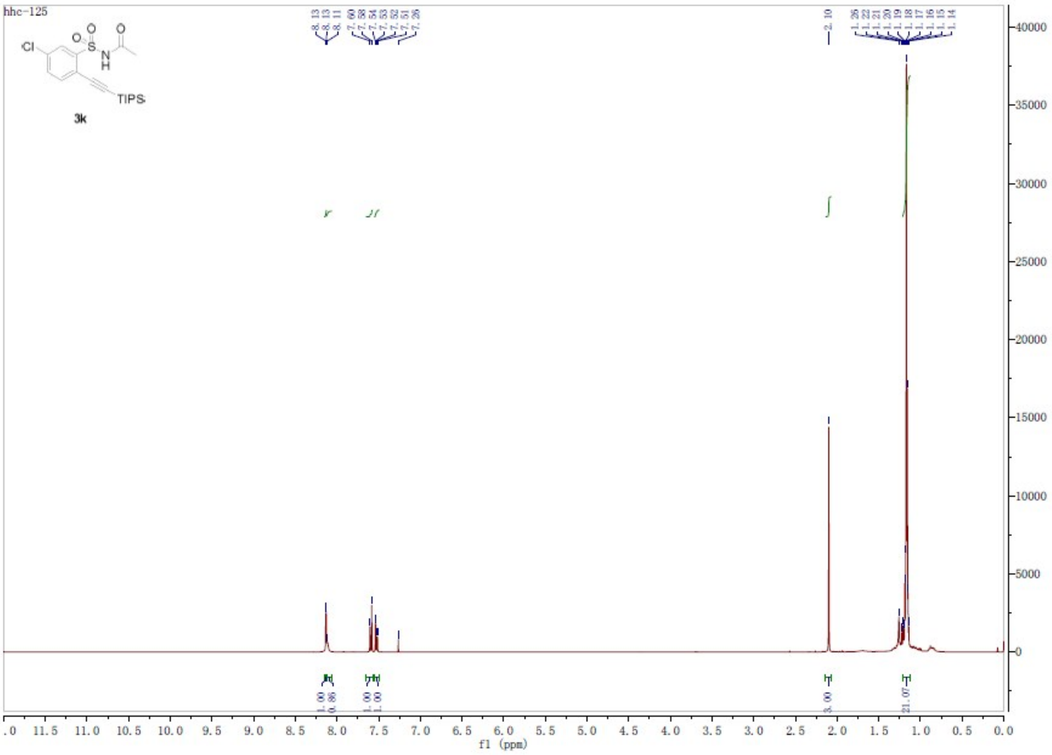

hhc-113
3h
F
TIPS
167.48 166.19 163.63
135.84 133.25 133.15
124.24 122.64 122.40
116.06 115.84
103.57 101.20
77.34 77.02 76.70
23.32 18.64 11.33
f1 (ppm)

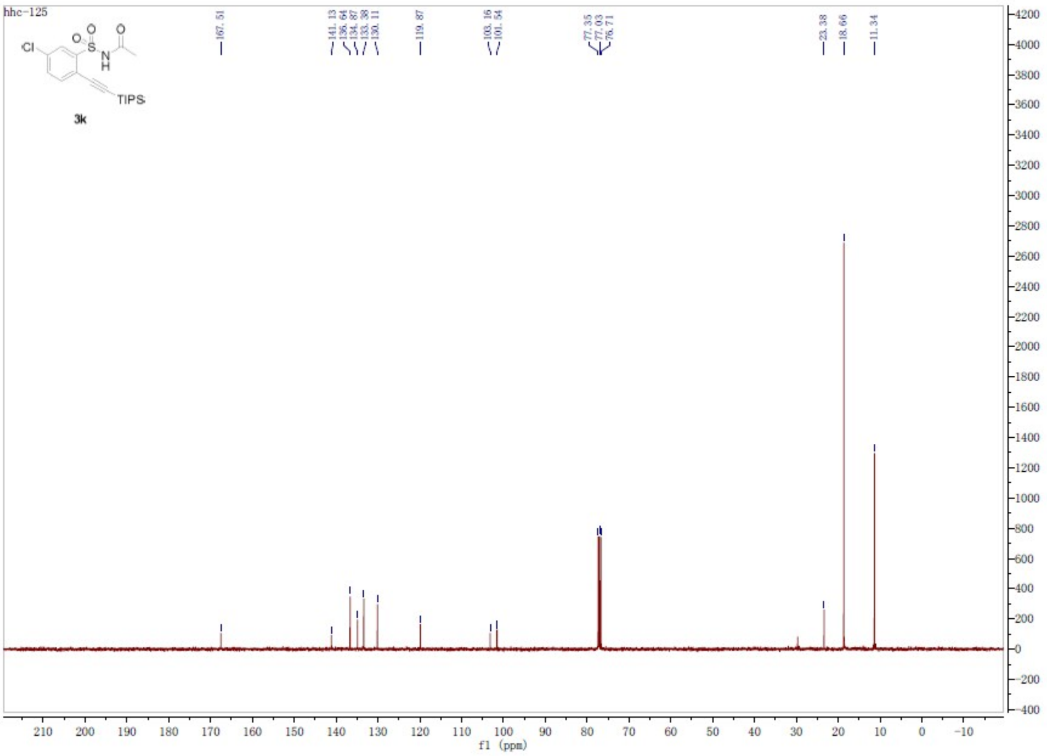

Cl
O
O
S
N
H
O
TIPS
3i
8.09
8.07
7.62
7.62
7.48
7.47
7.45
7.45
7.26
2.08
1.19
1.17
1.16
1.02
1.00
1.06
3.00
21.00
.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

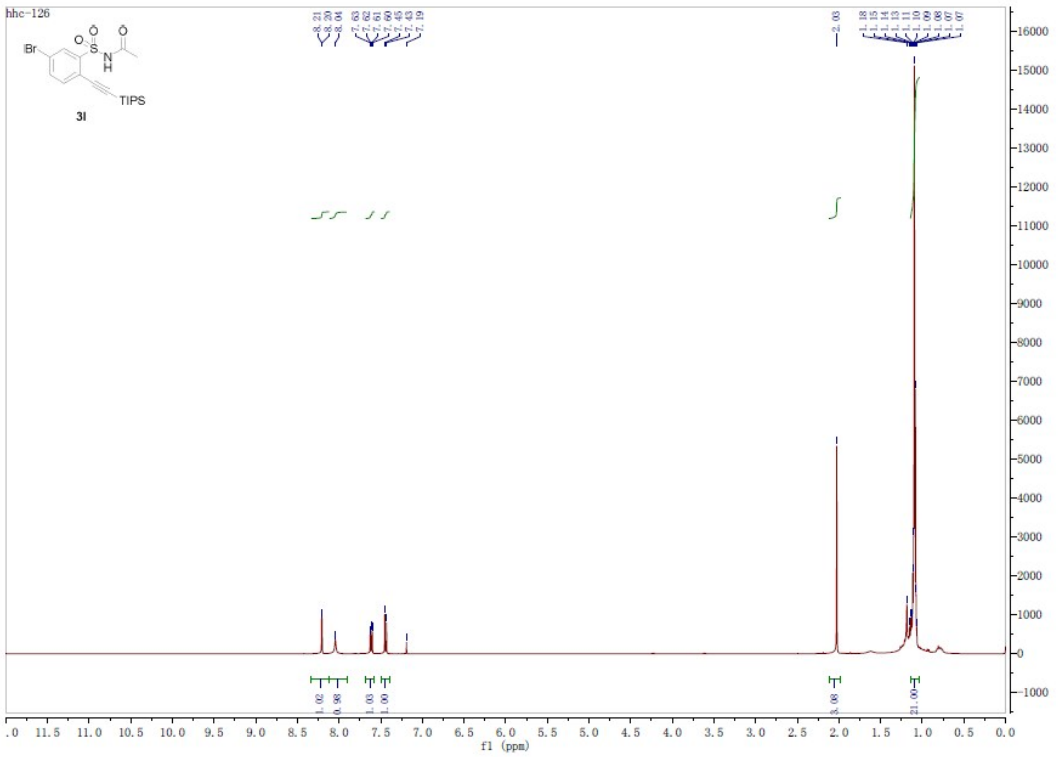

167.48
139.88
138.10
135.20
131.65
128.77
123.18
103.63
101.15
77.34
77.02
76.71
23.33
18.66
11.33
Cl
O
O
S
N
H
O
TIPS
3i
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

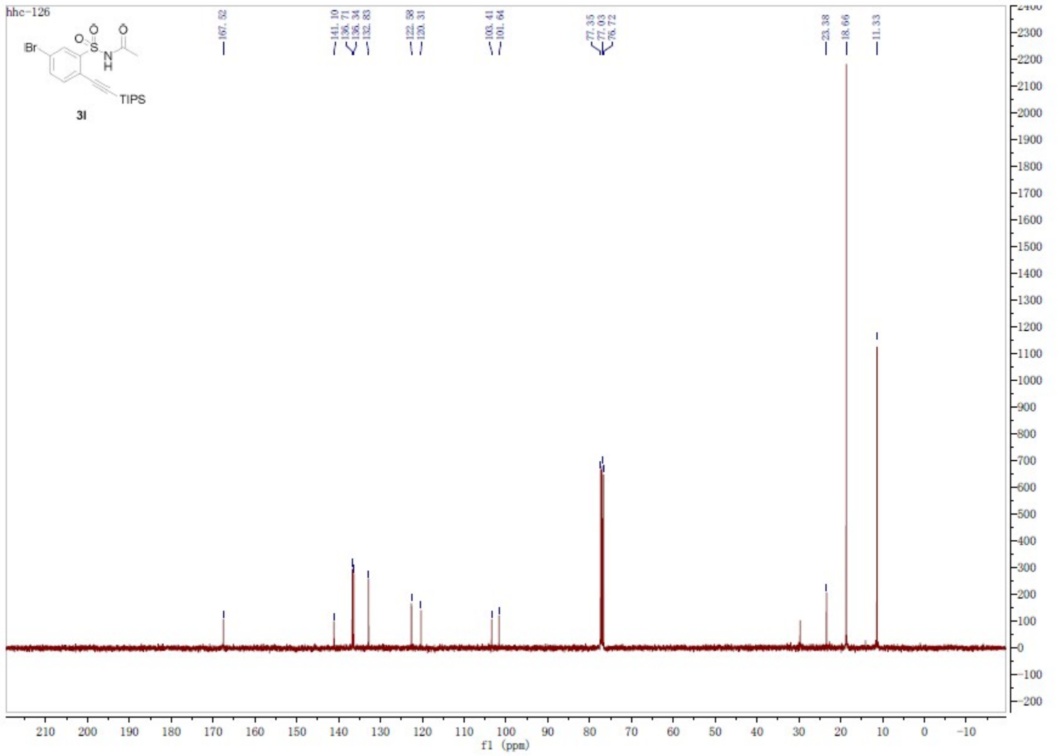

hhc-109
Br
TIPS
3j
8.06
8.01
7.99
7.78
7.78
7.64
7.64
7.62
7.62
7.26
2.09
1.26
1.24
1.23
1.22
1.22
1.21
1.19
1.17
1.16
0.94
1.07
1.02
1.00
3.06
21.07
f1 (ppm)

