

Supporting Information

Rh(II)-Catalyzed Branch-Selective C–H Alkylation of Aryl Sulfonamides with Vinylsilanes

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1. General information.

All chemicals were measured and added to a J-Young Schlenk tube or a sealed vial under an atmosphere of air. The reaction vial was then closed and kept in an oil bath. ^1H NMR (400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz), and ^{19}F NMR (376 Hz) spectra were recorded on a JEOL ECS-400 spectrometer in CDCl_3 with tetramethylsilane as an internal standard. All ^1H NMR chemical shifts were recorded in ppm (δ) and referenced to tetramethylsilane. All $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts are given in ppm (δ) relative to carbon resonances in CDCl_3 at δ 77.16. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer; absorptions are reported in reciprocal centimetres with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-700 spectrometer. Melting points were determined using a Stanford Research Systems apparatus. Flash column chromatography was performed using SiO_2 F60 (0.040–0.0663 mm, 230-400 mesh). Some compounds were isolated by LC-908 HPLC (GPC) or HPLC (Phenomenex Luna 5u Silica (2) 100 $\times$ 21.20 mm column with hexane/EtOAc as an eluent).

2. Materials.

$[\text{Rh}(\text{OAc})(\text{cod})]_2$ was prepared from $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ by following a literature procedure.¹ $\text{RhCl}(\text{PPh}_3)_3$, $[\text{Rh}(\text{OAc})_2]_2$, and $[\text{RhCp}^*\text{Cl}_2]_2$ were used as received from Tokyo Chemical Industry (TCI). The sulfonamides listed in Table S1 were prepared according to a literature

procedure.² PhSO₂NHAc was prepared according to the literature procedure.³ PhSO₂NH₂ and PhSO₂NHPh were used as received from TCI. All chemicals were used as received without further purification. Solvents (DCM, toluene, EtOAc, hexane, and CDCl₃) were used without further purification.

General procedure for the preparation of sulfonamide starting materials.

In a dry three-necked round bottom flask, 8-aminoquinoline (1.441 g, 10.0 mmol, 1.0 equiv) and triethylamine (1.8 mL, 13.0 mmol, 1.3 equiv) were dissolved in CH₂Cl₂ (25 mL). After cooling the reaction mixture to 0 °C, a suitable sulfonyl chloride (10.0 mmol, 1.0 equiv) in 15 mL of CH₂Cl₂ was added portion wise over a period of about 10 minutes. The resulting mixture was allowed to warm to room temperature and then stirred overnight. After the reaction reached completion, the crude mixture was washed with saturated aqueous NaHCO₃ (20 mL) and a brine solution (20 mL). The aqueous layer was washed three times with 20 mL portions of CH₂Cl₂. The combined organic phases were then dried over anhydrous Na₂SO₄ and the volatiles were evaporated to dryness. The resulting crude mixture was purified by flash chromatography on silica gel (eluent: hexane/EtOAc/acetone = 10/3/1).

Table S1. Synthesis sulfonamide starting materials.

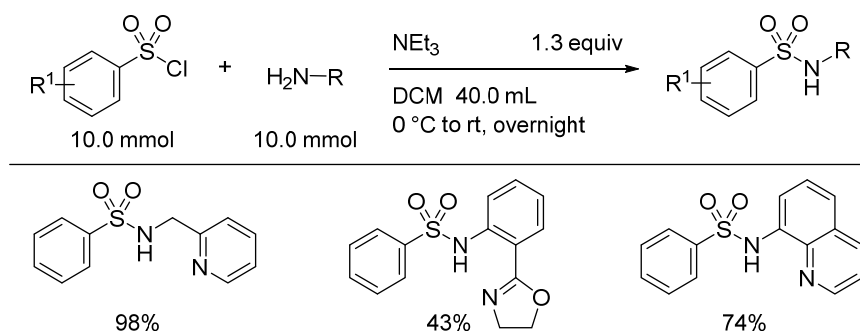
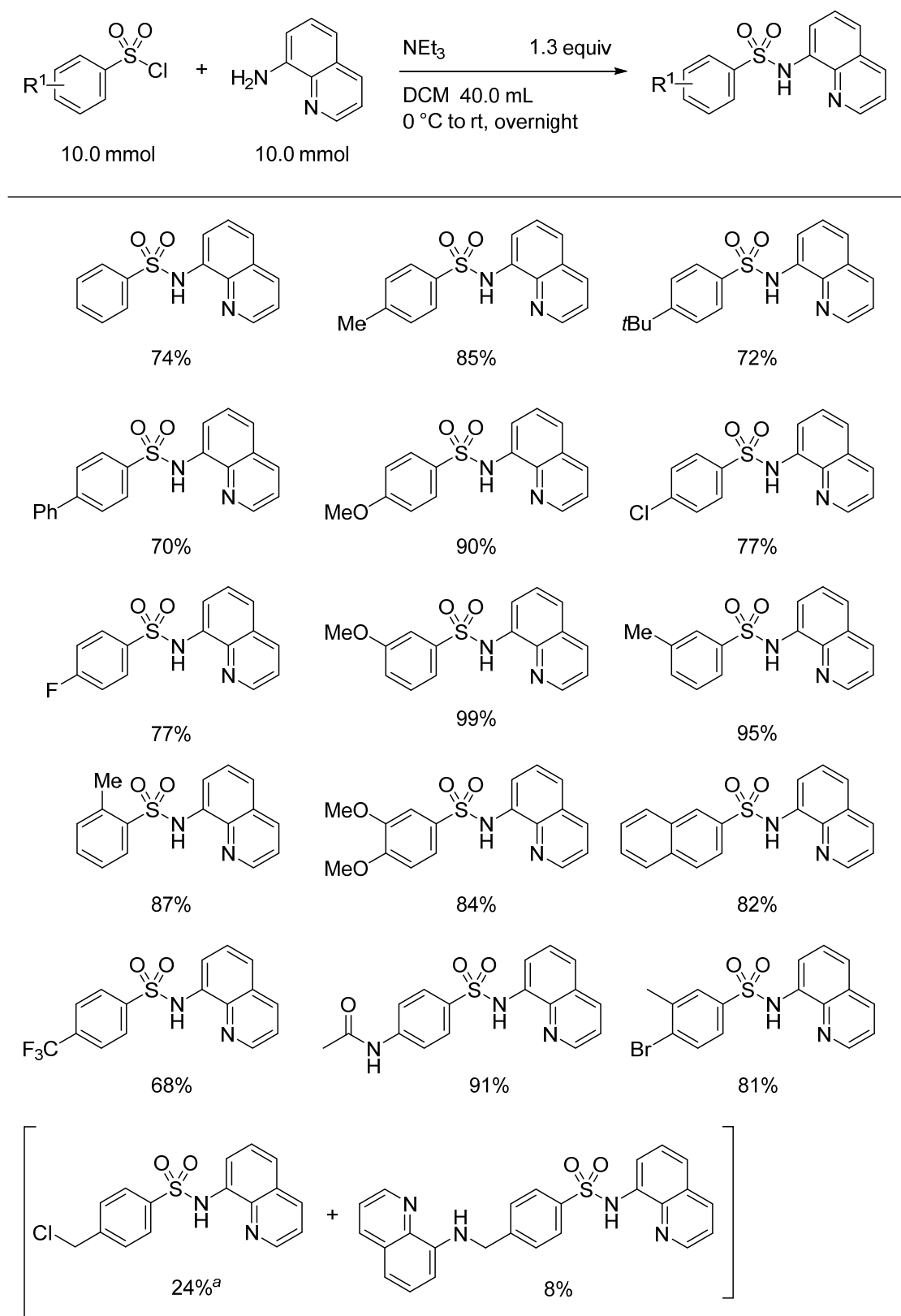


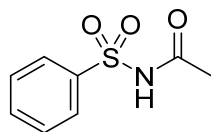
Table S2. Synthesis sulfonamide starting materials.



^a – 4-(Bromomethyl)benzenesulfonyl chloride (cas no.- 66176-39-4) was used as a starting material.

3. Spectral data of starting materials

N-(phenylsulfonyl)acetamide



R_f - 0.13 (hexane/EtOAc = 1/1). White solid. **MP** – 126 °C.

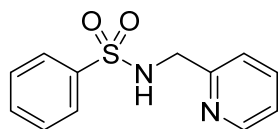
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 8.13 – 8.01 (m, 2H), 7.70 – 7.65 (m, 1H), 7.61 – 7.53 (m, 2 H), 2.09 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 168.46, 138.51, 134.28, 129.24, 128.39, 23.66.

IR (neat, v/cm⁻¹) 3249 w, 2992 w, 2884 w, 1696 s, 1451 s, 1338 m, 1243 m, 1162 s, 1090 s, 997 w, 856 s, 758 m, 721 m.

HRMS [M+H]⁺ Calcd for C₈H₁₀NO₃S: 200.0376, found 200.0382.

N-(pyridin-2-ylmethyl)benzenesulfonamide



R_f - 0.13 (hexane/EtOAc = 1/1). White solid. **MP** – 82 °C.

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 8.46 – 8.41 (m, 1H), 7.90 – 7.80 (m, 2H), 7.59 (td, *J* = 7.7, 1.8 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.47 – 7.40 (m, 2H), 7.20 – 7.10 (m, 2H), 6.22 (s, 1H), 4.27 (d, *J* = 5.5 Hz, 2H).

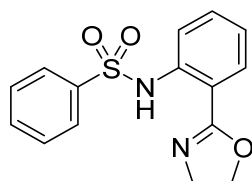
¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 154.85, 149.07, 139.72, 136.98, 132.66, 129.10, 127.23, 122.79, 122.12, 47.53.

IR (neat, v/cm⁻¹) 3276 w, 3065 w, 2858 w, 1444 m, 1326 s, 1156 s, 1092 s, 1073 m, 754 s,

720 m, 689 s.

HRMS $[M+H]^+$ Calcd for $C_{12}H_{13}N_2O_2S$: 249.0692, found 249.0702.

***N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzenesulfonamide**



R_f - 0.20 (hexane/EtOAc = 4/1). White solid. **MP** – 147 °C.

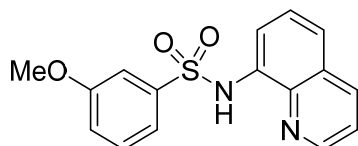
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 12.39 (s, 1H), 7.87 (dd, J = 8.2, 0.8 Hz, 2H), 7.74 (dd, J = 7.9, 1.5 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 7.3 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.38 – 7.32 (m, 1H), 7.01 (t, J = 7.6 Hz, 1H), 4.36 (t, J = 9.5 Hz, 2H), 4.13 (t, J = 9.5 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 164.63, 139.96, 139.10, 132.88, 132.54, 129.48, 129.01, 127.29, 122.58, 118.05, 113.75, 66.59, 54.58.

IR (neat, ν/cm^{-1}) 3064 w, 2979 w, 2881 w, 1635 s, 1584 m, 1500 s, 1445 m, 1336 s, 1286 m, 1257 s, 1158 s, 1137 m, 1092 s, 1063 s, 942 s, 752 s, 687 s.

HRMS Calcd for $C_{15}H_{14}N_2O_3S$: 302.0725, found 302.0724.

3-methoxy-*N*-(quinolin-8-yl)benzenesulfonamide (1a)



R_f - 0.11 (hexane/EtOAc = 5/1). White solid. **MP** – 105 °C.

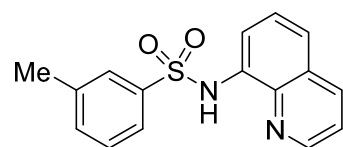
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.24 (s, 1H), 8.79 – 8.69 (m, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 6.8 Hz, 1H), 7.54 – 7.34 (m, 5H), 7.28 – 7.19 (m, 1H), 7.00 – 6.88 (m, 1H), 3.71 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 159.74, 148.82, 140.51, 138.62, 136.41, 133.80, 130.01, 128.29, 126.93, 122.38, 122.10, 119.58, 119.53, 115.32, 111.78, 55.64.

IR (neat, v/cm⁻¹) 3253 w, 3070 w, 3009 w, 2938 w, 1503 s, 1470 s, 1370 s, 1308 s, 1243 s, 1159 s, 1088 s, 1037 m, 825 s, 790 s, 758 s, 687 s.

HRMS Calcd for C₁₆H₁₄N₂O₃S: 314.0725, found 314.0726.

3-methyl-*N*-(quinolin-8-yl)benzenesulfonamide (**1b**)



R_f - 0.34 (hexane/EtOAc = 5/1). White solid. **MP** –94 °C.

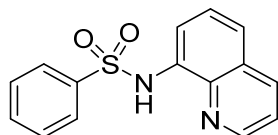
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.24 (s, 1H), 8.79 – 8.72 (m, 1H), 8.13 – 8.04 (m, 1H), 7.81 (dd, *J* = 6.1, 2.7 Hz, 1H), 7.77 – 7.66 (m, 2H), 7.49 – 7.36 (m, 3H), 7.25 – 7.20 (m, 2H), 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.76, 139.29, 139.22, 138.56, 136.37, 133.85, 128.82, 128.28, 127.66, 126.95, 124.45, 122.18, 122.08, 115.00, 21.35.

IR (neat, v/cm⁻¹) 3259 w, 3060 w, 2960 w, 2922 w, 1503 s, 1412 m, 1368 s, 1334 m, 1307 s, 1156 s, 1087 s, 922 m, 824 m, 789 s, 756 m, 687 s.

HRMS Calcd for C₁₆H₁₄N₂O₂S: 298.0776, found 298.0773.

N-(quinolin-8-yl)benzenesulfonamide (**1c**)



R_f - 0.31 (hexane/EtOAc = 7/3). White solid. **MP** – 134 °C.

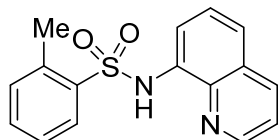
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.25 (s, 1H), 8.74 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.07 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.97 – 7.87 (m, 2H), 7.83 (dd, *J* = 6.5, 2.3 Hz, 1H), 7.49 – 7.30 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.82, 139.40, 138.57, 136.36, 133.77, 133.01, 128.99, 128.26, 127.28, 126.91, 122.31, 122.09, 115.14.

IR (neat, v/cm⁻¹) 3216 w, 3069 w, 2927 w, 1503 m, 1470 w, 1356 m, 1306 m, 1164 s, 1089 m, 906 s, 786 m, 727 s, 685 s.

HRMS Calcd for C₁₅H₁₂N₂O₂S: 284.0619, found 284.0621.

2-methyl-N-(quinolin-8-yl)benzenesulfonamide (**1d**)



R_f - 0.16 (hexane/EtOAc = 4/1). Off-white solid. **MP** – 109 °C.

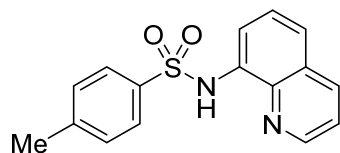
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.35 (s, 1H), 8.84 – 8.74 (m, 1H), 8.15 – 8.04 (m, 2H), 7.67 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.48 – 7.29 (m, 4H), 7.29 – 7.20 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 2.74 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.78, 138.31, 137.54, 137.20, 136.43, 133.74, 133.13, 132.73, 130.33, 128.30, 126.99, 126.05, 122.15, 121.81, 114.11, 20.35.

IR (neat, v/cm⁻¹) 3279 w, 3064 w, 2968 w, 2929 w, 1503 s, 1470 s, 1411 s, 1364 s, 1308 s, 1165 s, 922 m, 792 m, 754 s, 692 m.

HRMS Calcd for C₁₆H₁₄N₂O₂S: 298.0776, found 298.0774.

4-methyl-*N*-(quinolin-8-yl)benzenesulfonamide (1e)



R_f - 0.17 (hexane/EtOAc = 4/1). White solid. **MP** – 156 °C.

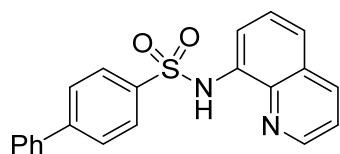
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.22 (s, 1H), 8.75 (d, *J* = 4.1 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.75 (m, 3H), 7.49 – 7.36 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.78, 143.85, 138.59, 136.56, 136.37, 133.97, 129.64, 128.30, 127.37, 126.97, 122.11, 122.06, 114.97, 21.58.

IR (neat, v/cm⁻¹) 3261 m, 3050 w, 2923 w, 2854 w, 1503 s, 1470 m, 1366 s, 1305 s, 1159 s, 1087 s, 920 m, 825 m, 791 s, 759 m, 662 s.

HRMS Calcd for C₁₆H₁₄N₂O₂S: 298.0776, found 298.0774.

***N*-(quinolin-8-yl)-[1,1'-biphenyl]-4-sulfonamide (1f)**



R_f - 0.17 (hexane/EtOAc = 4/1). White crystalline solid. **MP** – 158 °C.

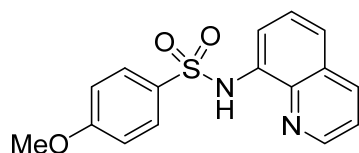
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.29 (s, 1H), 8.76 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.00 – 7.92 (m, 2H), 7.87 (dd, *J* = 5.4, 3.5 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.50 – 7.30 (m, 8H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.85, 145.87, 139.24, 138.65, 138.08, 136.43, 133.87, 129.08, 128.57, 128.35, 127.85, 127.62, 127.33, 127.01, 122.33, 122.12, 115.20.

IR (neat, v/cm⁻¹) 3259 w, 3065 w, 3032 w, 1594 m, 1503 s, 1370 s, 1308 s, 1163 s, 1090 s, 921 m, 792 m, 759 s, 695 m, 673 s.

HRMS Calcd for C₂₁H₁₆N₂O₂S: 360.0932, found 360.0929.

4-methoxy-*N*-(quinolin-8-yl)benzenesulfonamide (1g)



R_f - 0.14 (hexane/EtOAc = 4/1). White solid. **MP** – 93 °C.

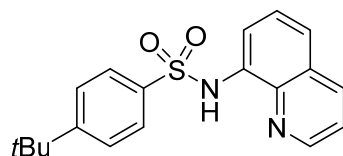
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.19 (s, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.08 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.88 – 7.75 (m, 3H), 7.49 – 7.36 (m, 3H), 6.85 – 6.76 (m, 2H), 3.74 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 163.14, 148.76, 138.63, 136.40, 134.04, 131.10, 129.51, 128.31, 126.97, 122.12, 122.06, 115.09, 114.17, 55.60.

IR (neat, v/cm⁻¹) 3260 w, 3069 w, 3012 w, 2944 w, 1595 s, 1578 m, 1501 s, 1413 m, 1367 s, 1306 s, 1259 s, 1155 s, 1089 s, 1025 m, 919 m, 826 s, 792 s, 758 m, 667 m.

HRMS Calcd for C₁₆H₁₄N₂O₃S: 314.0725, found 314.0730.

4-(*tert*-butyl)-*N*-(quinolin-8-yl)benzenesulfonamide (1h)



R_f - 0.24 (hexane/EtOAc = 4/1). White crystalline solid. **MP** – 174 °C.

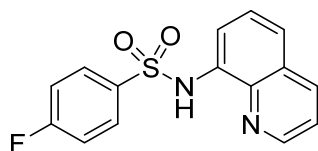
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.24 (s, 1H), 8.75 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.89 – 7.76 (m, 3H), 7.49 – 7.33 (m, 5H), 1.23 (s, 9H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 156.78, 148.73, 138.53, 136.54, 136.36, 134.00, 128.28, 127.14, 127.02, 126.06, 122.05, 121.98, 114.74, 35.18, 31.08.

IR (neat, v/cm⁻¹) 3208 m, 3062 w, 2961 m, 2904 w, 2968 w, 1503 s, 1469 m, 1413 m, 1333 s, 1167 s, 1085 s, 1057 m, 919 s, 824 m, 789 s, 755 s, 672 s.

HRMS Calcd for C₁₉H₂₀N₂O₂S: 340.1245, found 340.1244.

4-fluoro-*N*-(quinolin-8-yl)benzenesulfonamide (1i)



R_f - 0.31 (hexane/EtOAc = 4/1). White solid. **MP** – 139 °C.

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.22 (s, 1H), 8.75 (dd, *J* = 4.0, 0.8 Hz, 1H), 8.11 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.88 – 7.79 (m, 1H), 7.53 – 7.39 (m, 3H), 7.08 – 6.97 (m, 2H).

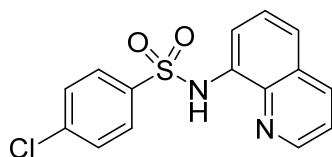
¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 165.27 (d, *J* = 255.1 Hz), 148.97, 138.69, 136.44, 135.41 (d, *J* = 3.2 Hz), 133.60, 130.07 (d, *J* = 9.5 Hz), 128.32, 126.92, 122.64, 122.20, 116.27 (d, *J* = 22.5 Hz), 115.51.

¹⁹F NMR (376 MHz, CDCl₃, 30 °C) δ -104.67.

IR (neat, v/cm⁻¹) 3259 w, 3106 w, 3071 w, 1592 m, 1503 s, 1413 m, 1372 s, 1236 m, 1170 s, 1156 s, 1089 s, 923 m, 839 s, 824 s, 792 s, 758 m, 667 m.

HRMS Calcd for C₁₅H₁₁FN₂O₂S: 302.0525, found 302.0531.

4-chloro-*N*-(quinolin-8-yl)benzenesulfonamide (1j)



R_f - 0.29 (hexane/EtOAc = 4/1). White solid. **MP** – 137 °C.

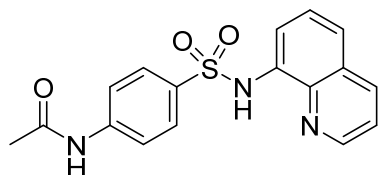
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.24 (s, 1H), 8.76 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.89 – 7.78 (m, 3H), 7.54 – 7.38 (m, 3H), 7.35 – 7.28 (m, 2H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.98, 139.54, 138.65, 137.91, 136.49, 133.50, 129.33, 128.78, 128.36, 126.95, 122.71, 122.23, 115.50.

IR (neat, v/cm⁻¹) 3257 w, 3090 w, 2987 w, 1581 w, 1503 s, 1471 m, 1414 m, 1372 s, 1309 s, 1166 s, 1088 s, 923 m, 825 s, 792 s, 754 s.

HRMS Calcd for C₁₅H₁₁ClN₂O₂S: 318.0230, found 318.0233.

***N*-(4-(*N*-(quinolin-8-yl)sulfamoyl)phenyl)acetamide (1k)**



R_f - 0.03 (hexane/EtOAc = 5/1). White solid. **MP** – 194 °C.

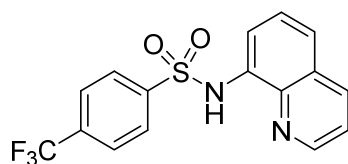
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.23 (s, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.87 – 7.77 (m, 3H), 7.55 – 7.32 (m, 6H), 2.13 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 168.61, 148.88, 142.16, 138.64, 136.45, 134.16, 133.79, 128.72, 128.35, 126.98, 122.39, 122.14, 119.15, 115.26, 24.83.

IR (neat, ν/cm^{-1}) 3359 w, 3242 w, 3187 w, 3109 w, 3054 w, 2925 w, 1682 s, 1592 s, 1528 s, 1503 s, 1311 s, 1159 s, 1089 s, 921 m, 826 s, 791 s, 749 m, 728 s.

HRMS (EI^+) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$ 341.0834; found 341.0839.

***N*-(quinolin-8-yl)-4-(trifluoromethyl)benzenesulfonamide (1l)**



R_f - 0.64 (hexane/EtOAc = 3/2). White solid. **MP** – 130 °C.

¹H NMR (400 MHz, CDCl_3 , 30 °C) δ 9.29 (s, 1H), 8.76 (dd, J = 4.2, 1.6 Hz, 1H), 8.12 (dd, J = 8.3, 1.6 Hz, 1H), 8.03 (dd, J = 8.8, 0.6 Hz, 2H), 7.86 (dd, J = 7.3, 1.6 Hz, 1H), 7.66 – 7.54 (m, 2H), 7.47 (m, 3H).

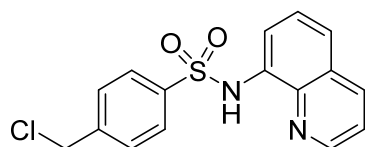
¹³C NMR (101 MHz, CDCl_3 , 30 °C) δ 149.08, 142.99, 138.67, 136.51, 134.64 (q, J = 33.0 Hz), 133.27, 128.39, 127.83, 126.95, 126.20 (q, J = 3.5 Hz), 123.20 (d, J = 273.0 Hz), 122.96, 122.30, 115.61.

¹⁹F NMR (376 MHz, CDCl_3 , 30 °C) δ -63.15.

IR (neat, ν/cm^{-1}) 3255 w, 3065 w, 1504 m, 1413 m, 1375 m, 1321 s, 1169 s, 1131 s, 1092 m, 1062 s, 845 m, 826 m, 792 m, 713 s.

HRMS Calcd for $\text{C}_{16}\text{H}_{11}\text{F}_3\text{N}_2\text{O}_2\text{S}$: 352.0493, found 352.0493.

4-(chloromethyl)-*N*-(quinolin-8-yl)benzenesulfonamide (1m)



R_f - 0.63 (hexane/EtOAc = 3/2). Off-white solid. **MP** – 164 °C.

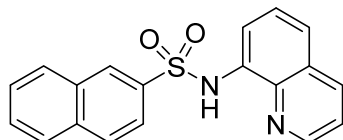
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.25 (s, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.96 – 7.87 (m, 2H), 7.83 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.55 – 7.32 (m, 5H), 4.49 (s, 2H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.91, 142.44, 139.38, 138.61, 136.41, 133.64, 129.03, 128.33, 127.75, 126.95, 122.47, 122.17, 115.18, 44.90.

IR (neat, v/cm⁻¹) 3258 w, 3057 w, 1504 s, 1471 m, 1412 s, 1372 s, 1335 m, 1309 s, 1165 s, 1090 s, 924 m, 825 m, 792 m, 757 m, 694 s.

HRMS Calcd for C₁₆H₁₃ClN₂O₂S: 332.0386, found 332.0388.

***N*-(quinolin-8-yl)naphthalene-2-sulfonamide (1n)**



R_f - 0.14 (hexane/EtOAc = 4/1). Off-white solid. **MP** – 152 °C.

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.36 (s, 1H), 8.73 (dt, *J* = 3.5, 1.6 Hz, 1H), 8.52 (d, *J* = 1.5 Hz, 1H), 8.06 – 7.99 (m, 1H), 7.93 – 7.83 (m, 3H), 7.80 – 7.70 (m, 2H), 7.58 – 7.48 (m, 2H), 7.44 – 7.32 (m, 3H).

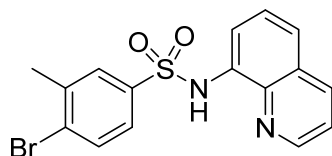
¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.80, 138.53, 136.35, 136.30, 134.96, 133.77, 131.98, 129.43, 129.33, 128.99, 128.90, 128.26, 127.88, 127.52, 126.91, 122.33, 122.26, 122.08, 114.99.

IR (neat, v/cm⁻¹) 3260 w, 3057 w, 2992 w, 1734 m, 1503 s, 1470 m, 1412 s, 1372 s, 1334

m, 1308 s, 1241 m, 1162 s, 1075 m, 823 s, 792 s, 757 s.

HRMS Calcd for C₁₉H₁₄N₂O₂S: 334.0776, found 334.0773.

4-bromo-3-methyl-N-(quinolin-8-yl)benzenesulfonamide (1o)



R_f - 0.66 (hexane/EtOAc = 3/2). White solid. **MP** – 126 °C.

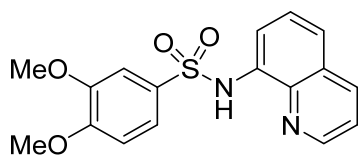
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.23 (s, 1H), 8.76 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.85 – 7.74 (m, 2H), 7.60 – 7.38 (m, 5H), 2.33 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.92, 139.35, 138.62, 138.50, 136.44, 133.59, 133.02, 130.50, 129.20, 128.35, 126.94, 125.98, 122.54, 122.19, 115.24, 23.07.

IR (neat, v/cm⁻¹) 3258 w, 3068 w, 2983 w, 1503 s, 1469 m, 1412 m, 1371 s, 1335 m, 1308 s, 1240 m, 1161 s, 1029 s, 924 m, 824 s, 791 s, 757 m, 700 s.

HRMS Calcd for C₁₆H₁₃BrN₂O₂S: 375.9881, found 375.9879.

3,4-dimethoxy-N-(quinolin-8-yl)benzenesulfonamide (1p)



R_f - 0.08 (hexane/EtOAc = 4/1). White solid. **MP** – 134 °C.

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.18 (s, 1H), 8.75 (d, *J* = 3.3 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.84 (dd, *J* = 6.8, 1.9 Hz, 1H), 7.52 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.49 – 7.38 (m, 3H), 7.32 (d, *J* = 1.9 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H).

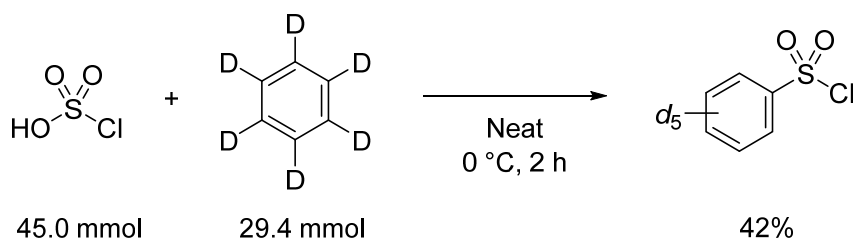
¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 152.80, 148.98, 148.81, 138.83, 136.45, 134.09, 131.10, 128.35, 126.94, 122.39, 122.09, 121.52, 115.66, 110.37, 109.68, 56.21, 56.15.

IR (neat, v/cm⁻¹) 3256 w, 3077 w, 3008 w, 2964 w, 2935 w, 1587 m, 1504 s, 1469 m, 1410 m, 1368 m, 1333 m, 1308 m, 1262 s, 1156 s, 1139 s, 1089 s, 1020 s, 920 m, 825 m, 792 s, 731 m.

HRMS Calcd for C₁₇H₁₆N₂O₄S: 344.0831, found 344.0835.

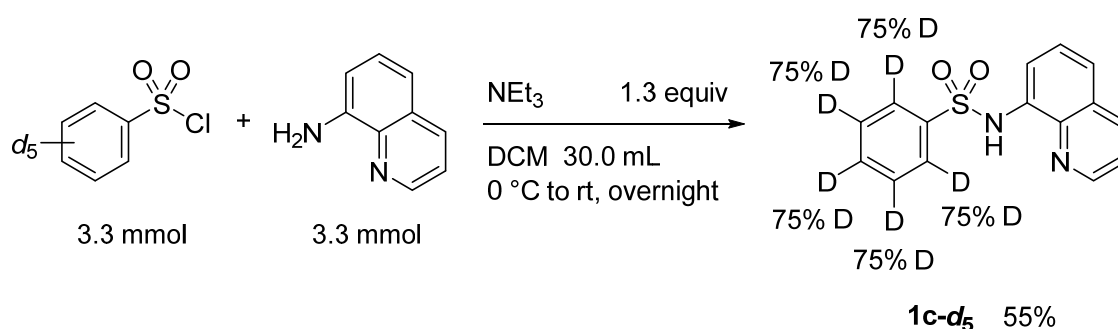
4. Preparation of deuterated sulfonamide **1c-d₅**.

In an oven dried two-necked round bottom flask, chlorosulfonic acid (3.0 mL, 45.0 mmol, 1 equiv) was added dropwise to benzene-*d*₆ (2.6 mL, 29.4 mmol, 0.65 equiv) at 0 °C. The ice bath was then removed and the resulting mixture was stirred for an additional 2 h at room temperature. The mixture was then diluted with 40 mL of CH₂Cl₂ and poured into 50 mL of ice water. The organic layer was separated and washed with water (2 X 25 mL), and dried over Na₂SO₄. The organic phase was evaporated to give a colorless oil. The product was purified by column chromatography (eluent- EtOAc/hexane) to give 2.3 g (42%) of benzenesulfonyl chloride-*d*₅ as a clear colorless oil.⁴



Benzenesulfonyl chloride-*d*₅ was used for the preparation of sulfonamide **1c-d₅**. In a dry

three-necked round bottom flask, 8-aminoquinoline (476 mg, 3.3 mmol, 1.0 equiv) and triethylamine (0.6 mL, 4.29 mmol, 1.3 equiv) were dissolved in CH₂Cl₂ (20 mL). After cooling the reaction mixture to 0 °C, benzenesulfonyl chloride-*d*₅ (600 mg, 3.3 mmol, 1.0 equiv) in 10 mL of CH₂Cl₂ was added dropwise over a period of 10 minutes. The resulting mixture was allowed to warm to room temperature and then stirred overnight. After the reaction reached completion, the crude mixture was washed with saturated aqueous NaHCO₃ (20 mL). The aqueous layer was then washed with 3 x 20 mL of CH₂Cl₂. The combined organic phases were dried over anhydrous Na₂SO₄ and the volatiles were evaporated to dryness. The resulting crude mixture was purified by flash chromatography on silica gel (eluent: hexane/EtOAc/acetone = 10/3/1) to yield of 521 mg (55 % yield) of sulfonamide **1c-d₅**.



¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.25 (s, 1H), 8.82 – 8.70 (m, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.95 – 7.79 (m, 0.5H of arene), 7.87 – 7.79 (m, 1H), 7.51 – 7.32 (m, 3H of quinoline moiety, and 0.82 H of arene moiety).

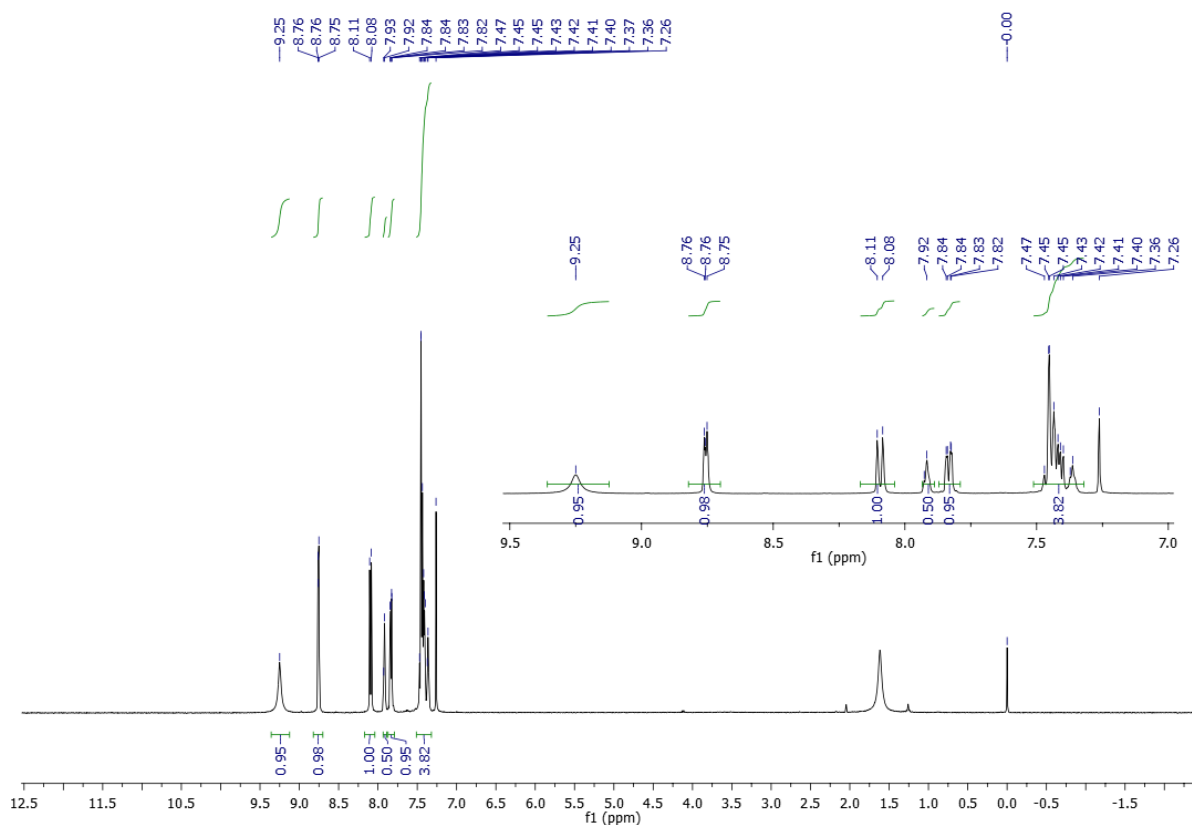
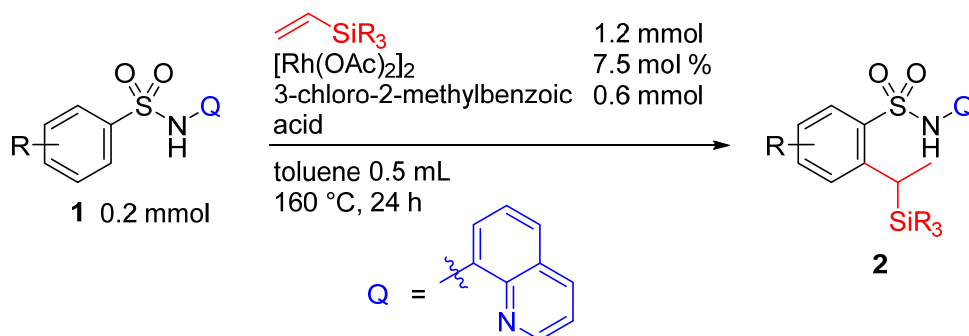


Figure S1. ^1H spectrum of **1c-d₅** in CDCl_3 .

5. General procedure for the branch-alkylation of sulfonamide derivatives.

In an oven dried sealed tube or J-Young Schlenk, $[\text{Rh}(\text{OAc})_2]_2$ (6.6 mg, 0.015 mmol, 0.075 equiv), sulfonamide (0.2 mmol, 1.0 equiv), and the acid additive (0.4 mmol, 2.0 equiv), along with 0.5 mL of toluene were added. Vinylsilane (1.2 mmol, 6.0 equiv) was added to the reaction and the mixture was kept for 24 h at 160 °C in an oil bath, in which the temperature of the oil bath was determined by a thermometer. After 24 h, the crude mixture was washed with saturated aqueous NaHCO_3 (5 mL) and a brine solution (5 mL). The aqueous layer was washed 5 times with 10 mL portions of CH_2Cl_2 and the organic layer was then dried under vacuum. The resulting crude mixture was purified by flash chromatograph

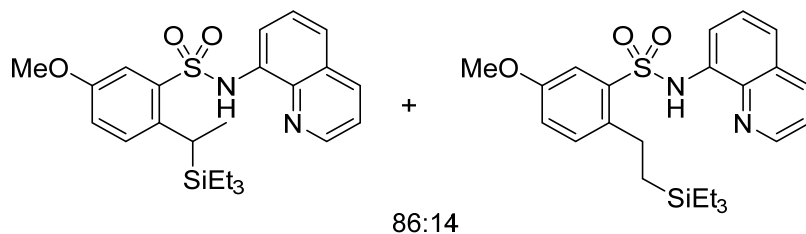
on NH-silica (eluent- hexane/EtOAc/acetone). If required, the product was purified further by LC-908 HPLC (GPC).



6. Spectral data of products

5-methoxy-*N*-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide (2aa) and

5-methoxy-*N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)benzenesulfonamide



R_f - 0.36 (hexane/EtOAc = 4/1). Yellow solid. **MP** – 85 °C.

Note: Some peaks are overlapped with the minor isomer (linear).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.32 (s, 1H), 8.77 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.69 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.59 (d, *J* = 2.8 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.92 (dd, *J* = 8.6, 2.8 Hz, 1H), 3.72 (s, linear), 3.71 (s, 3H), 3.29 (q, *J* = 7.4 Hz, 1H), 3.07 – 2.97 (m, linear), 1.12 (d, *J* = 7.4 Hz, 3H), 1.02 – 0.94 (m, linear), 0.85 (t, *J* = 7.9 Hz, 9H), 0.66 – 0.50 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 155.96, 148.65, 139.23, 138.21, 136.96, 136.33, 134.02, 131.25, 128.23, 126.97, 122.07, 121.67, 119.47, 114.48, 114.05, 55.61, 22.59, 17.63, 7.65, 2.79.

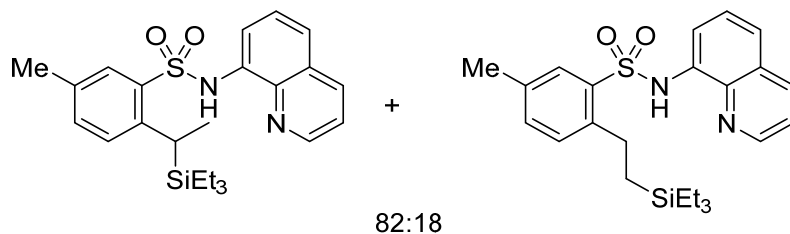
Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 157.08, 137.32, 136.78, 133.83, 131.75, 121.76, 119.29, 114.75, 55.68, 26.12, 13.18, 3.31.

IR (neat, v/cm⁻¹) 3286 w, 3068 w, 2952 m, 2909 m, 2874 m, 1604 w, 1504 s, 1470 s, 1413 m, 1365 m, 1308 s, 1287 m, 1272 m, 1239 s, 1158 s, 1040 m, 923 m, 825 m, 791 m, 741 m.

HRMS Calcd for C₂₄H₃₂N₂O₃SSi: 456.1903, found 456.1900.

5-methyl-*N*-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide (2ba) and 5-methyl-*N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)benzenesulfonamide



R_f - 0.5 (hexane/EtOAc = 4/1). White solid. **MP** – 76 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.29 (s, 1H), 8.77 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.11 – 8.06 (m, 1H), 7.91 (s, 1H), 7.65 (dt, *J* = 7.0, 1.9 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.21 – 7.06 (m, 2H), 3.32 (q, *J* = 7.4 Hz, 1H), 3.11 – 3.00 (m, linear), 2.30 (s, linear), 2.28 (s, 3 H), 1.12 (d, *J* = 7.4 Hz, 3H), 1.04 – 0.93 (m, linear), 0.85 (t, *J* = 7.9 Hz, 9H), 0.66 – 0.48 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.59, 144.47, 138.24, 136.29, 136.00, 134.13, 134.01, 133.65, 130.59, 130.14, 128.23, 126.98, 122.04, 121.49, 113.89, 23.18, 20.88, 17.58, 7.67, 2.80.