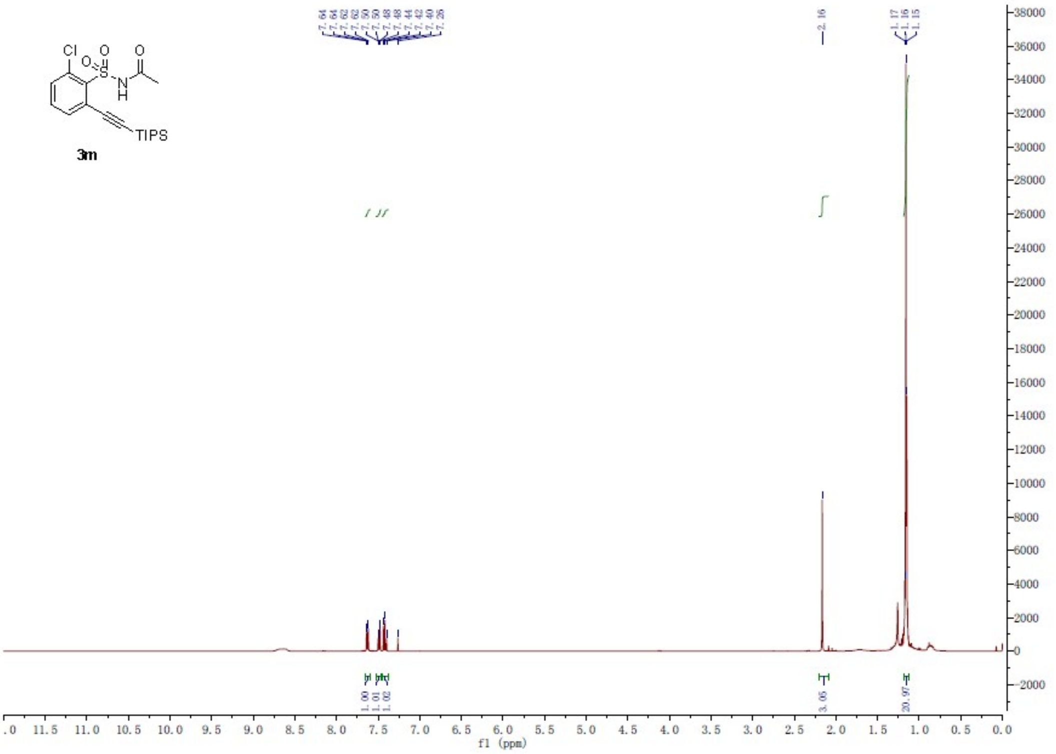

hhc-109
Br
TIPS
3j
167.46
138.64
138.05
131.77
131.56
128.22
123.20
103.71
101.06
23.35
18.67
11.34
f1 (ppm)

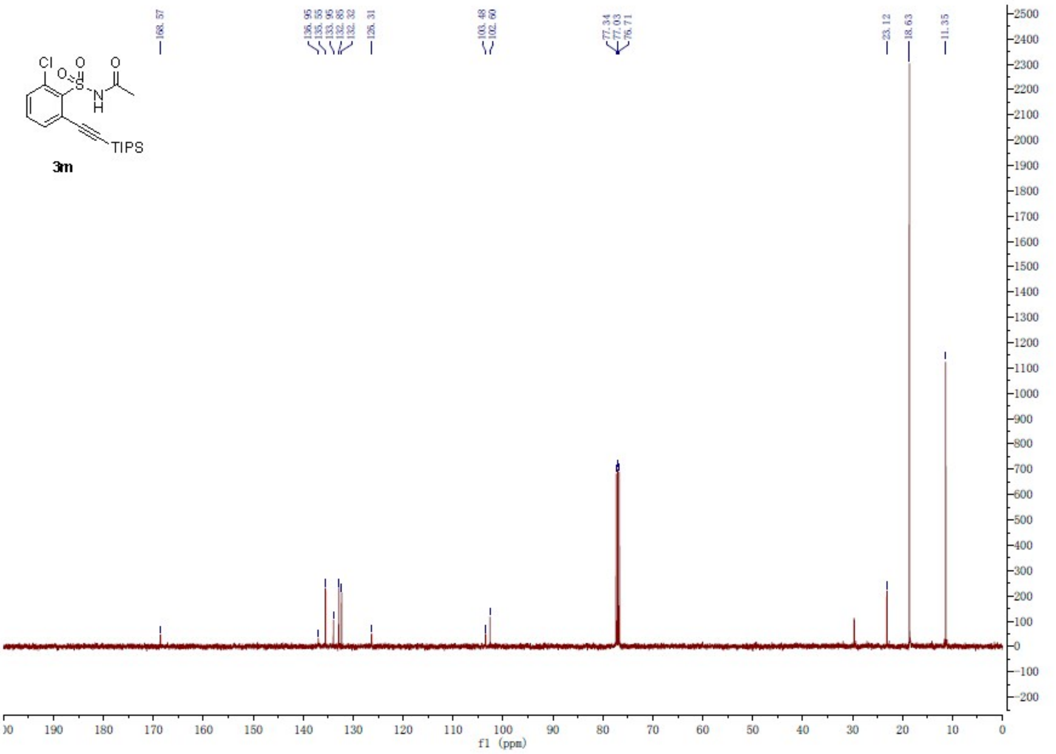

hhc-125
Cl
O
S
O
N
H
O
TIPS
3k
8.13
8.13
8.11
7.60
7.58
7.54
7.53
7.52
7.51
7.26
2.10
1.26
1.22
1.21
1.20
1.19
1.18
1.17
1.16
1.15
1.14
1.00
0.86
1.00
1.00
3.00
21.07
40000
35000
30000
25000
20000
15000
10000
5000
0
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

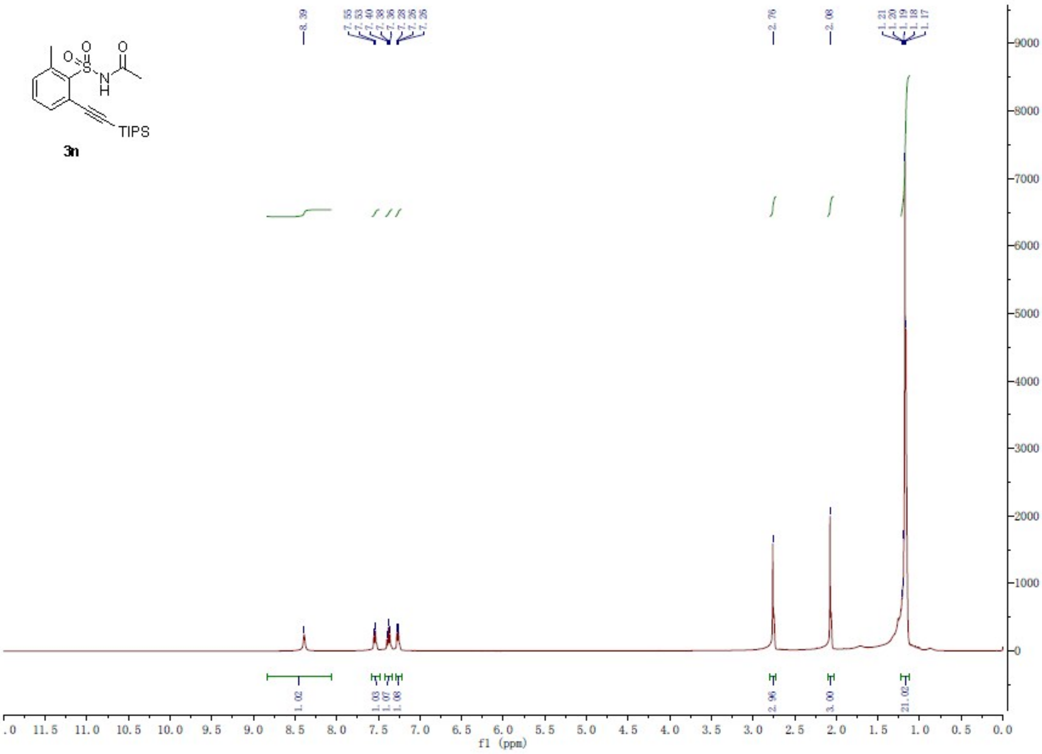

hhc-125
Cl
O
S
O
N
H
O
TIPS
3k
167.51
141.13
136.64
134.87
133.38
130.11
119.87
103.16
101.54
77.35
77.03
76.71
23.38
18.66
11.34
4200
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


hhc-126
Br
TIPS
3l
8.21
8.20
8.04
7.63
7.62
7.61
7.60
7.45
7.43
7.19
2.03
1.18
1.15
1.14
1.13
1.11
1.10
1.09
1.08
1.07
1.07
1.02
0.98
1.03
1.00
3.08
21.00
f1 (ppm)

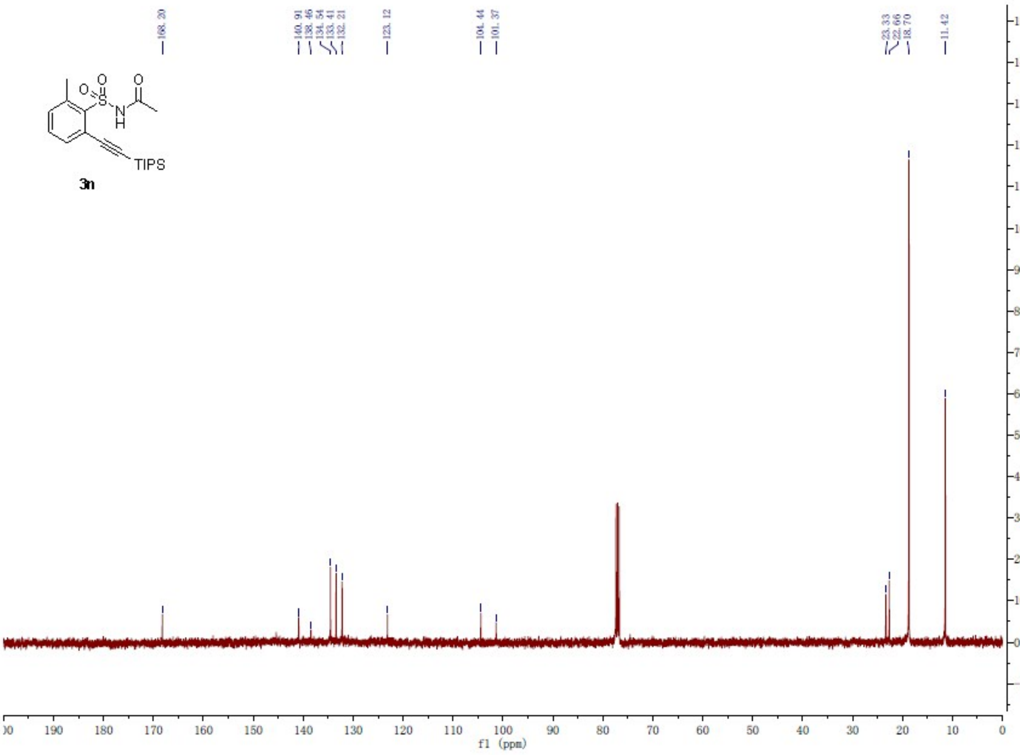

hhc-126
Br
TIPS
3l
167.52
141.10
136.71
136.34
132.83
122.58
120.31
103.41
101.64
77.35
77.03
76.72
23.38
18.66
11.33
f1 (ppm)


Cl
O
O
S
N
H
O
TIPS
3m
7.64
7.64
7.62
7.62
7.50
7.50
7.48
7.48
7.44
7.42
7.40
7.26
2.16
1.17
1.16
1.15
1.00
1.01
1.02
3.06
20.97
f1 (ppm)

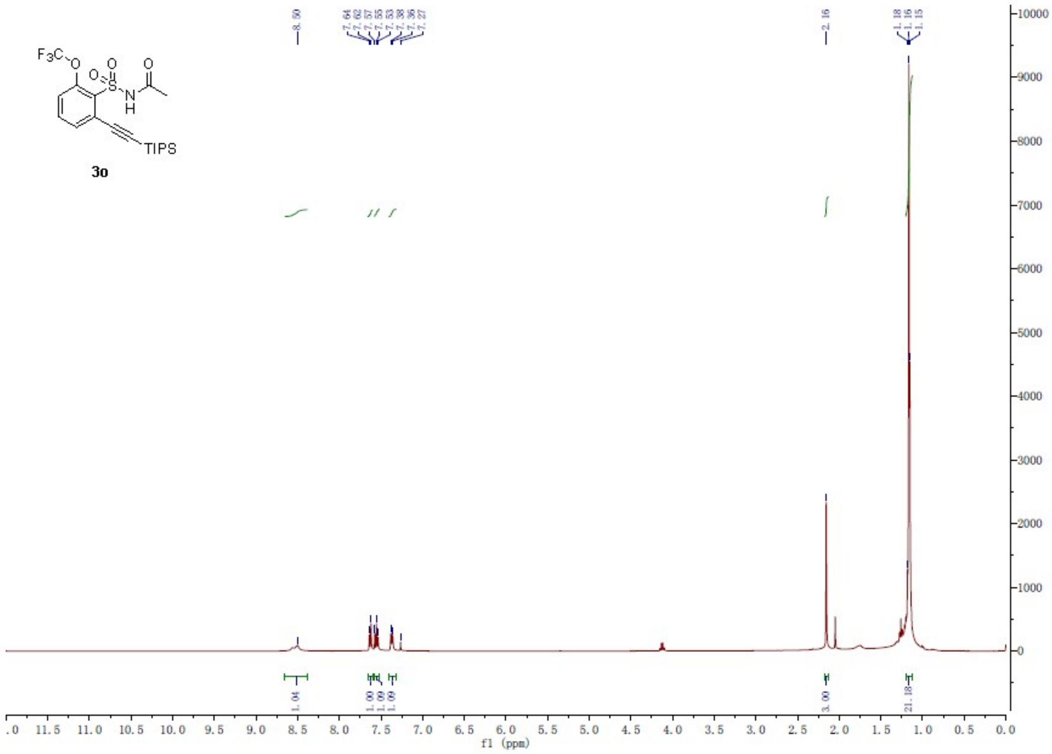

Cl
O
O
S
N
H
O
TIPS
3m
168.57
136.95
135.55
133.95
132.85
132.32
126.31
103.48
102.60
77.34
77.03
76.71
23.12
18.63
11.35
f1 (ppm)

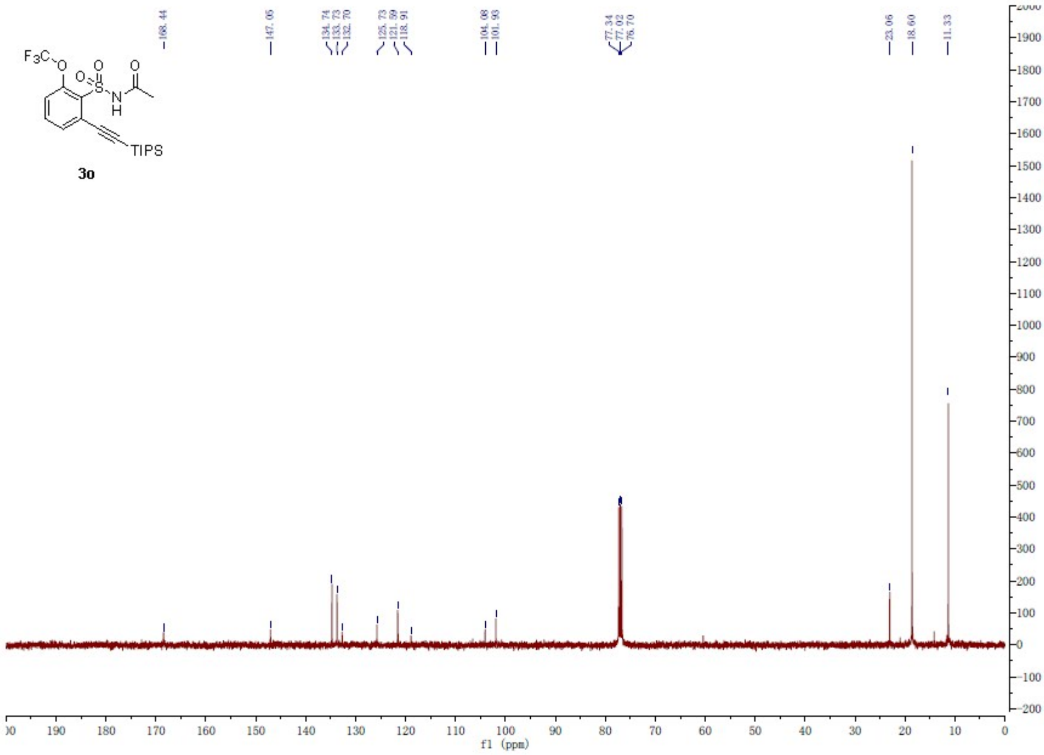


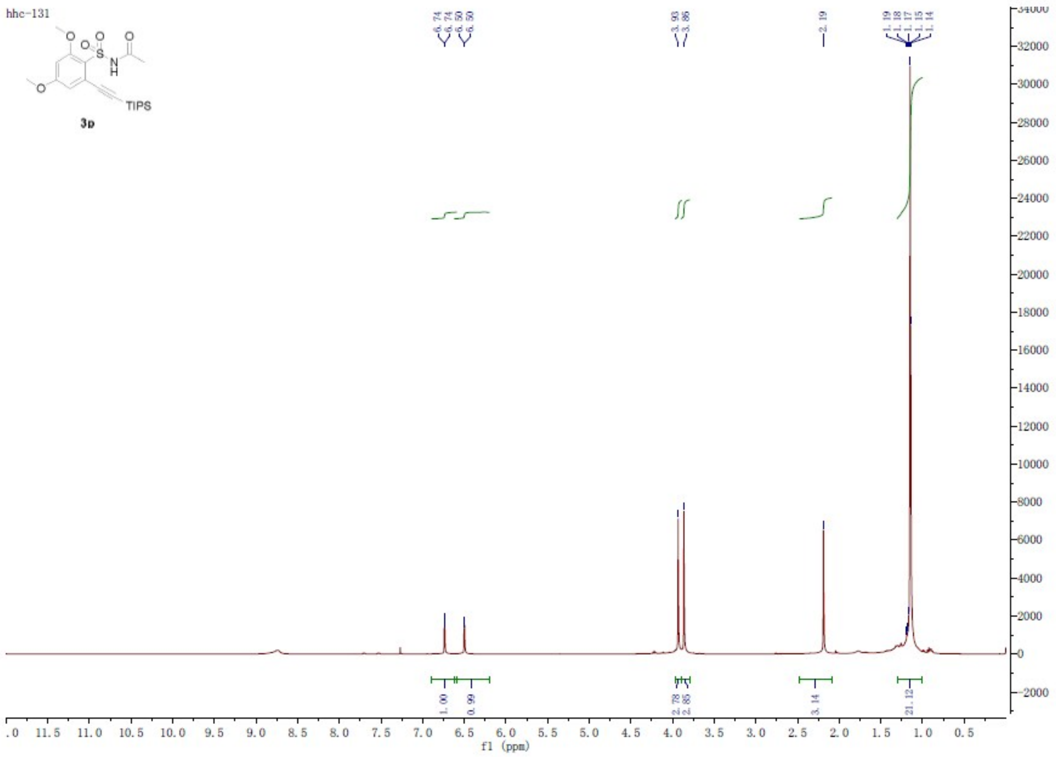
8.39
7.55
7.53
7.40
7.38
7.36
7.28
7.26
7.25
2.76
2.08
1.21
1.20
1.19
1.18
1.17
TIPS
3n
1.02
1.03
1.07
1.08
2.96
3.00
21.02
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