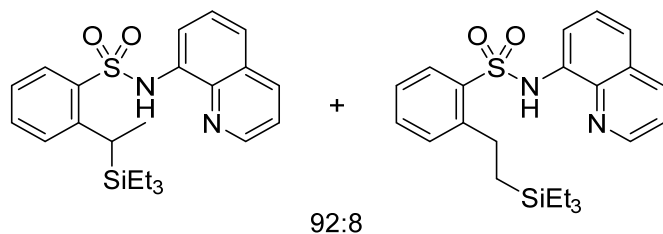
Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 148.62, 142.00, 136.34, 135.53, 133.99, 130.44, 128.26, 122.07, 121.57, 26.53, 20.91, 13.06, 7.61, 3.31.

IR (neat, v/cm⁻¹) 3299 w, 3059 w, 2952 m, 2911 m, 2874 m, 1662 s, 1504 s, 1470 s, 1363 s, 1334 m, 1308 s, 1236 m, 1159 s, 1089 m, 825 m, 790 s, 746 s, 714 s, 697 s.

HRMS Calcd for C₂₄H₃₂N₂O₂SSi: 440.1954, found 440.1960.

***N*-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide (2ca) and *N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)benzenesulfonamide**



R_f - 0.28 (hexane/EtOAc = 4/1). White solid. **MP** – 123 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.32 (s, 1H), 8.78 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.09 (td, *J* = 8.3, 1.6 Hz, 2H), 7.65 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.46 – 7.33 (m, 4H), 7.21 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.16 – 7.07 (m, 1H), 3.38 (q, *J* = 7.4 Hz, 1H), 3.14 – 3.07 (m, linear), 1.16 (d, *J* = 7.4 Hz, 3H), 1.04 – 0.95 (m, linear), 0.85 (t, *J* = 7.9 Hz, 9H), 0.67 – 0.51 (m, 6H).

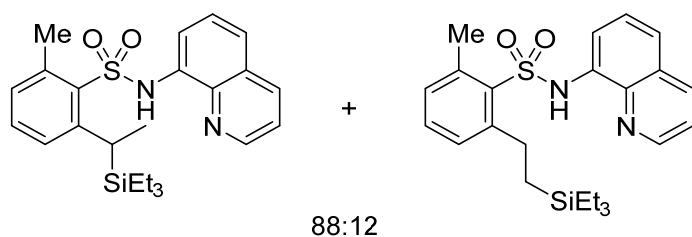
Note: Traces of linear isomer present in isolated compound, and thus in ¹³C NMR spectrum no peak corresponding to linear isomer was observed.

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.64, 147.78, 138.24, 136.36, 136.33, 134.11, 132.72, 130.36, 130.22, 128.27, 127.03, 124.28, 122.09, 121.56, 113.96, 23.83, 17.51, 7.65, 2.79.

IR (neat, v/cm⁻¹) 3266 w, 3063 w, 2953 m, 2909 m, 2875 m, 1591 m, 1504 s, 1470 s, 1413 m, 1307 s, 1245 s, 1159 s, 1061 m, 921 m, 788 m, 764 s, 731 s.

HRMS Calcd for C₂₃H₃₀N₂O₂SSi: 426.1797, found 426.1792.

2-methyl-*N*-(quinolin-8-yl)-6-(1-(triethylsilyl)ethyl)benzenesulfonamide (2da) and 2-methyl-*N*-(quinolin-8-yl)-6-(2-(triethylsilyl)ethyl)benzenesulfonamide



R_f - 0.49 (hexane/EtOAc = 4/1). White solid. **MP** – 103 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.34 (s, 1H), 8.76 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.07 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.50 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.44 – 7.31 (m, 3H), 7.21 – 7.07 (m, 2H), 6.93 (d, *J* = 6.8 Hz, 1H), 4.00 (q, *J* = 7.3 Hz, 1H), 3.23 – 3.17 (m, linear), 2.82 (s, 3H), 2.81 (s, linear), 1.26 (d, *J* = 7.3 Hz, 3H), 1.05 – 0.95 (m, linear), 0.87 (t, *J* = 7.9 Hz, 9H), 0.69 – 0.48 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 149.98, 148.60, 139.52, 138.29, 136.31, 135.39, 134.35, 131.55, 129.61, 128.29, 126.92, 122.06, 121.41, 113.51, 24.12, 23.35, 17.64, 7.68, 2.70.

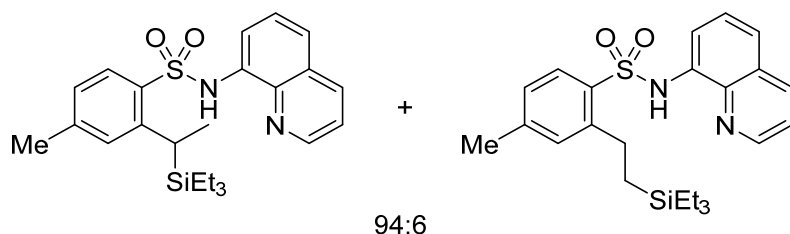
Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 148.67, 148.24, 139.26, 135.81, 132.28, 131.07, 129.92, 121.62, 113.81, 29.70, 23.17, 15.36, 3.37.

IR (neat, v/cm^{-1}) 3302 w, 2953 m, 2909 m, 2874 m, 1739 m, 1579 m, 1504 s, 1469 m, 1412 m, 1365 s, 1309 m, 1166 s, 1088 m, 918 w, 792 s, 730 s.

HRMS Calcd for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_2\text{SSi}$: 440.1954, found 440.1955.

4-methyl-*N*-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide (2ea) and 4-methyl-*N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)benzenesulfonamide



R_f - 0.50 (hexane/EtOAc = 4/1). Off-white solid. **MP** – 112 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl_3 , 30 °C) δ 9.29 (s, 1H), 8.76 (dd, J = 4.2, 1.6 Hz, 1H), 8.07 (dd, J = 8.2, 1.6 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.64 (dd, J = 7.0, 1.9 Hz, 1H), 7.45 – 7.33 (m, 3H), 6.98 (s, 1H), 6.91 (dd, J = 8.2, 1.1 Hz, 1H), 3.34 (q, J = 7.4 Hz, 1H), 3.10 – 3.02 (m, linear), 2.29 (s, linear), 2.26 (s, 3H), 1.14 (d, J = 7.4 Hz, 3H), 1.06 – 0.95 (m, linear), 0.85 (t, J = 7.9 Hz, 9H), 0.67 – 0.50 (m, 6H).

¹³C NMR (101 MHz, CDCl_3 , 30 °C) δ 148.56, 147.49, 143.24, 138.17, 136.29, 134.15, 133.37, 130.84, 130.54, 128.21, 126.97, 125.09, 122.02, 121.39, 113.75, 23.51, 21.57, 17.43, 7.63, 2.75.

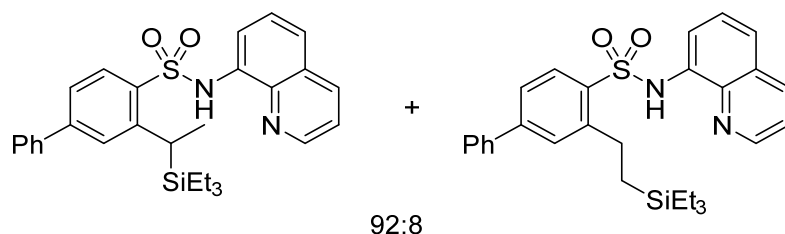
Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 148.48, 144.93, 143.87, 140.76, 133.24, 131.35, 130.37, 130.17, 129.06, 128.03, 126.87, 126.33, 121.44, 113.43, 26.84, 21.50, 13.01, 7.56, 3.56.

IR (neat, v/cm^{-1}) 3285 w, 3027 w, 2953 m, 2912 m, 2875 m, 1739 s, 1504 s, 1470 m, 1414 m, 1365 s, 1308 m, 1216 m, 1162 s, 1089 w, 922 w, 759 m, 735 m.

HRMS Calcd for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_2\text{SSi}$: 440.1954, found 440.1945.

***N*-(quinolin-8-yl)-3-(1-(triethylsilyl)ethyl)-[1,1'-biphenyl]-4-sulfonamide (2fa) and *N*-(quinolin-8-yl)-3-(2-(triethylsilyl)ethyl)-[1,1'-biphenyl]-4-sulfonamide**



R_f - 0.47 (hexane/EtOAc = 4/1). White solid. **MP** – 96 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl_3 , 30 °C) δ 9.36 (s, 1H), 8.78 (dd, J = 4.2, 1.6 Hz, 1H), 8.14 (d, J = 8.3 Hz, 1H), 8.08 (dd, J = 8.3, 1.6 Hz, 1H), 7.70 (dd, J = 6.7, 2.1 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.44 – 7.31 (m, 8H), 3.43 (q, J = 7.4 Hz, 1H), 3.20 – 3.12 (m, linear), 1.21 (d, J = 7.4 Hz, 3H), 1.06 – 0.96 (m, linear), 0.88 (t, J = 7.9 Hz, 9H), 0.69 – 0.57 (m, 6H).

¹³C NMR (101 MHz, CDCl_3 , 30 °C) δ 148.65, 148.14, 145.21, 139.60, 138.25, 136.35, 135.08, 134.08, 130.96, 129.06, 128.80, 128.39, 128.27, 127.21, 127.02, 122.97, 122.09, 121.61, 113.98, 23.92, 17.60, 7.68, 2.87.

Selected ¹³C NMR peak for linear isomer (minor) are as follows:

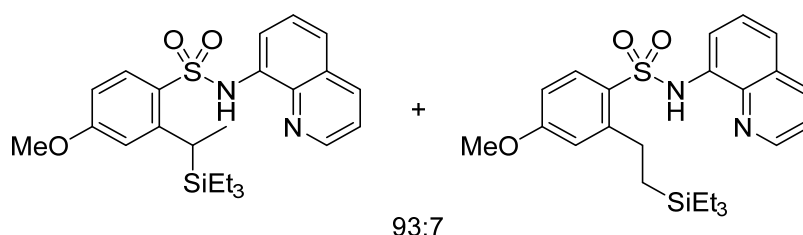
δ 129.37, 127.37, 124.29, 27.17, 13.12, 7.59, 3.34.

IR (neat, ν/cm^{-1}) 3285 w, 3062 w, 2953 m, 2908 w, 2874 m, 1595 m, 1503 m, 1469 m, 1413 m, 1366 m, 1308 m, 1241 m, 1164 m, 1088 m, 920 m, 792 m, 758 m, 734 m, 670 m.

HRMS Calcd for $\text{C}_{29}\text{H}_{34}\text{N}_2\text{O}_2\text{SSi}$: 502.2110, found 502.2105.

4-methoxy-*N*-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide (2ga) and

4-methoxy-*N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)benzenesulfonamide



R_f - 0.42 (hexane/EtOAc = 4/1). White solid. **MP** – 96 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl_3 , 30 °C) δ 9.27 (s, 1H), 8.76 (dd, J = 4.2, 1.6 Hz, 1H), 8.11 – 8.04 (m, 2H), 7.63 (dd, J = 7.0, 1.9 Hz, 1H), 7.44 – 7.33 (m, 3H), 6.66 (d, J = 2.6 Hz, 1H), 6.62 (dd, J = 8.9, 2.6 Hz, 1H), 3.77 (s, linear), 3.75 (s, 3H), 3.33 (q, J = 7.4 Hz, 1H), 3.09 – 3.01 (m, linear), 1.11 (d, J = 7.4 Hz, 3H), 1.01 – 0.94 (m, linear), 0.86 (t, J = 7.9 Hz, 9H), 0.68 – 0.53 (m, 6H).

¹³C NMR (101 MHz, CDCl_3 , 30 °C) δ 162.76, 149.99, 148.55, 138.22, 136.34, 134.18, 132.93, 128.24, 126.99, 122.02, 121.41, 115.72, 113.86, 109.07, 55.37, 23.88, 17.47, 7.66, 2.74.

Selected ¹³C NMR peak for linear isomer (minor) are as follows:

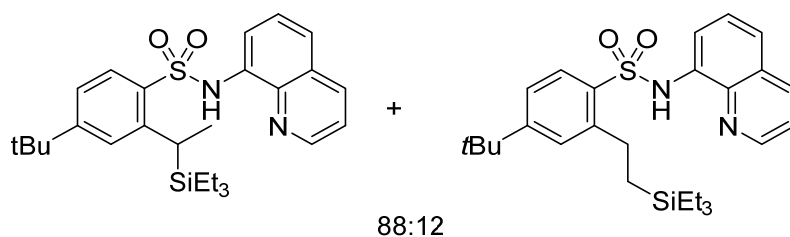
δ 163.20, 147.33, 140.67, 116.29, 113.74, 111.91, 109.87, 55.49, 26.93, 12.53, 3.30.

IR (neat, ν/cm^{-1}) 3285 w, 2952 m, 2908 w, 2874 m, 1594 s, 1503 s, 1469 s, 1413 m, 1362 m, 1306 s, 1235 m, 1160 s, 1087 m, 1059 s, 919 m, 755 s, 729 s, 711 s.

HRMS Calcd for C₂₄H₃₂N₂O₃SSi: 456.1903, found 456.1907.

4-(*tert*-butyl)-*N*-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide (2ha)

and 4-(*tert*-butyl)-*N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)benzenesulfonamide



R_f - 0.41 (hexane/EtOAc = 4/1). White solid. **MP** – 212 °C.

Note: Branch isomer (major) was isolated in pure form.

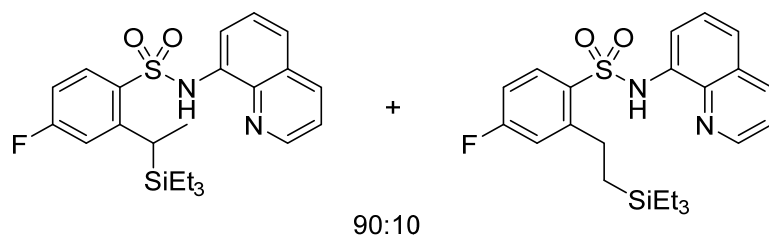
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.29 (s, 1H), 8.78 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.23 (d, *J* = 2.0 Hz, 1H), 7.12 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.35 (q, *J* = 7.4 Hz, 1H), 1.24 (s, 9H), 1.19 (d, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.62 – 0.54 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 156.03, 148.58, 147.13, 138.21, 136.31, 134.32, 133.66, 130.11, 128.26, 127.61, 127.11, 122.04, 121.49, 121.28, 113.71, 35.04, 31.08, 23.84, 17.81, 7.65, 2.92.

IR (neat, ν/cm⁻¹) 3241 m, 2955 m, 2910 m, 2875 m, 1503 m, 1469 m, 1371 s, 1306 m, 1239 s, 1167 s, 1055 m, 733 m, 664 m.

HRMS Calcd for C₂₇H₃₈N₂O₂SSi: 482.2423, found 482.2421.

4-fluoro-*N*-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide (2ia) and 4-fluoro-*N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)benzenesulfonamide



R_f - 0.49 (hexane/EtOAc = 4/1). Off-white solid. **MP** – 99 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.30 (s, 1H), 8.77 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.13 – 8.06 (m, 2H), 7.65 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.46 – 7.35 (m, 3H), 6.85 (dd, *J* = 10.5, 2.6 Hz, 1H), 6.79 (ddd, *J* = 8.9, 7.4, 2.6 Hz, 1H), 3.38 (qd, *J* = 7.4, 2.0 Hz, 1H), 3.14 – 3.06 (m, linear), 1.12 (d, *J* = 7.4 Hz, 3H), 1.06 – 0.94 (m, linear), 0.87 (t, *J* = 7.9 Hz, 9H), 0.68 – 0.51 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 165.17 (d, *J* = 253.9 Hz), 151.49 (d, *J* = 8.6 Hz), 148.74, 138.29, 136.39, 133.83, 133.17 (d, *J* = 9.8 Hz), 132.16 (d, *J* = 2.0 Hz), 128.27, 126.95, 122.15, 121.89, 116.69 (d, *J* = 22.2 Hz), 114.22, 111.48 (d, *J* = 22.2 Hz), 24.39, 17.26, 7.58, 2.63.

Selected ¹³C NMR peak for linear isomer (minor) are as follows:

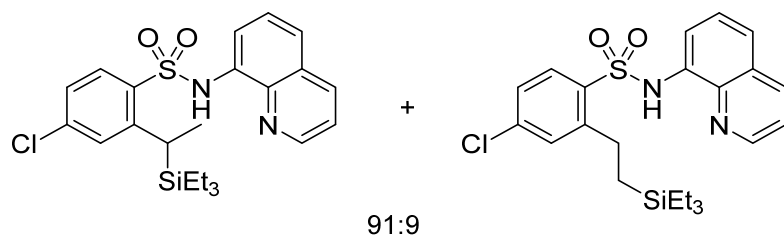
δ 148.61, 139.57, 135.35, 126.87, 26.93, 12.32, 7.53, 3.28.

¹⁹F NMR (376 MHz, 30 °C) δ -105.44 (linear), -105.92 (branch).

IR (neat, v/cm⁻¹) 3280 w, 2979 w, 2955 m, 2908 w, 2876 m, 1771 m, 1601 m, 1577 m, 1504 m, 1469 m, 1414 m, 1309 m, 1245 s, 1162 s, 1057 m, 923 m, 792 m, 756 m, 739 m.

HRMS Calcd for C₂₃H₂₉FN₂O₂SSi: 444.1703, found 444.1709.

4-chloro-*N*-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide (2ja) and 4-chloro-*N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)benzenesulfonamide



R_f - 0.40 (hexane/EtOAc = 4/1). Off-white solid. **MP** – 81 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.37 (s, 1H), 8.83 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.71 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.20 (d, *J* = 2.2 Hz, 1H), 7.13 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.41 (q, *J* = 7.4 Hz, 1H), 3.18 – 3.10 (m, linear), 1.19 (d, *J* = 7.4 Hz, 3H), 1.10 – 1.01 (m, linear), 0.92 (t, *J* = 7.9 Hz, 9H), 0.71 – 0.58 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 149.89, 148.76, 139.12, 138.24, 136.43, 134.72, 133.73, 131.81, 130.05, 128.29, 126.98, 124.47, 122.18, 121.97, 114.21, 24.15, 17.24, 7.60, 2.63.

Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 135.18, 131.68, 130.55, 128.47, 125.84, 114.12, 26.89, 12.57, 3.29.

IR (neat, ν/cm⁻¹) 3278 w, 3069 w, 2954 m, 2909 m, 2875 m, 1581 m, 1504 s, 1469 s, 1413 s, 1308 s, 1245 m, 1168 s, 1088 m, 922 m, 859 s, 824 m, 792 m, 753 s, 730 s.

HRMS Calcd for C₂₃H₂₉ClN₂O₂SSi: 460.1408, found 460.1415.

***N*-(4-(*N*-(quinolin-8-yl)sulfamoyl)-3-(1-(triethylsilyl)ethyl)phenyl)acetamide (2ka)**
and *N*-(4-(*N*-(quinolin-8-yl)sulfamoyl)-3-(2-(triethylsilyl)ethyl)phenyl)acetamide



Note: Some peaks are overlapped with the linear isomer (minor).

¹³C NMR (101 MHz, CDCl₃, 30 °C) NMR (101 MHz,) δ 168.73, 149.57, 148.68, 142.02, 138.27, 136.35, 134.02, 131.82, 128.28, 126.98, 122.10, 121.73, 121.64, 120.05, 114.56, 113.94, 24.88, 24.10, 17.49, 7.66, 2.72.

δ 146.69, 142.34, 136.40, 133.80, 131.07, 128.32, 121.73, 120.62, 115.93, 27.01, 24.82, 12.72, 7.61, 3.32.

HRMS Calcd for C₂₅H₃₃N₃O₃SSi: 483.2012, found 483.2015.

(21a) and *N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)-4-

S28

90:10

Note: Some peaks are overlapped with the linear isomer (minor).

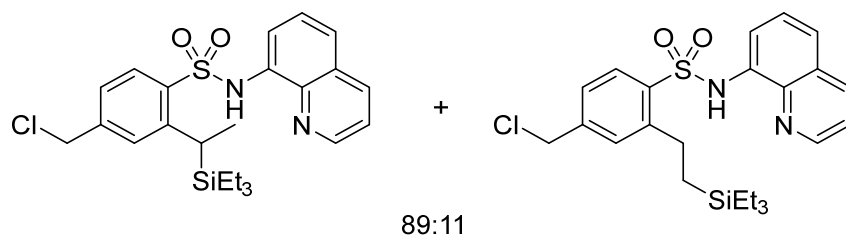
¹³C NMR (101 MHz, CDCl₃, 30 °C) 149.08, 148.86, 139.72, 138.24, 136.48, 134.22 (q, *J* = 32.6 Hz), 133.59, 130.67, 128.35, 127.08 (q, *J* = 3.5 Hz), 127.00, 123.43 (q, *J* = 272.0 Hz), 122.26, 122.20, 121.00 (q, *J* = 3.5 Hz), 114.32, 24.38, 17.35, 7.53, 2.65.

8 148.74, 146.29, 140.25, 139.43, 136.52, 130.49, 27.11, 12.80, 7.60, 3.31.

IR (neat, v/cm^{-1}) 3274 w, 2955 w, 2912 w, 2877 w, 1739 m, 1504 s, 1412 s, 1370 s, 1330 s, 1310 s, 1170 s, 1132 s, 1092 s, 924 m, 825 m, 792 m, 700 s.

4-(chloromethyl)-*N*-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide

(2ma) and **4-(chloromethyl)-*N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)benzenesulfonamide**



R_f - 0.63 (hexane/EtOAc = 3/2). White solid. **MP** – 108 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.32 (s, 1H), 8.78 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.14 – 8.03 (m, 2H), 7.66 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.48 – 7.35 (m, 3H), 7.23 (d, *J* = 1.8 Hz, 1H), 7.11 (dd, *J* = 8.3, 1.8 Hz, 1H), 4.54 – 4.41 (m, 2H), 3.38 (q, *J* = 7.4 Hz, 1H), 3.16 – 3.07 (m, linear), 1.18 (d, *J* = 7.4 Hz, 3H), 1.06 – 0.95 (m, linear), 0.85 (t, *J* = 7.9 Hz, 9H), 0.67 – 0.53 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.72, 148.43, 141.92, 138.25, 136.38, 136.26, 133.96, 130.72, 130.21, 128.30, 127.03, 124.10, 122.14, 121.73, 114.03, 45.21, 23.96, 17.45, 7.62, 2.77.

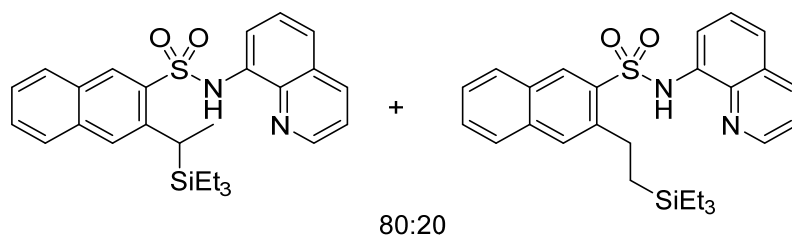
Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 145.74, 136.74, 130.63, 125.66, 121.82, 45.10, 26.96, 12.89, 3.33.

IR (neat, ν/cm⁻¹) 3283 w, 2953 m, 2875 w, 1739 s, 1504 s, 1470 m, 1367 s, 1309 m, 1232 s, 1165 s, 1089 w, 1058 w, 792 m, 757 m, 737 m, 674 m.

HRMS Calcd for C₂₄H₃₁ClN₂O₂SSi: 474.1564, found 474.1568.

***N*-(quinolin-8-yl)-3-(1-(triethylsilyl)ethyl)naphthalene-2-sulfonamide (2na) and *N*-(quinolin-8-yl)-3-(2-(triethylsilyl)ethyl)naphthalene-2-sulfonamide**



R_f - 0.43 (hexane/EtOAc = 4/1). White solid. **MP** – 111 °C.

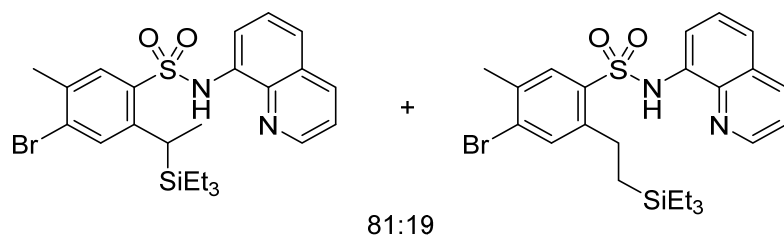
¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.40 (s, 1H), 8.78 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.73 – 8.69 (m, 1H), 8.05 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.92 – 7.83 (m, 1H), 7.75 – 7.65 (m, 2H), 7.59 (s, 1H), 7.54 – 7.47 (m, 1H), 7.46 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 6.44 (d, *J* = 18.8 Hz, alkenylated product) 3.40 (q, *J* = 7.4 Hz, 1H), 3.31 – 3.24 (m, linear), 1.27 (d, *J* = 7.4 Hz, 3H), 1.08 – 0.98 (m, linear), 0.86 (t, *J* = 7.9 Hz, 9H), 0.73 – 0.55 (m, 6H).

Selected ^{13}C NMR peak for linear isomer (minor) are as follows:

IR (neat, v/cm^{-1}) 3284 w, 3053 w, 2952 w, 2907 w, 2874 w, 1626 w, 1582 w, 1503 s, 1470 m, 1412 m, 1308 m, 1244 w, 1162 s, 921 w, 791 m, 744 s.

HRMS Calcd for C₂₇H₃₂N₂O₂SSi: 476.1954, found 476.1945.

4-bromo-5-methyl-N-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide



R_f - 0.71 (hexane/EtOAc = 3/2). Red solid. **MP** – 64 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.29 (s, 1H), 8.79 – 8.76 (m, 1H), 8.11 (dt, *J* = 8.3, 1.7 Hz, 1H), 7.95 (s, linear), 7.93 (s, 1H), 7.68 – 7.64 (m, 1H), 7.47 – 7.37 (m, 3H), 7.33 (s, 1H), 3.31 – 3.23 (q, *J* = 7.4 Hz, 1H), 3.11 – 2.96 (m, linear), 2.34 (s, linear), 2.32 (s, 3H), 1.11 (d, *J* = 7.4 Hz, 3H), 1.03 – 0.95 (m, linear), 0.87 (t, *J* = 7.9 Hz, 9H), 0.67 – 0.53 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 148.72, 146.65, 138.30, 136.39, 135.32, 134.13, 133.92, 133.83, 131.95, 130.34, 128.30, 126.99, 122.15, 121.88, 114.18, 23.41, 22.42, 17.40, 7.63, 2.67.

Selected ¹³C NMR peak for linear isomer (minor) are as follows:

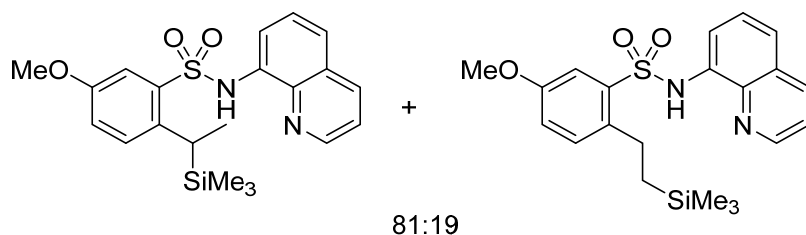
δ 148.60, 143.85, 136.44, 135.65, 134.22, 133.63, 131.66, 130.61, 128.33, 126.90, 121.95, 114.14, 26.33, 22.47, 12.66, 7.60, 3.30.

IR (neat, v/cm⁻¹) 3281 w, 2952 m, 2909 w, 2874 m, 1503 s, 1469 s, 1413 m, 1376 m, 1309 m, 1241 w, 1167 s, 930 s, 824 w, 792 m, 726 m, 703 s.

HRMS Calcd for C₂₄H₃₁BrN₂O₂SSi: 518.1059, found 518.1059.

5-methoxy-*N*-(quinolin-8-yl)-2-(1-(trimethylsilyl)ethyl)benzenesulfonamide (2ab)

and 5-methoxy-*N*-(quinolin-8-yl)-2-(2-(trimethylsilyl)ethyl)benzenesulfonamide



R_f - 0.34 (hexane/EtOAc = 4/1). White solid. **MP** – 98 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.46 (s, 1H), 9.40 (s, linear), 8.92 – 8.84 (m, 1H), 8.25 – 8.15 (m, 1H), 7.85 – 7.77 (m, 1H), 7.74 – 7.68 (m, 1H), 7.57 – 7.46 (m, 3H), 7.17 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.09 – 6.99 (m, 1H), 3.84 (s, 3H), 3.34 – 3.24 (m, 1H), 3.18 – 3.09 (m, linear), 1.27 (d, *J* = 7.4 Hz, 3H), 0.96 – 0.87 (m, linear), 0.19 (s, linear), 0.05 (s, 9H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 155.89, 148.67, 139.06, 138.30, 136.89, 136.38, 134.05, 130.20, 128.27, 127.02, 122.09, 121.73, 119.59, 114.58, 114.21, 55.65, 24.56, 16.69, -2.65.

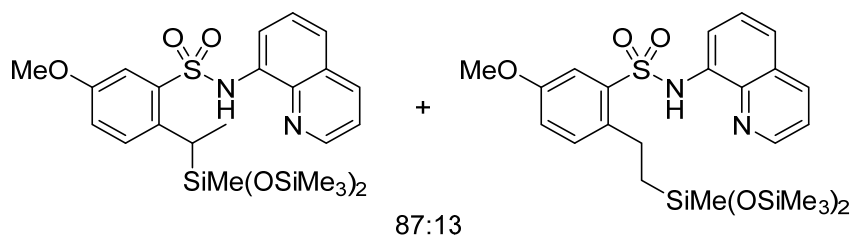
Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 157.10, 138.24, 137.33, 136.64, 133.83, 131.81, 119.31, 114.88, 114.00, 55.72, 26.14, 18.15, -1.67.

IR (neat, v/cm⁻¹) 3275 w, 3071 w, 2955 m, 2900 w, 2837 w, 1504 s, 1471 m, 1413 m, 1365 m, 1308 m, 1245 s, 1159 s, 1088 m, 1042 m, 841 s, 792 m, 757 m, 693 m.

HRMS Calcd for C₂₁H₂₆N₂O₃SSi: 414.1433, found 414.1430.

2-(1-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)ethyl)-5-methoxy-N-(quinolin-8-yl)benzenesulfonamide (2ac) and 2-(2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)ethyl)-5-methoxy-N-(quinolin-8-yl)benzenesulfonamide



R_f - 0.43 (hexane/EtOAc = 4/1). White solid. **MP** – 115 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.40 (s, 1H), 9.38 (s, linear), 8.85 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.77 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.69 (d, *J* = 2.8 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.8 Hz, 1H), 3.81 (s, 3H), 3.80 (s, linear), 3.19 – 3.10 (m, 1H, overlapped with linear isomer), 1.17 (d, *J* = 7.3 Hz, 3H), 0.92 – 0.85 (m, linear), 0.24 (s, 9H), 0.21 (s, linear), 0.09 (s, 9H), -0.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 156.21, 148.62, 138.24, 137.84, 137.43, 136.33, 134.09, 131.39, 128.26, 127.01, 122.08, 121.61, 119.38, 114.51, 113.98, 55.67, 25.80, 16.52, 1.93, 1.80, -1.31.

Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 157.10, 148.69, 138.31, 137.53, 136.59, 133.95, 132.11, 121.76, 119.33, 114.67, 114.16, 25.65, 19.52, 2.04, -0.27.

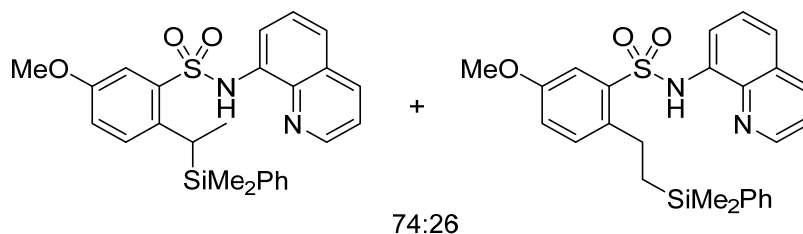
IR (neat, ν/cm⁻¹) 3288 w, 2957 w, 2900 w, 2838 w, 1503 m, 1471 w, 1366 w, 1309 w, 1254 s, 1160 s, 1044 s, 924 w, 841 s, 791 s, 756 s.

HRMS Calcd for C₂₅H₃₈N₂O₅SSi₃: 562.1809, found 562.1816.

2-(1-(dimethyl(phenyl)silyl)ethyl)-5-methoxy-*N*-(quinolin-8-yl)benzenesulfonamide

(2ad) and 2-(2-(dimethyl(phenyl)silyl)ethyl)-5-methoxy-*N*-(quinolin-8-yl)benzenesulfonamide

yl)benzenesulfonamide



R_f - 0.30 (hexane/EtOAc = 4/1). Off-white solid. **MP** – 135 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.32 (s, 1H), 9.25 (s, linear), 8.72 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.67 (dd, *J* = 4.2, 1.6 Hz, linear), 8.08 (ddd, *J* = 8.2, 2.8, 1.6 Hz, 1H), 7.74 – 7.64 (m, 1H), 7.59 (t, *J* = 2.8 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.45 – 7.31 (m, 6H), 7.14 (d, *J* = 8.5 Hz, linear), 6.95 – 6.82 (m, 2H), 3.72 (s, linear), 3.71 (s, 3H), 3.41 (q, *J* = 7.4 Hz, 1H), 3.09 – 3.00 (m, linear), 1.11 (d, *J* = 7.4 Hz, 3H), 1.10 – 1.04 (m, linear), 0.38 (s, 3H), 0.22 (s, 3H), 0.20 (s, linear).

Combined ¹³C NMR peaks for branch (major) and linear (minor) isomers are as follows:

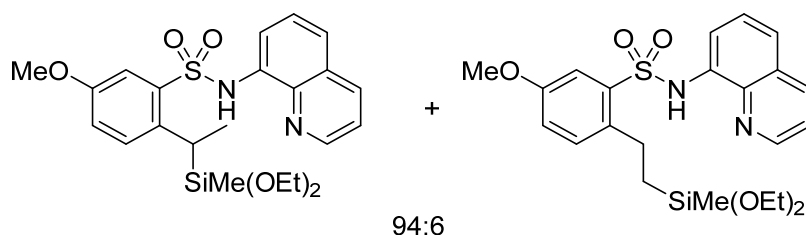
¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 157.15, 156.05, 148.72, 148.67, 139.04, 138.32, 138.25, 137.62, 137.38, 137.12, 136.43, 136.35, 134.57, 134.04, 133.81, 133.74, 132.02, 130.56, 129.20, 129.07, 128.25, 127.92, 127.77, 127.00, 122.08, 121.80, 119.44, 119.34, 114.85, 114.48, 114.39, 114.12, 55.71 (linear), 55.64 (branch), 26.31 (linear), 24.48 (branch), 17.54 (linear), 16.90 (branch), -3.06 (branch), -3.27 (linear), -5.34 (branch).

IR (neat, v/cm⁻¹) 3281 w, 3069 w, 3050 w, 2958 w, 2902 w, 1503 s, 1471 m, 1370 m, 1308 m, 1241 s, 1160 s, 1045 m, 923 m, 822 s, 792 m, 701 m.

HRMS Calcd for C₂₆H₂₈N₂O₃SSi: 476.1590, found 476.1598.

2-(1-(diethoxy(methyl)silyl)ethyl)-5-methoxy-N-(quinolin-8-yl)benzenesulfonamide

(2ae) and 2-(2-(diethoxy(methyl)silyl)ethyl)-5-methoxy-*N*-(quinolin-8-yl)benzenesulfonamide



R_f - 0.49 (hexane/EtOAc = 3/2). White solid. **MP** – 91 °C.

Note: Branch isomer was isolated in a pure form.

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.34 (s, 1H), 8.78 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.68 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.61 (d, *J* = 2.8 Hz, 1H), 7.48 – 7.33 (m, 4H), 6.95 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.80 – 3.69 (m, 5H), 3.63 (q, *J* = 7.0 Hz, 3H), 3.25 (q, *J* = 7.4 Hz, 1H), 1.24 – 1.13 (m, 6H), 1.08 (t, *J* = 7.0 Hz, 3H), -0.04 (s, 3H).

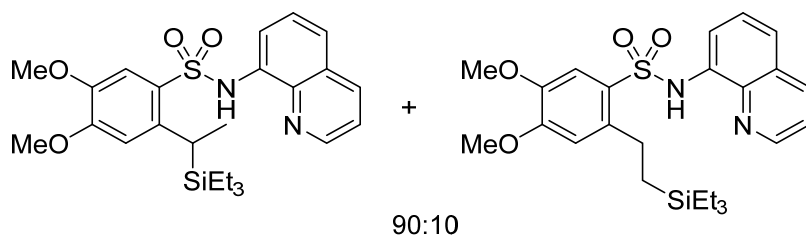
¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 156.38, 148.67, 138.32, 137.50, 137.27, 136.35, 134.12, 132.03, 128.31, 127.04, 122.12, 121.65, 119.60, 114.56, 114.00, 58.71, 58.64, 55.68, 24.37, 18.47, 18.41, 16.87, -5.73.

IR (neat, v/cm⁻¹) 3279 w, 3056 w, 2972 m, 2927 w, 1758 s, 1504 s, 1472 m, 1373 s, 1323 m, 1241 s, 1164 s, 1087 s, 1063 s, 825 m, 795 m, 698 w.

HRMS Calcd for C₂₃H₃₀N₂O₅SSi: 474.1645, found 474.1644.

4,5-dimethoxy-*N*-(quinolin-8-yl)-2-(1-(triethylsilyl)ethyl)benzenesulfonamide (2pa)

and 4,5-dimethoxy-*N*-(quinolin-8-yl)-2-(2-(triethylsilyl)ethyl)benzenesulfonamide



R_f - 0.19 (hexane/EtOAc = 4/1). White solid. **MP** – 94 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.28 (s, 1H), 8.77 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.68 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.56 (s, 1H), 7.45 – 7.34 (m, 3H), 6.71 (s, linear), 6.62 (s, 1H), 3.85 (s, linear), 3.81 (s, 3H), 3.81 (s, 3H), 3.34 (q, *J* = 7.4 Hz, 1H), 3.06 – 2.98 (m, linear), 1.10 (d, *J* = 7.4 Hz, 3H), 1.02 – 0.96 (m, linear), 0.87 (t, *J* = 7.9 Hz, 9H), 0.68 – 0.52 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 152.21, 148.62, 145.13, 141.52, 138.31, 136.36, 134.18, 128.24, 127.59, 126.94, 122.04, 121.63, 114.17, 113.05, 112.10, 56.21, 55.89, 23.20, 17.54, 7.69, 2.82.

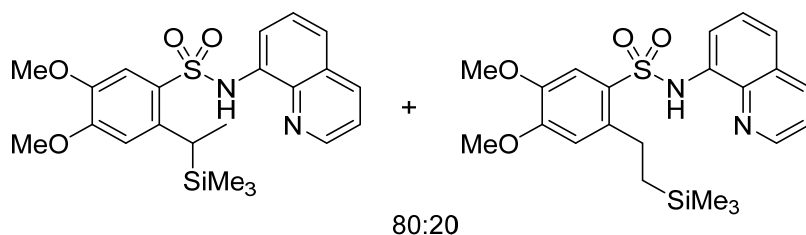
Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 152.44, 146.09, 140.25, 139.20, 134.00, 127.82, 121.73, 114.21, 113.10, 112.70, 56.32, 56.05, 26.78, 13.35, 7.61, 3.30.

IR (neat, ν/cm⁻¹) 3284 w, 2953 m, 2907 w, 2874 m, 1505 s, 1469 m, 1308 m, 1262 s, 1167 m, 1146 s, 1050 m, 793 m, 755 m, 739 m.

HRMS Calcd for C₂₅H₃₄N₂O₄SSi: 486.2009, found 486.2011.

4,5-dimethoxy-*N*-(quinolin-8-yl)-2-(1-(trimethylsilyl)ethyl)benzenesulfonamide (2pb)
and 4,5-dimethoxy-*N*-(quinolin-8-yl)-2-(2-(trimethylsilyl)ethyl)benzenesulfonamide



R_f - 0.22 (hexane/EtOAc = 4/1). Off-white solid. **MP** – 85 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.29 (s, 1H), 8.76 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.08 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.69 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.55 (s, linear), 7.54 (s, 1H), 7.45 – 7.33 (m, 3H), 6.70 (s, linear), 6.55 (s, 1H), 3.83 (s, linear), 3.81 (s, linear), 3.81 (s, 3H), 3.78 (s, 3H), 3.22 (q, *J* = 7.3 Hz, 1H), 3.06 – 2.95 (m, linear), 1.13 (d, *J* = 7.3 Hz, 3H), 0.84 – 0.76 (m, linear), 0.09 (s, linear), -0.04 (s, 9H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 152.28, 148.63, 145.02, 141.26, 138.37, 136.35, 134.17, 128.24, 127.47, 126.91, 122.03, 121.70, 114.27, 113.12, 111.01, 56.21, 55.84, 25.11, 16.54, -2.68.

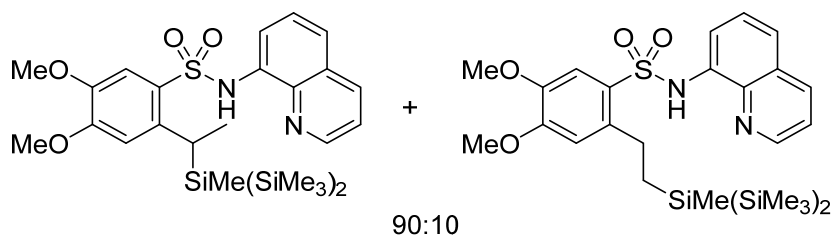
Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 152.42, 146.05, 139.02, 138.30, 136.38, 133.96, 127.78, 114.08, 113.18, 112.76, 56.32, 56.06, 26.77, 18.26, -1.69.

IR (neat, ν/cm⁻¹) 3280 w, 3006 w, 2954 m, 2872 w, 1739 m, 1504 s, 1469 m, 1361 m, 1262 s, 1218 m, 1167 m, 1145 s, 1050 m, 917 w, 838 s, 793 m, 758 m.