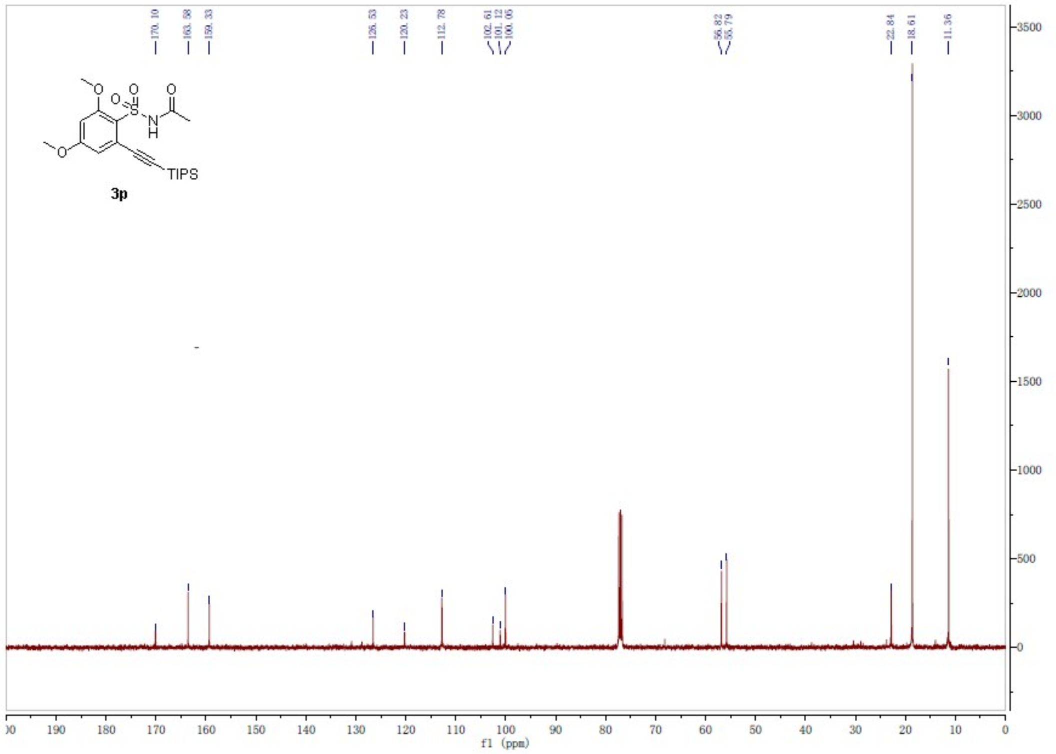


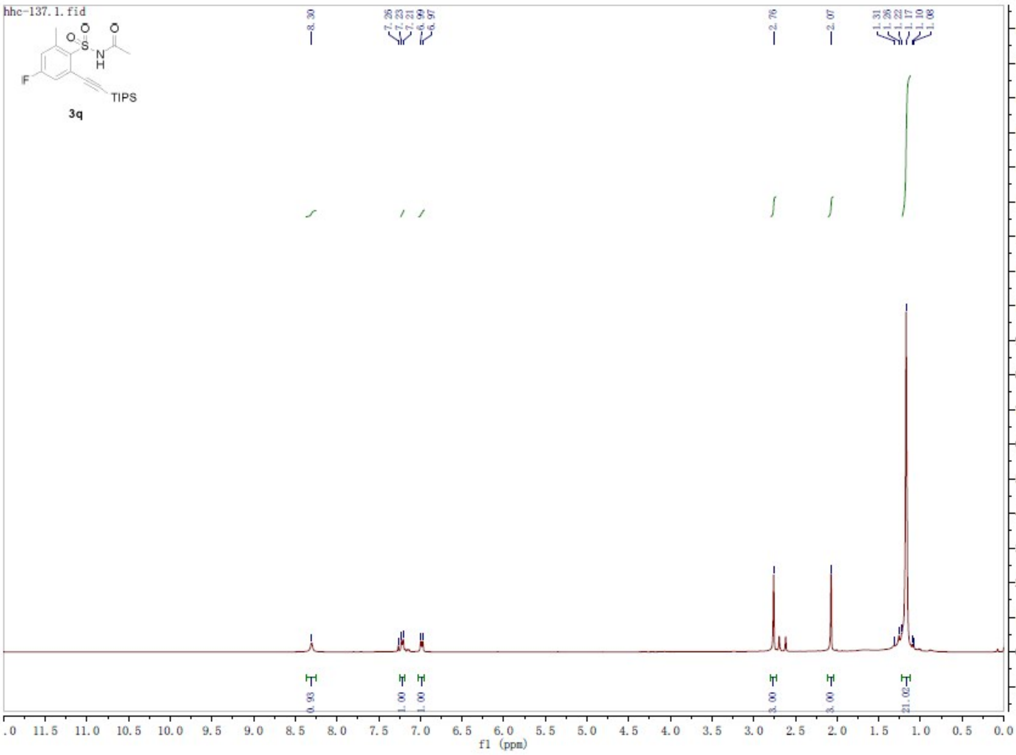
168.20
140.91
138.46
134.54
133.41
132.21
123.12
104.44
101.37
23.33
22.66
18.70
11.42
TIPS
3n
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

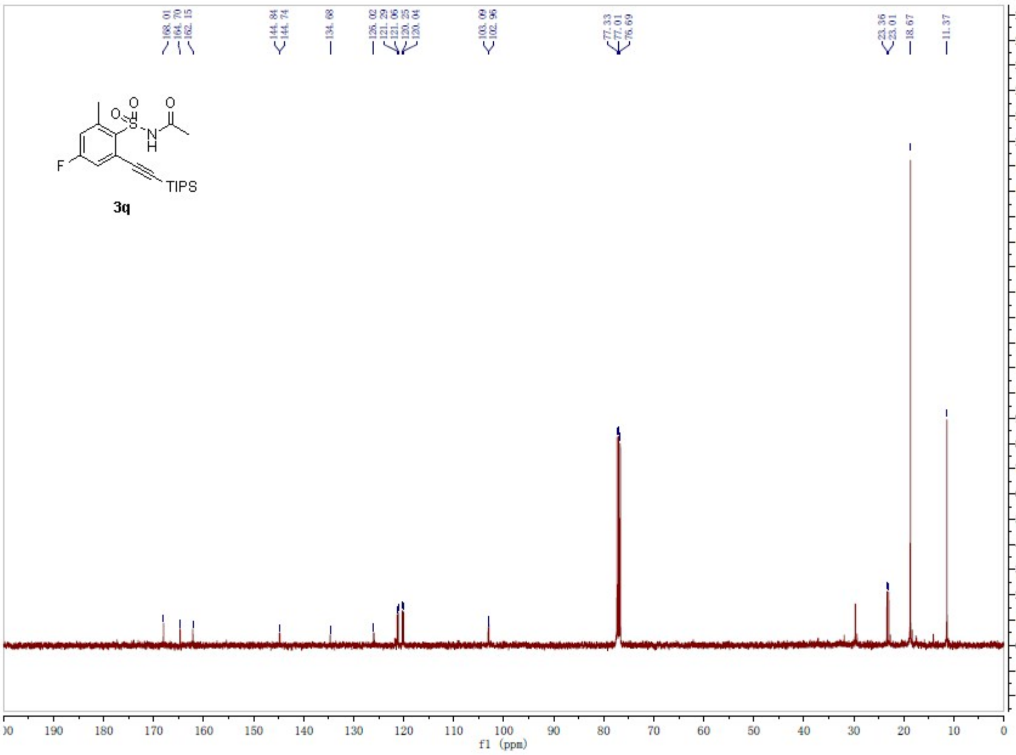

F3C O O O S N H O
TIPS
3o
8.50
7.64
7.62
7.57
7.55
7.53
7.38
7.36
7.27
2.16
1.18
1.16
1.15
1.04
1.00
1.09
1.09
3.00
21.18
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

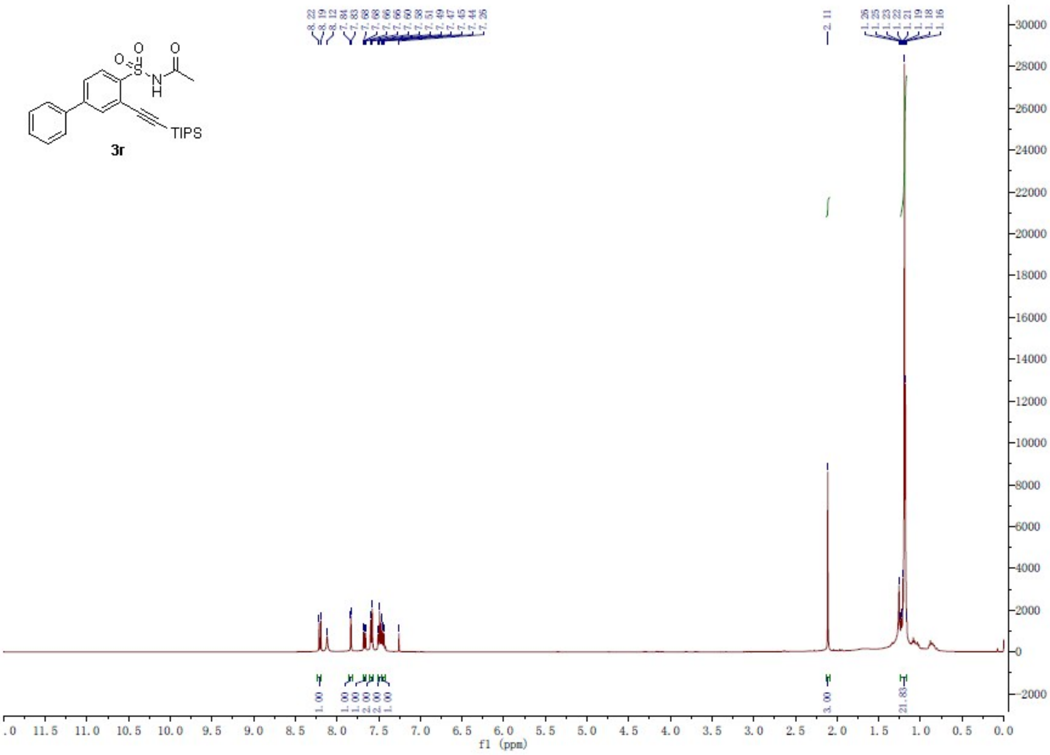

F3C O O O S N H O
TIPS
3o
168.44
147.05
134.74
133.73
132.70
125.73
121.59
118.91
104.08
101.93
77.34
77.02
76.70
23.06
18.60
11.33
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

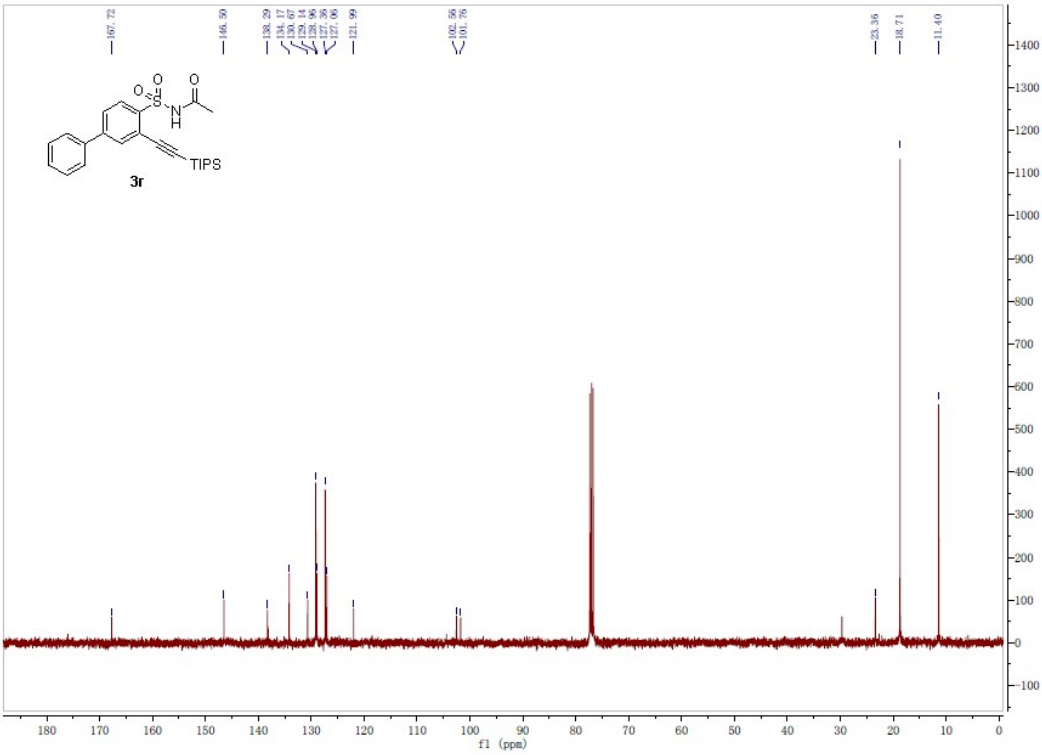

hhc-131
TIPS
3p
6.74
6.74
6.50
6.50
3.93
3.86
2.19
1.19
1.18
1.17
1.15
1.14
1.00
0.99
2.78
2.85
3.14
21.12
f1 (ppm)