HRMS Calcd for C₂₂H₂₈N₂O₄SSi: 444.1539, found 444.1535.

2-(1-(1,1,1,2,3,3,3-heptamethyltrisilan-2-yl)ethyl)-4,5-dimethoxy-*N*-(quinolin-8-yl)benzenesulfonamide (2pc) and 2-(2-(1,1,1,2,3,3,3-heptamethyltrisilan-2-yl)ethyl)-4,5-dimethoxy-*N*-(quinolin-8-yl)benzenesulfonamide



R_f - 0.34 (hexane/EtOAc = 4/1). Off-white solid. **MP** – 105 °C.

Note: Some peaks are overlapped with the linear isomer (minor).

¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.27 (s, 1H), 8.78 – 8.72 (m, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.65 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.56 (s, 1H), 7.53 (s, linear), 7.44 – 7.32 (m, 3H), 6.80 (s, 1H), 6.68 (s, linear), 3.81 (s, 3H), 3.80 (s, 3H), 3.09 (q, *J* = 7.4 Hz, 1H), 3.06 – 3.01 (m, linear), 1.06 (d, *J* = 7.4 Hz, 3H), 0.83 – 0.78 (m, linear), 0.17 (s, 9H), 0.13 (s, linear), -0.01 (s, 9H), -0.11 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 30 °C) δ 152.28, 148.57, 145.34, 140.22, 138.26, 136.31, 134.17, 128.22, 128.00, 126.93, 122.02, 121.53, 113.93, 113.03, 112.17, 56.24, 55.89, 26.41, 16.49, 1.90, 1.78, -1.35.

Selected ¹³C NMR peak for linear isomer (minor) are as follows:

δ 152.38, 148.64, 146.15, 138.95, 134.06, 121.73, 114.09, 56.00, 26.32, 19.68, 2.00, -0.25.

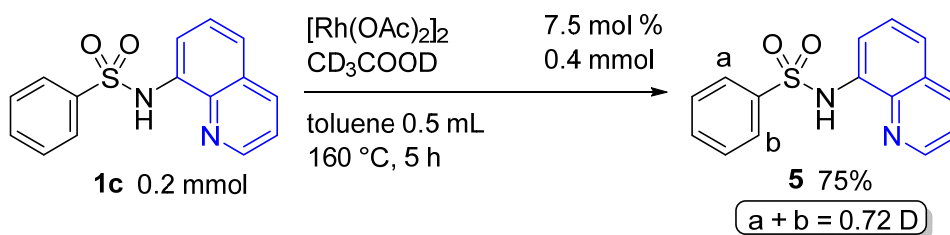
IR (neat, ν/cm⁻¹) 3286 w, 3005 w, 2957 w, 2903 w, 2844 w, 1505 s, 1469 m, 1308 m, 1259 s, 1220 m, 1168 m, 1145 s, 1051 s, 841 s, 791 s, 755 s.

HRMS Calcd for C₂₆H₄₀N₂O₆SSi₃: 592.1915, found 592.1905.

7. Deuterium labelling experiments

In an oven dried sealed tube or J-Young Schlenk, [Rh(OAc)₂]₂ (6.6 mg, 0.015 mmol, 0.075

equiv), the sulfonamide or deuterated sulfonamide (0.2 mmol, 1.0 equiv), and an acid additive (0.4 mmol, 2.0 equiv) were added to 0.5 mL of toluene. Triethylvinylsilane (170.8 mg, 222 μ L, 1.2 mmol, 6.0 equiv) was then added and the reaction mixture was kept for 5 h at 160 $^{\circ}$ C in an oil bath. The crude mixture was washed with saturated aqueous NaHCO_3 (5 mL) and a brine solution (5 mL). The aqueous layer was washed with 5 x 10 mL of CH_2Cl_2 and the organic layer was then dried under a vacuum. The resulting crude mixture was purified by flash chromatography on NH-silica (eluent- hexane/EtOAc/acetone). The crude product was further purified by HPLC. The percent of D/H exchange was determined by ^1H and ^2H NMR spectroscopy.



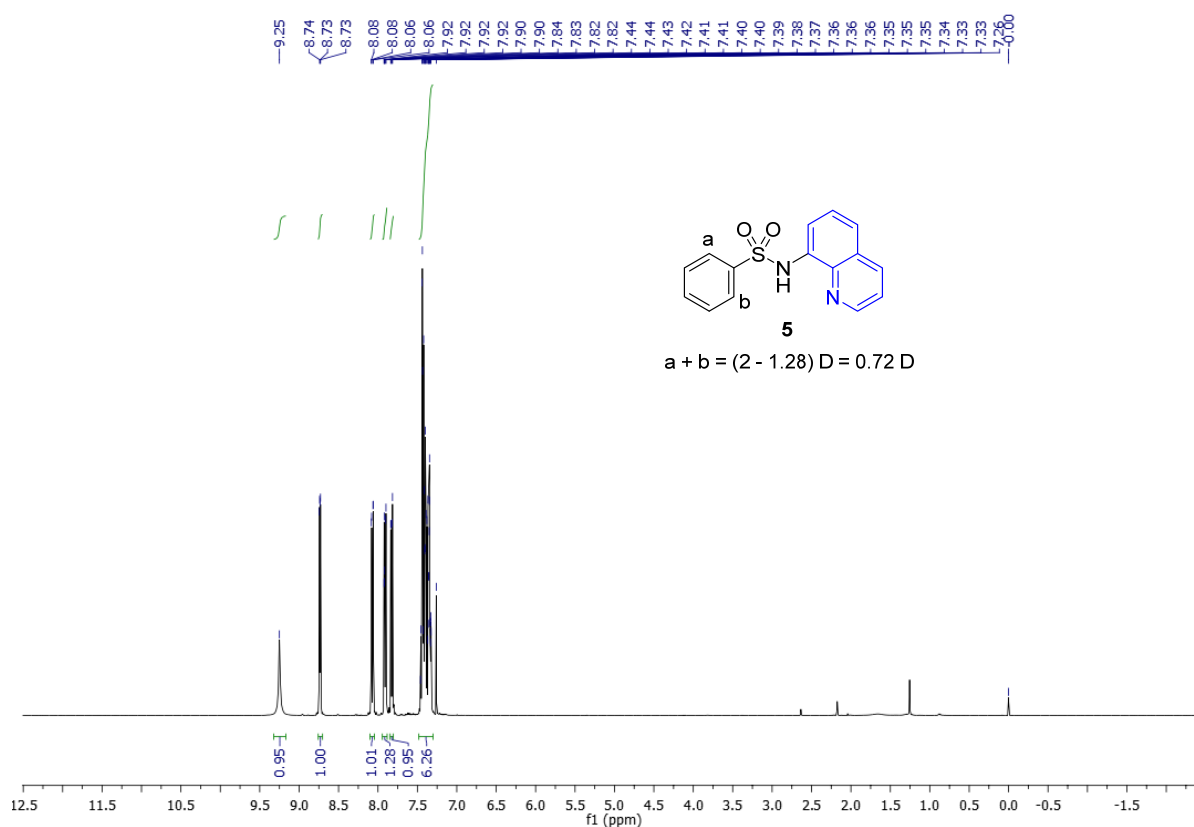
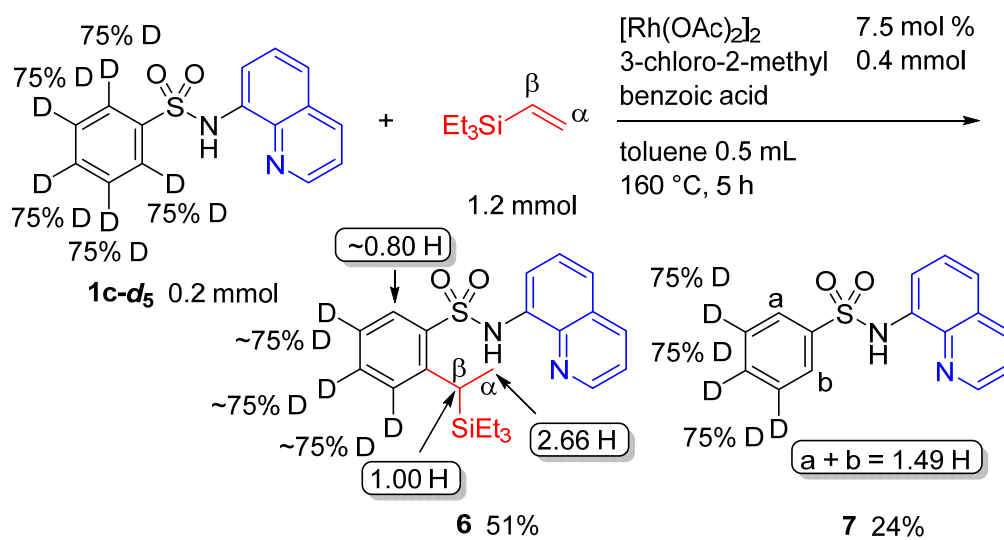


Figure S2. ^1H spectrum of **5** in CDCl_3 .

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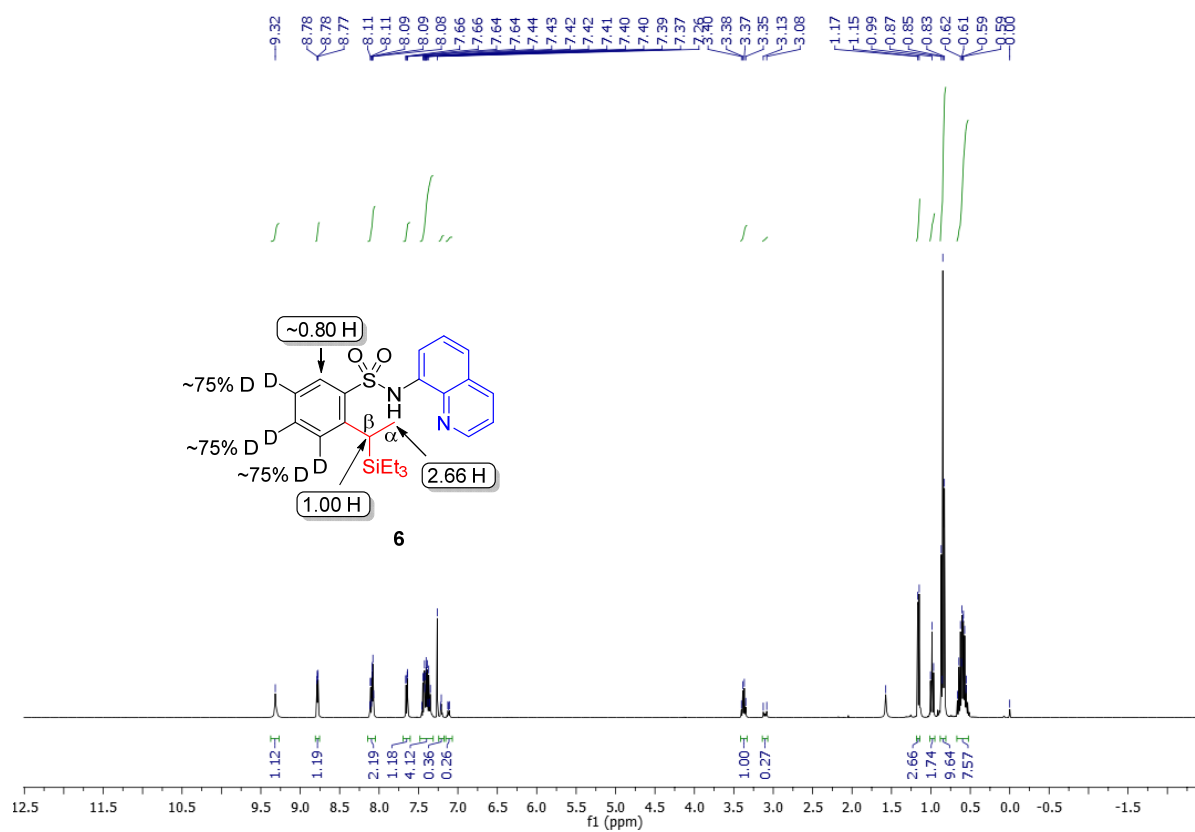


Figure S3. ^1H spectrum of **6** in CDCl_3 .

~

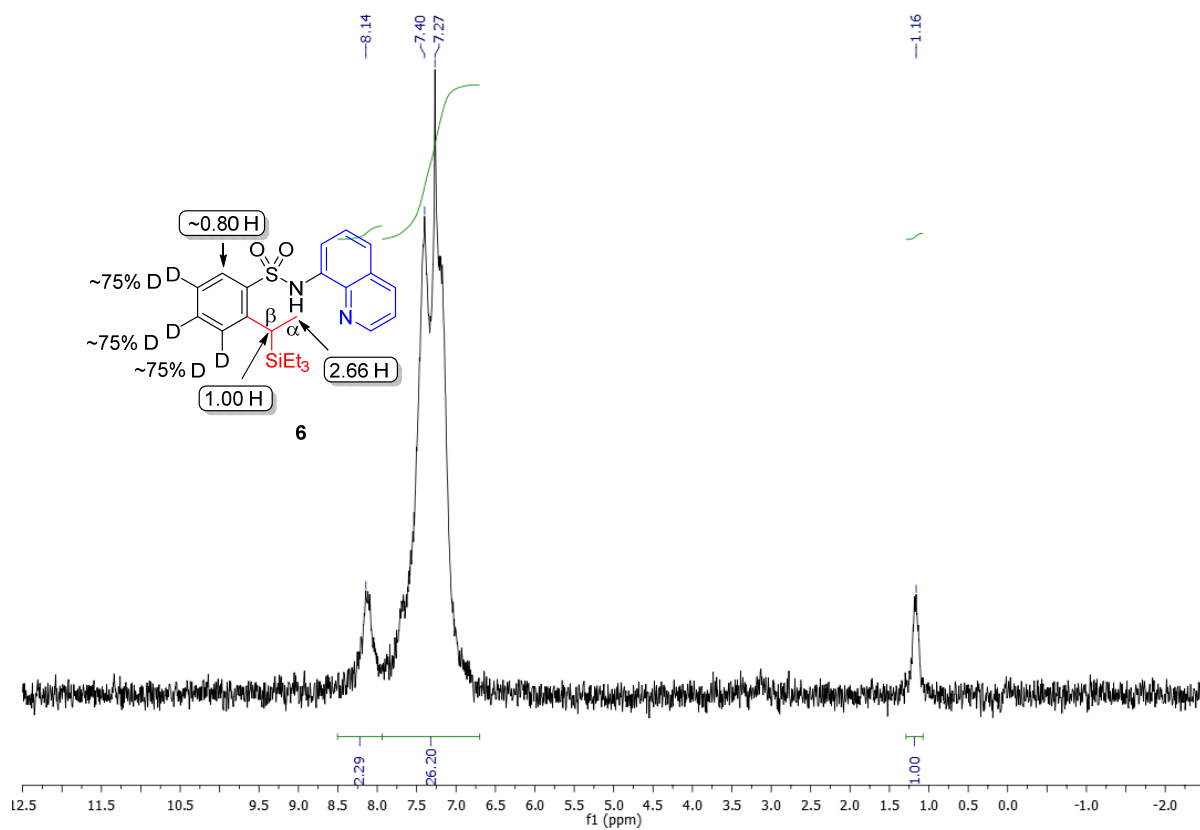


Figure S4. ^2H spectrum of **6** in CDCl_3 .

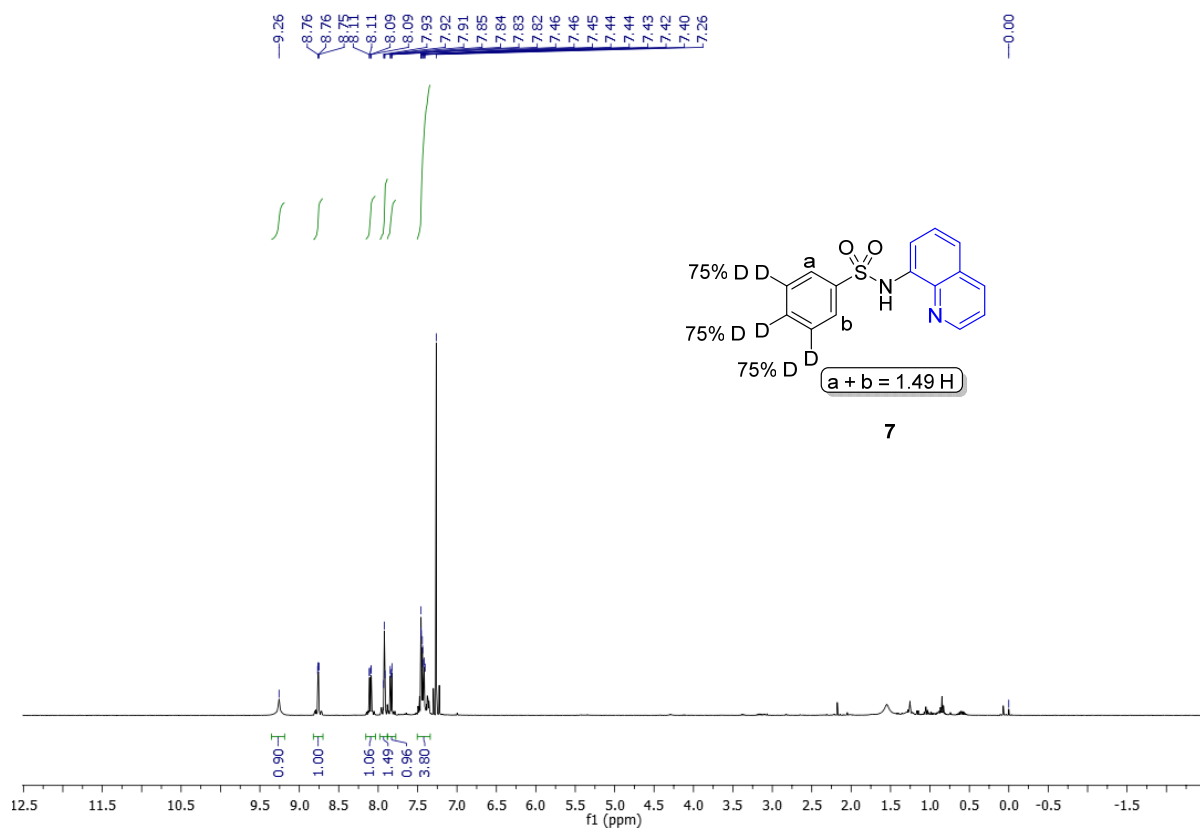


Figure S5. ^1H spectrum of **7** in CDCl_3 .

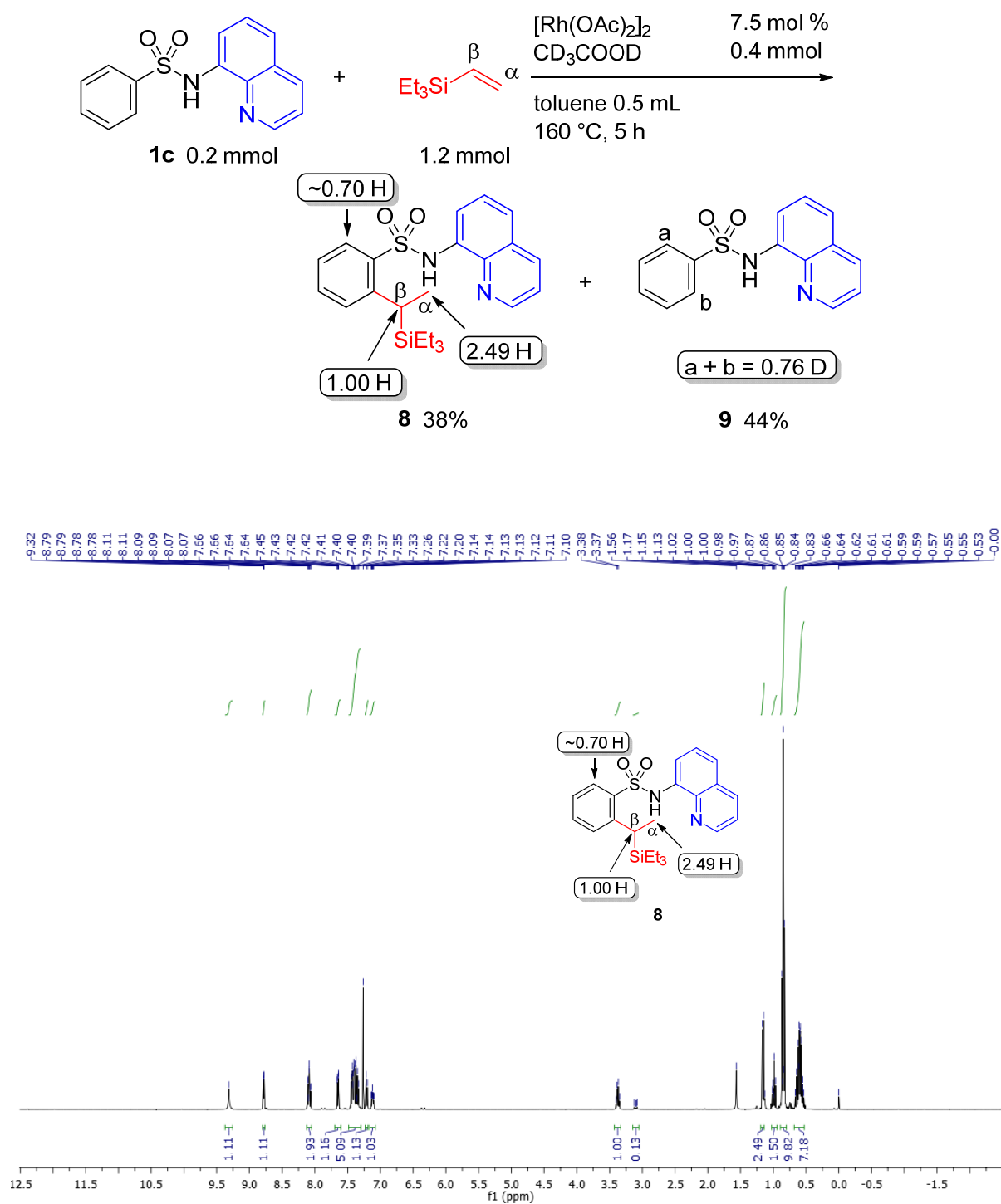


Figure S6. ^1H spectrum of **8** in CDCl_3 .

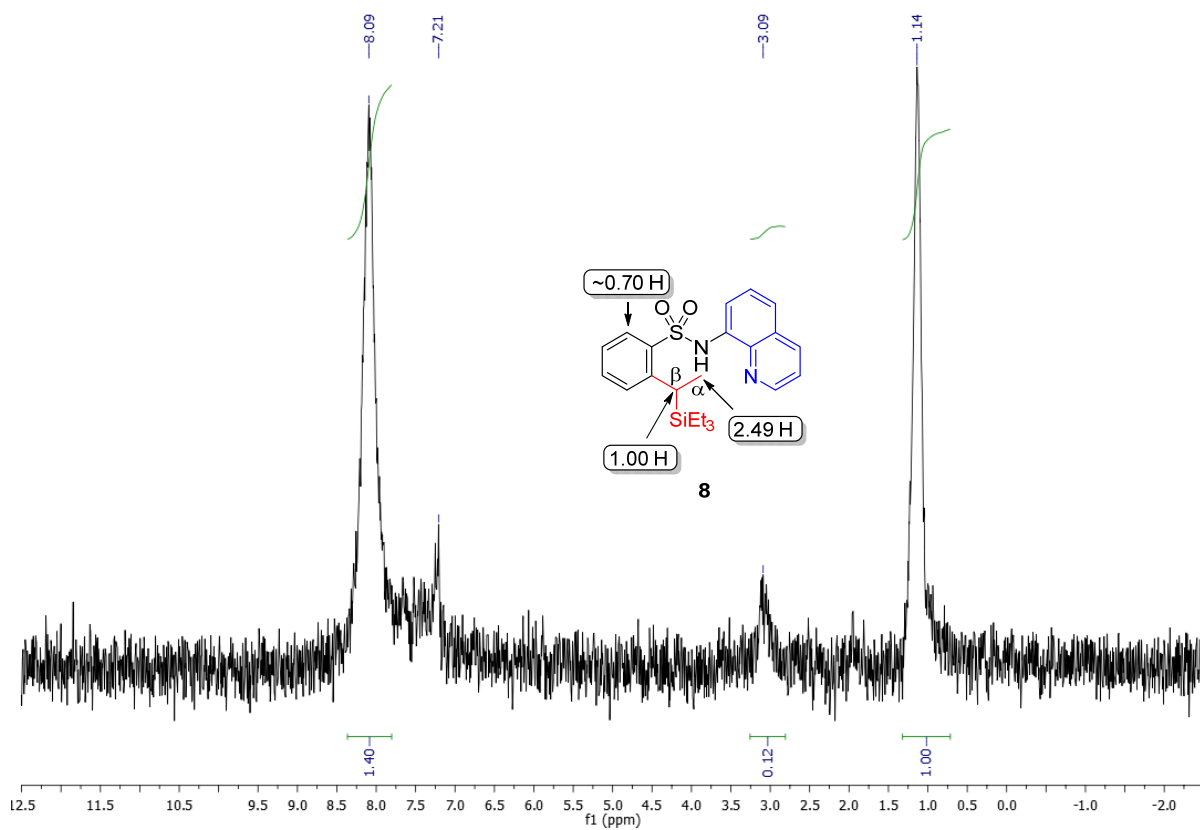


Figure S7. ^2H spectrum of **8** in CDCl_3 .

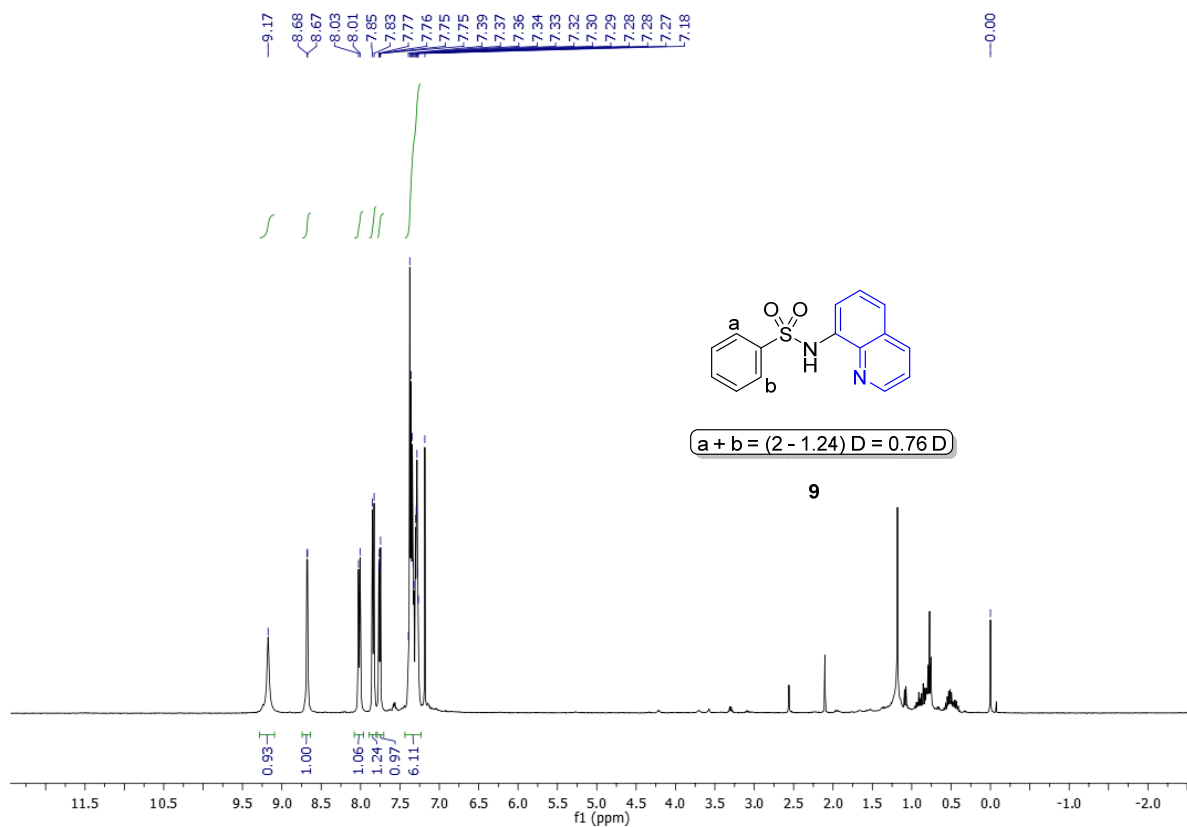


Figure S8. ^1H spectrum of **9** in CDCl_3 .

Two reactions were carried out in two different oven dried J-Young Schlenks, that involved reacting $[\text{Rh}(\text{OAc})_2]_2$ (6.6 mg, 0.015 mmol, 0.075 equiv), the sulfonamide or the deuterated sulfonamide (0.2 mmol, 1.0 equiv), and an acid additive (0.4 mmol, 2.0 equiv) in 0.5 mL of toluene. Triethylvinylsilane (170.8 mg, 222 μL , 1.2 mmol, 6.0 equiv) was then added to the reaction mixture was kept at 160 $^\circ\text{C}$ in an oil bath. The conversion of starting material at different reaction times were determined from crude NMR. Plots of $1/[\text{S}] - 1/[\text{S}]_0$ vs time for **1c** and **1c-d₅** provided the k_{H} and k_{D} . The ratio of k_{H} and k_{D} was determined to be 1.056, suggesting that the C–H activation step is not a rate limiting step.

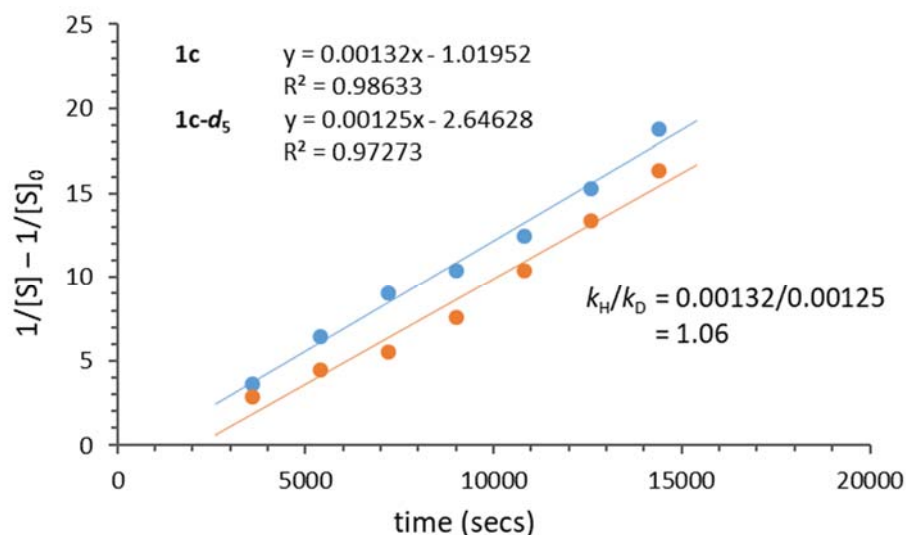
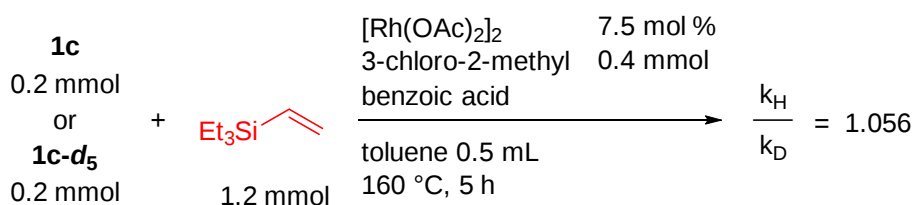


Figure S9. KIE plots for the reaction of **1c** or **1c-d₅** with triethylvinylsilane. $k_{\text{H}}/k_{\text{D}} = 0.00132/0.00125 = 1.056$

8. X-ray structure of **2ga** and **10**

To provide further evidence, compound **2ga** was crystallized from a mixture of EtOAc/hexane (2:5) and structural and crystallographic information for compound **2ga** is given below.

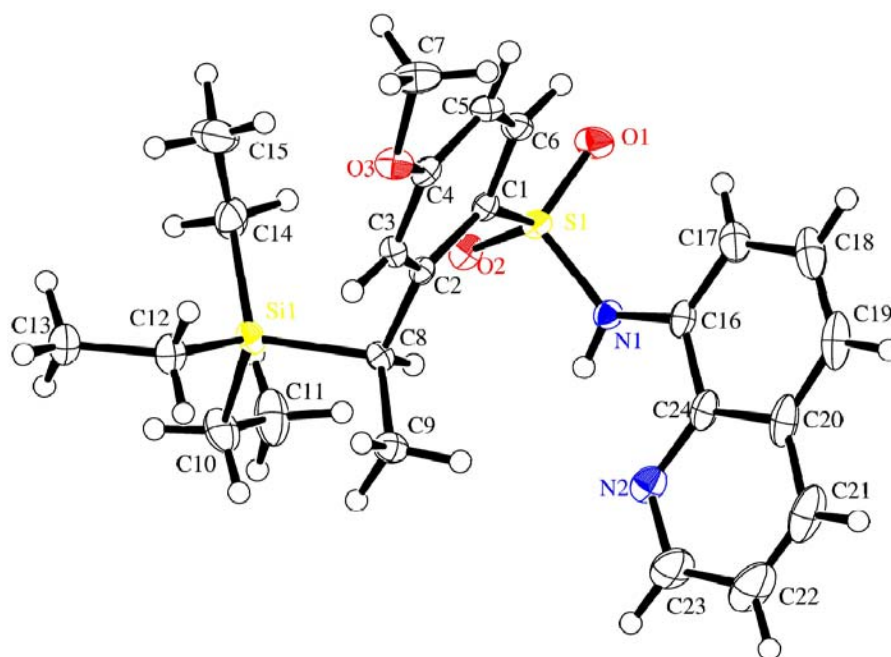


Figure S10. The structure of **2ga** was determined by the X-ray diffraction. Hydrogen atoms are not labelled for clarity. Thermal ellipsoids are drawn at the 50% probability level.

CCDC 1910136 contains supplementary crystallographic data for compound **2ga**. Colorless prisms of $C_{24}H_{32}N_2O_3SSi$ having approximate dimensions of 0.500 x 0.200 x 0.100 mm was mounted in a loop. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo- $K\alpha$ radiation. The data were collected at a temperature of $-150 \pm 1^\circ\text{C}$ to a maximum 2θ value of 62.0° . A total of 400 oscillation images were collected. A sweep of the data was done using ω scans from -22.0

to 26.0° in 0.50° step, at $\chi = -99.0$ and $\phi = -30.0^\circ$. The exposure rate was $61.7 \text{ [sec./}^\circ]$. The detector swing angle was -5.49° . A second sweep was performed using ω scans from -26.0 to 19.0° in 0.50° step, at $\chi = -99.0^\circ$ and $\phi = 120.0^\circ$. The exposure rate was $61.7 \text{ [sec./}^\circ]$. The detector swing angle was -5.49° . Another sweep was performed using ω scans from -76.0 to -32.0° in 0.50° step, at $\chi = -57.0^\circ$ and $\phi = -150.0^\circ$. The exposure rate was $61.7 \text{ [sec./}^\circ]$. The detector swing angle was -5.49° . Another sweep was performed using ω scans from -26.0 to 37.0° in 0.50° step, at $\chi = -99.0^\circ$ and $\phi = -180.0^\circ$. The exposure rate was $61.7 \text{ [sec./}^\circ]$. The detector swing angle was 5.65° . The crystal-to-detector distance was 34.00 mm . Readout was performed in the 0.172 mm pixel mode.

The structure was solved by direct methods⁵ and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed using the CrystalStructure⁶ crystallographic software package except for refinement, which was performed using SHELXL97.⁷

Table S3. Crystal Data

Empirical Formula	C ₂₄ H ₃₂ N ₂ O ₃ SSi
Formula Weight	456.67
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.500 X 0.200 X 0.100 mm
Crystal System	monoclinic
Lattice Type	I-centered
Lattice Parameters	a = 14.4384(4) Å b = 16.0496(6) Å c = 20.7130(6) Å β = 96.573(3)° V = 4768.3(3) Å ³
Space Group	I2/a (#15)
Z value	8
D _{calc}	1.272 g/cm ³
F ₀₀₀	1952.00
m(MoKa)	2.137 cm ⁻¹

Table S4. Intensity Measurements

Diffractometer	XtaLAB P200
Radiation	MoK α ($\lambda = 0.71073$ Å) multi-layer mirror monochromated
Voltage, Current	50kV, 1mA
Temperature	-150.0°C
Detector Aperture	83.8 x 70.0 mm
Data Images	400 exposures
ω oscillation Range ($\chi=-99.0$, $\phi=-30.0$)	-22.0 - 26.0°
Exposure Rate	61.7 sec./°
Detector Swing Angle	-5.49°
ω oscillation Range ($\chi=-99.0$, $\phi=120.0$)	-26.0 - 19.0°
Exposure Rate	61.7 sec./°
Detector Swing Angle	-5.49°
ω oscillation Range ($\chi=-57.0$, $\phi=-150.0$)	-76.0 - -32.0°
Exposure Rate	61.7 sec./°
Detector Swing Angle	-5.49°
ω oscillation Range ($\chi=-99.0$, $\phi=-180.0$)	-26.0 - 37.0°
Exposure Rate	61.7 sec./°
Detector Swing Angle	5.65°
Detector Position	34.00 mm
Pixel Size	0.172 mm
$2\theta_{\max}$	62.0°
No. of Reflections Measured	Total: 16863 Unique: 6120 ($R_{\text{int}} = 0.0334$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.123 - 0.979)

Table S5. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0549 \cdot P)^2 + 0.4375 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	62.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6120
No. Variables	408
Reflection/Parameter Ratio	15.00
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0364
Residuals: R (All reflections)	0.0502
Residuals: wR2 (All reflections)	0.0996
Goodness of Fit Indicator	1.083
Max Shift/Error in Final Cycle	0.008
Maximum peak in Final Diff. Map	0.35 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.31 e ⁻ /Å ³

Table S6. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S1	O1	1.4326(10)	S1	O2	1.4342(9)
S1	N1	1.6322(11)	S1	C1	1.7626(12)
Si1	C8	1.9123(13)	Si1	C10	1.8788(18)
Si1	C12	1.8735(15)	Si1	C14	1.8749(18)
O3	C4	1.3650(15)	O3	C7	1.4326(19)
N1	C16	1.4207(17)	N2	C23	1.318(2)
N2	C24	1.3604(19)	C1	C2	1.4067(17)
C1	C6	1.3896(18)	C2	C3	1.3958(17)
C2	C8	1.5145(18)	C3	C4	1.3913(18)
C4	C5	1.3852(18)	C5	C6	1.3858(18)
C8	C9	1.541(2)	C10	C11	1.535(2)
C12	C13	1.532(2)	C14	C15	1.524(3)
C16	C17	1.370(2)	C16	C24	1.419(2)
C17	C18	1.417(2)	C18	C19	1.361(3)
C19	C20	1.402(3)	C20	C21	1.408(3)
C20	C24	1.4246(18)	C21	C22	1.355(3)
C22	C23	1.406(3)			

Table S7. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O1	S1	O2	118.19(6)	O1	S1	N1	107.79(6)
O1	S1	C1	107.72(6)	O2	S1	N1	105.74(6)
O2	S1	C1	110.86(5)	N1	S1	C1	105.82(5)
C8	Si1	C10	107.18(6)	C8	Si1	C12	109.73(6)
C8	Si1	C14	112.16(6)	C10	Si1	C12	108.90(7)
C10	Si1	C14	108.50(8)	C12	Si1	C14	110.27(7)
C4	O3	C7	116.62(10)	S1	N1	C16	123.31(9)
C23	N2	C24	117.69(13)	S1	C1	C2	123.16(10)
S1	C1	C6	115.53(9)	C2	C1	C6	121.18(11)
C1	C2	C3	116.49(11)	C1	C2	C8	124.78(10)
C3	C2	C8	118.70(11)	C2	C3	C4	122.05(11)
O3	C4	C3	115.28(11)	O3	C4	C5	123.96(12)
C3	C4	C5	120.75(11)	C4	C5	C6	118.09(12)
C1	C6	C5	121.41(12)	Si1	C8	C2	112.44(8)
Si1	C8	C9	110.91(9)	C2	C8	C9	112.50(11)
Si1	C10	C11	114.77(13)	Si1	C12	C13	114.28(11)
Si1	C14	C15	116.41(13)	N1	C16	C17	123.74(13)
N1	C16	C24	116.19(12)	C17	C16	C24	120.02(12)
C16	C17	C18	119.87(16)	C17	C18	C19	121.34(17)
C18	C19	C20	119.97(14)	C19	C20	C21	123.61(14)
C19	C20	C24	119.55(14)	C21	C20	C24	116.84(15)
C20	C21	C22	120.05(16)	C21	C22	C23	118.96(19)
N2	C23	C22	123.75(18)	N2	C24	C16	118.28(12)
N2	C24	C20	122.60(13)	C16	C24	C20	119.11(13)

Spectral data of complex 10 and 11.

The sulfonamide **1c** (28.4 mg, 0.1 mmol, 1.0 equiv) and $[\text{Rh}(\text{OAc})_2]_2$ (22.1 mg, 0.05 mmol, 0.5 equiv) was added to 0.5 mL of toluene in an oven dried J-Young flask under a N_2 atmosphere. The sealed reaction vessel was placed in an oil bath at 120 °C for 4 hours. The reaction mixture was then allowed cool to room temperature and allowed to stand for 2 days, at which time, dark green colored crystals **10** were formed in the solution, one of which was used for a single crystal measurement. Structural and crystallographic information for the Rh-complex **10** is given below.

A dark green crystal was isolated and washed with hexane (3 x 2 mL) and then dried under a vacuum. A ^1H NMR spectrum of the sparingly soluble crystalline material indicated that the sample was the complex **11**. In the Rh-complex **10**, two molecules of acetic acid are coordinated at the axial positions. Because the interaction of acetic acid and the Rh-center is quite fragile, the weakly coordinated acetic acids were released while washing the complex with hexane and drying under a vacuum to give **11**.

The complex **11** was also obtained when the reaction of the sulfonamide **1c** (28.4 mg, 0.1 mmol, 1.0 equiv) and $[\text{Rh}(\text{OAc})_2]_2$ (22.1 mg, 0.05 mmol, 0.5 equiv) in the presence of 3-chloro-2-methyl benzoic acid (34.1 mg, 0.2 mmol, 2.0 equiv) was carried out.