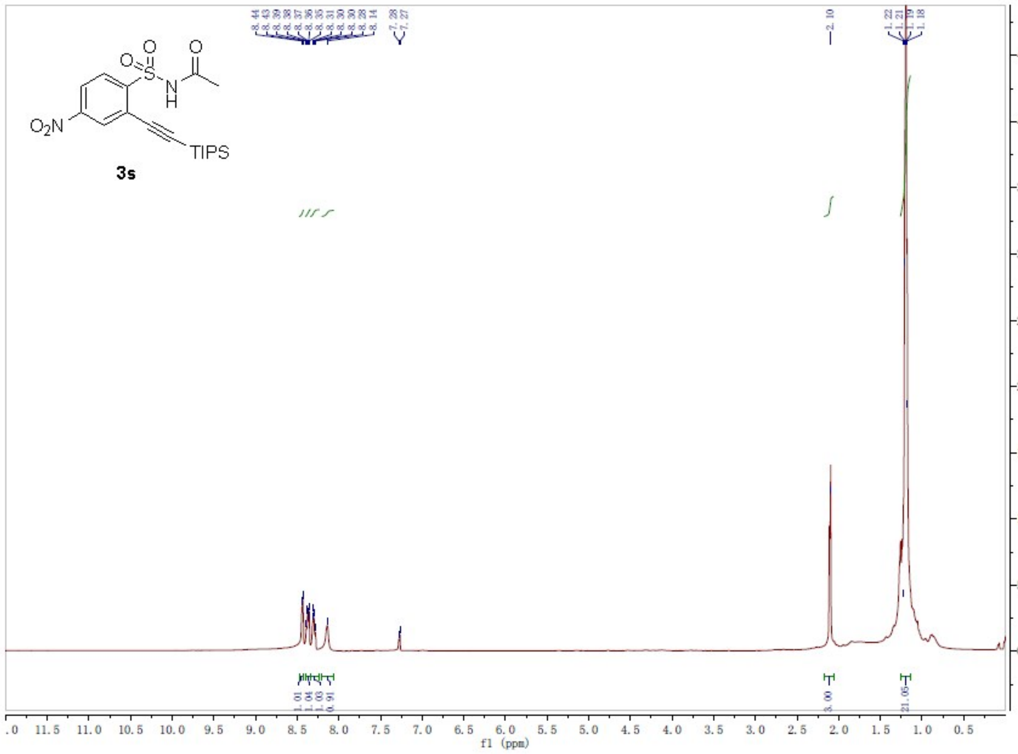

170.10
163.58
159.33
126.53
120.23
112.78
102.61
101.12
100.05
56.82
55.79
22.84
18.61
11.36
TIPS
3p
f1 (ppm)

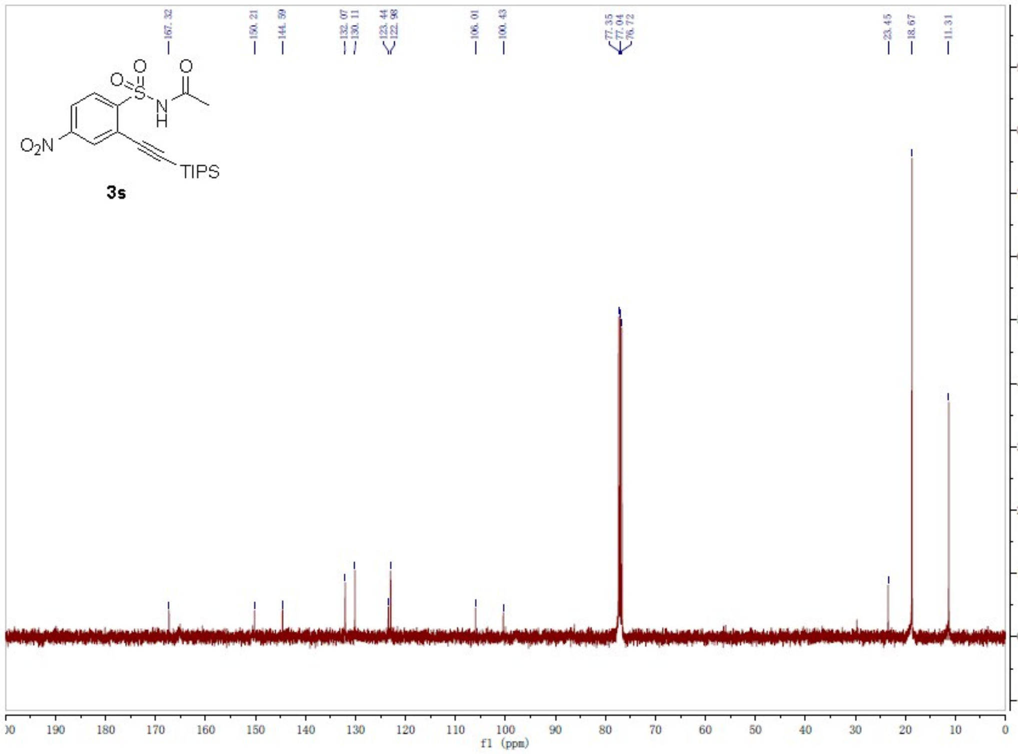

hhc-137.1.fid
3q
F
TIPS
O
S
N
H
8.30
7.25
7.23
7.21
6.99
6.97
2.76
2.07
1.31
1.26
1.22
1.17
1.10
1.08
0.93
1.00
1.00
3.00
3.00
21.02
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

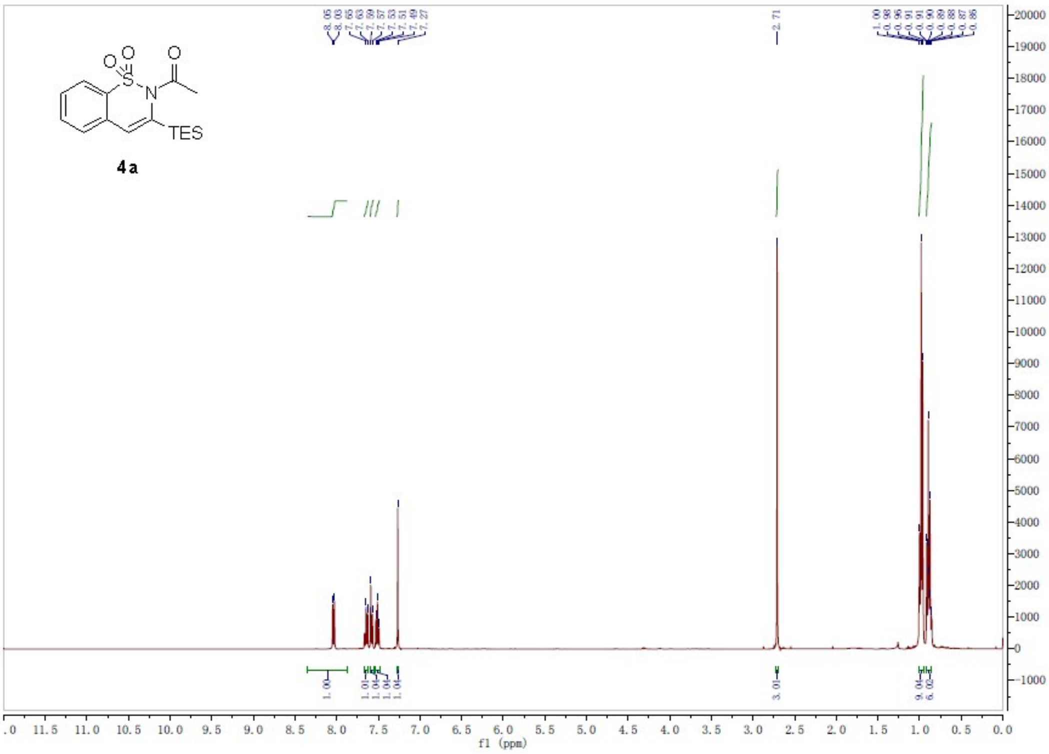

3q
F
TIPS
O
S
N
H
168.01
164.70
162.15
144.84
144.74
134.68
126.02
121.29
121.06
120.25
120.04
103.09
102.96
77.33
77.01
76.69
23.36
23.01
18.67
11.37
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

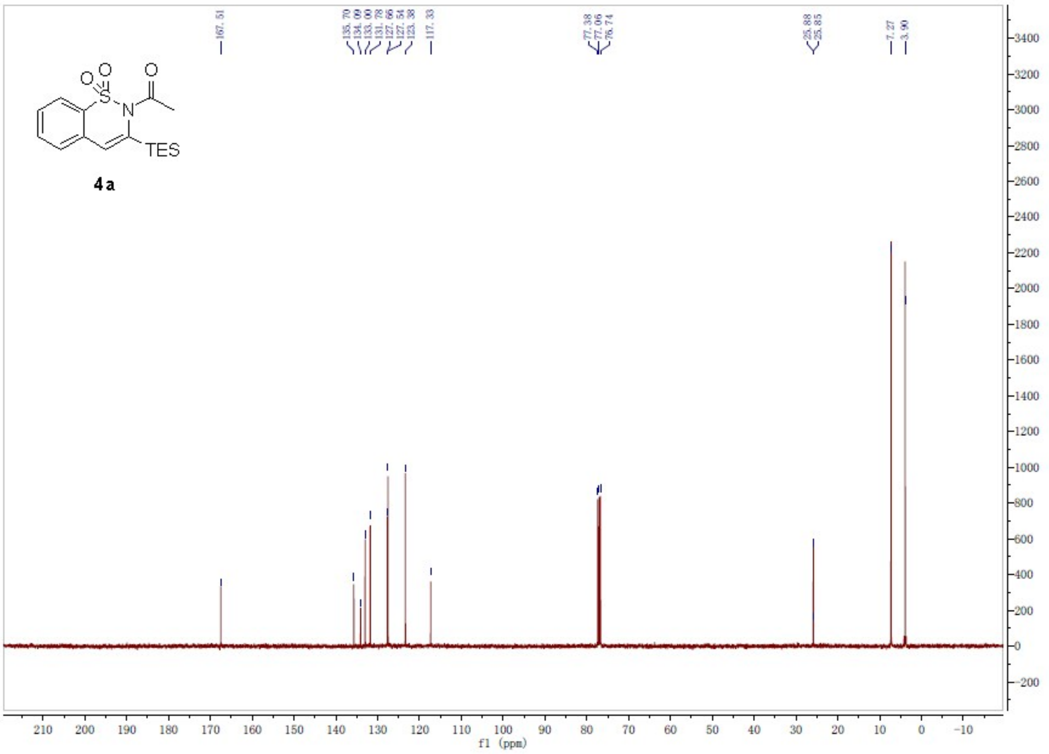

8.22
8.19
8.12
7.84
7.83
7.68
7.68
7.66
7.65
7.60
7.58
7.51
7.49
7.47
7.45
7.44
7.26
2.11
1.26
1.25
1.23
1.22
1.21
1.19
1.18
1.16
O
O
S
N
H
O
TIPS
3r
1.00
1.00
1.00
2.00
2.00
1.00
3.00
21.83
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