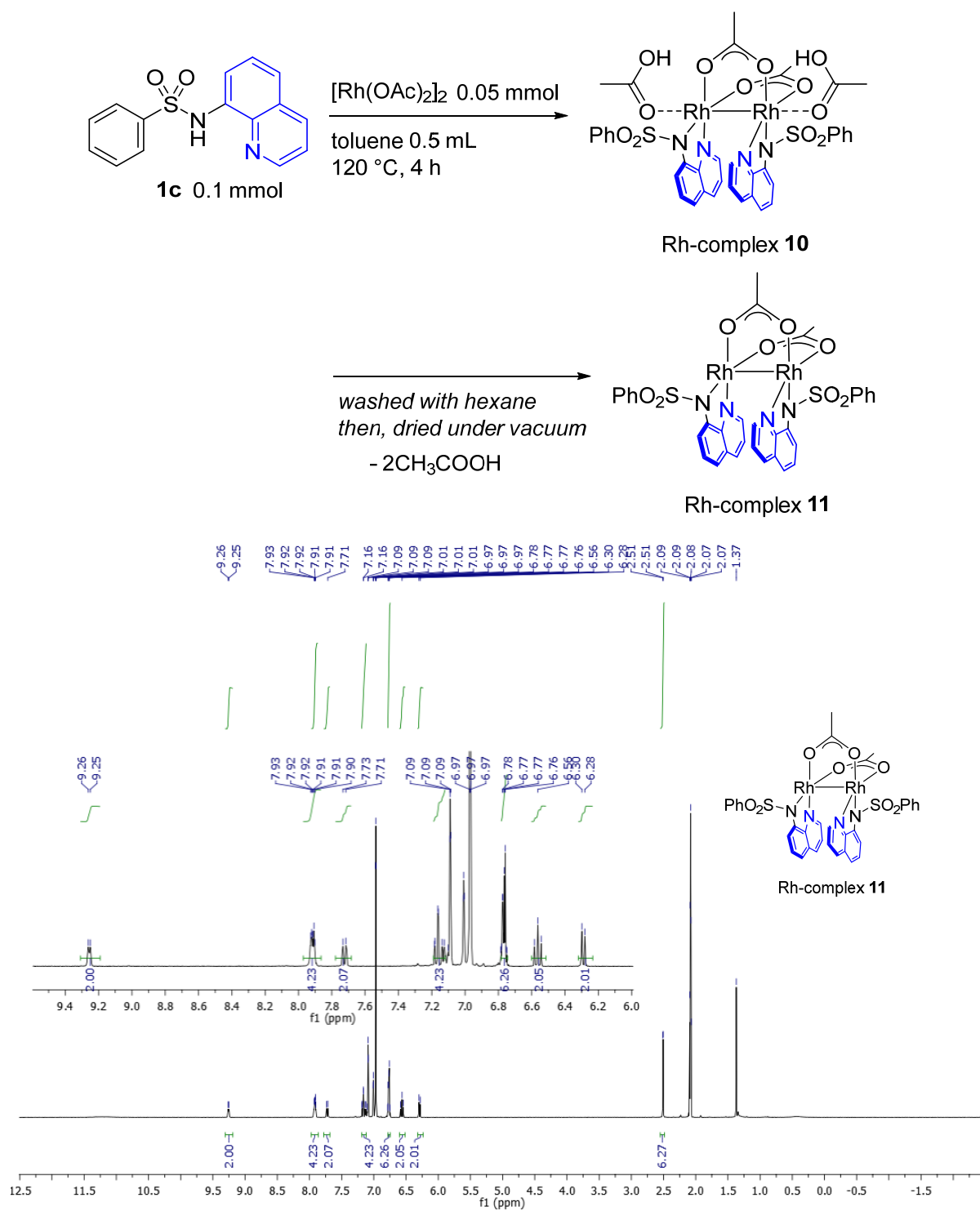


Figure S11. ^1H NMR of complex 11 in $\text{toluene-}d_8$.

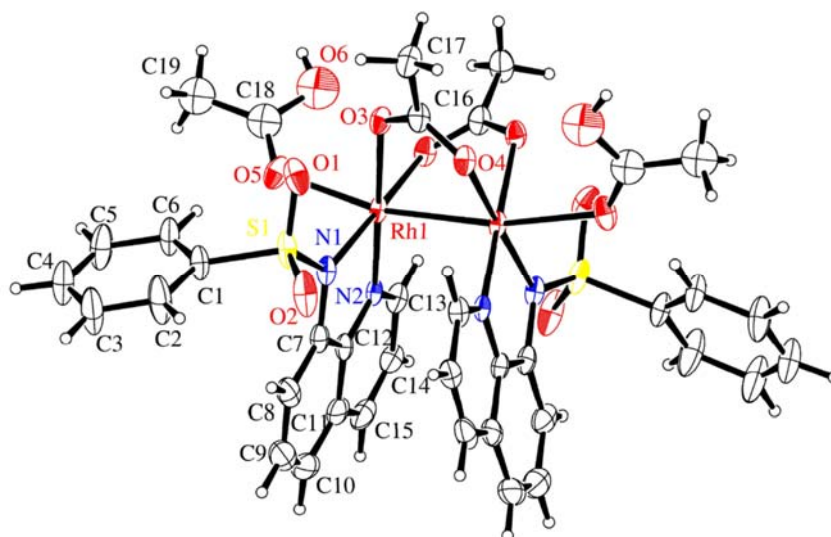


Figure S12. The structure of **10** was determined by the X-ray diffraction. Hydrogen atoms and the other part of the complex are not labelled for clarity. Thermal ellipsoids are drawn at the 30% probability level.

CCDC 1918726 contains supplementary crystallographic data for complex **10**. A dark green prism crystal of $C_{38}H_{36}N_4O_{12}Rh_2S_2$ having approximate dimensions of 0.200 x 0.200 x 0.100 mm was mounted in a loop. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-K α radiation. The data were collected at a temperature of $-150 \pm 1^\circ\text{C}$ to a maximum 2θ value of 61.7° . A total of 592 oscillation images were collected. A sweep of data was done using ω scans from -44.0 to -19.0° in 0.50° step, at $\chi = 108.0^\circ$ and $\phi = 93.0^\circ$. The exposure rate was 7.6 [sec./ $^\circ$]. The detector swing angle was -5.34° . A second sweep was performed using ω scans from -3.0 to 22.0° in 0.50° step, at $\chi = -108.0^\circ$ and $\phi = -3.0^\circ$. The exposure rate was 7.6 [sec./ $^\circ$]. The detector swing angle was 5.34° . Another sweep was performed using ω scans from -25.0 to 21.0° in 0.50° step, at $\chi = -99.0^\circ$ and $\phi = -90.0^\circ$. The exposure rate was 7.6 [sec./ $^\circ$]. The detector swing angle was -5.34° . Another sweep was performed using ω scans from -19.0

to 27.0° in 0.50° step, at $\chi = -99.0^\circ$ and $\phi = -150.0^\circ$. The exposure rate was 7.6 [sec./°]. The detector swing angle was -5.34°. Another sweep was performed using ω scans from -23.0 to 31.0° in 0.50° step, at $\chi = -99.0^\circ$ and $\phi = -60.0^\circ$. The exposure rate was 7.6 [sec./°]. The detector swing angle was 5.34°. Another sweep was performed using ω scans from -11.0 to 27.0° in 0.50° step, at $\chi = -99.0^\circ$ and $\phi = 90.0^\circ$. The exposure rate was 7.6 [sec./°]. The detector swing angle was -5.34°. Another sweep was performed using ω scans from -12.0 to 19.0° in 0.50° step, at $\chi = -99.0^\circ$ and $\phi = 150.0^\circ$. The exposure rate was 7.6 [sec./°]. The detector swing angle was -5.34°. Another sweep was performed using ω scans from -12.0 to 19.0° in 0.50° step, at $\chi = -99.0^\circ$ and $\phi = 120.0^\circ$. The exposure rate was 7.6 [sec./°]. The detector swing angle was -5.34°. The crystal-to-detector distance was 35.00 mm. Readout was performed in the 0.172 mm pixel mode.

The structure was solved by direct methods⁵ and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while rest were refined isotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure⁶ crystallographic software package except for refinement, which was performed using SHELXL97.⁷

Table S8. Crystal Data

Empirical Formula	C ₃₈ H ₃₆ N ₄ O ₁₂ Rh ₂ S ₂
Formula Weight	1010.65
Crystal Color, Habit	darkgreen, prism
Crystal Dimensions	0.200 X 0.200 X 0.100 mm
Crystal System	monoclinic
Lattice Type	I-centered

Lattice Parameters

$$a = 17.4067(10) \text{ \AA}$$

$$b = 10.6112(10) \text{ \AA}$$

$$c = 22.164(2) \text{ \AA}$$

$$\beta = 98.333(7)^\circ$$

$$V = 4050.6(6) \text{ \AA}^3$$

Space Group

$$I2/a \text{ (#15)}$$

Z value

$$4$$

D_{calc}

$$1.657 \text{ g/cm}^3$$

F₀₀₀

$$2040.00$$

$\mu(\text{MoK}\alpha)$

$$9.828 \text{ cm}^{-1}$$

Table S9. Intensity Measurements

Diffractometer	XtaLAB P200
Radiation	MoK α ($\lambda = 0.71073$ Å) multi-layer mirror monochromated
Voltage, Current	50kV, 1mA
Temperature	-150.0°C
Detector Aperture	83.8 x 70.0 mm
Data Images	592 exposures
ω oscillation Range ($\chi = 108.0, \phi = 93.0$)	-44.0 - -19.0°
Exposure Rate	7.6 sec./°
Detector Swing Angle	-5.34°
ω oscillation Range ($\chi = -108.0, \phi = -3.0$)	-3.0 - 22.0°
Exposure Rate	7.6 sec./°
Detector Swing Angle	5.34°
ω oscillation Range ($\chi = -99.0, \phi = -90.0$)	-25.0 - 21.0°
Exposure Rate	7.6 sec./°
Detector Swing Angle	-5.34°
ω oscillation Range ($\chi = -99.0, \phi = -150.0$)	-19.0 - 27.0°
Exposure Rate	7.6 sec./°
Detector Swing Angle	-5.34°
ω oscillation Range ($\chi = -99.0, \phi = -60.0$)	-23.0 - 31.0°
Exposure Rate	7.6 sec./°
Detector Swing Angle	5.34°
ω oscillation Range ($\chi = -99.0, \phi = 90.0$)	-11.0 - 27.0°
Exposure Rate	7.6 sec./°
Detector Swing Angle	-5.34°
ω oscillation Range ($\chi = -99.0, \phi = 150.0$)	-12.0 - 19.0°
Exposure Rate	7.6 sec./°
Detector Swing Angle	-5.34°
ω oscillation Range ($\chi = -99.0, \phi = 120.0$)	-12.0 - 19.0°
Exposure Rate	7.6 sec./°
Detector Swing Angle	-5.34°
Detector Position	35.00 mm

Pixel Size	0.172 mm
$2\theta_{\text{max}}$	61.7°
No. of Reflections Measured	Total: 18791
	Unique: 5185 ($R_{\text{int}} = 0.0925$)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.620 - 0.906)

Table S10. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.1454 \cdot P)^2 + 49.2335 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	61.7°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5185
No. Variables	247
Reflection/Parameter Ratio	20.99
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0897
Residuals: R (All reflections)	0.1132
Residuals: wR2 (All reflections)	0.2618
Goodness of Fit Indicator	1.041
Max Shift/Error in Final Cycle	0.006
Maximum peak in Final Diff. Map	3.94 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-1.54 e ⁻ /Å ³

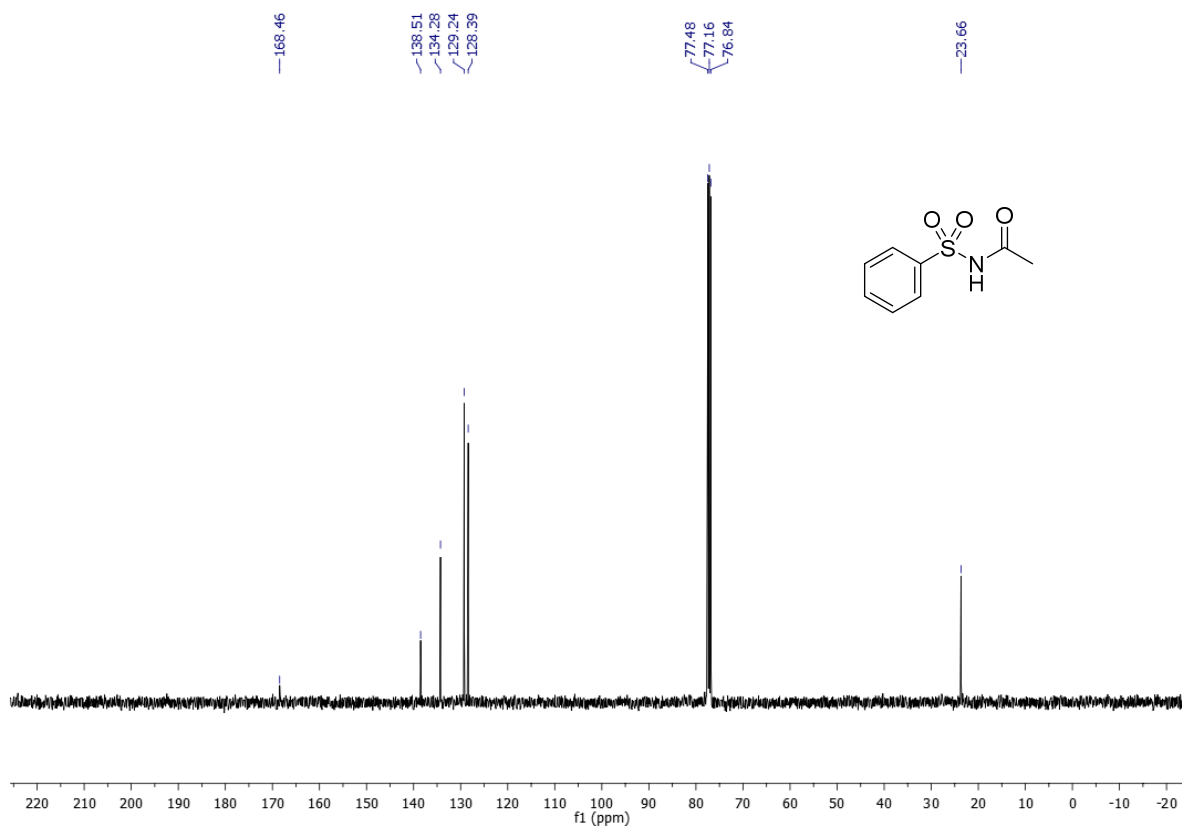
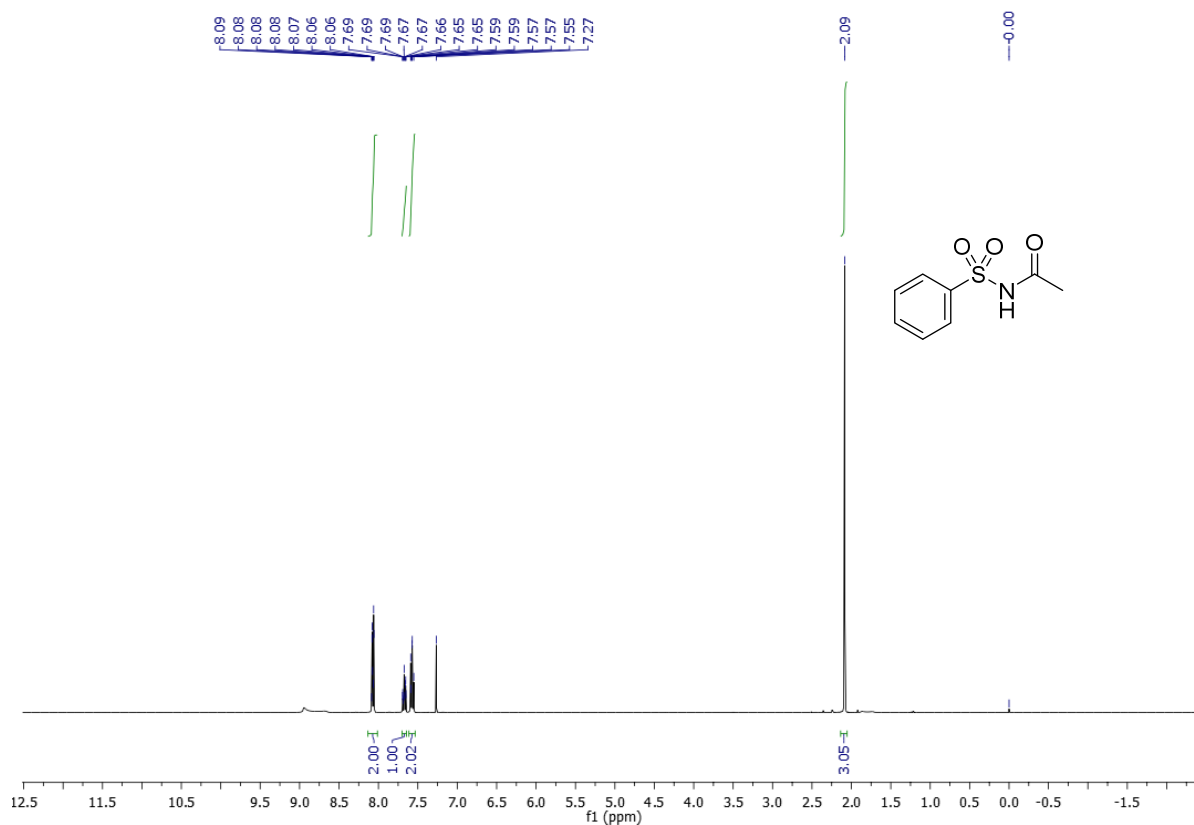
Table S11. Bond lengths (Å)

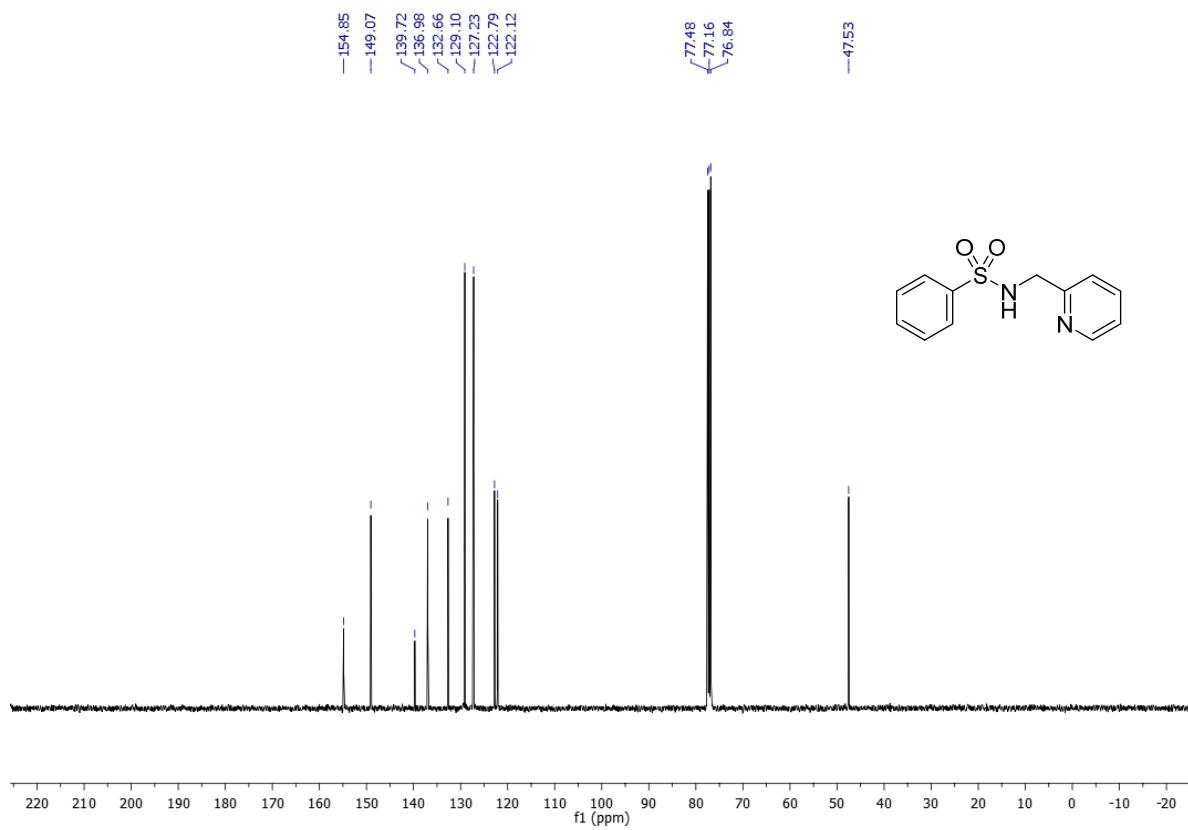
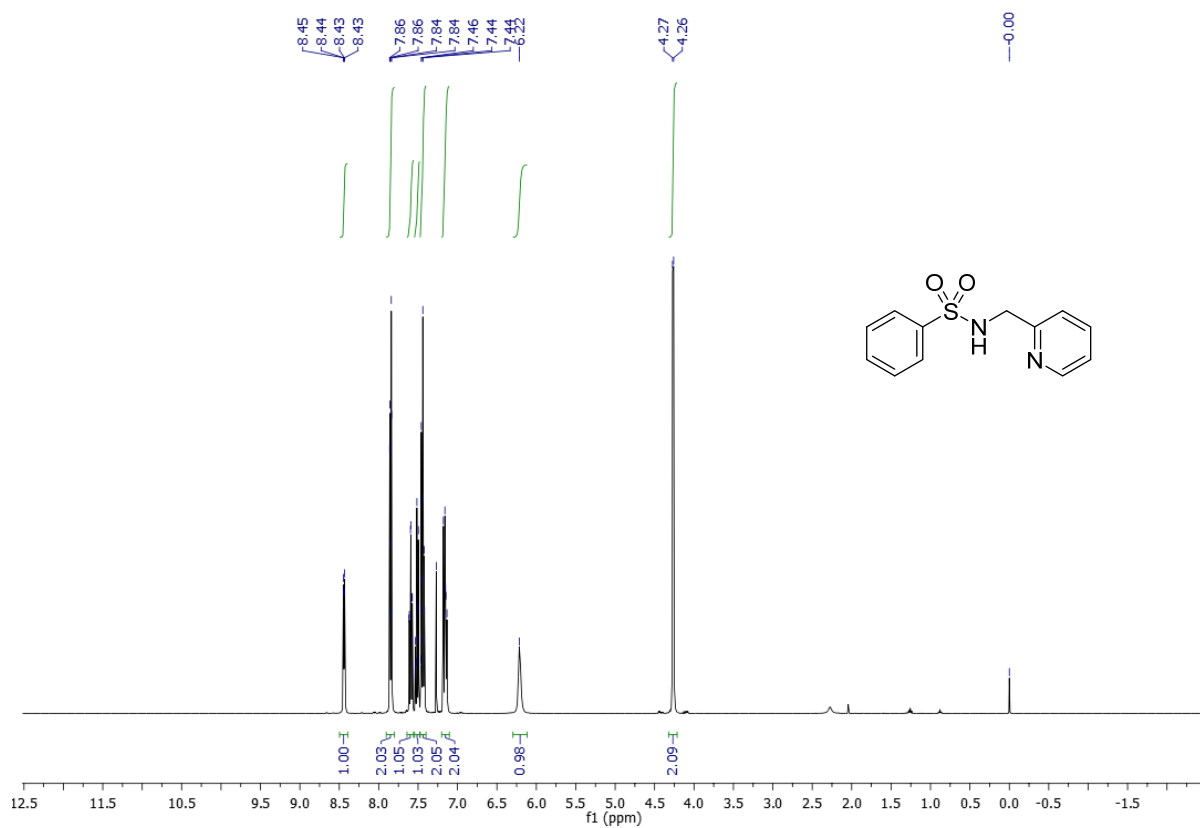
atom	atom	distance	atom	atom	distance
Rh1	Rh1 ¹	2.5178(7)	Rh1	O3	2.065(6)
Rh1	O4 ¹	2.066(6)	Rh1	O5	2.322(6)
Rh1	N1	2.062(6)	Rh1	N2	1.970(6)
S1	O1	1.457(9)	S1	O2	1.446(8)
S1	N1	1.617(6)	S1	C1	1.769(9)
O3	C16	1.276(10)	O4	C16	1.263(10)
O5	C18	1.209(18)	O6	C18	1.44(2)
N1	C7	1.426(11)	N2	C12	1.372(10)
N2	C13	1.335(9)	C1	C2	1.362(17)
C1	C6	1.388(14)	C2	C3	1.381(18)
C3	C4	1.36(2)	C4	C5	1.35(2)
C5	C6	1.384(14)	C7	C8	1.380(13)
C7	C12	1.421(12)	C8	C9	1.399(17)
C9	C10	1.38(2)	C10	C11	1.426(17)
C11	C12	1.427(13)	C11	C15	1.433(17)
C13	C14	1.399(13)	C14	C15	1.343(15)
C16	C17	1.472(14)	C18	C19	1.49(2)

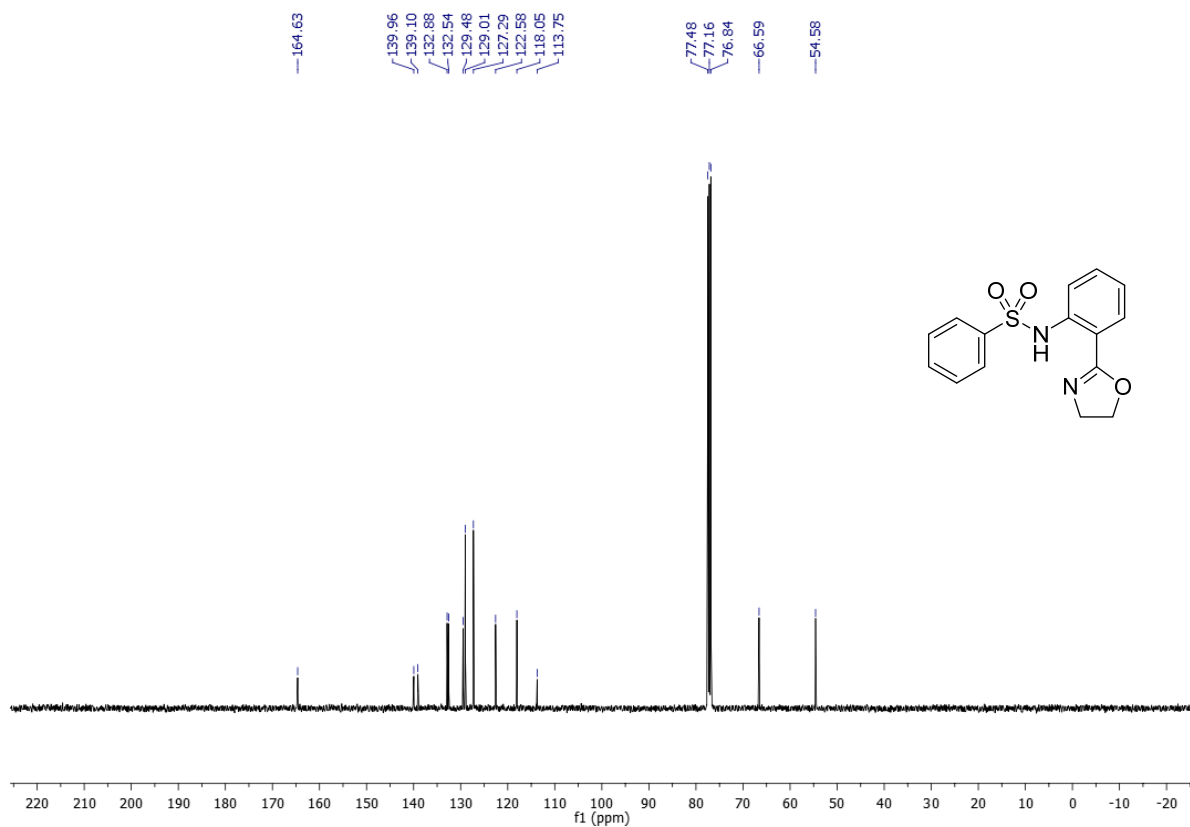
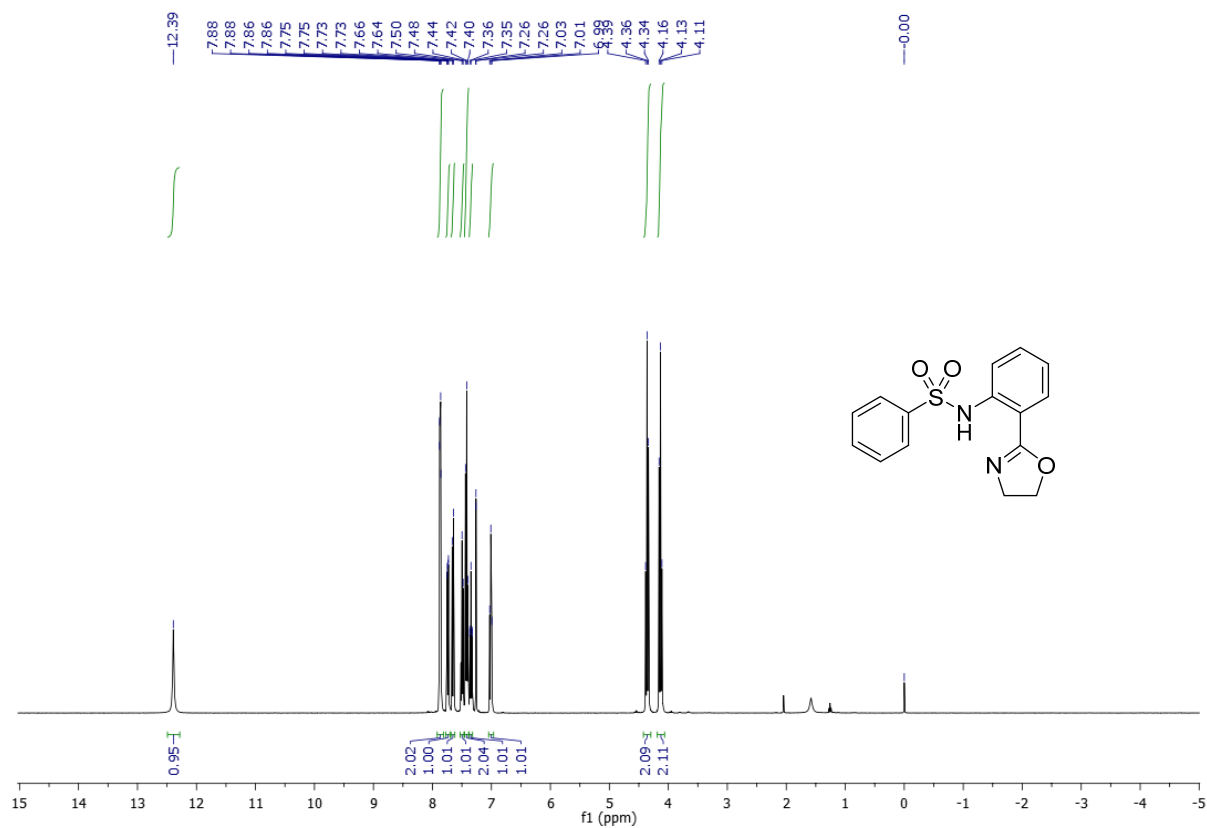
Table S12. Bond angles (°)

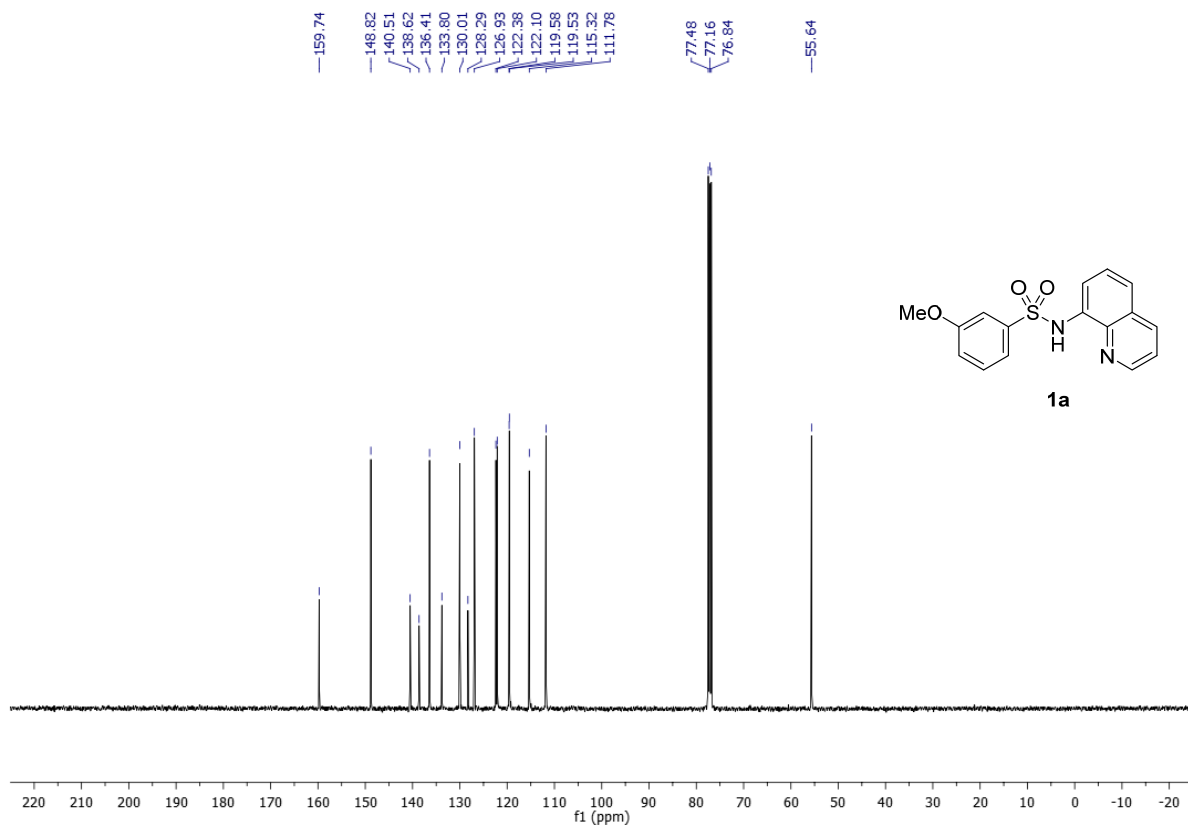
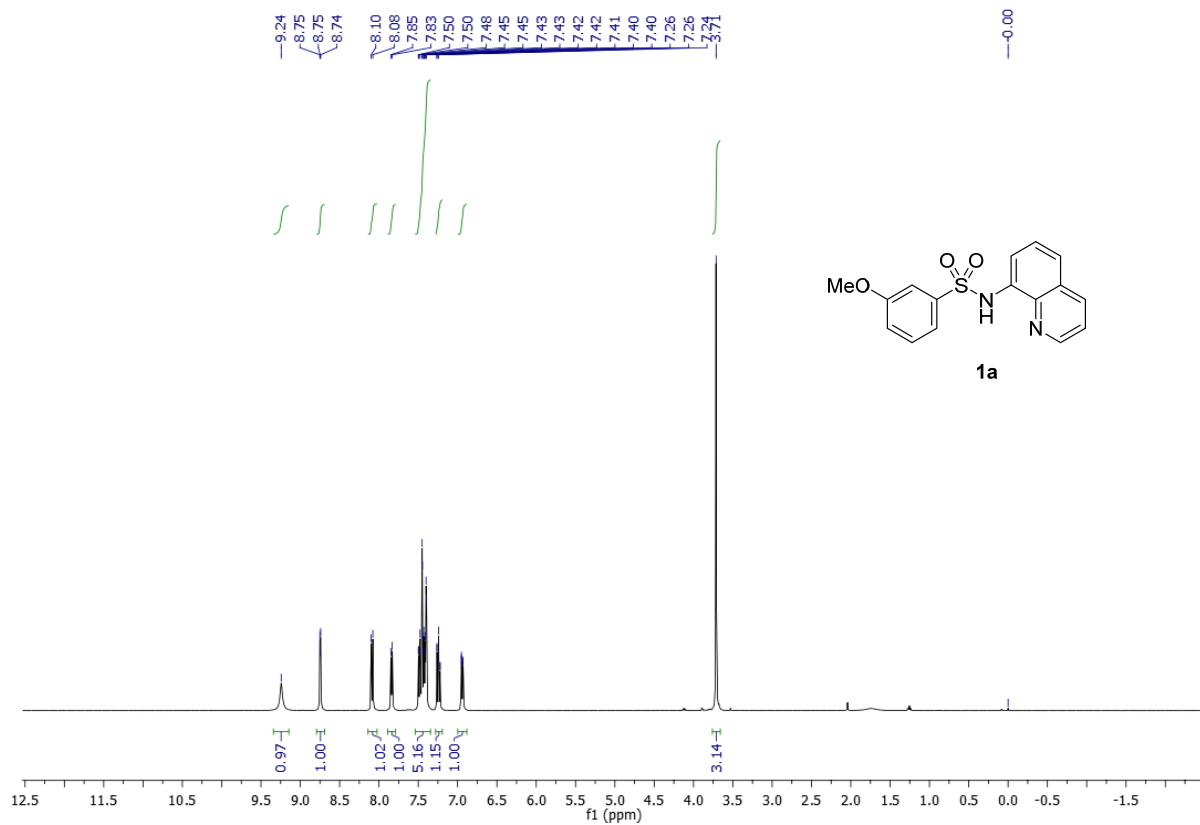
atom	atom	atom	angle	atom	atom	atom	angle
Rh1 ¹	Rh1	O3	83.69(15)	Rh1 ¹	Rh1	O4 ¹	83.80(15)
Rh1 ¹	Rh1	O5	167.56(19)	Rh1 ¹	Rh1	N1	99.86(17)
Rh1 ¹	Rh1	N2	97.56(15)	O3	Rh1	O4 ¹	84.5(2)
O3	Rh1	O5	88.1(2)	O3	Rh1	N1	99.2(2)
O3	Rh1	N2	178.6(2)	O4 ¹	Rh1	O5	86.1(2)
O4 ¹	Rh1	N1	175.1(2)	O4 ¹	Rh1	N2	95.0(2)
O5	Rh1	N1	90.7(2)	O5	Rh1	N2	90.5(2)
N1	Rh1	N2	81.3(2)	O1	S1	O2	117.3(5)
O1	S1	N1	108.5(4)	O1	S1	C1	107.0(5)
O2	S1	N1	110.9(4)	O2	S1	C1	106.0(4)
N1	S1	C1	106.5(4)	Rh1	O3	C16	119.4(6)
Rh1 ¹	O4	C16	119.1(5)	Rh1	O5	C18	129.2(8)
Rh1	N1	S1	128.4(4)	Rh1	N1	C7	112.2(4)
S1	N1	C7	118.9(5)	Rh1	N2	C12	115.3(5)
Rh1	N2	C13	125.4(6)	C12	N2	C13	119.3(7)
S1	C1	C2	122.1(8)	S1	C1	C6	119.7(7)
C2	C1	C6	118.1(9)	C1	C2	C3	120.8(13)
C2	C3	C4	120.2(15)	C3	C4	C5	120.4(11)
C4	C5	C6	119.5(11)	C1	C6	C5	120.9(11)
N1	C7	C8	127.8(8)	N1	C7	C12	113.5(7)
C8	C7	C12	118.5(8)	C7	C8	C9	120.1(11)
C8	C9	C10	123.3(12)	C9	C10	C11	118.2(11)
C10	C11	C12	118.6(11)	C10	C11	C15	124.4(11)
C12	C11	C15	117.0(9)	N2	C12	C7	117.5(7)
N2	C12	C11	121.2(8)	C7	C12	C11	121.3(8)
N2	C13	C14	122.2(8)	C13	C14	C15	120.4(9)
C11	C15	C14	120.0(10)	O3	C16	O4	122.8(8)
O3	C16	C17	119.4(8)	O4	C16	C17	117.9(8)
O5	C18	O6	120.1(13)	O5	C18	C19	127.2(13)
O6	C18	C19	110.3(14)				

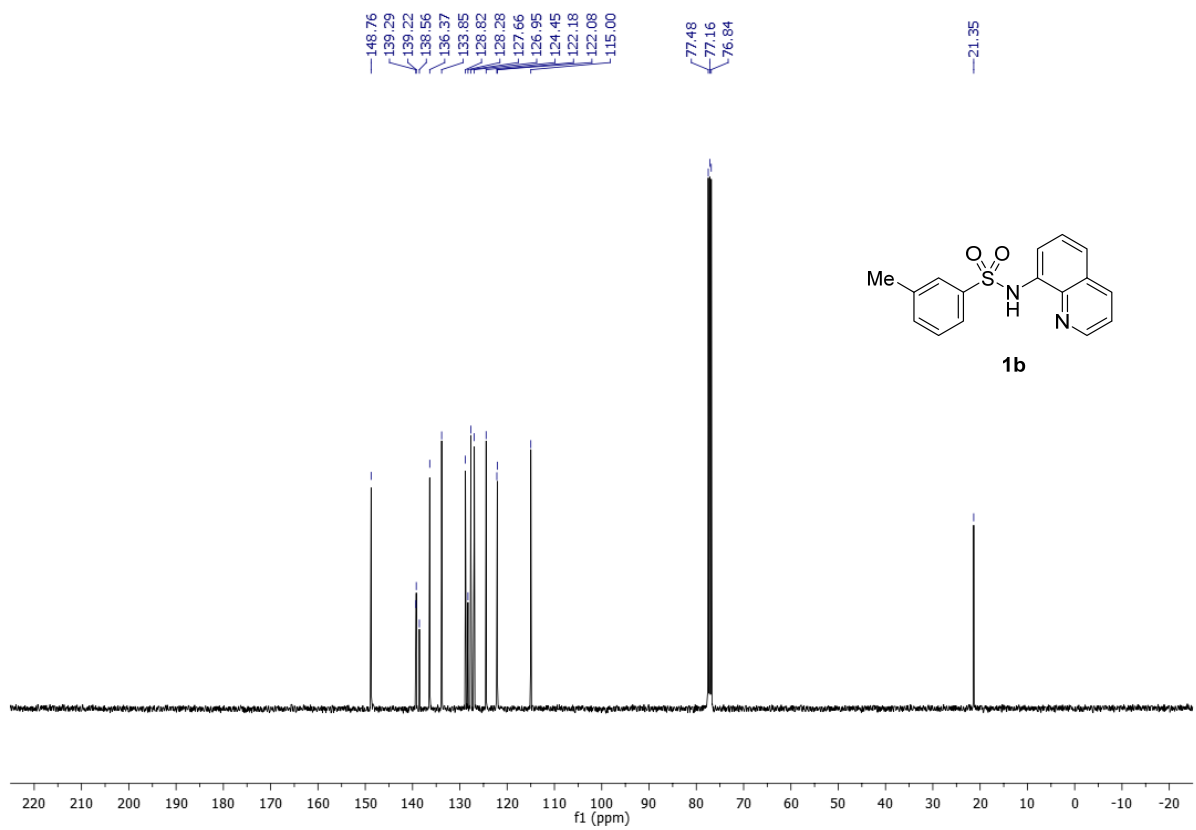
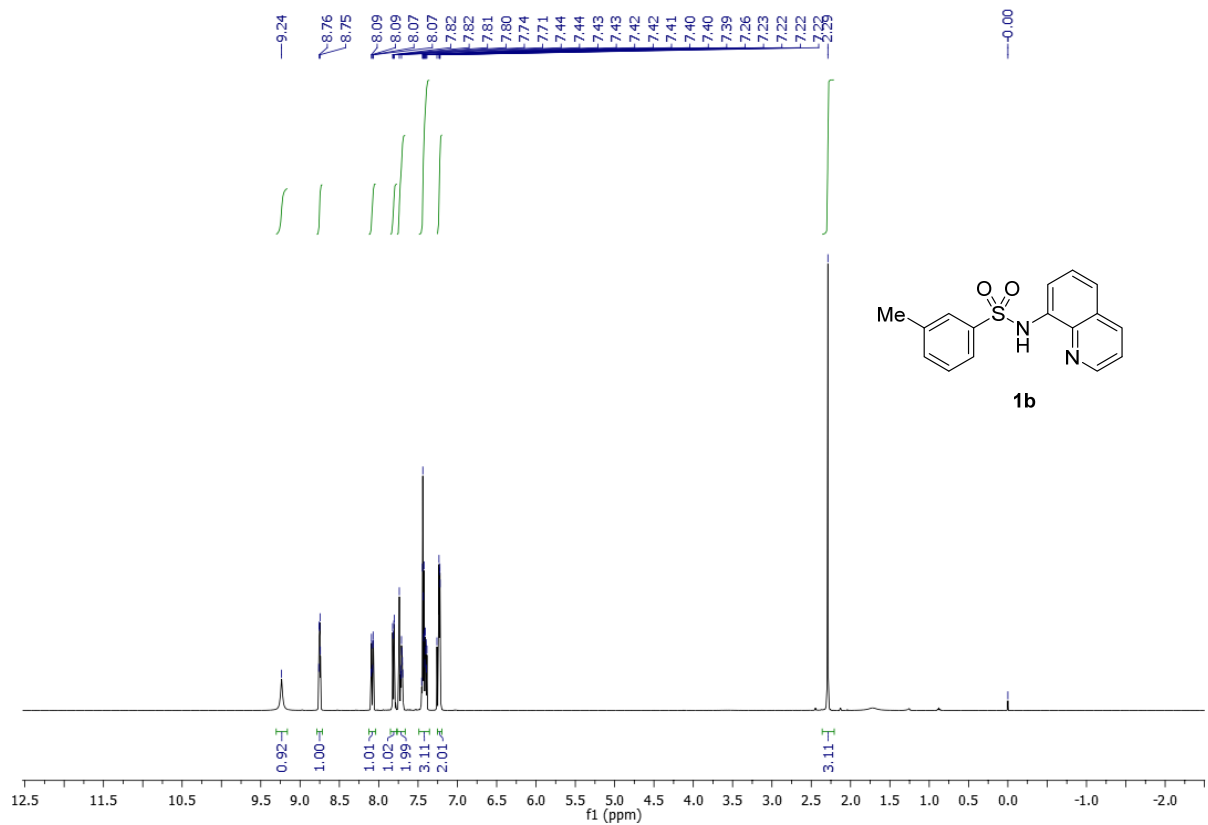
9. NMR spectra of starting materials

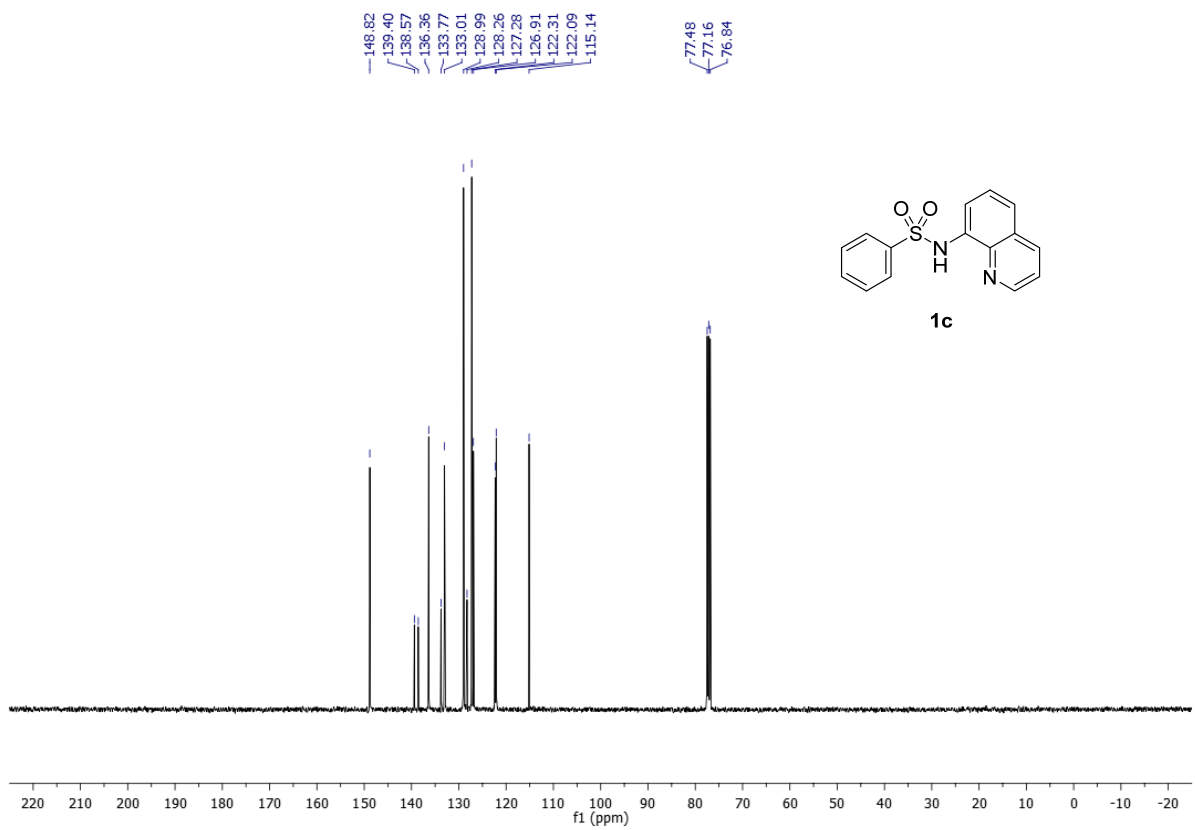
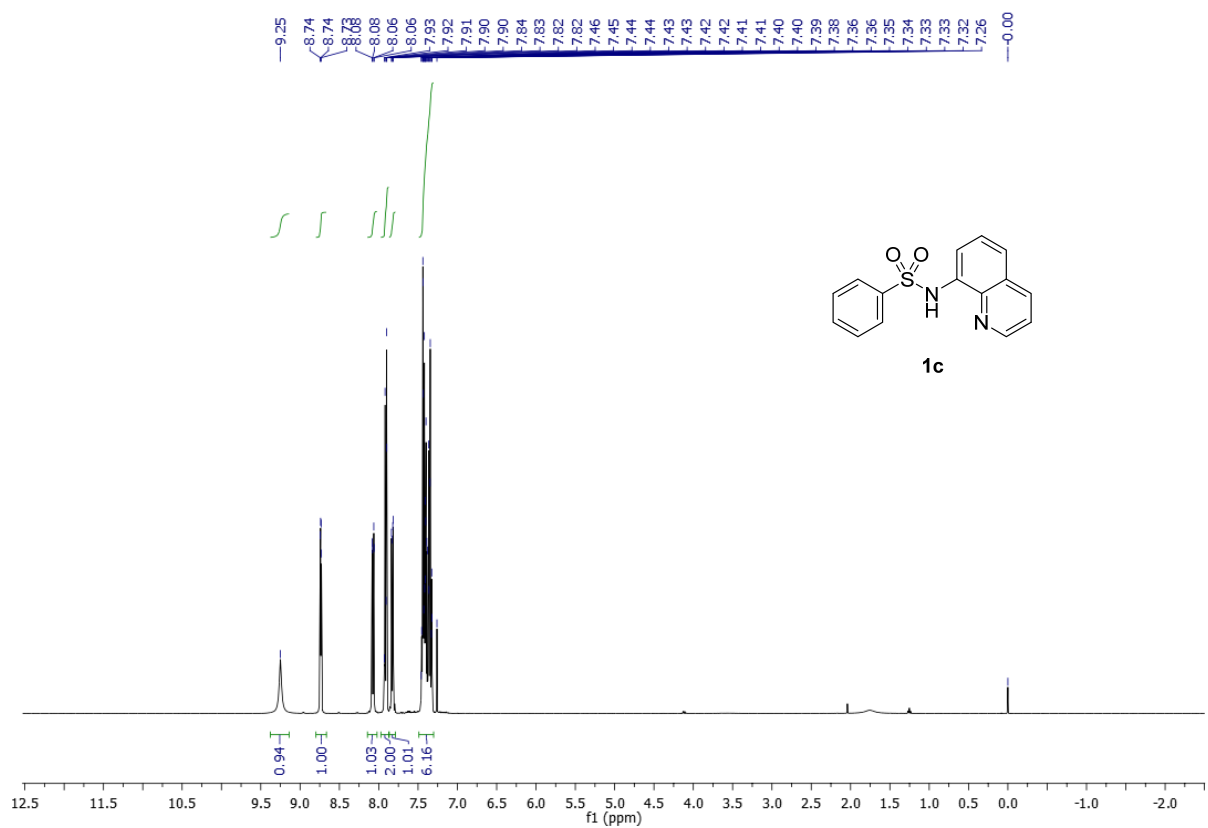


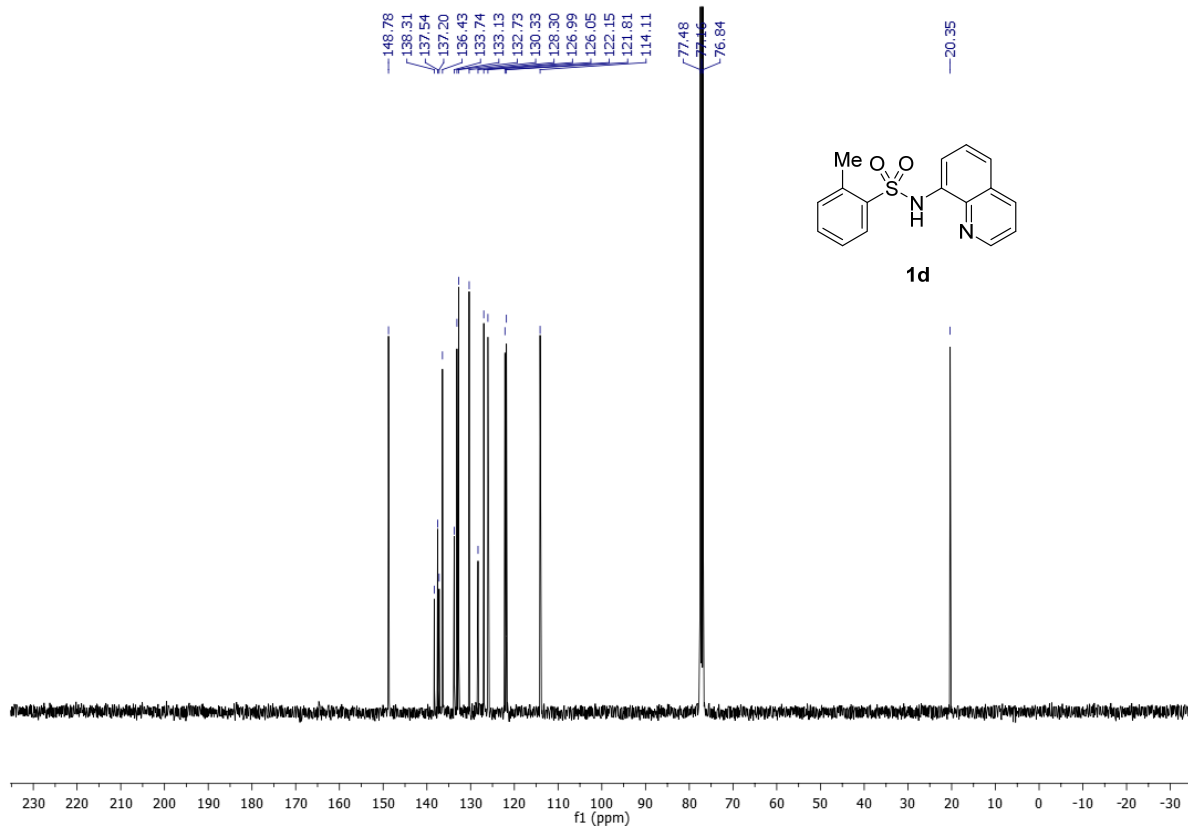
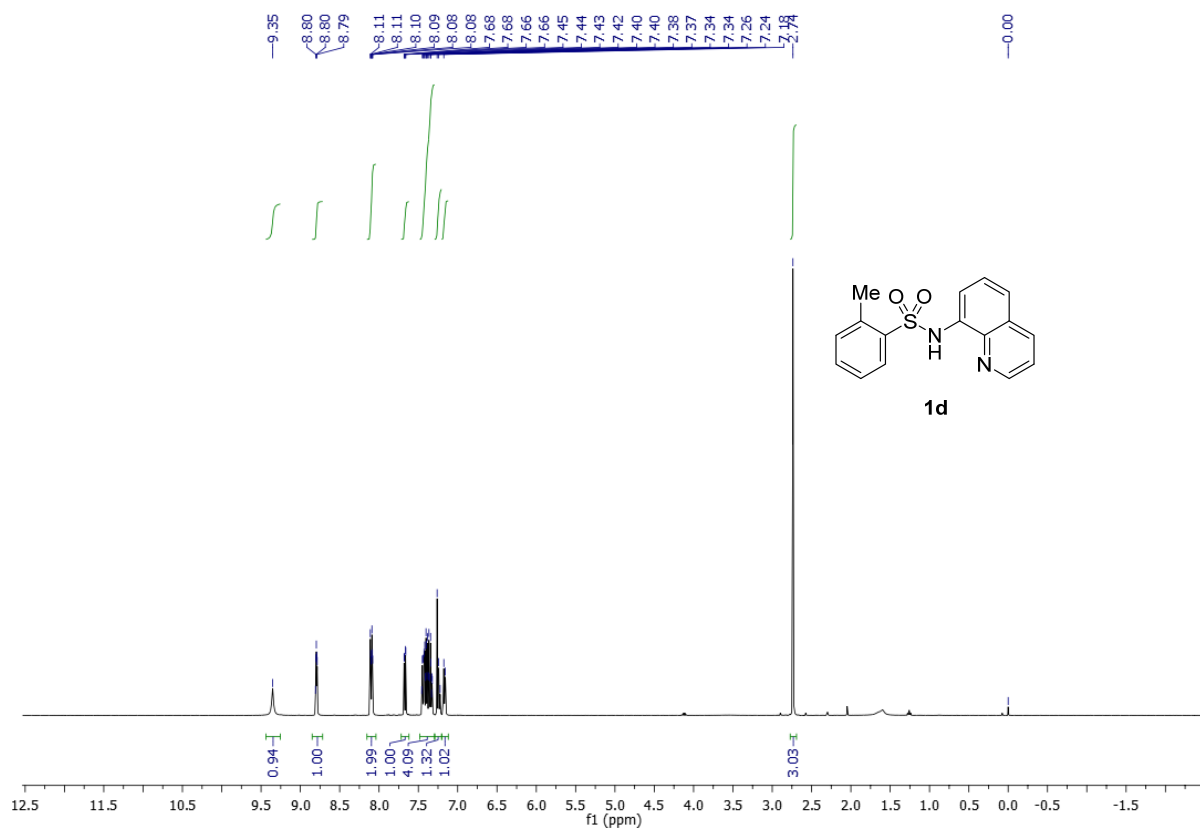


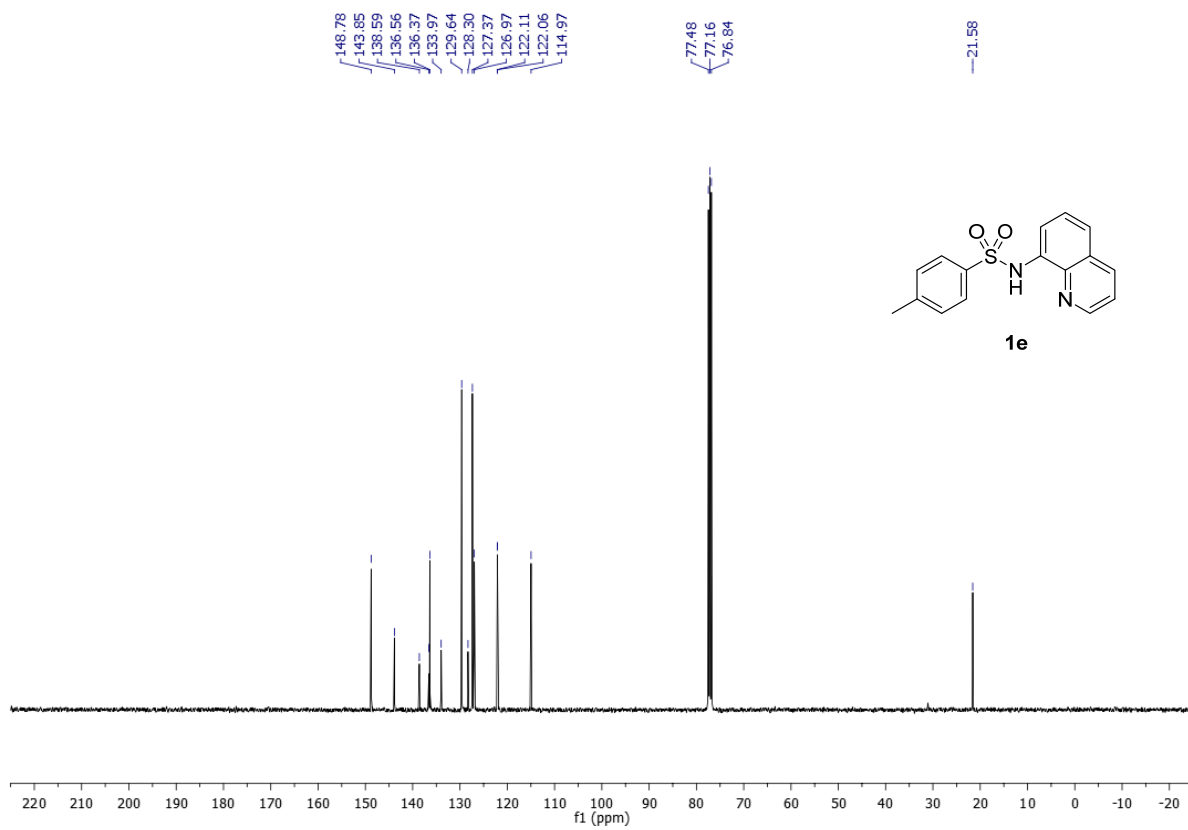
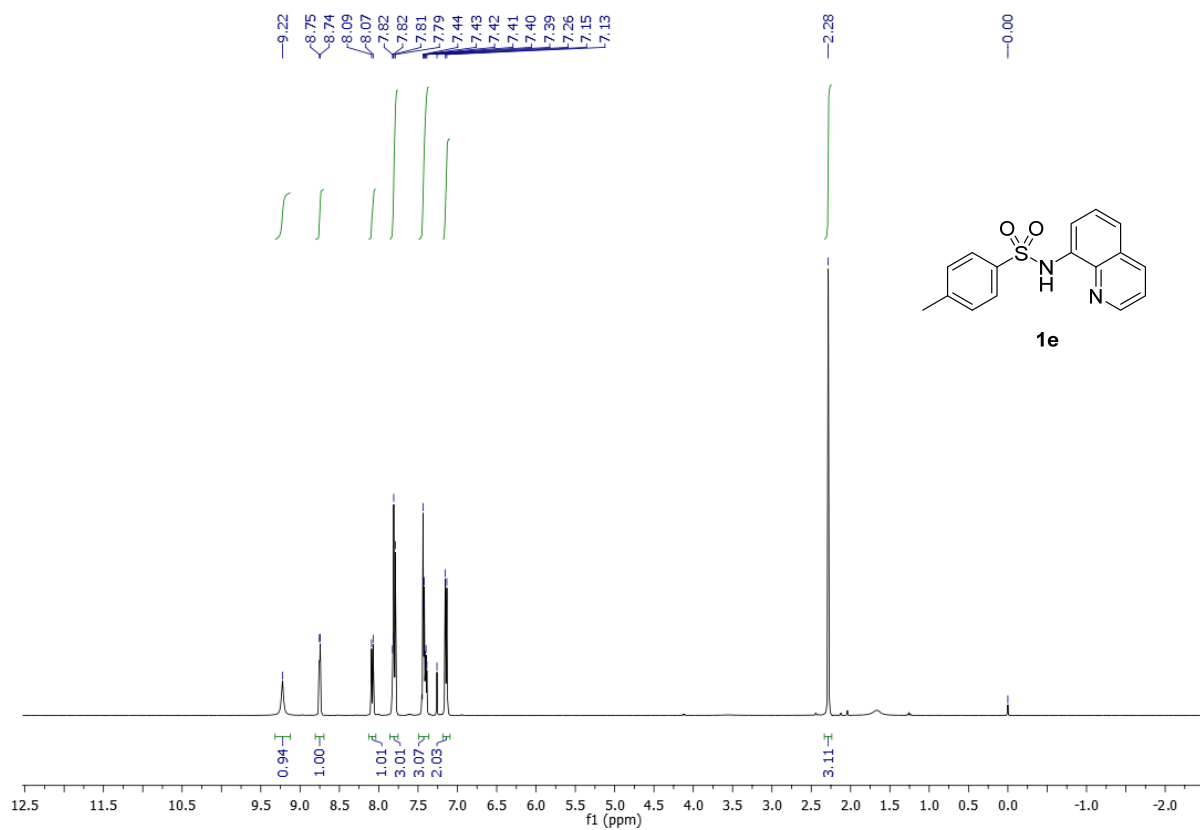


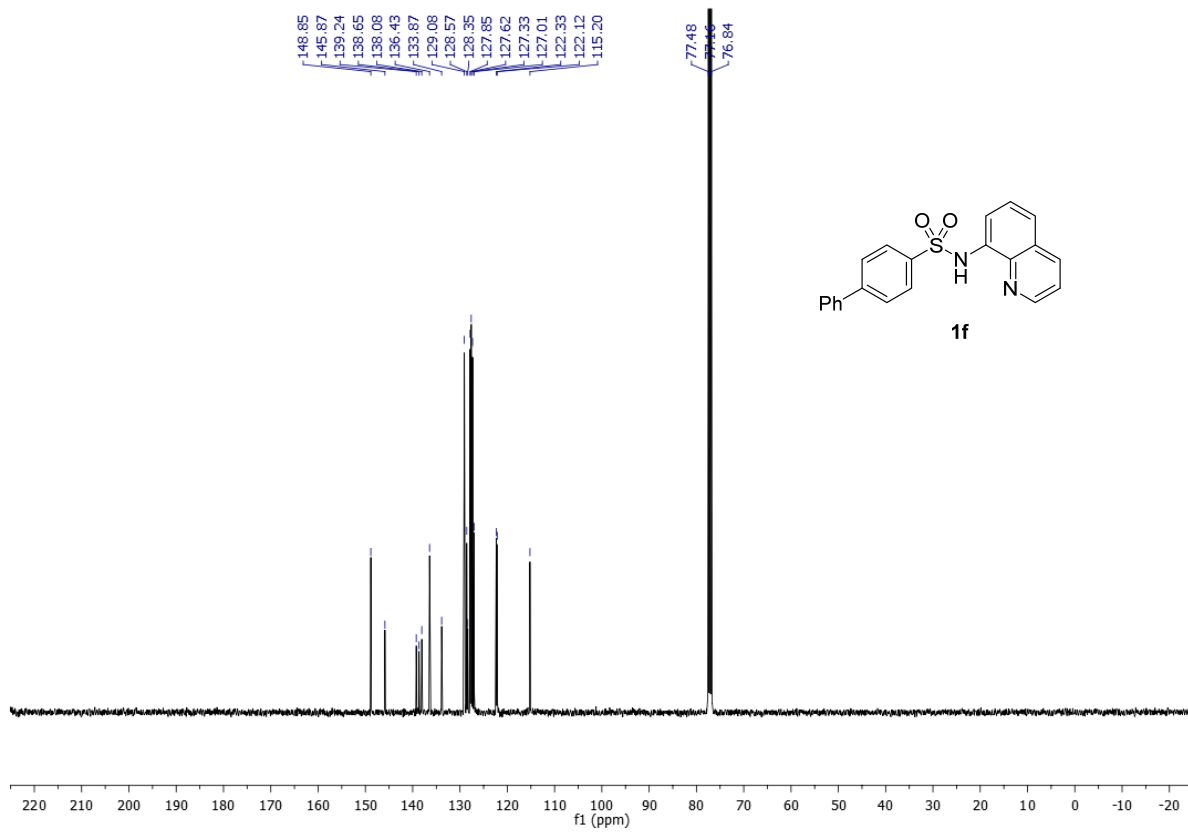
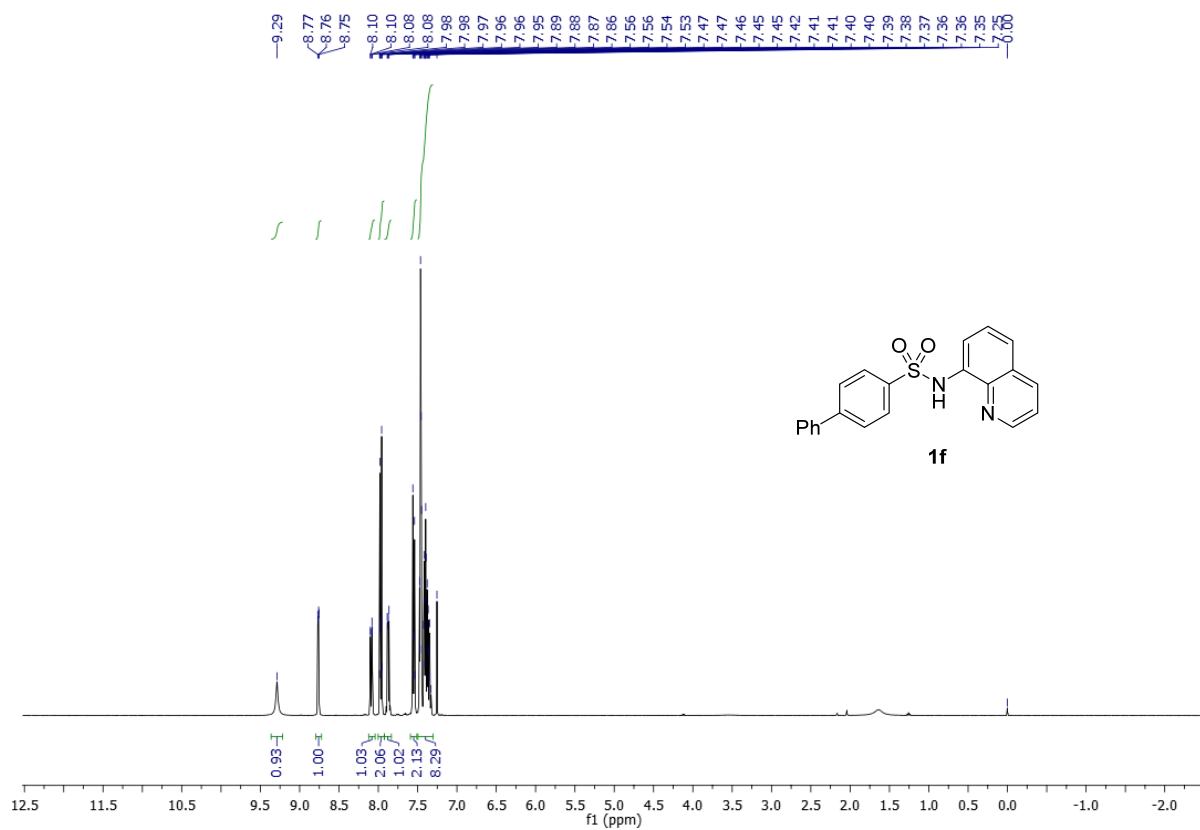


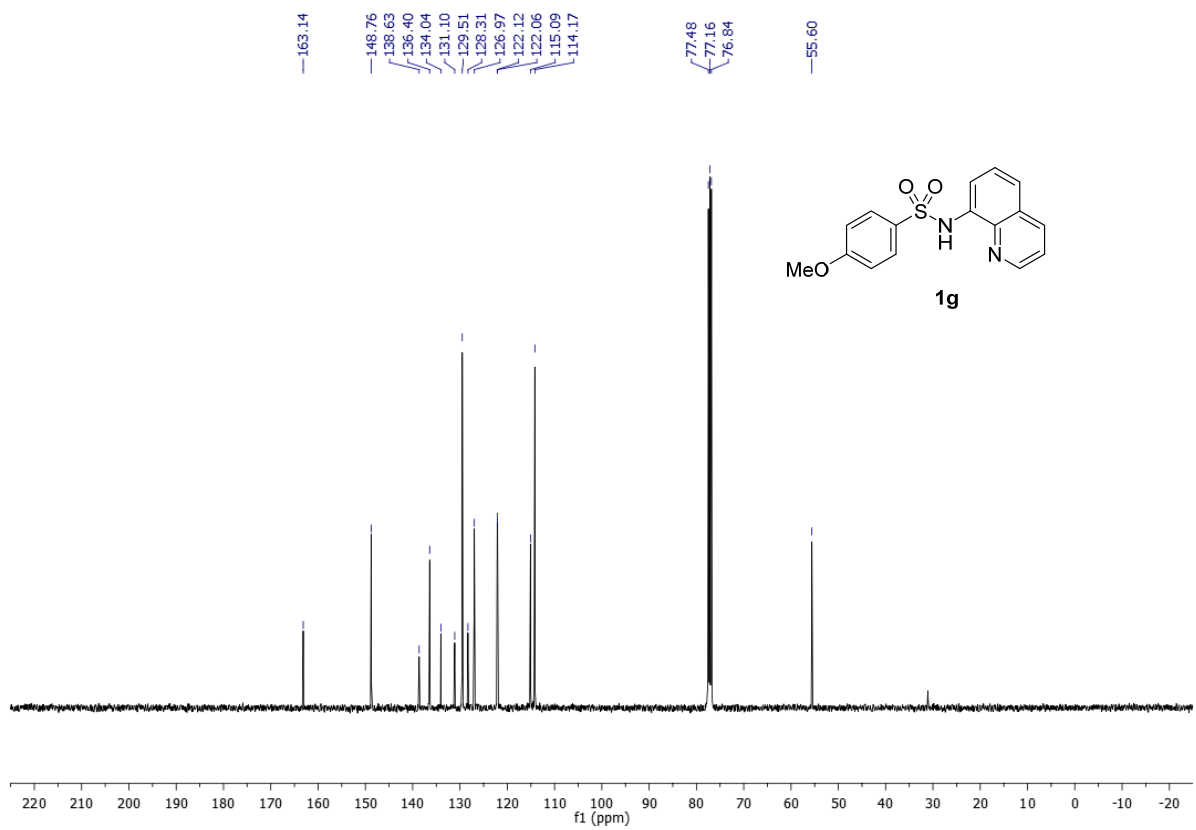
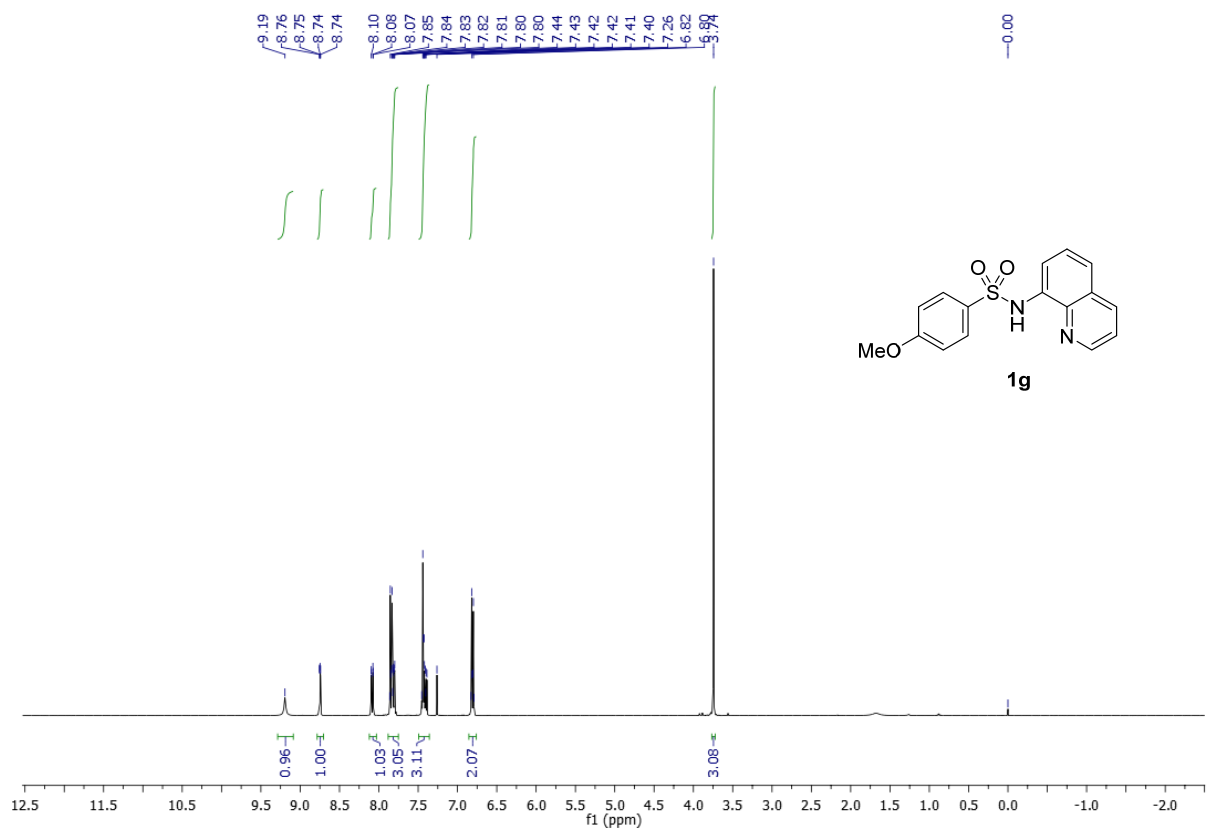


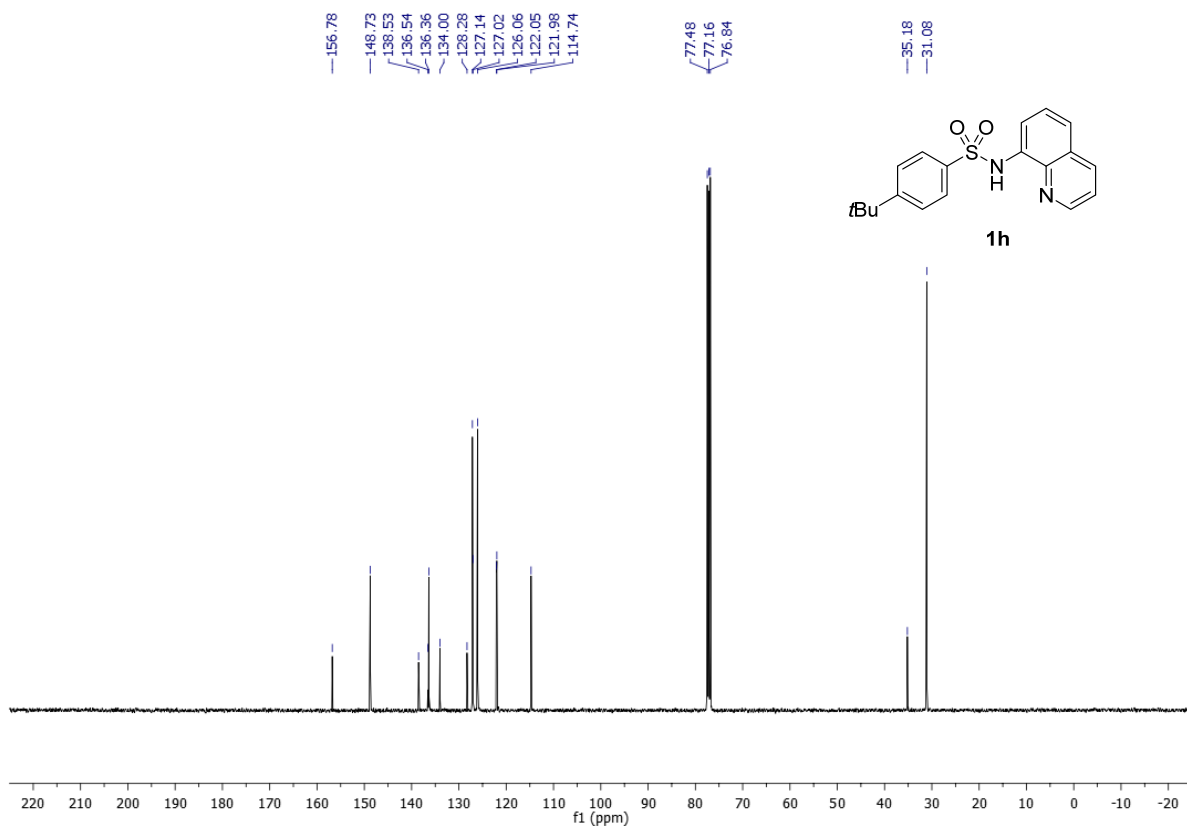
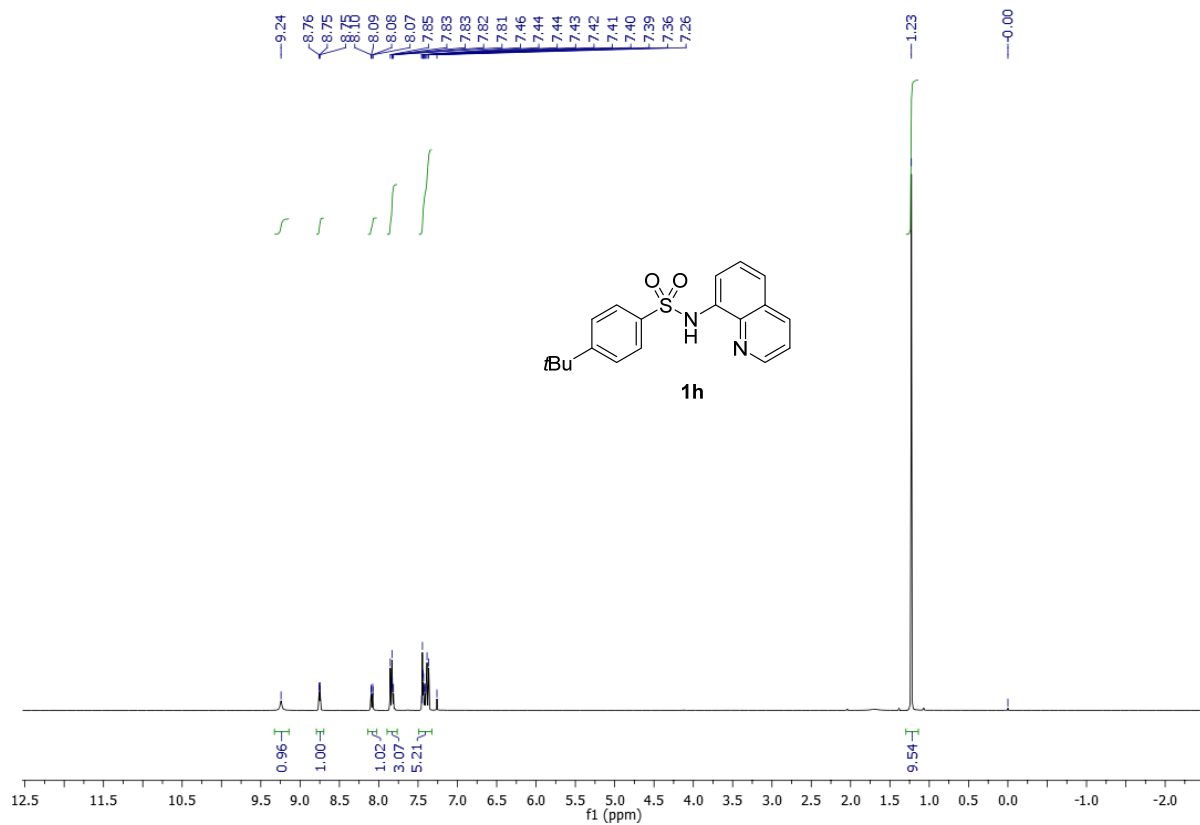