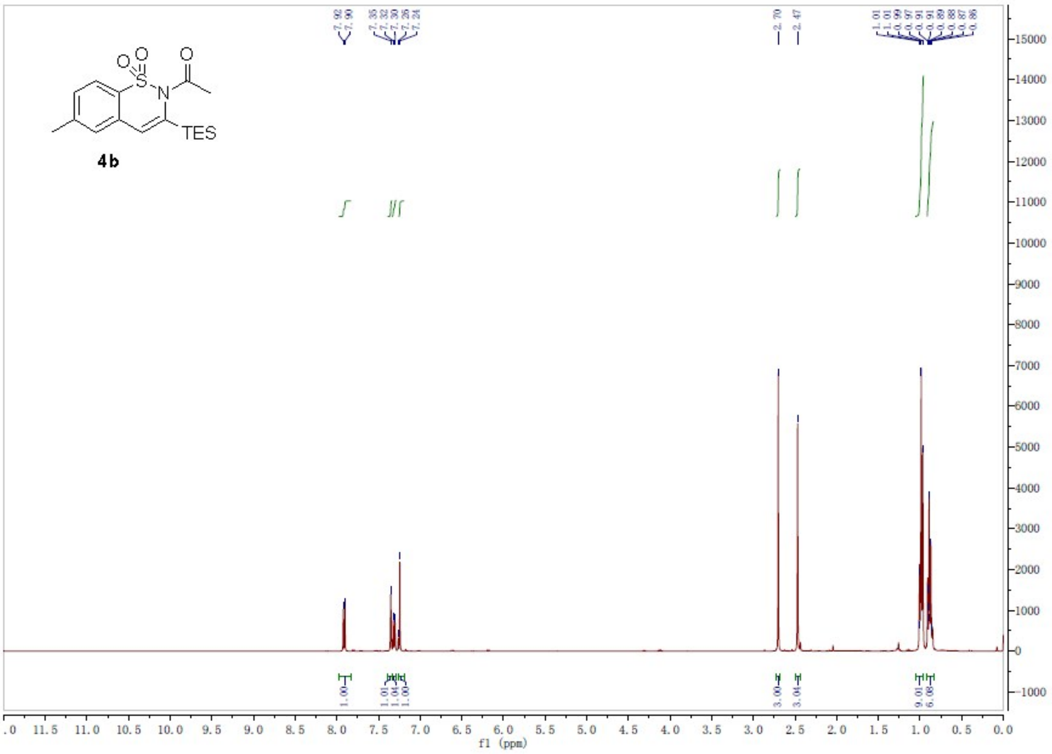

167.72
146.50
138.29
134.17
130.67
129.14
128.96
127.36
127.06
121.99
102.56
101.76
23.36
18.71
11.40
O
O
S
N
H
O
TIPS
3r
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

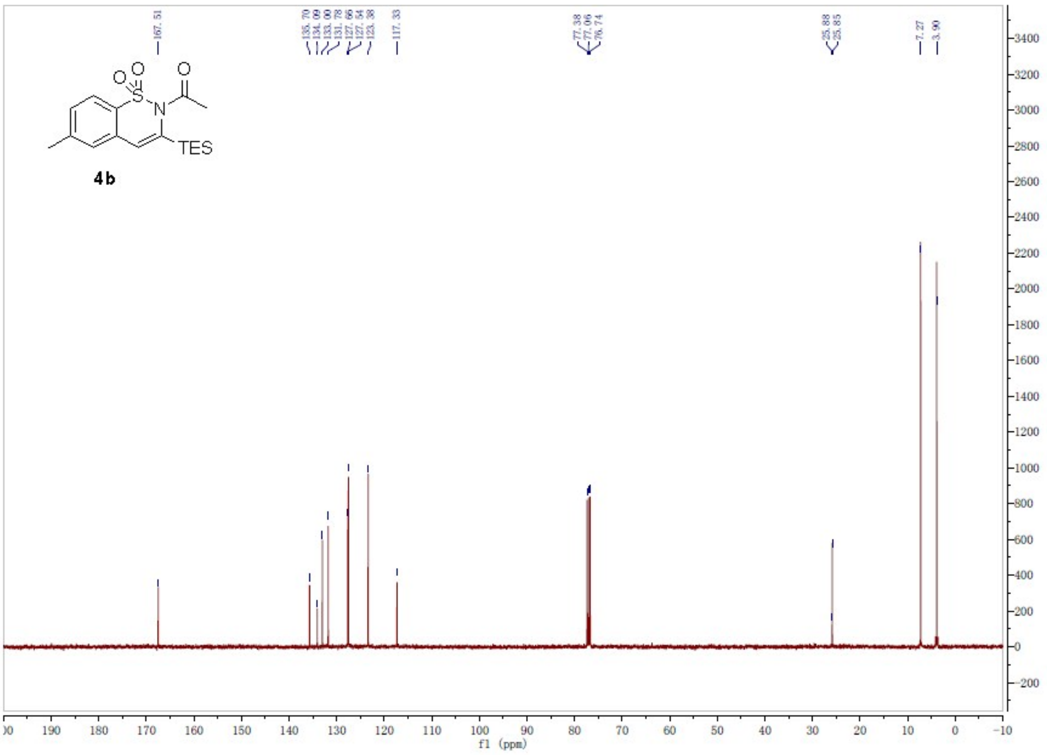

3s
TIPS
O2N
8.44
8.43
8.39
8.38
8.37
8.36
8.35
8.31
8.30
8.30
8.28
8.14
7.28
7.27
2.10
1.22
1.21
1.19
1.18
1.01
1.04
1.03
0.91
3.00
21.05
f1 (ppm)

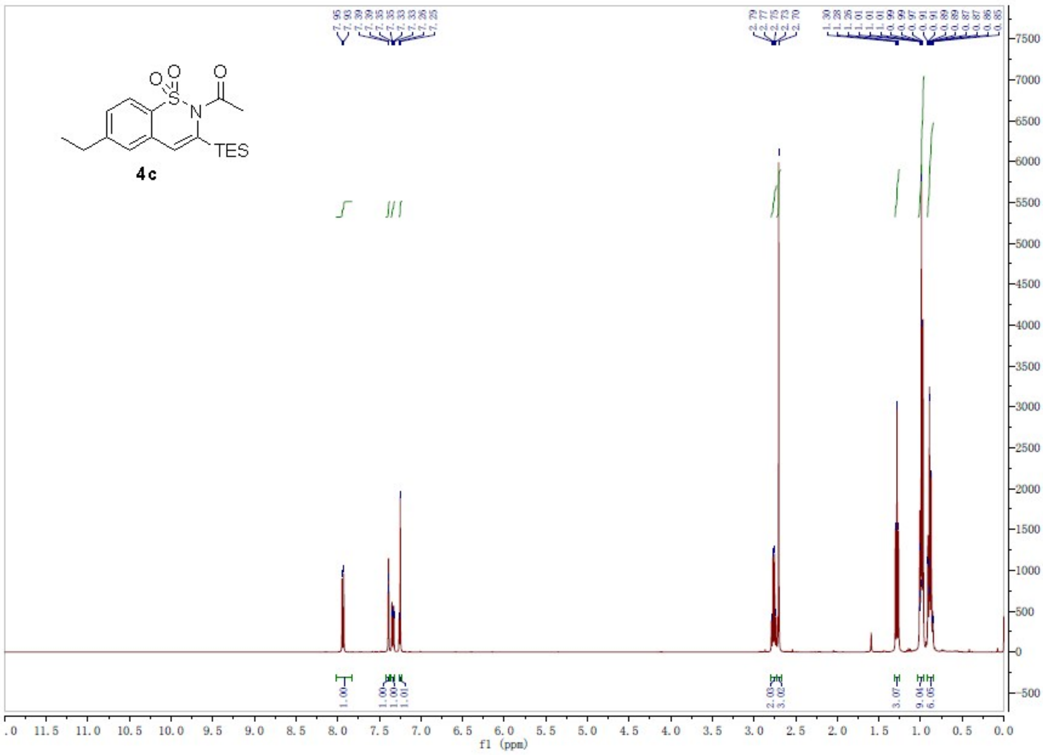

3s
TIPS
O2N
167.32
150.21
144.59
132.07
130.11
123.44
122.98
106.01
100.43
77.35
77.04
76.72
23.45
18.67
11.31
f1 (ppm)

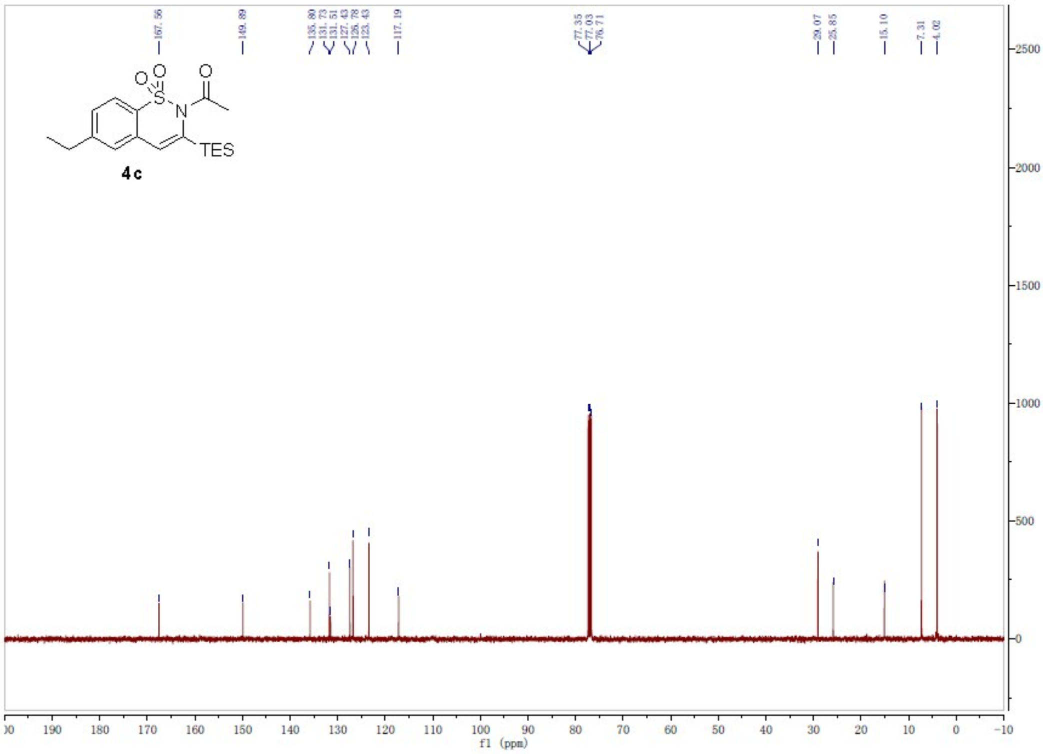

O
O
S
N
O
TES
4a
8.05
8.03
7.65
7.63
7.59
7.57
7.53
7.51
7.49
7.27
2.71
1.00
0.98
0.96
0.91
0.91
0.90
0.89
0.88
0.87
0.86
1.00
1.01
1.04
1.04
1.04
3.01
9.04
6.02
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