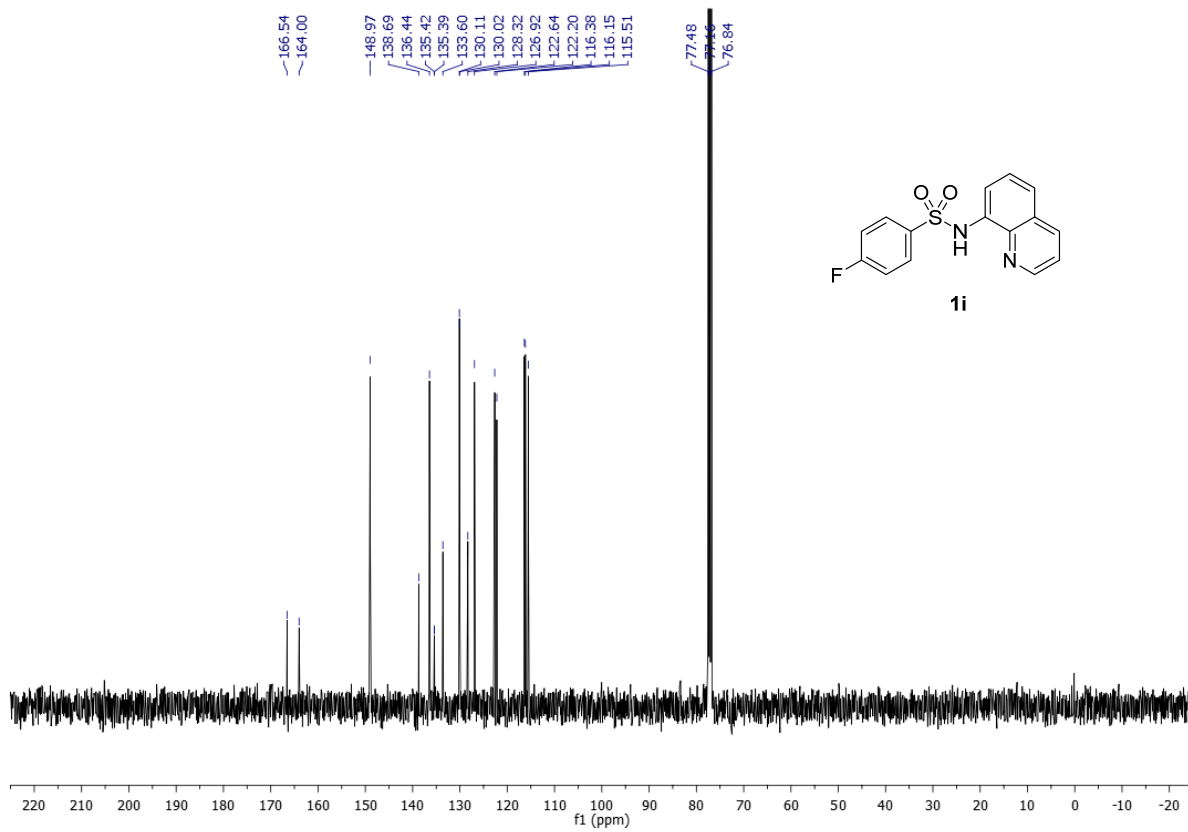
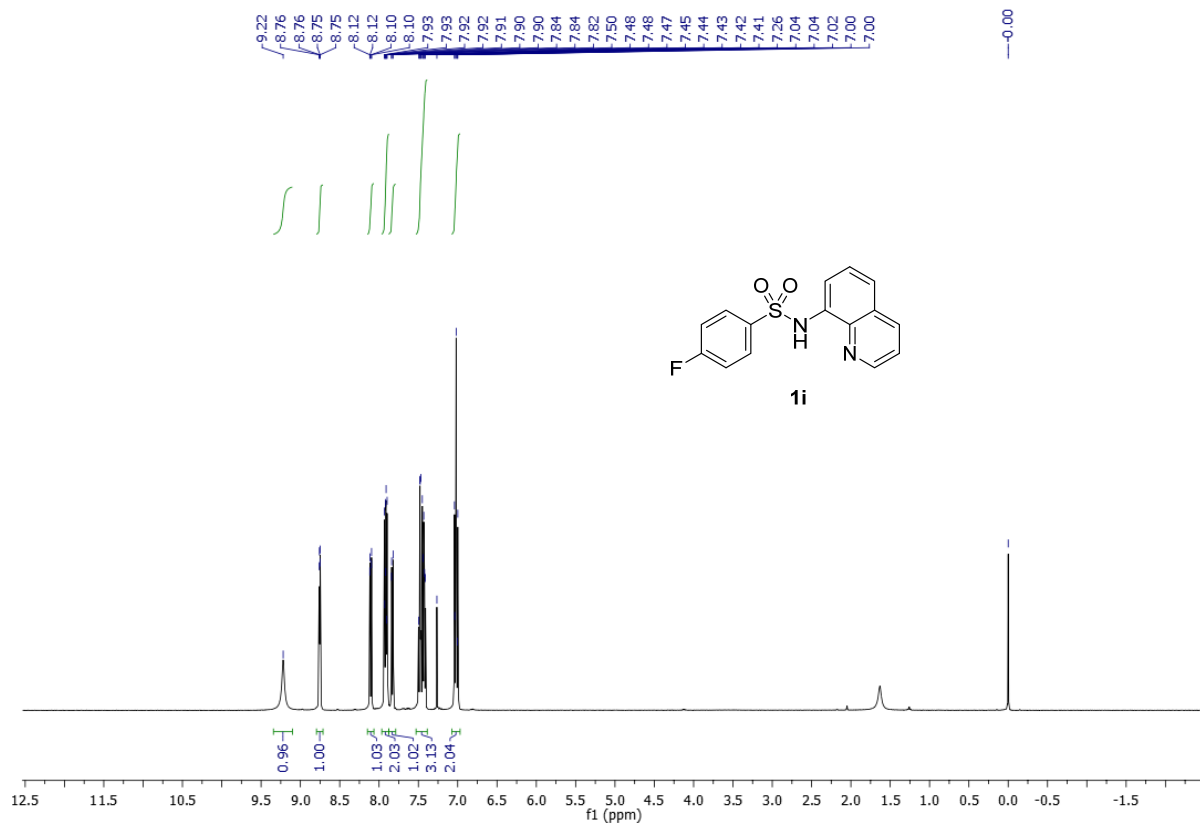


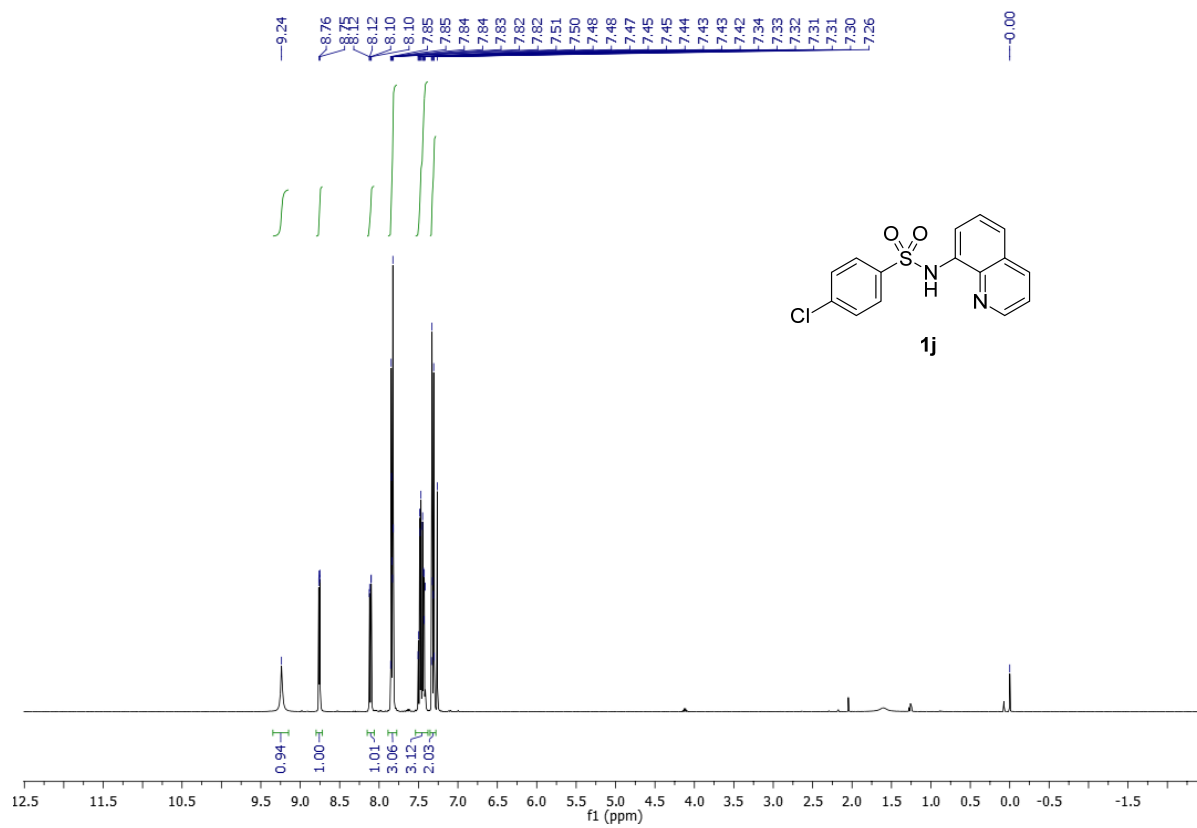
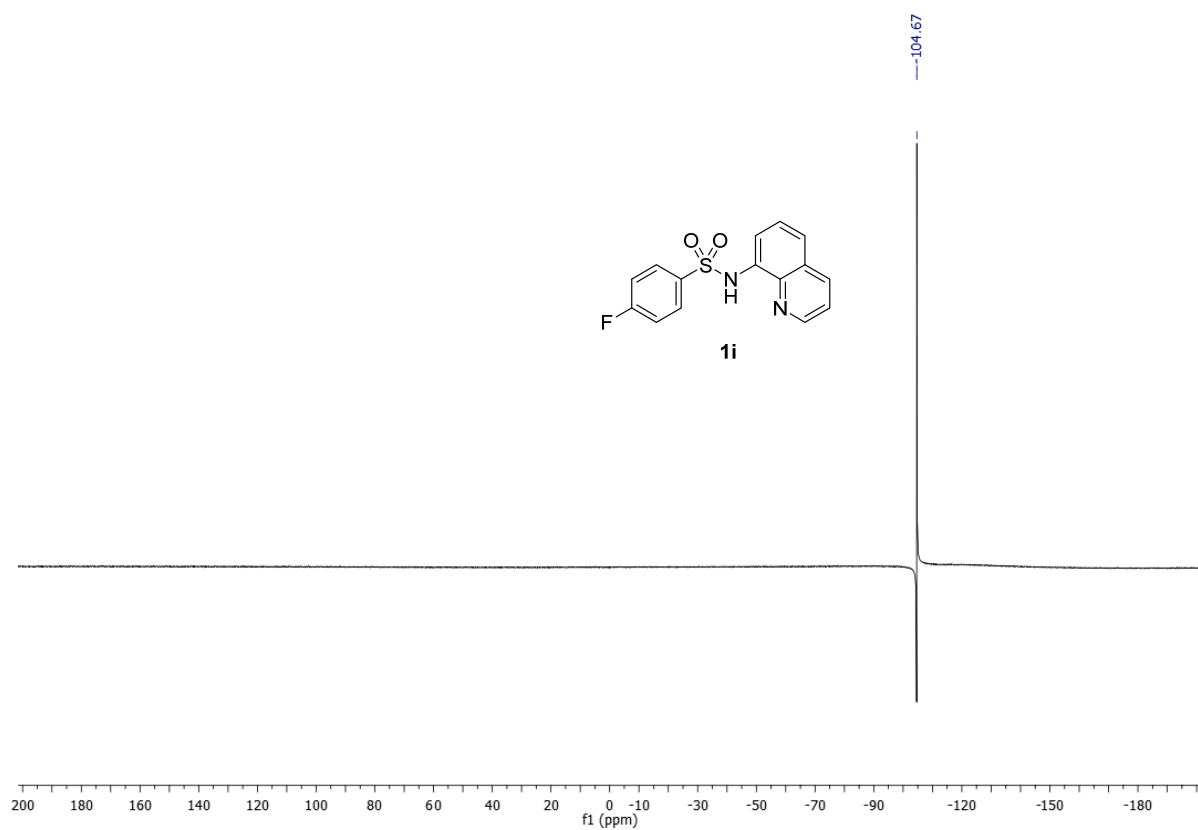


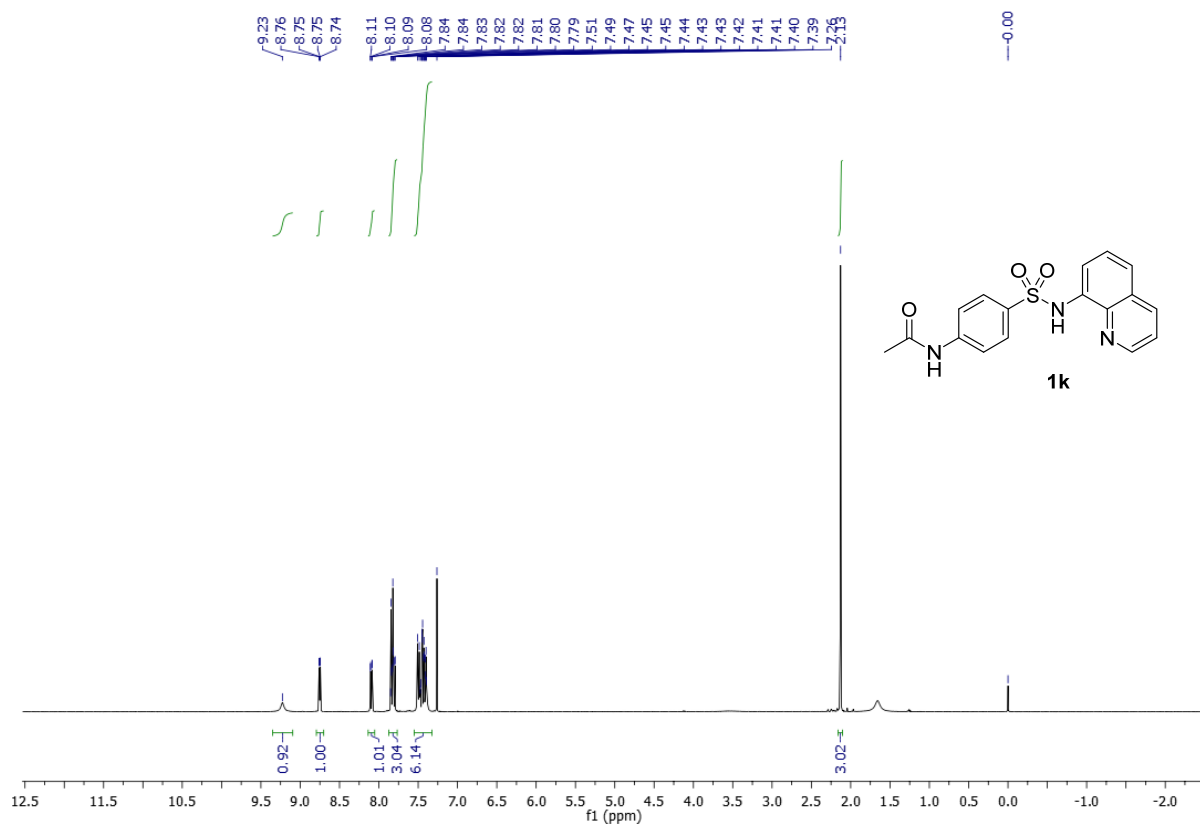
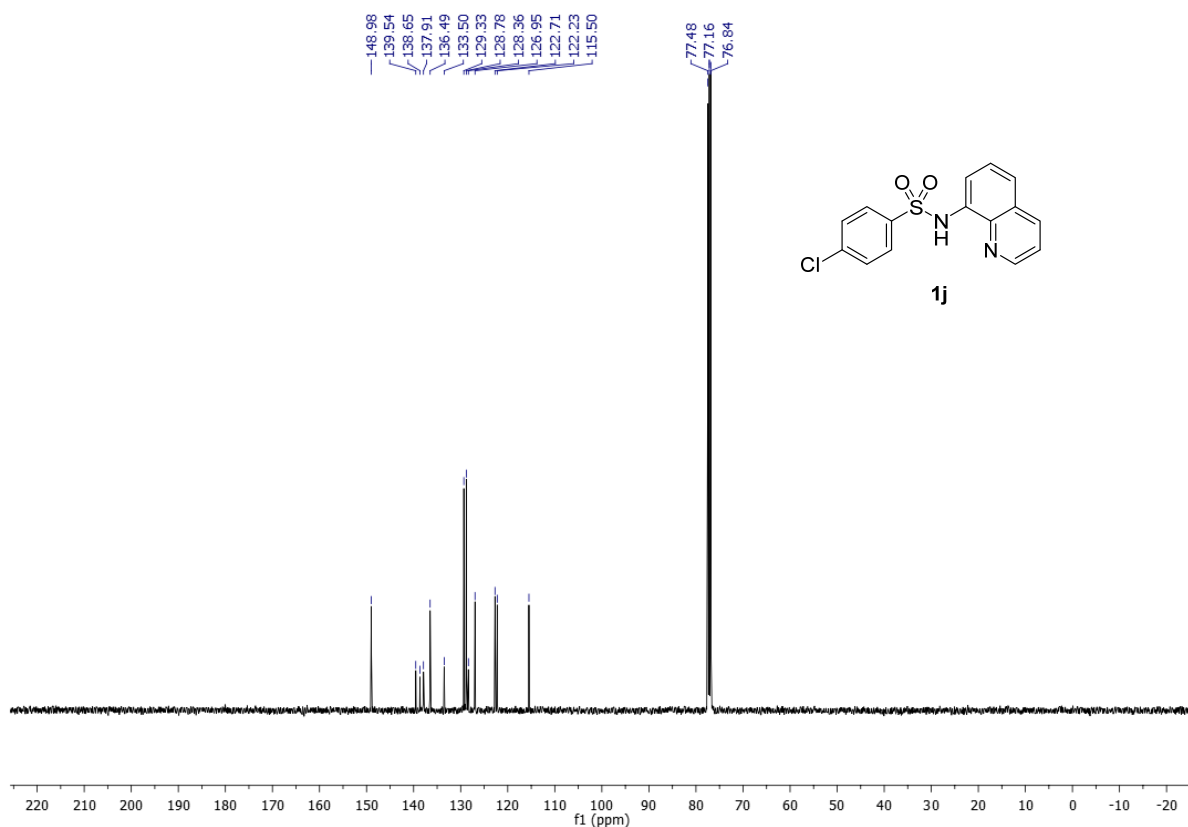


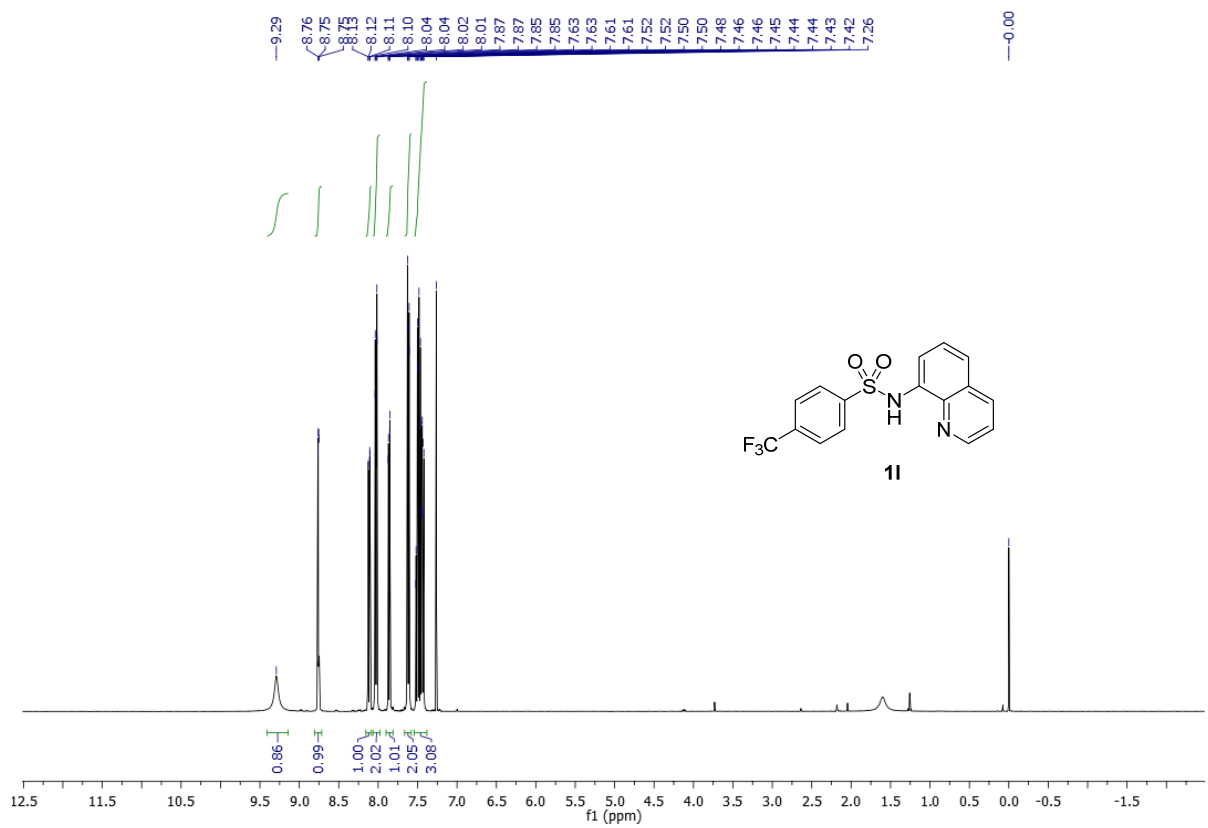
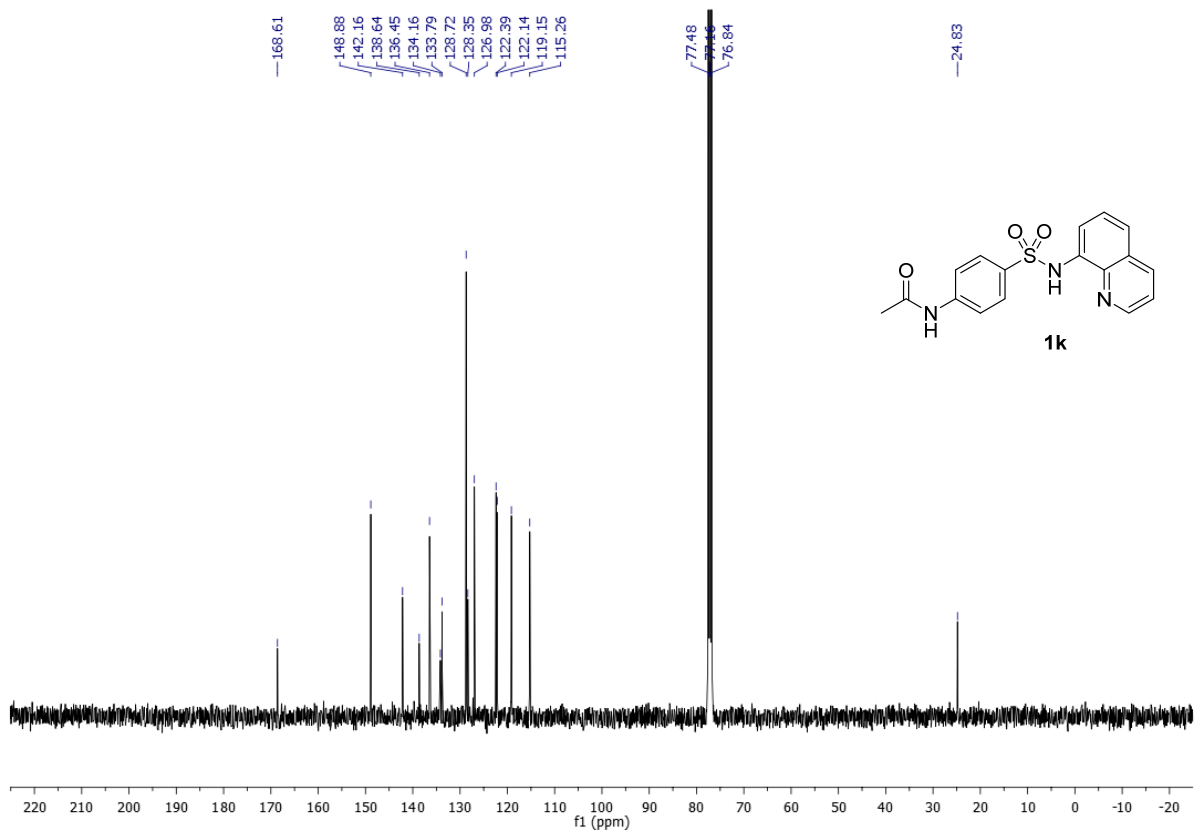


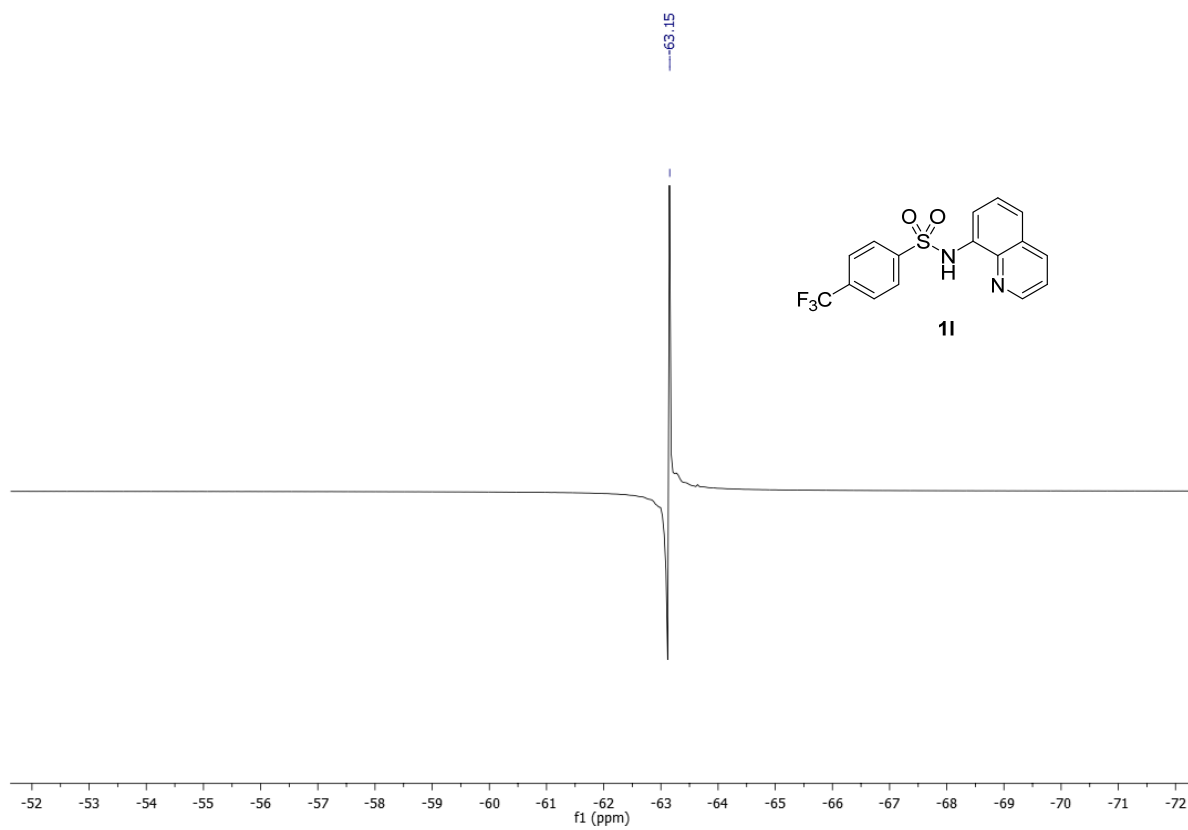
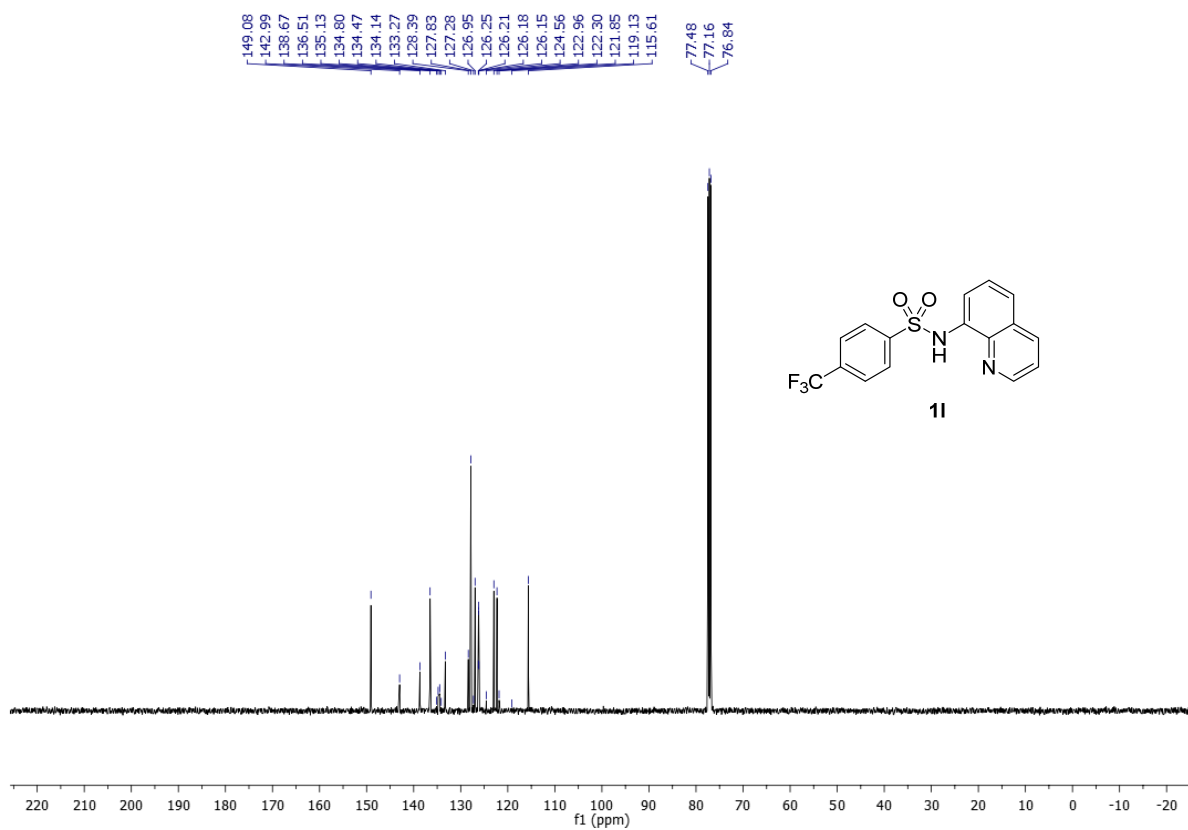


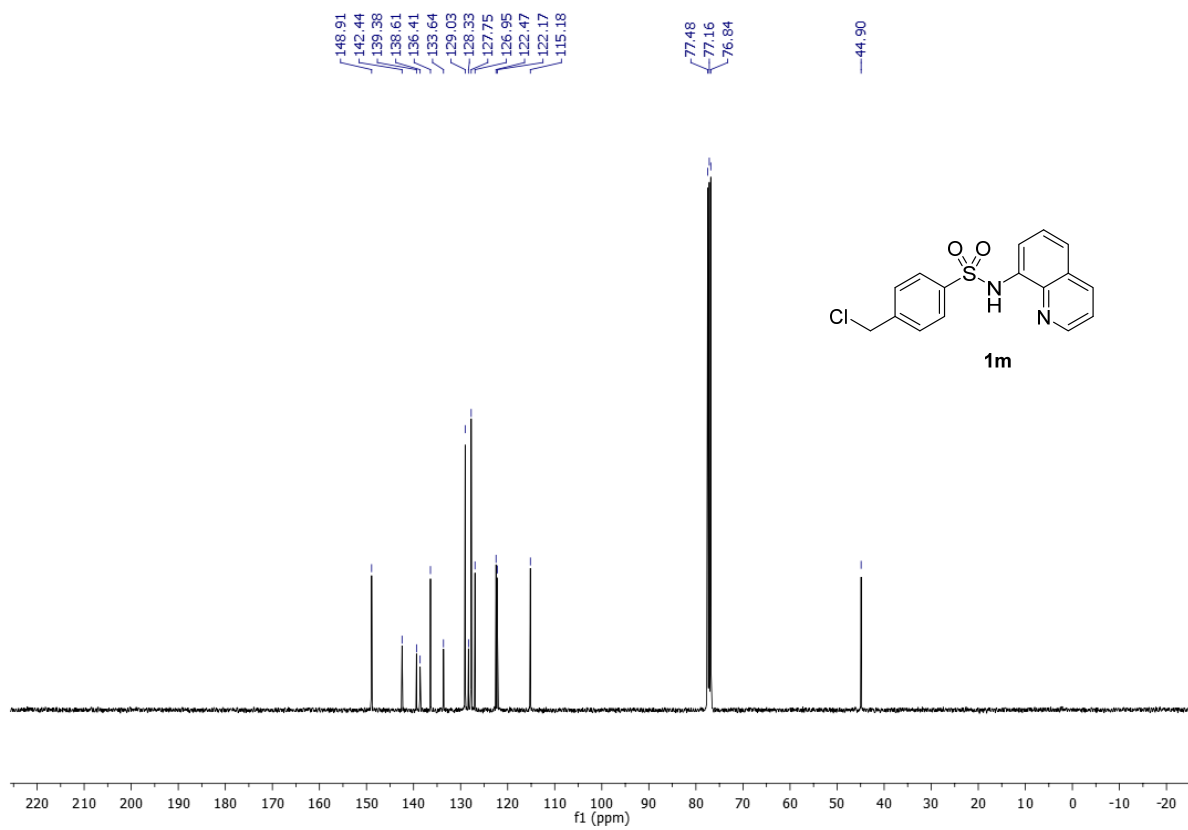
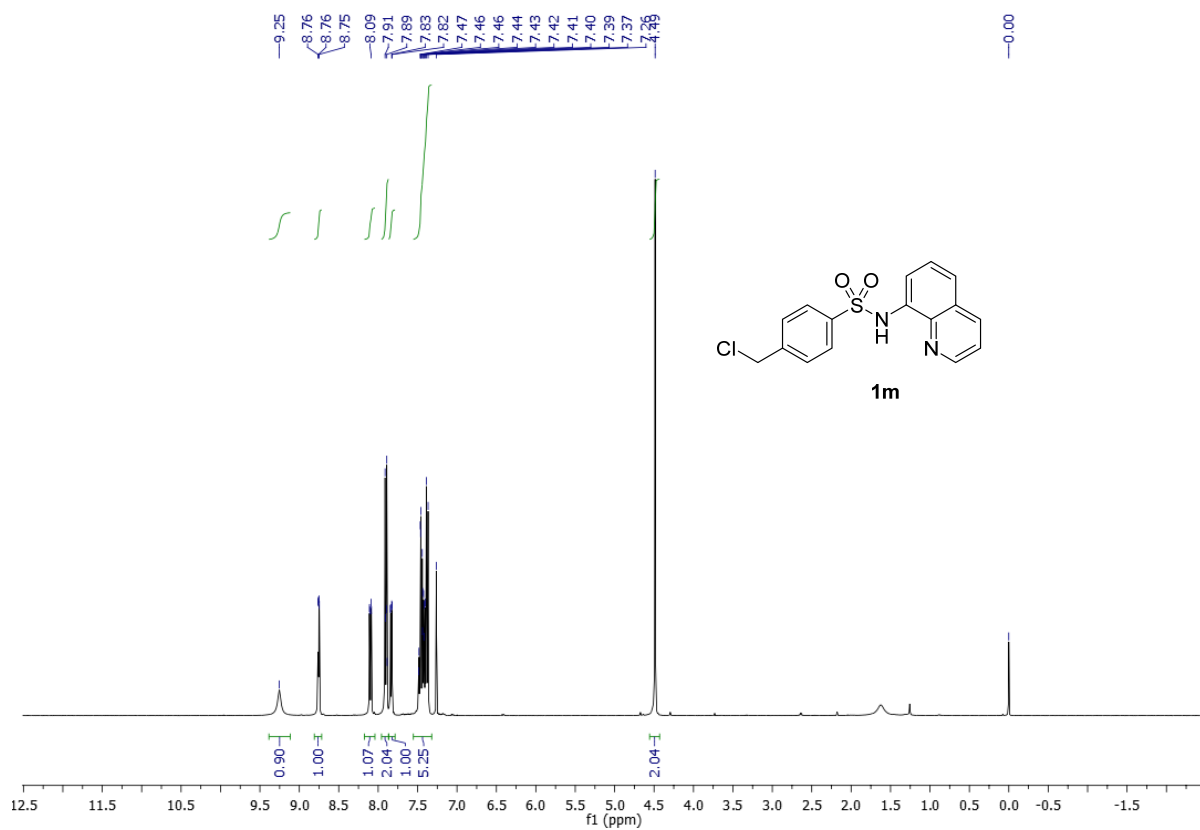


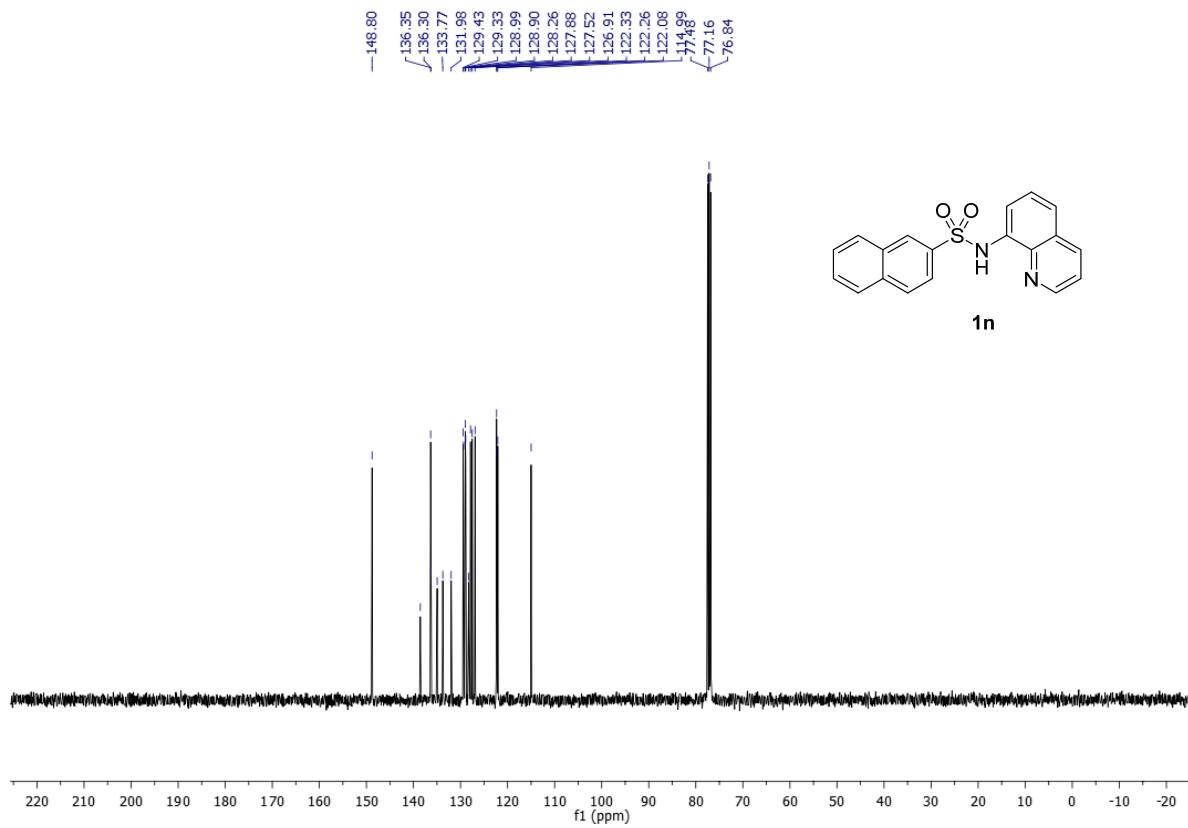
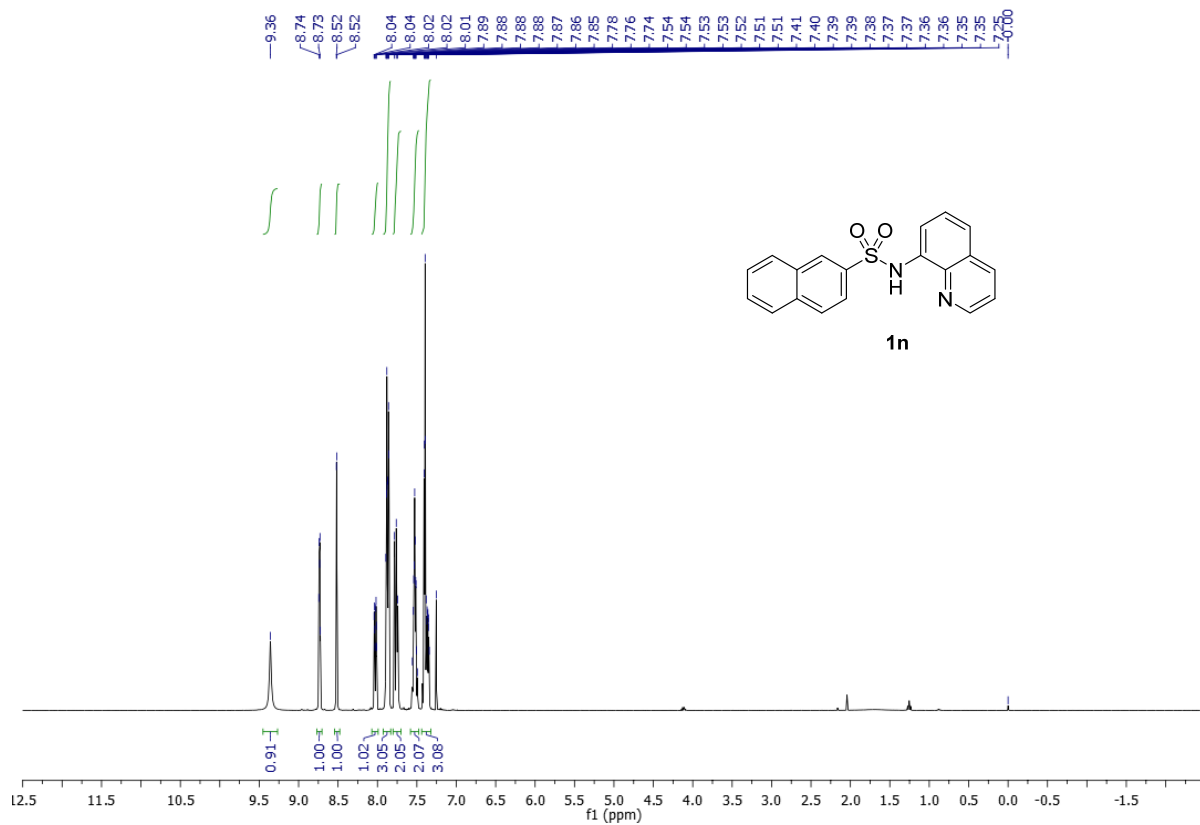


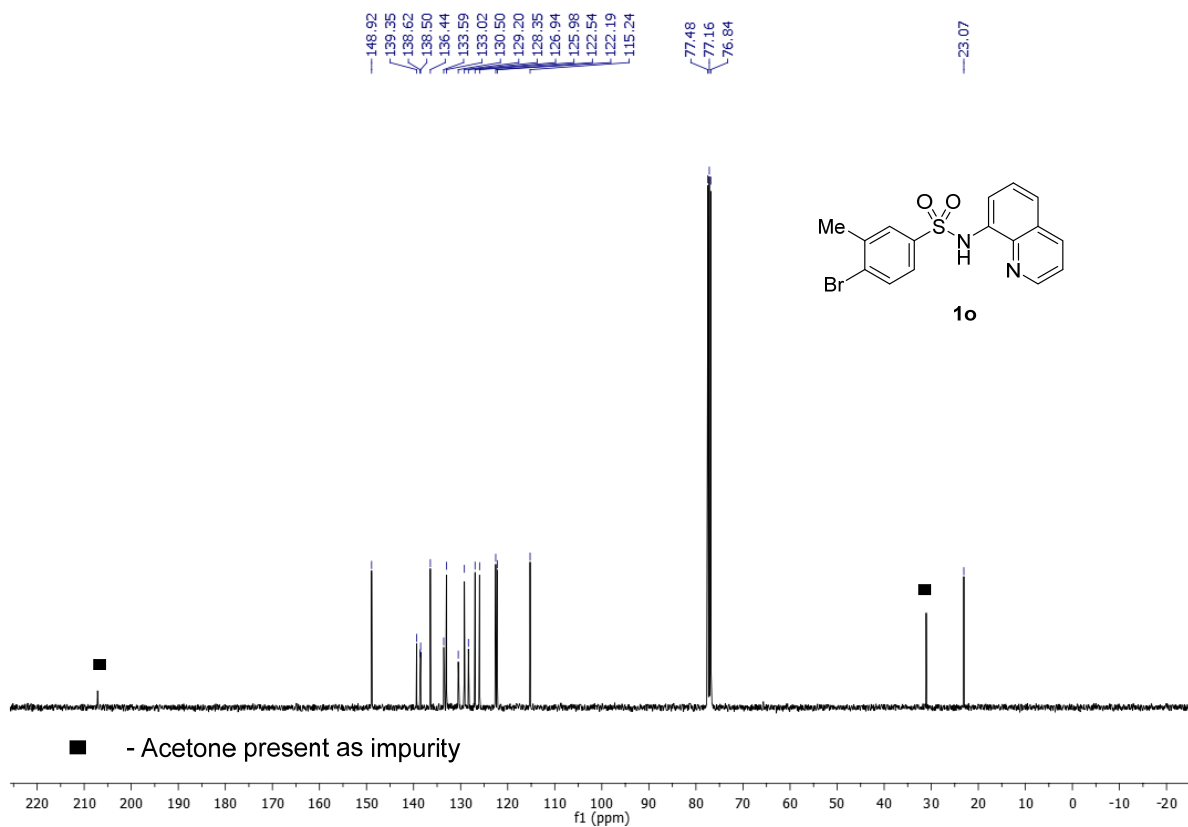
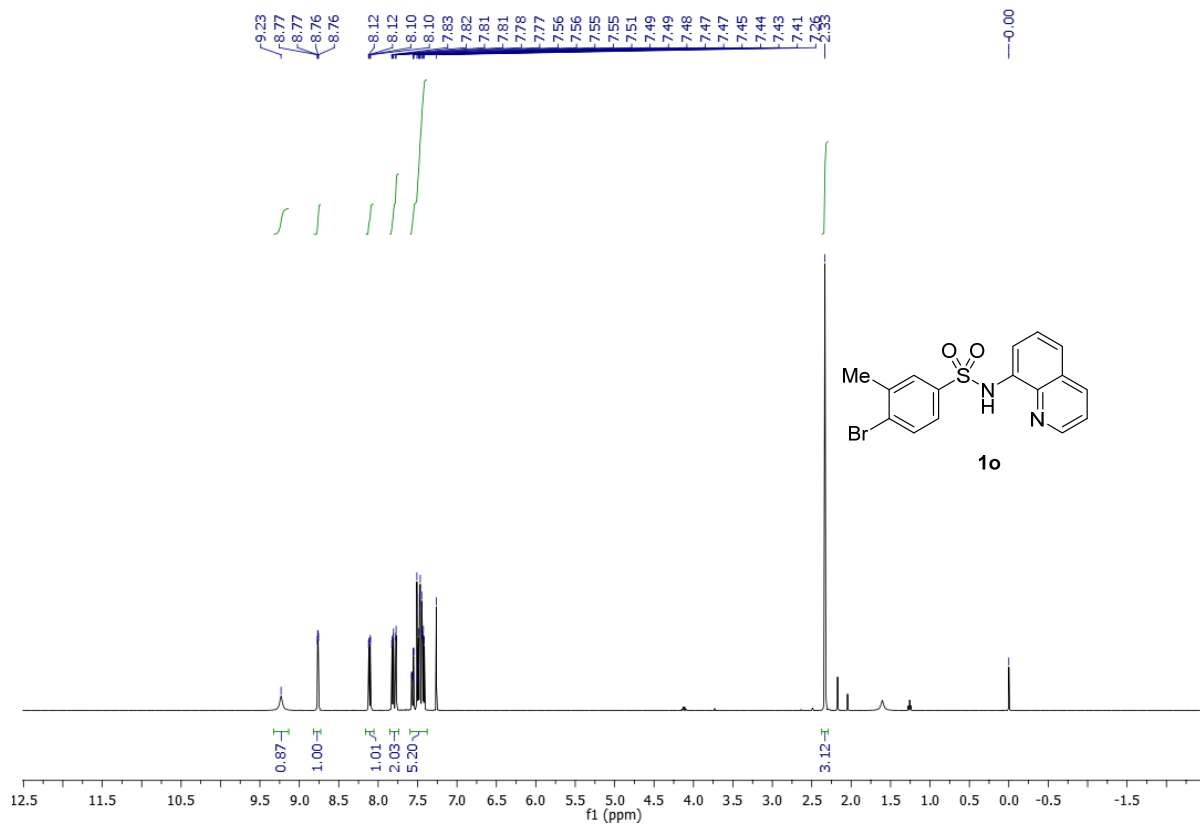


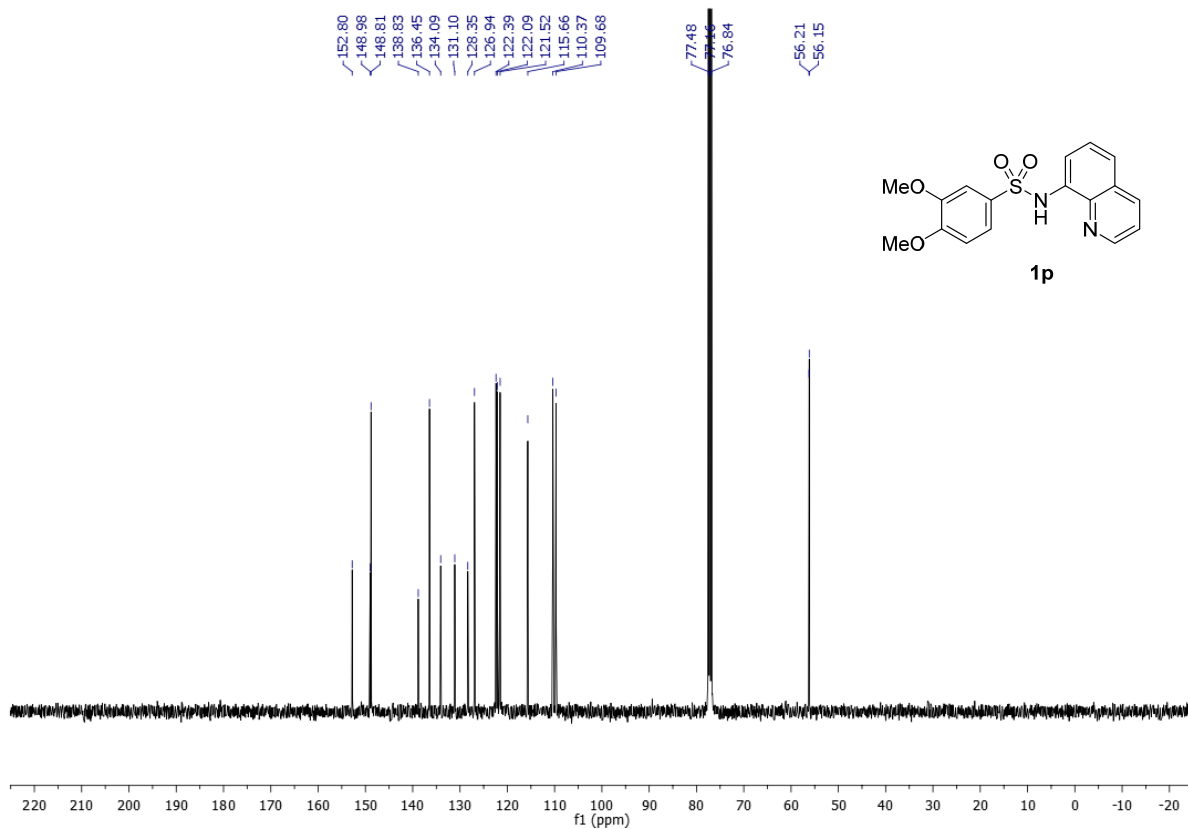
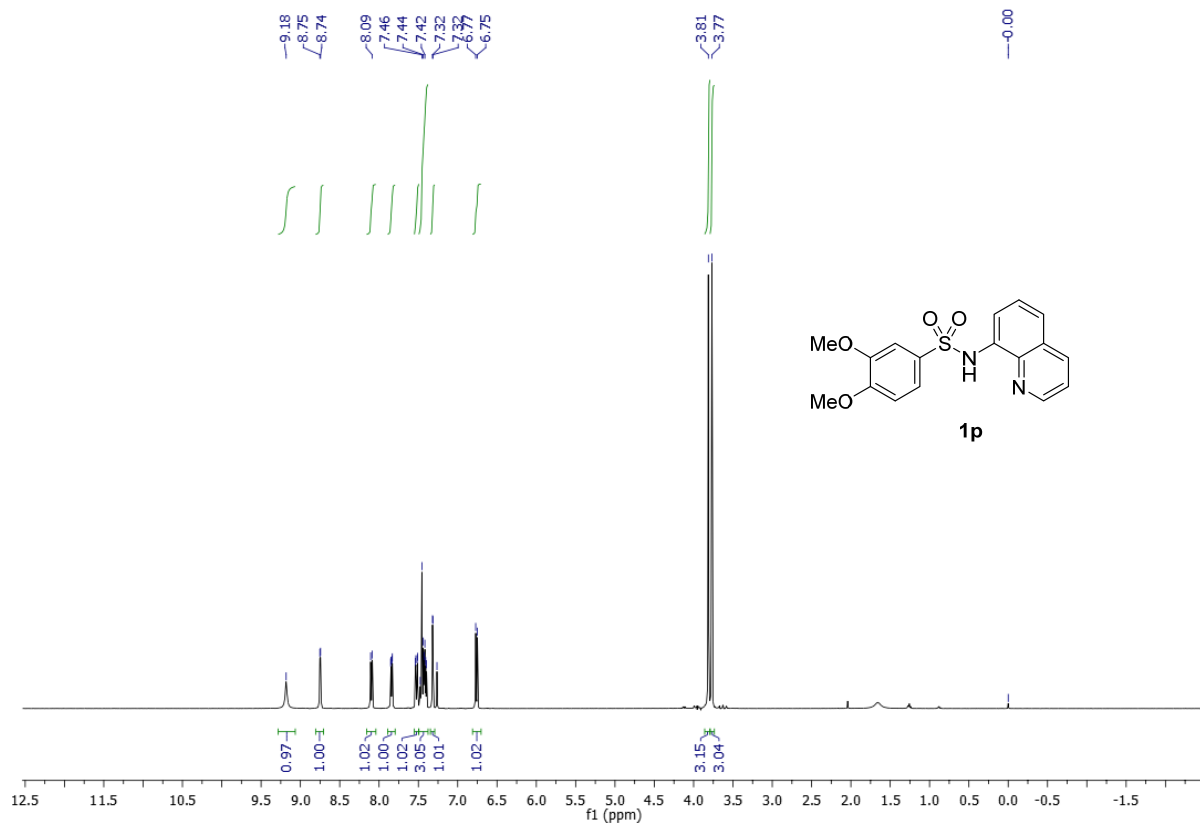




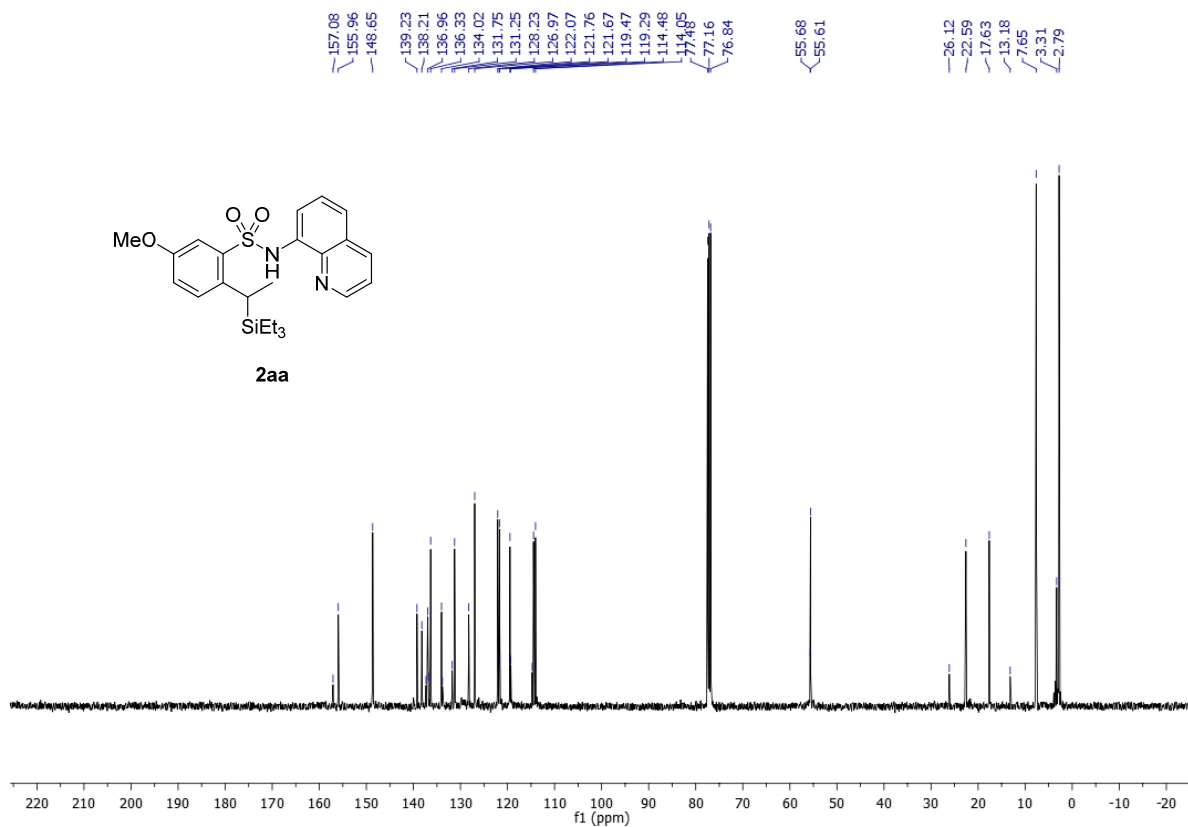
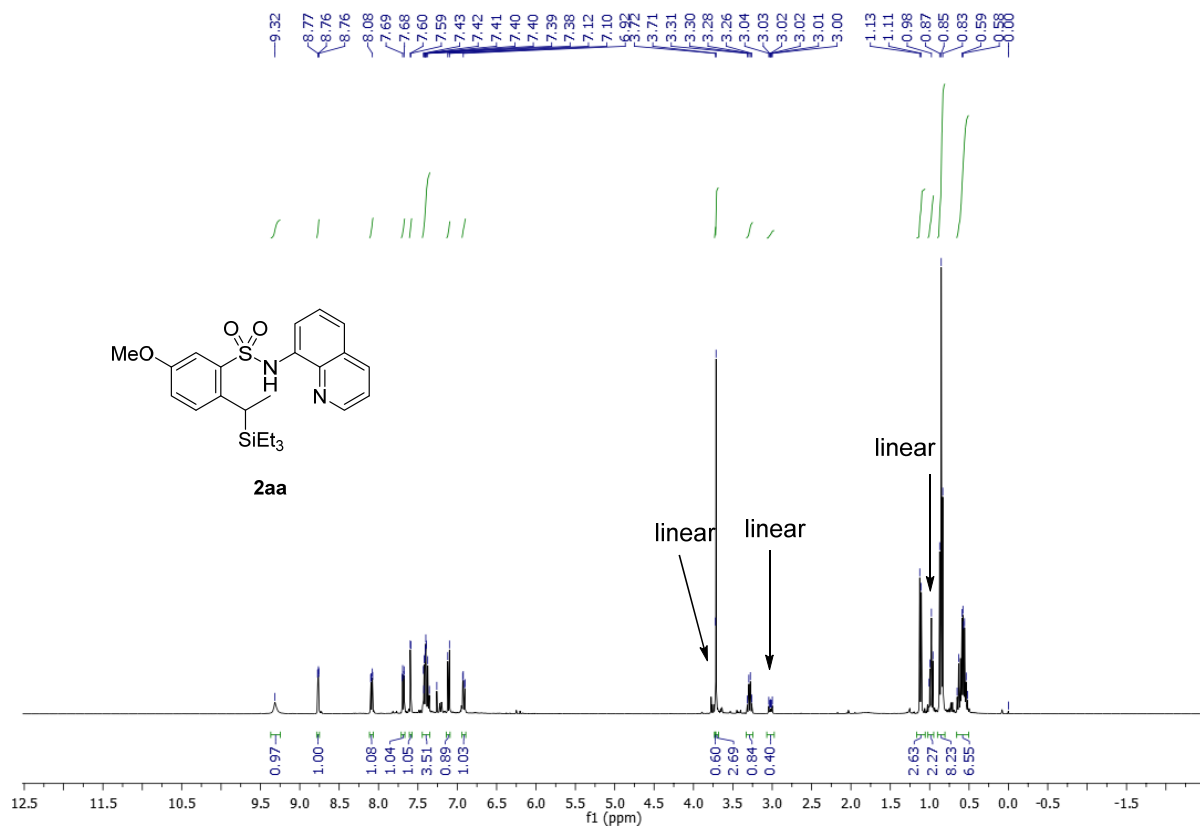


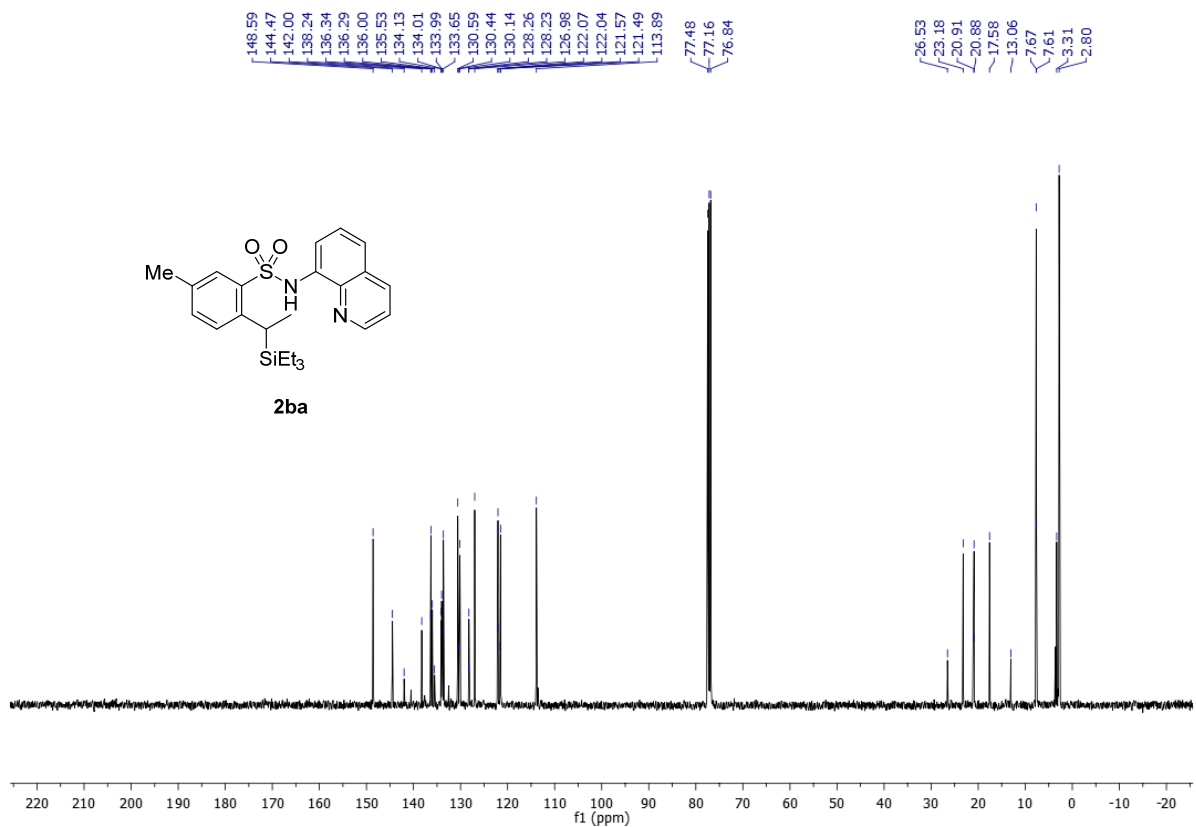
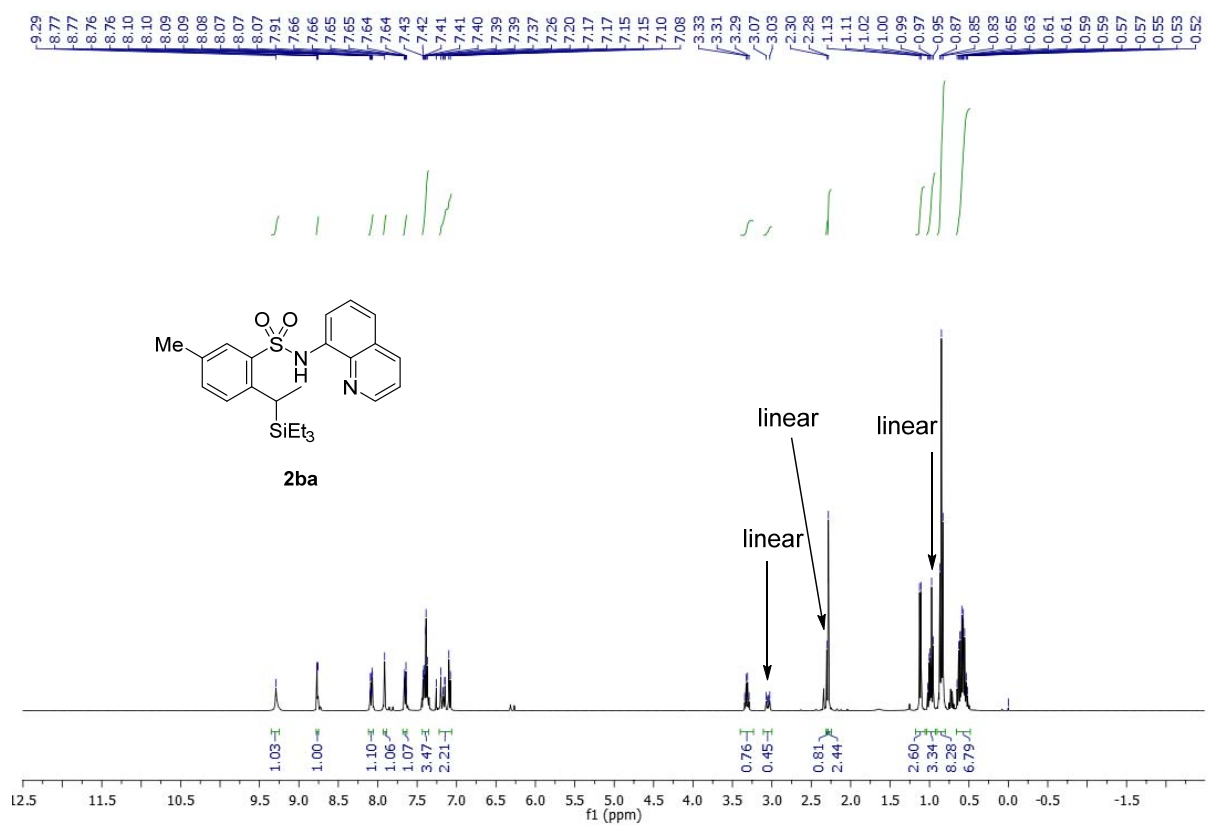


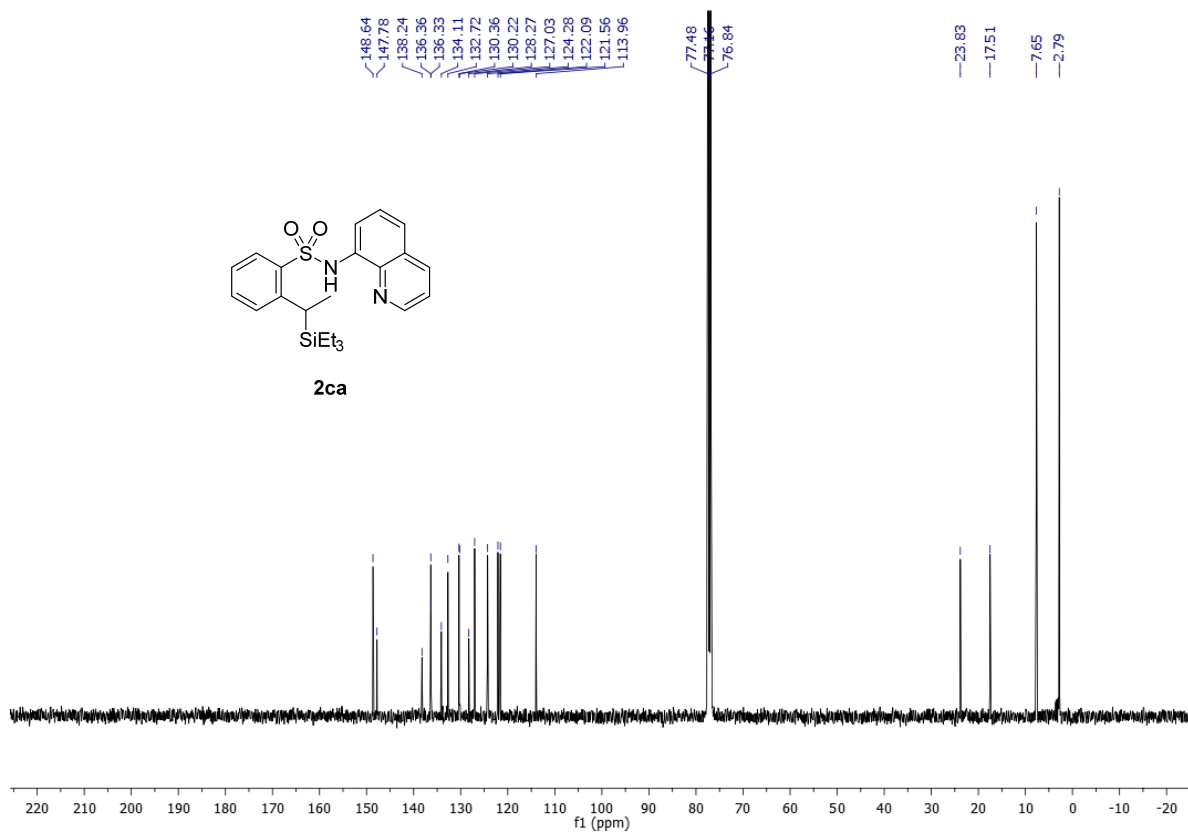
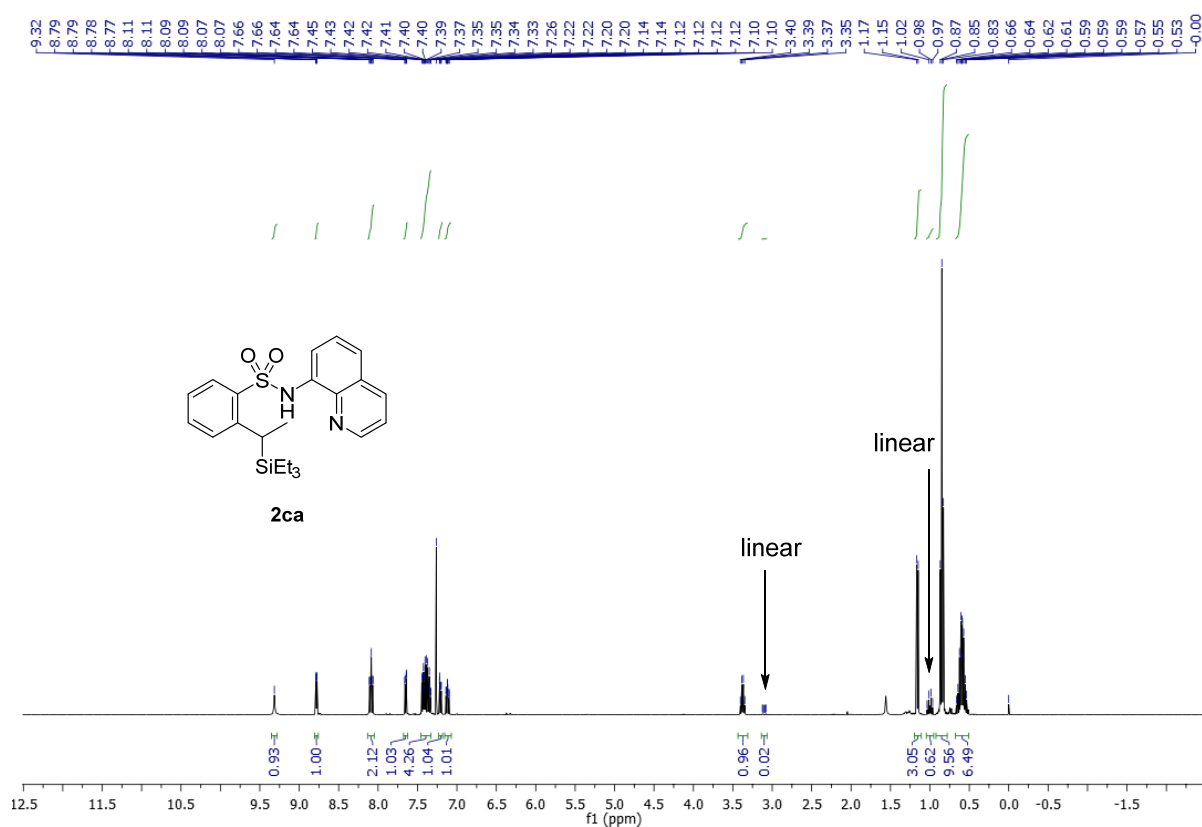


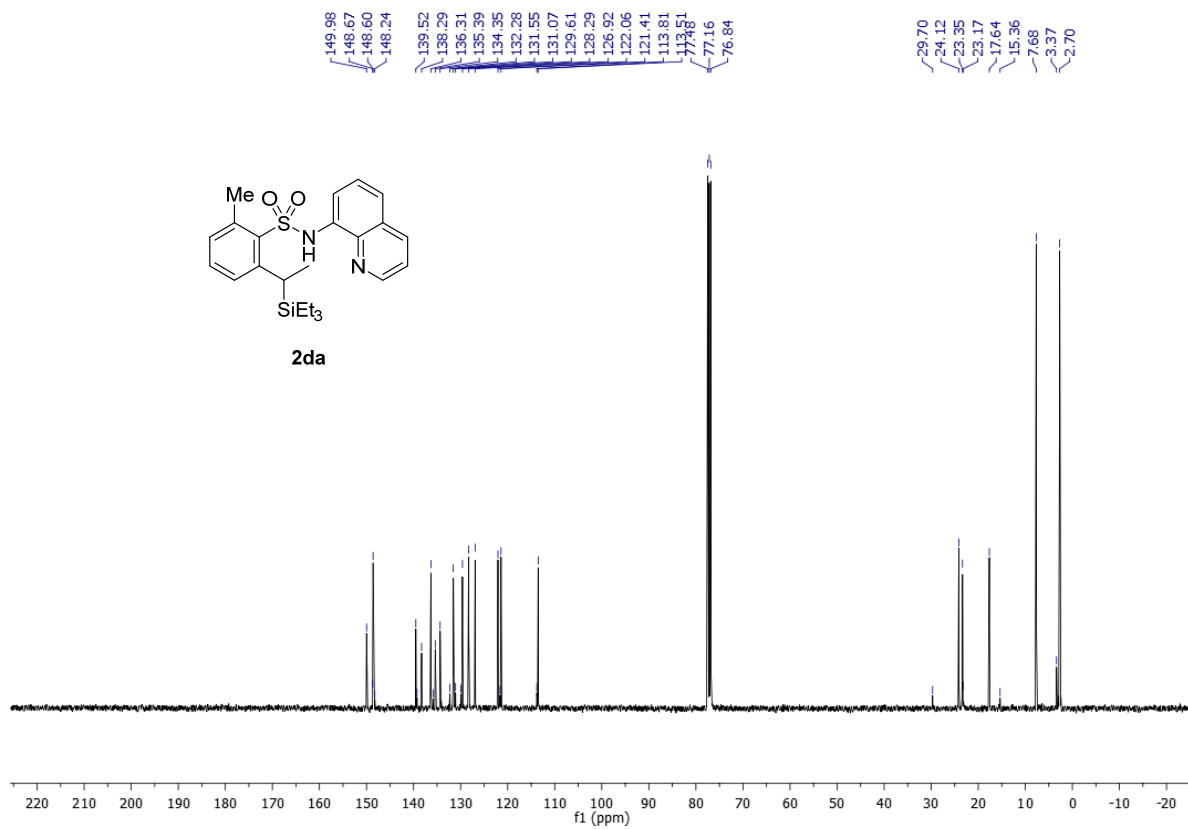
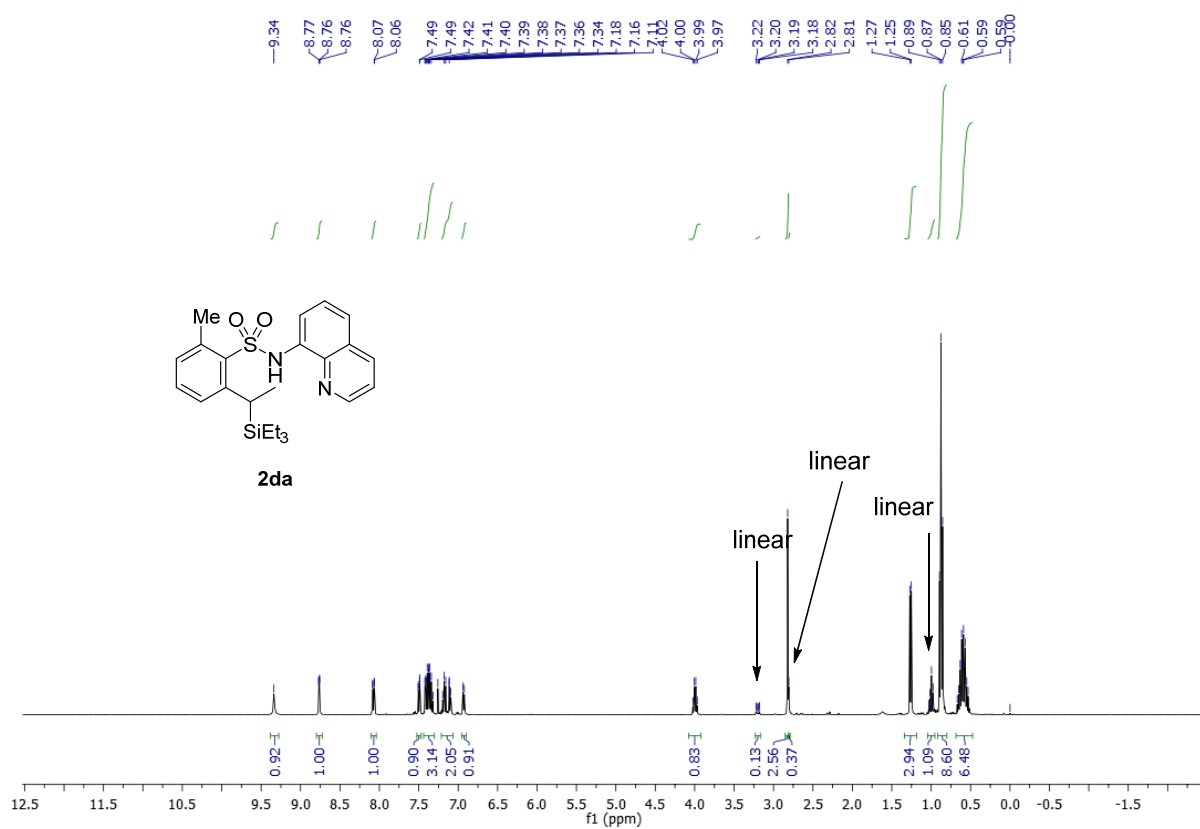


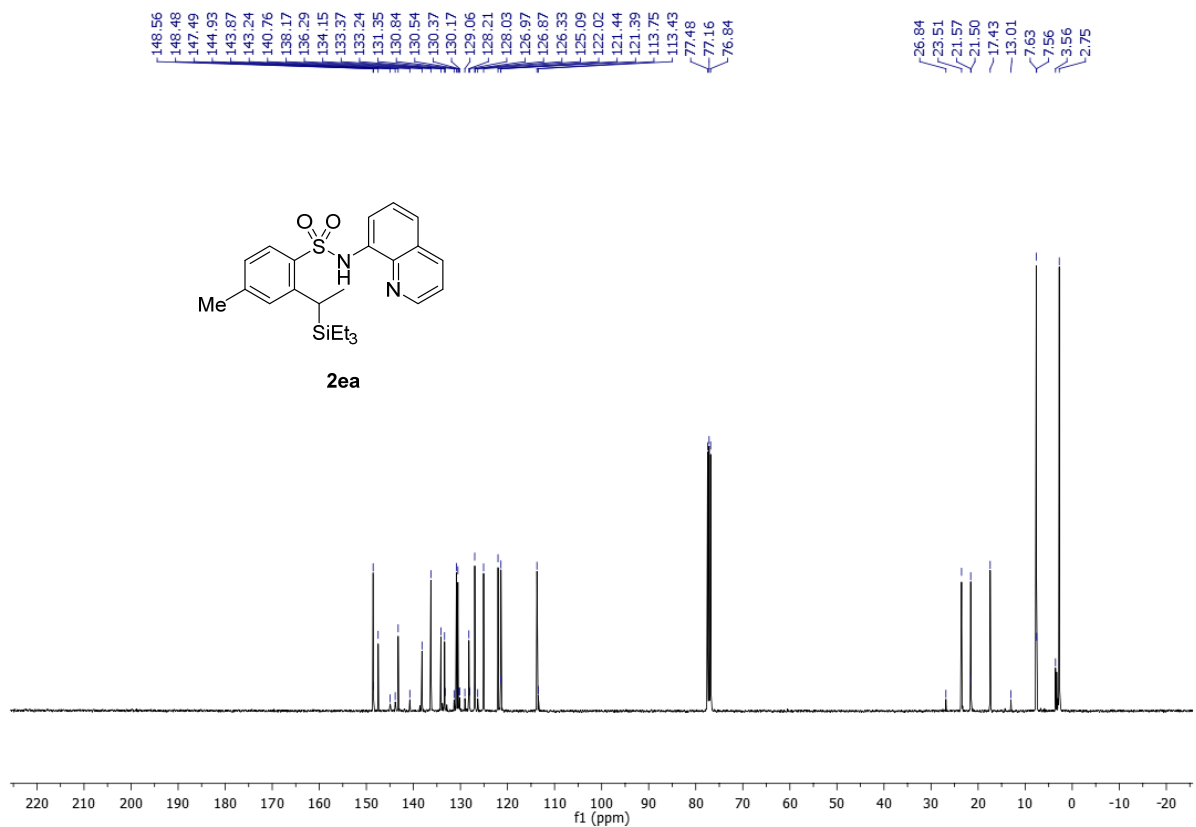
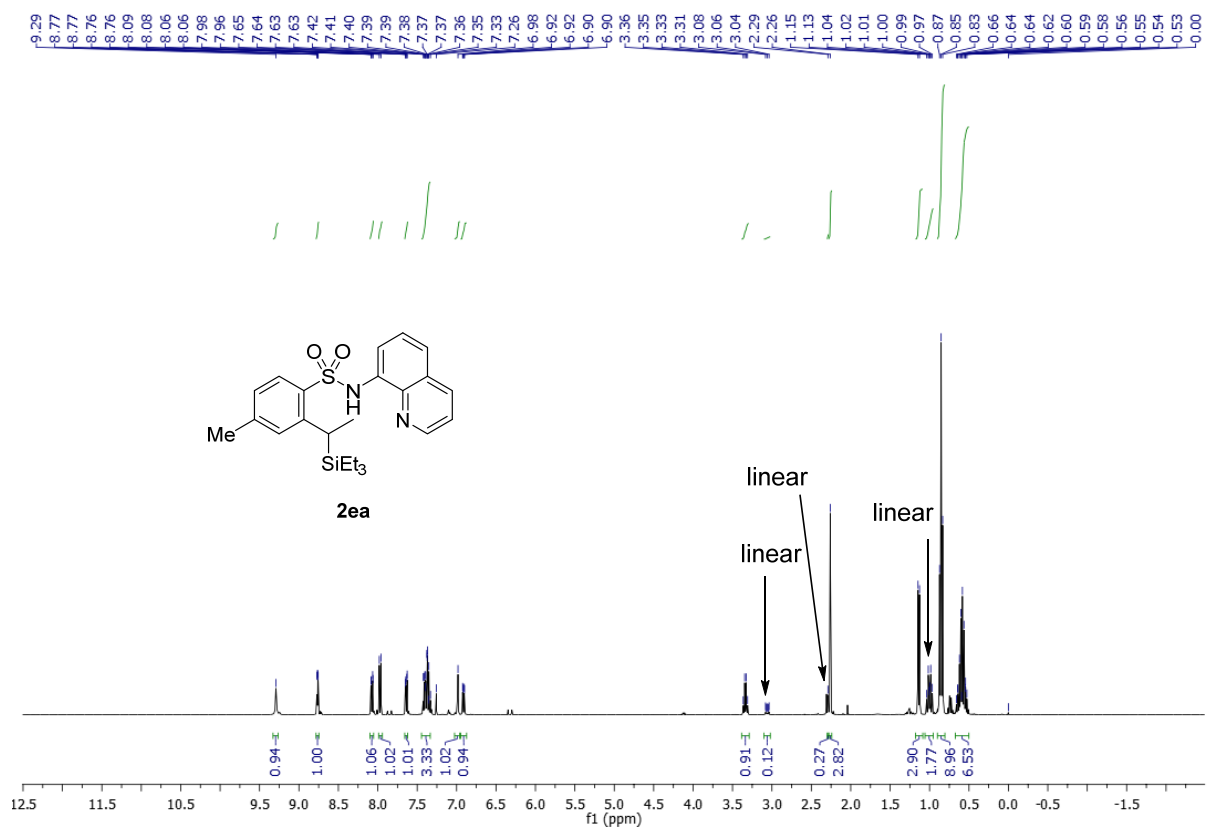
10. NMR spectra of products