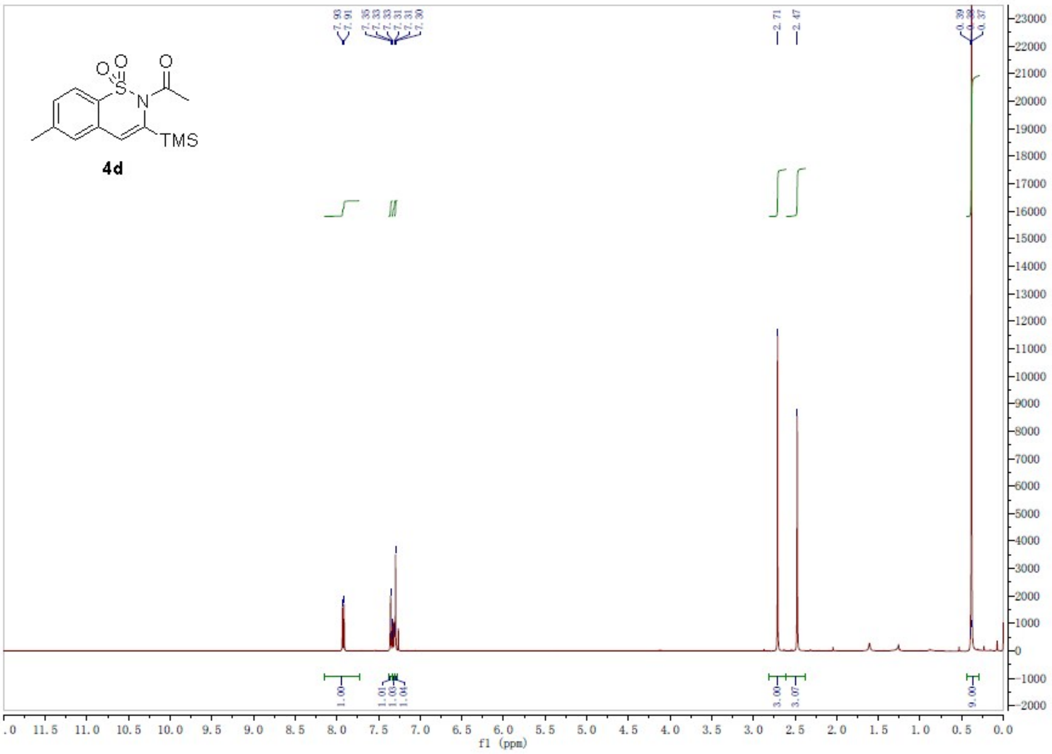

O
O
S
N
O
TES
4a
167.51
135.70
134.09
133.00
131.78
127.66
127.54
123.38
117.33
77.38
77.06
76.74
25.88
25.85
7.27
3.90
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

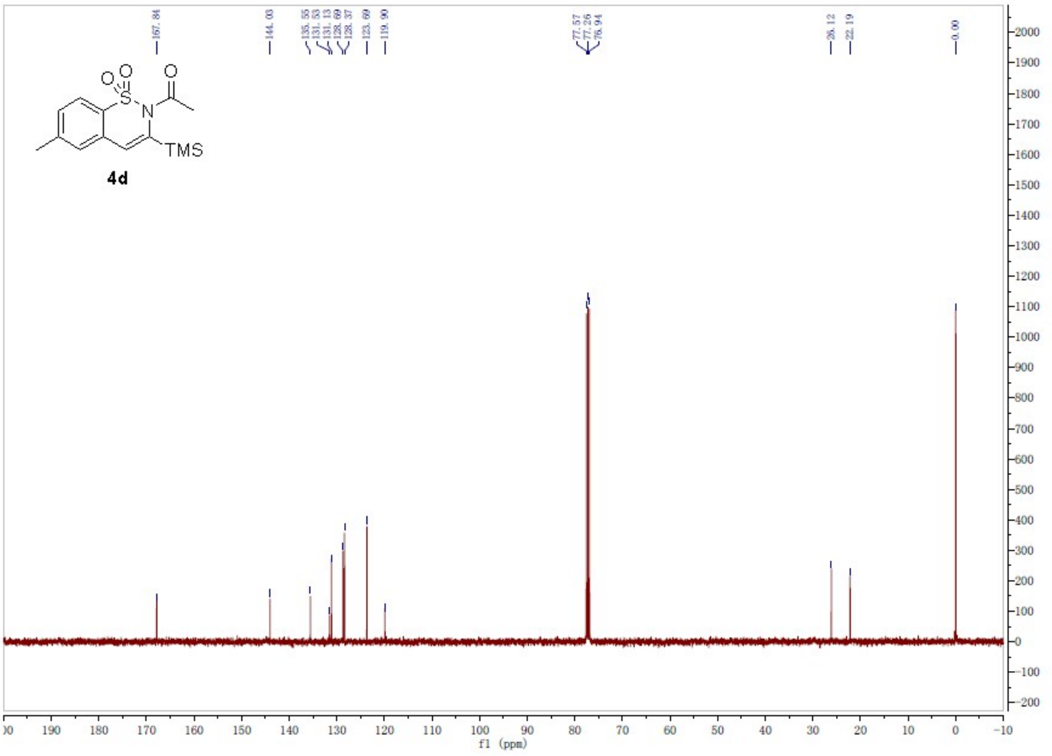

4b
TES
7.92
7.90
7.35
7.32
7.30
7.25
7.24
2.70
2.47
1.01
1.01
0.99
0.97
0.91
0.91
0.89
0.88
0.87
0.86
1.00
1.01
1.04
1.00
3.00
3.04
9.01
6.08
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

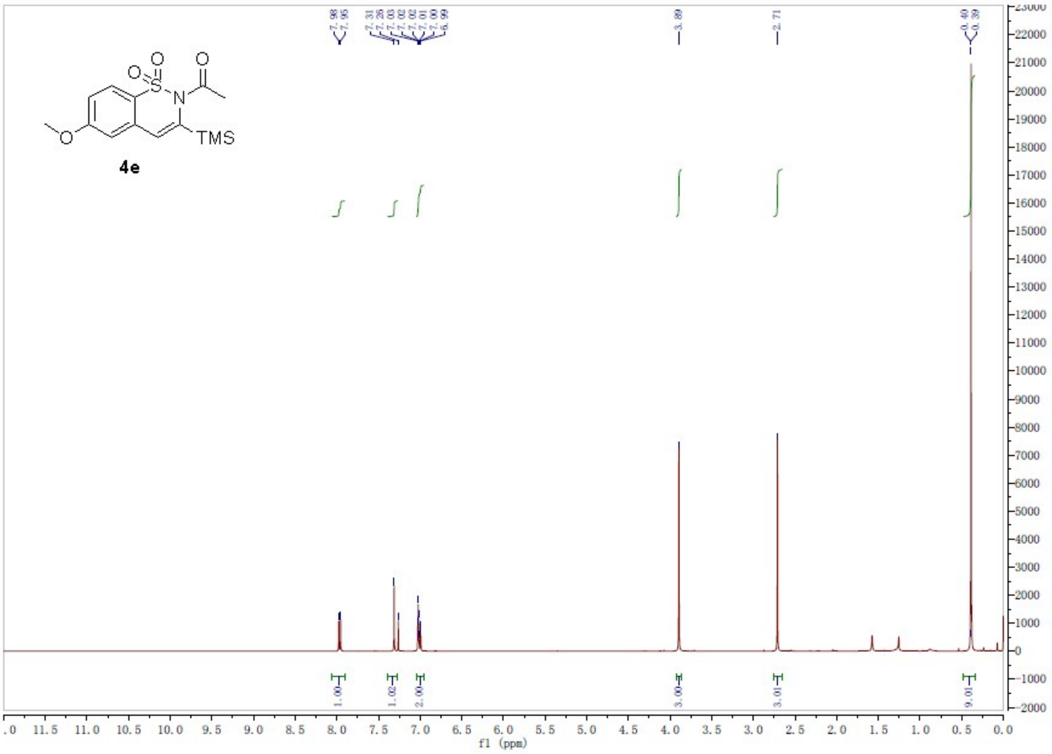

4b
TES
167.51
135.70
134.09
133.00
131.78
127.66
127.54
123.38
117.33
77.38
77.06
76.74
25.88
25.85
7.27
3.90
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

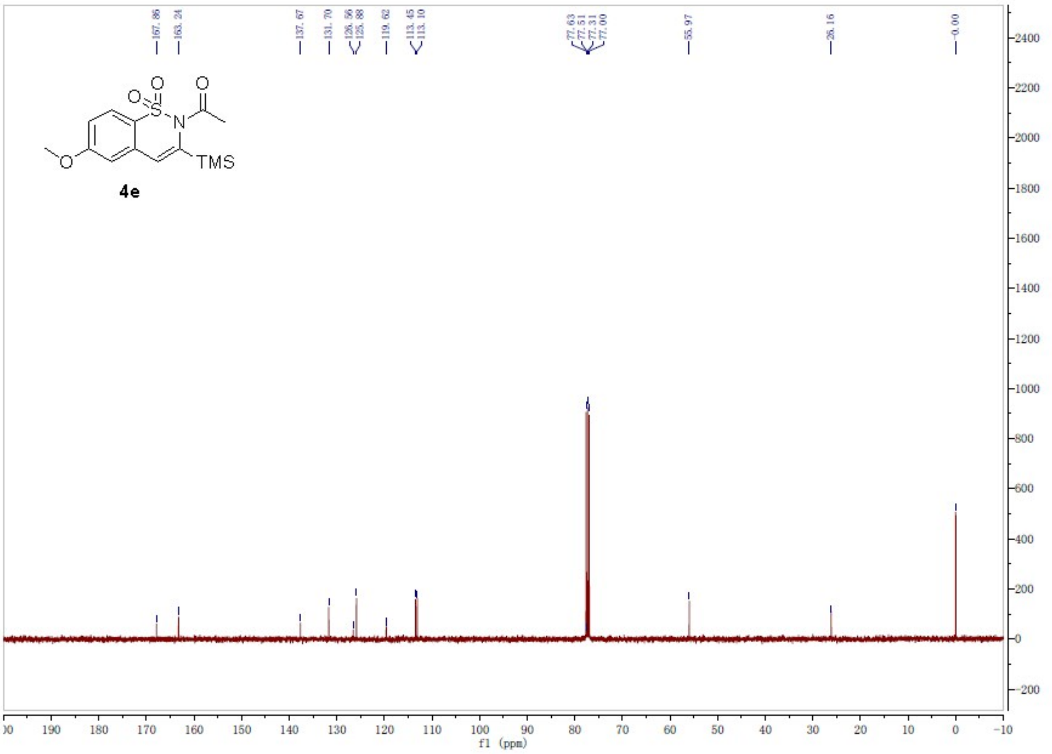

7.95
7.93
7.39
7.39
7.35
7.35
7.33
7.33
7.26
7.25
2.79
2.77
2.75
2.73
2.70
1.30
1.28
1.26
1.01
1.01
1.01
0.99
0.99
0.97
0.91
0.91
0.89
0.89
0.87
0.87
0.86
0.85
O
O
S
N
O
TES
4c
1.00
1.00
1.00
1.01
2.03
3.02
3.07
9.04
6.05
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

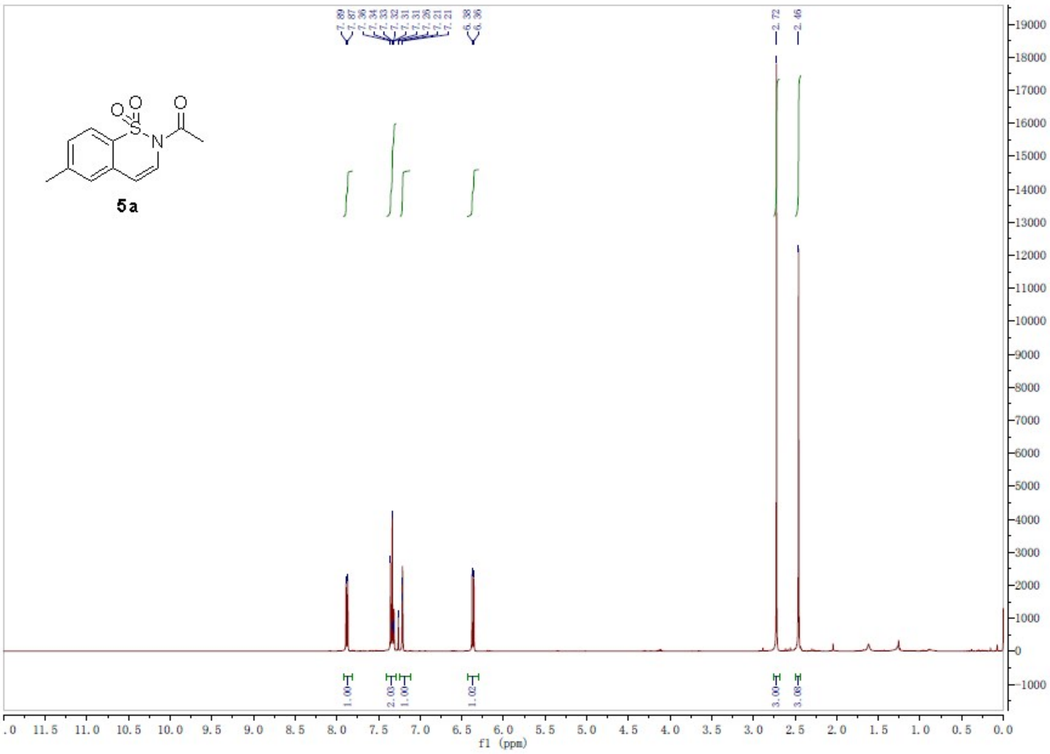

167.56
149.89
135.80
131.73
131.51
127.43
126.78
123.43
117.19
77.35
77.03
76.71
29.07
25.85
15.10
7.31
4.02
O
O
S
N
O
TES
4c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2500
2000
1500
1000
500
0

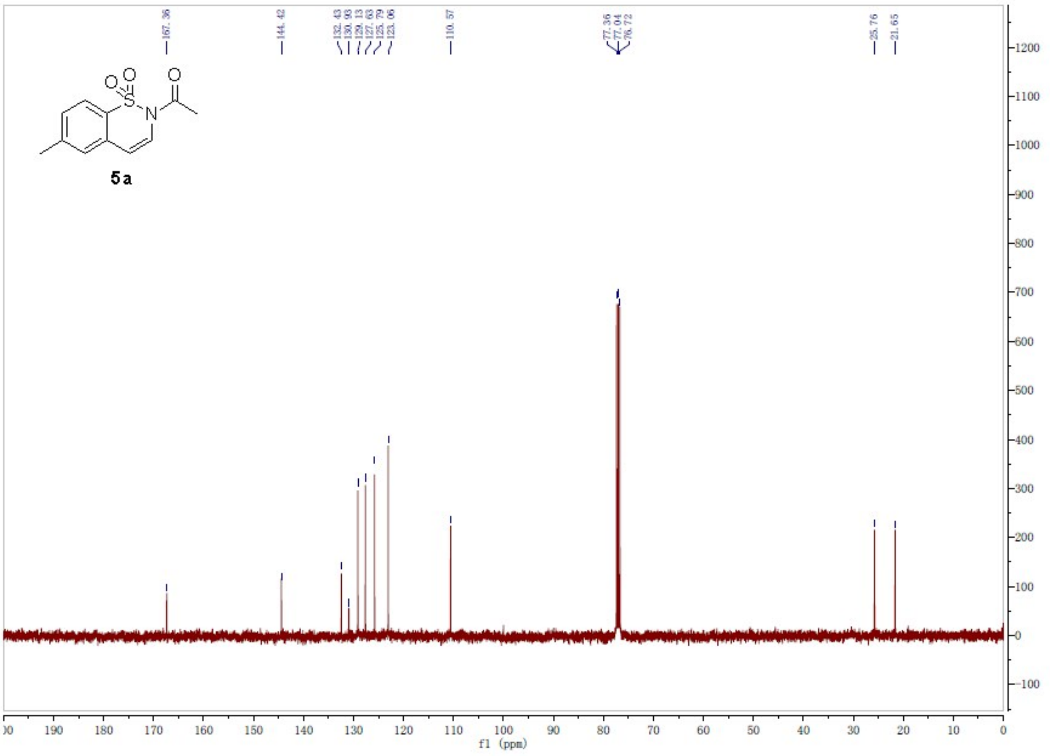

7.93
7.91
7.35
7.33
7.33
7.31
7.31
7.30
2.71
2.47
0.39
0.38
0.37
TMS
4d
1.00
1.01
1.03
1.04
3.00
3.07
9.00
f1 (ppm)

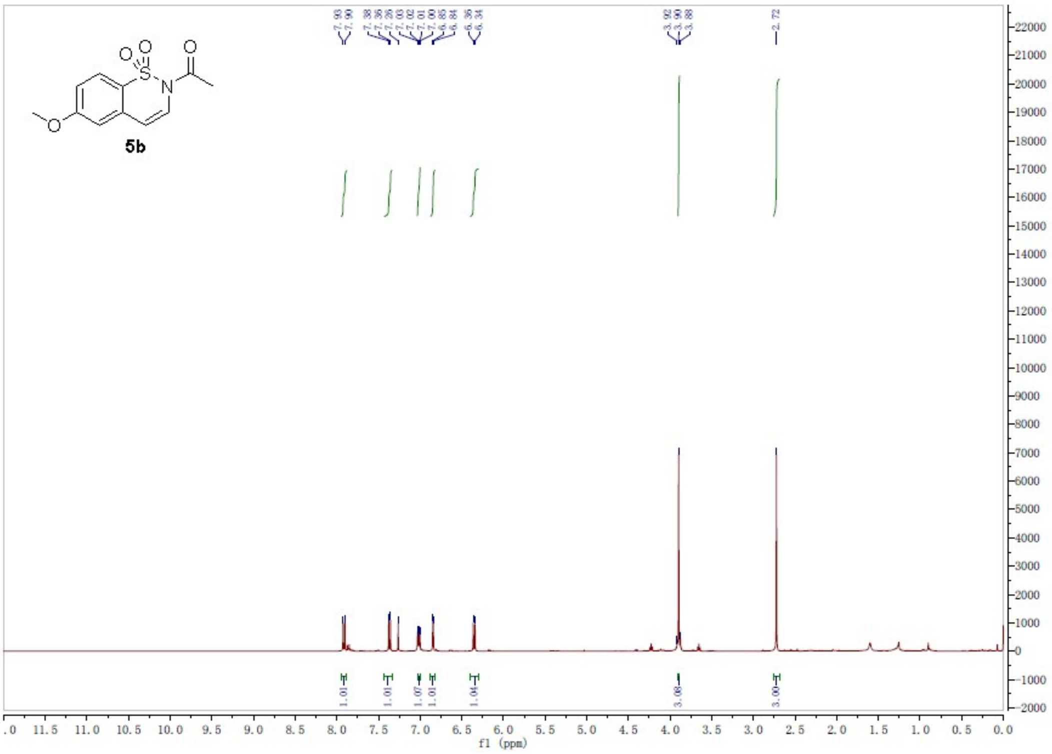

167.84
144.03
135.55
131.53
131.13
128.69
128.37
123.69
119.90
77.57
77.26
76.94
26.12
22.19
0.00
TMS
4d
f1 (ppm)

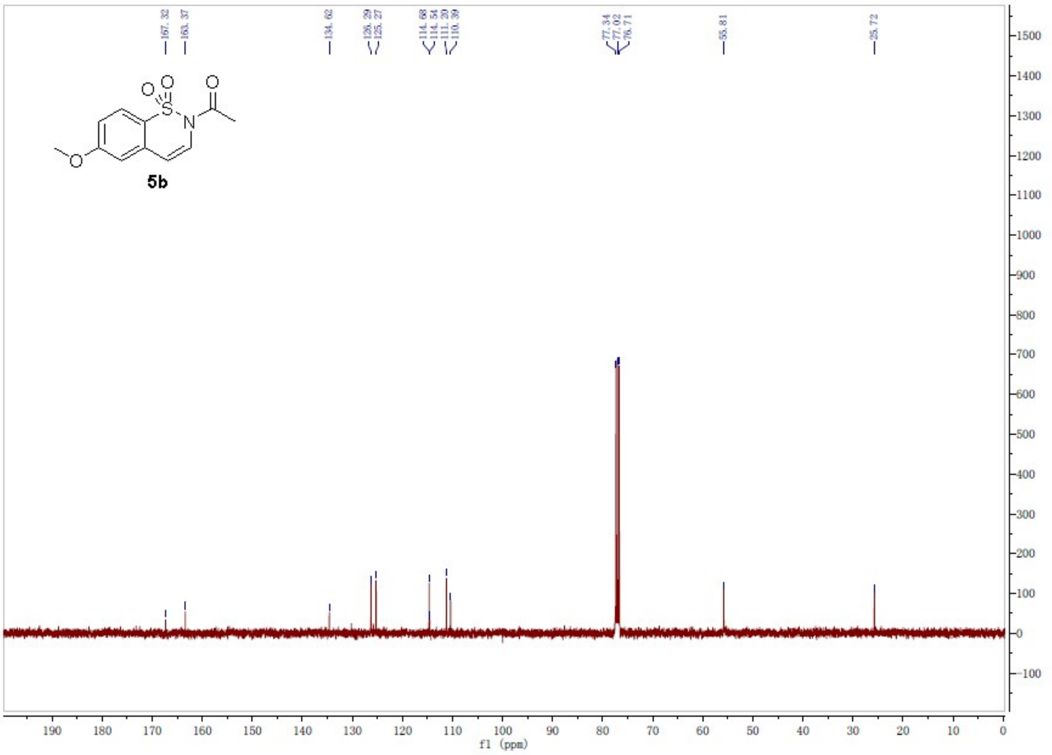

4e
O
O
S
N
O
O
TMS
7.98
7.95
7.31
7.26
7.03
7.02
7.02
7.01
7.00
6.99
3.89
2.71
0.40
0.39
1.00
1.02
2.00
3.00
3.01
9.01
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


4e
O
O
S
N
O
O
TMS
167.86
163.24
137.67
131.70
126.56
125.88
119.62
113.45
113.10
77.63
77.51
77.31
77.00
55.97
26.16
-0.00
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5a
7.89
7.87
7.36
7.34
7.33
7.32
7.31
7.31
7.26
7.21
7.21
6.38
6.36
2.72
2.46
1.00
2.03
1.00
1.02
3.00
3.08
f1 (ppm)


5a
167.36
144.42
132.43
130.93
129.13
127.63
125.79
123.06
110.57
77.36
77.04
76.72
25.76
21.65
f1 (ppm)


5b
7.93
7.90
7.38
7.36
7.29
7.03
7.02
7.01
7.00
6.85
6.84
6.36
6.34
3.92
3.90
3.88
2.72
1.01
1.01
1.07
1.01
1.04
3.08
3.00
f1 (ppm)


5b
167.32
163.37
134.62
126.29
125.27
114.68
114.54
111.20
110.39
77.34
77.02
76.71
55.81
25.72
f1 (ppm)