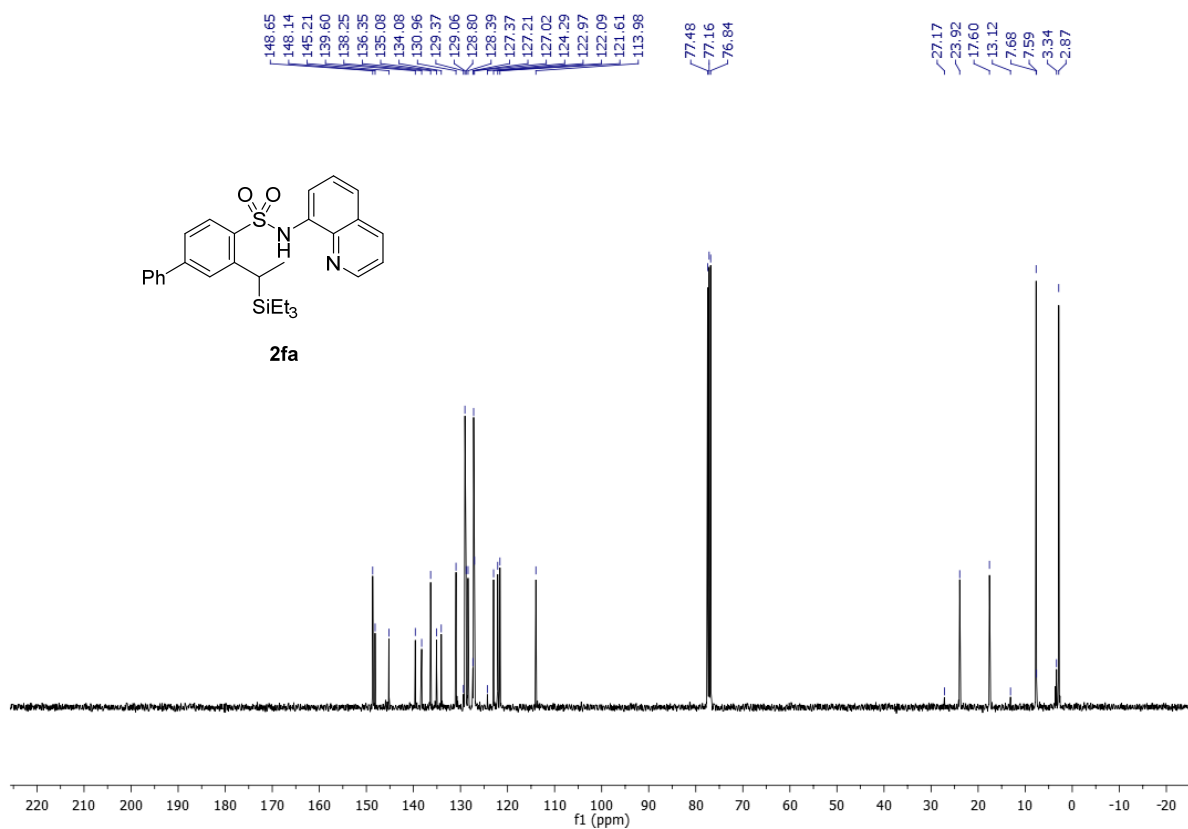
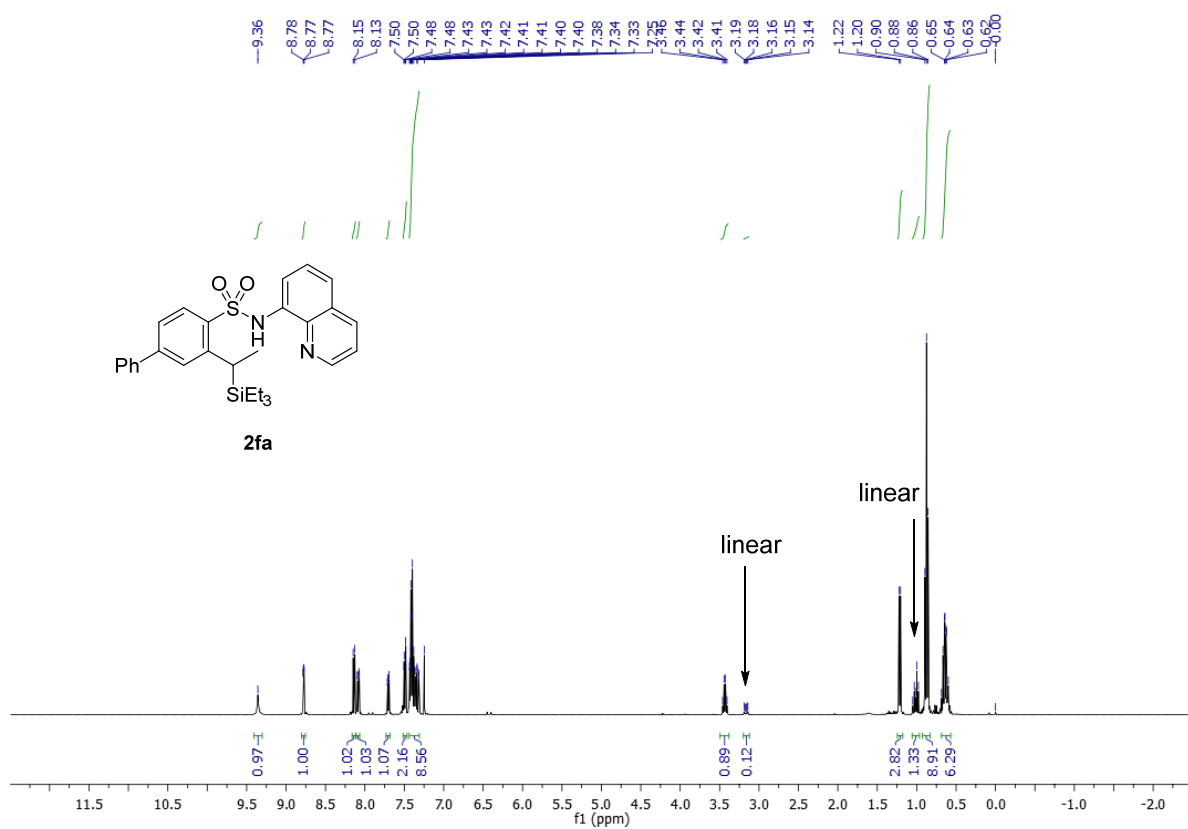


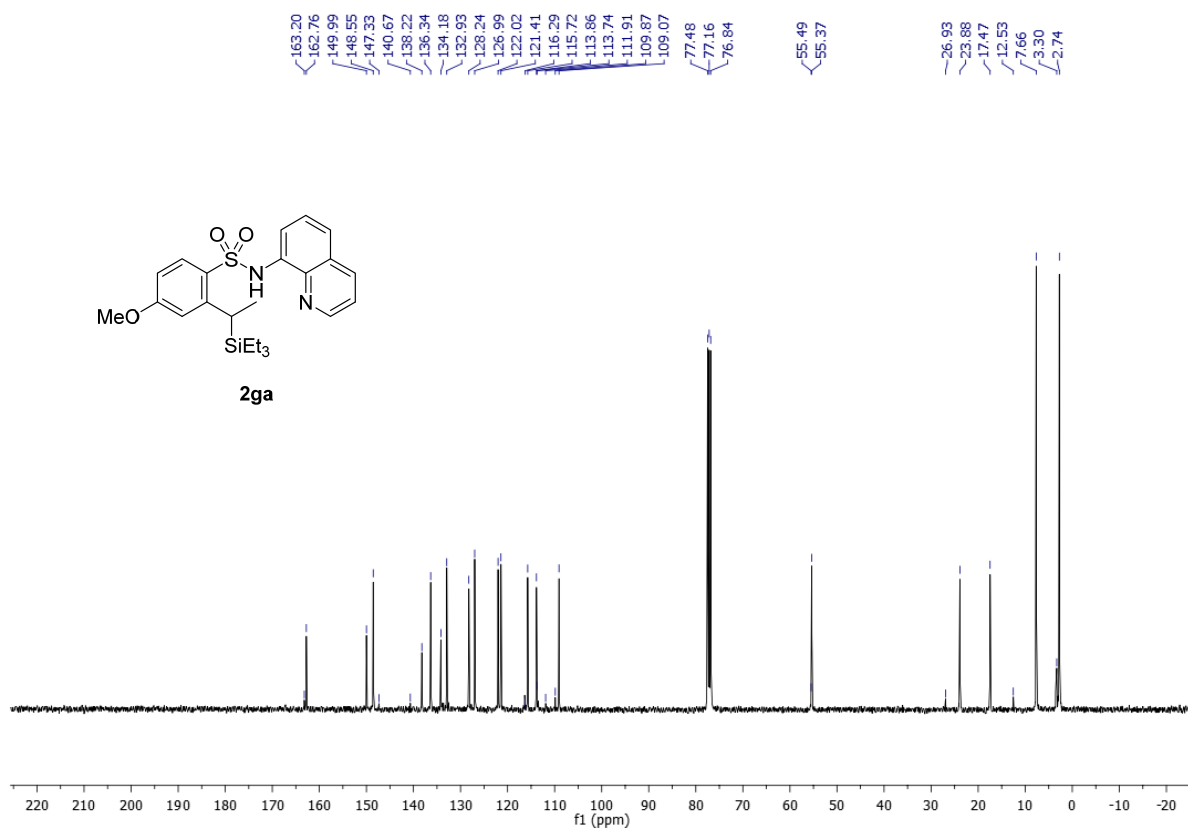
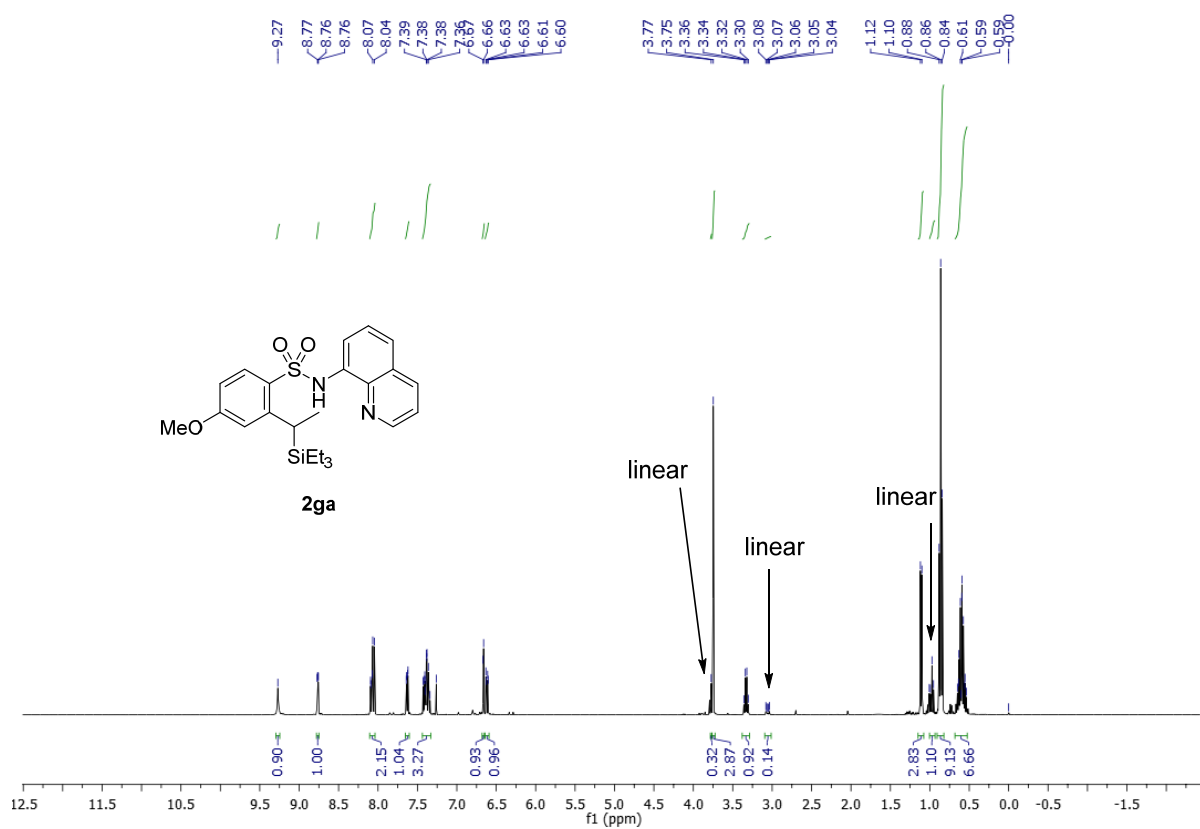


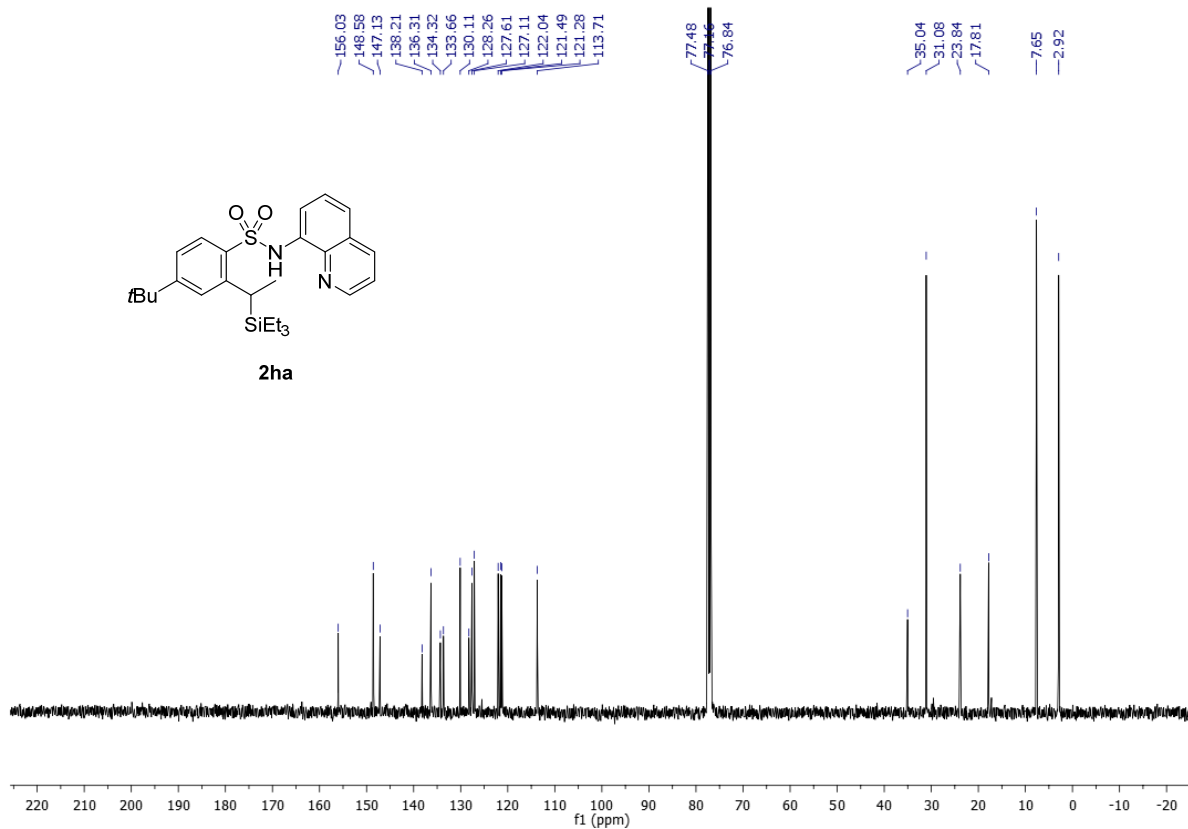
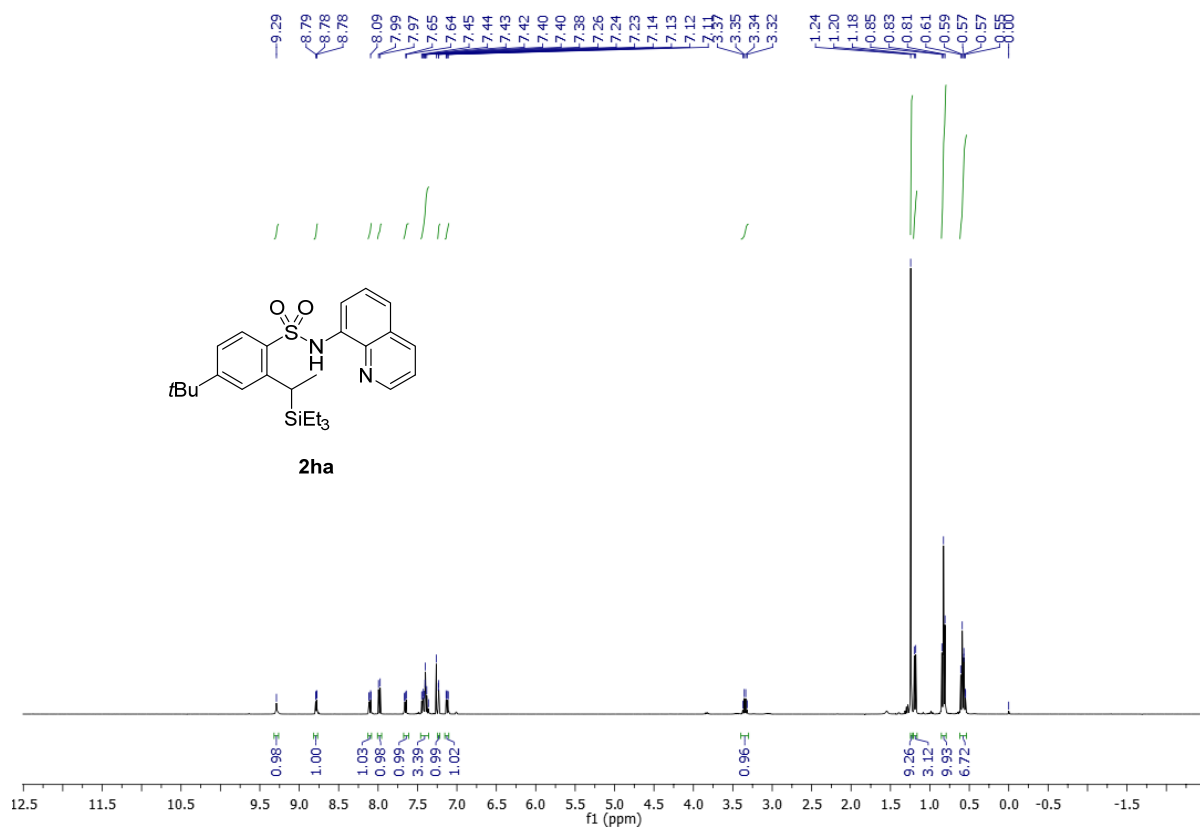


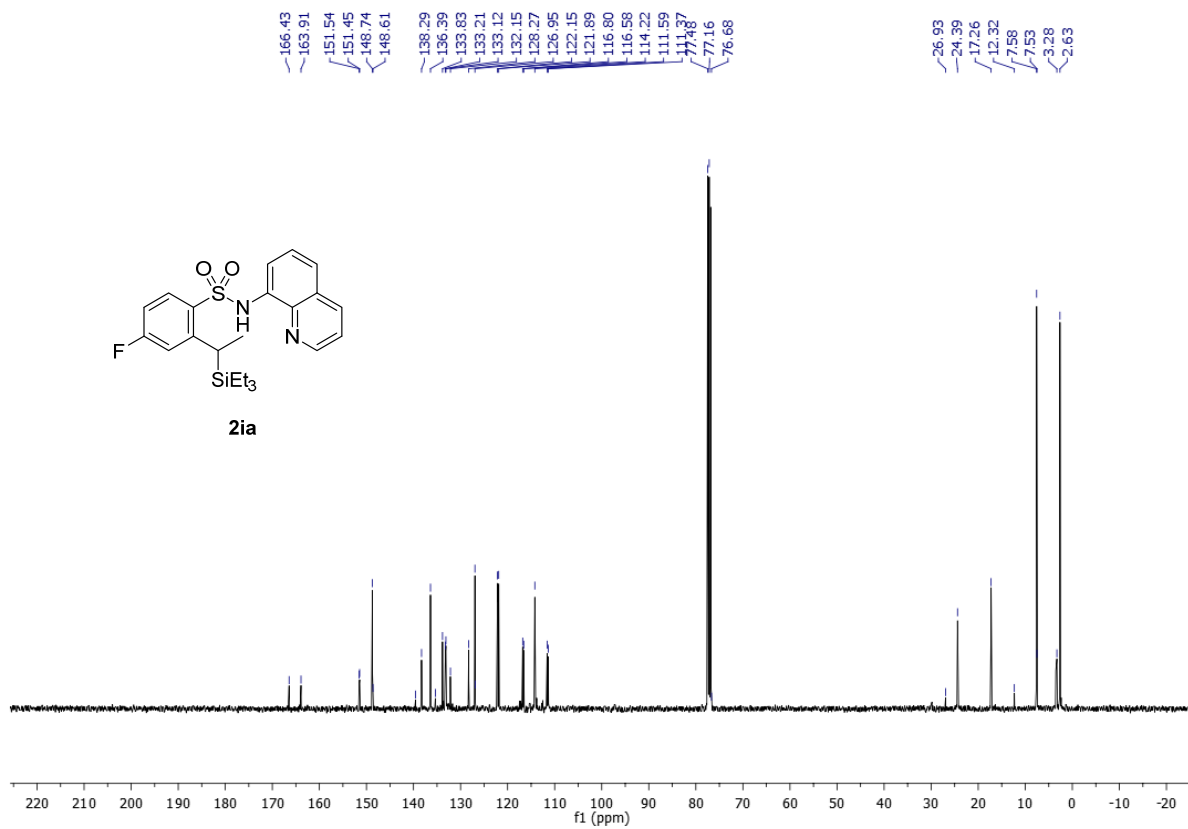
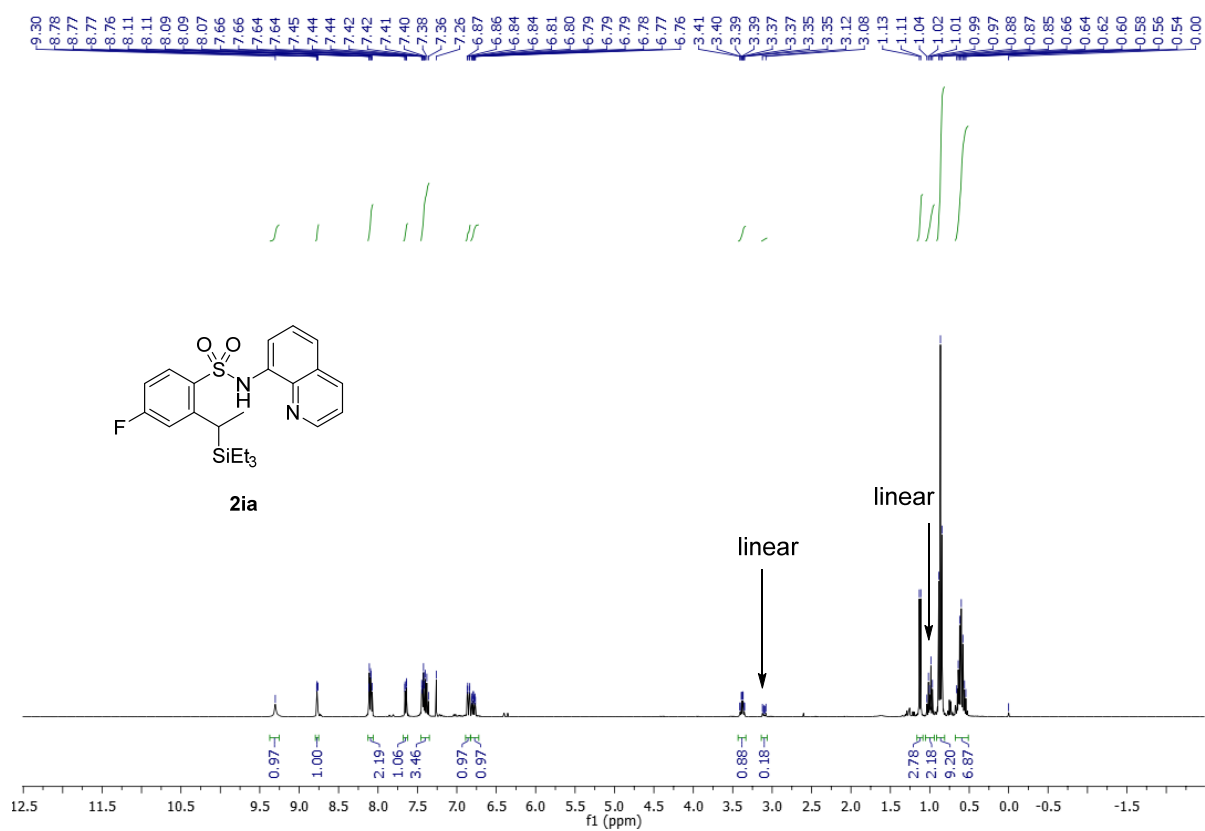


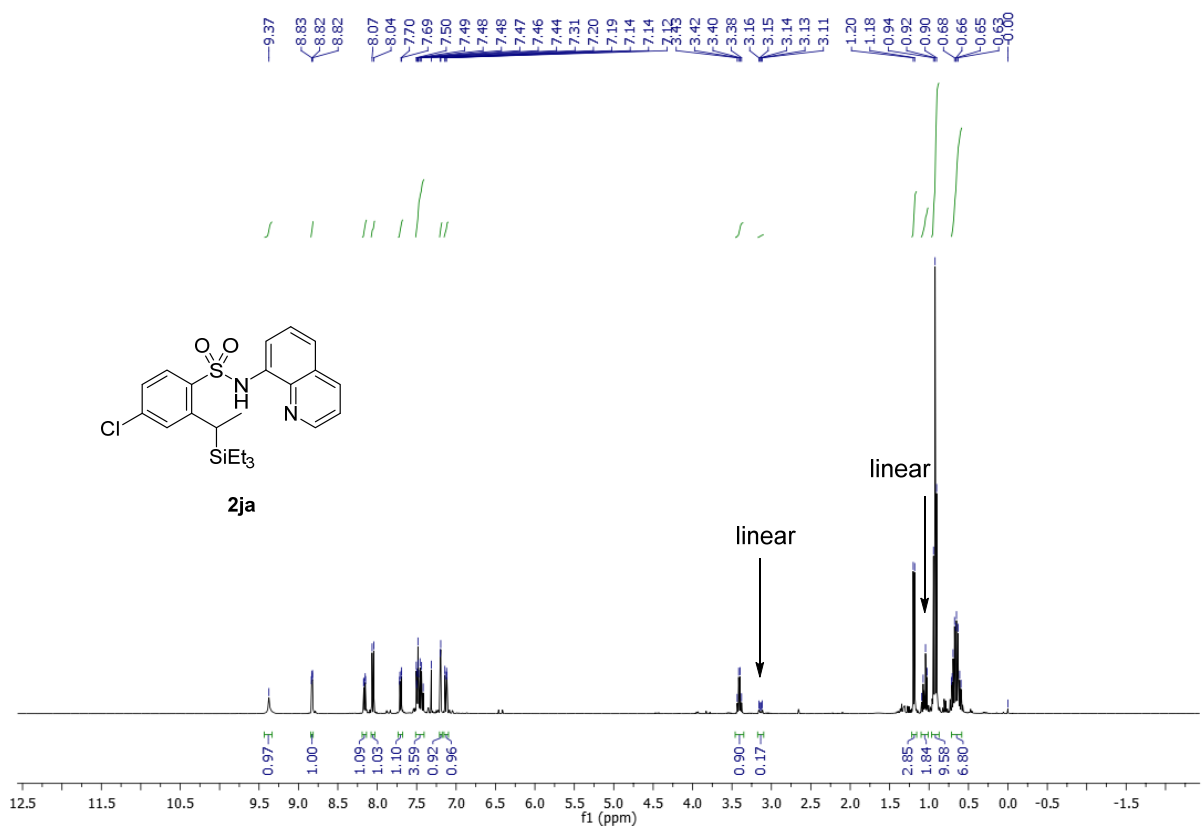
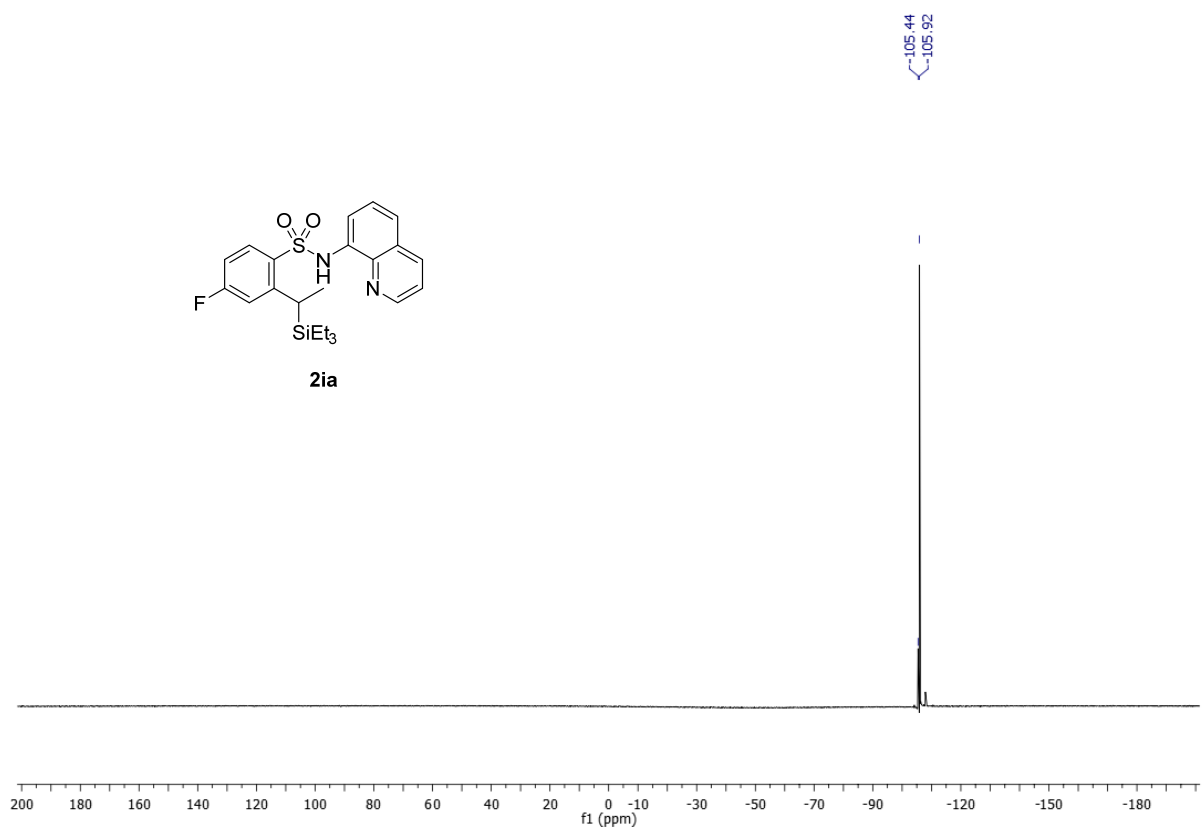


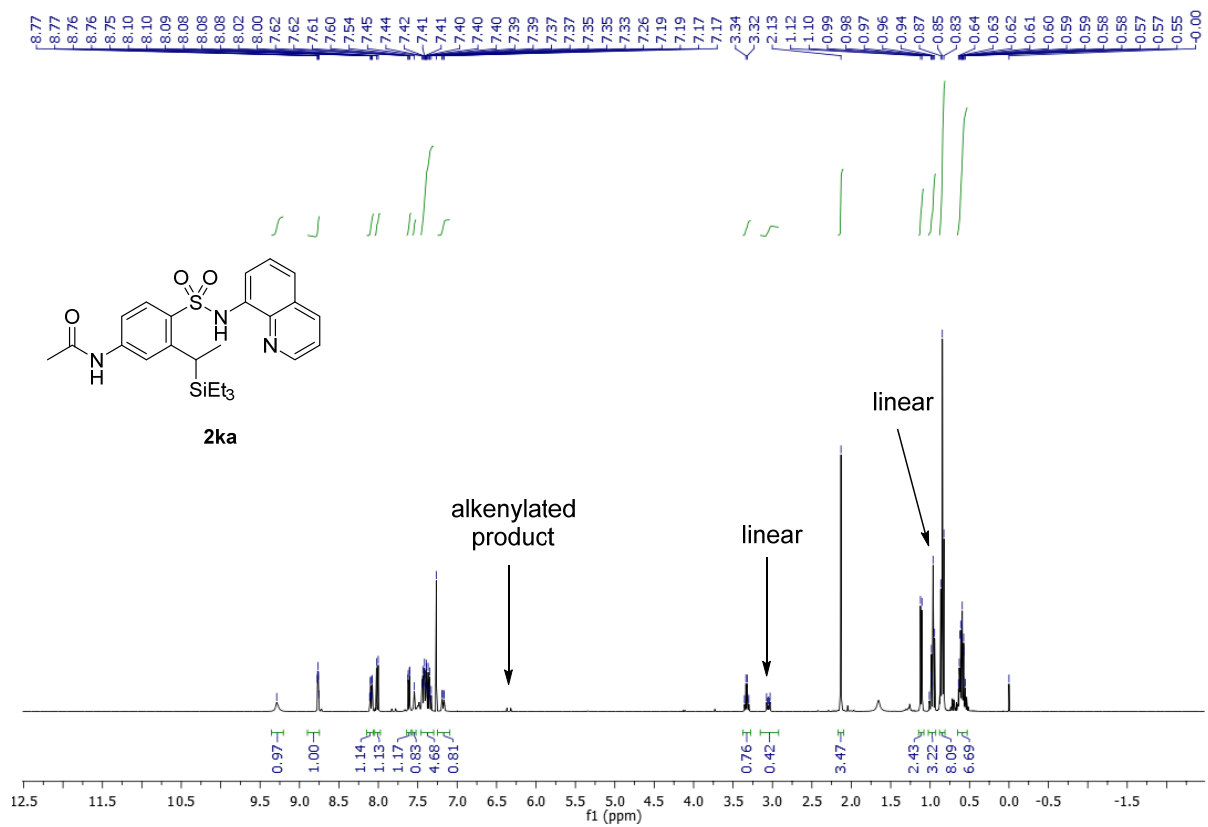
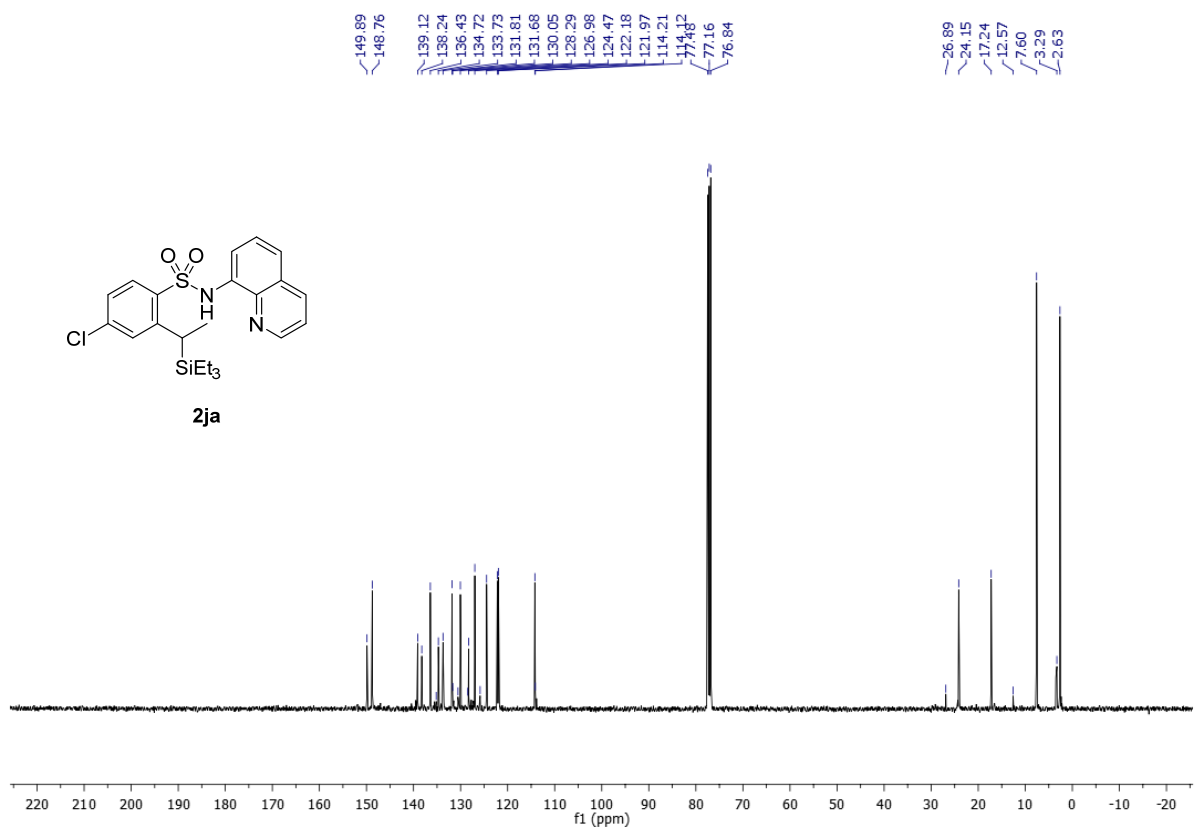


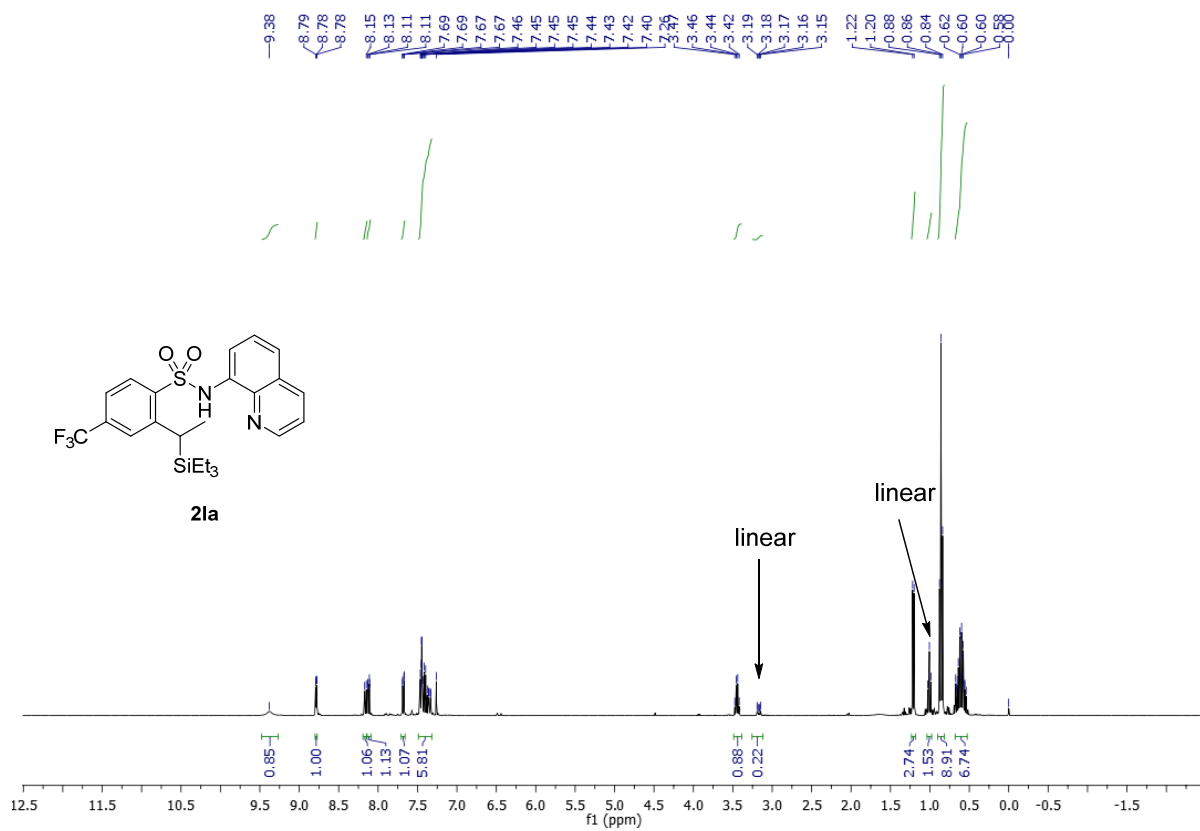
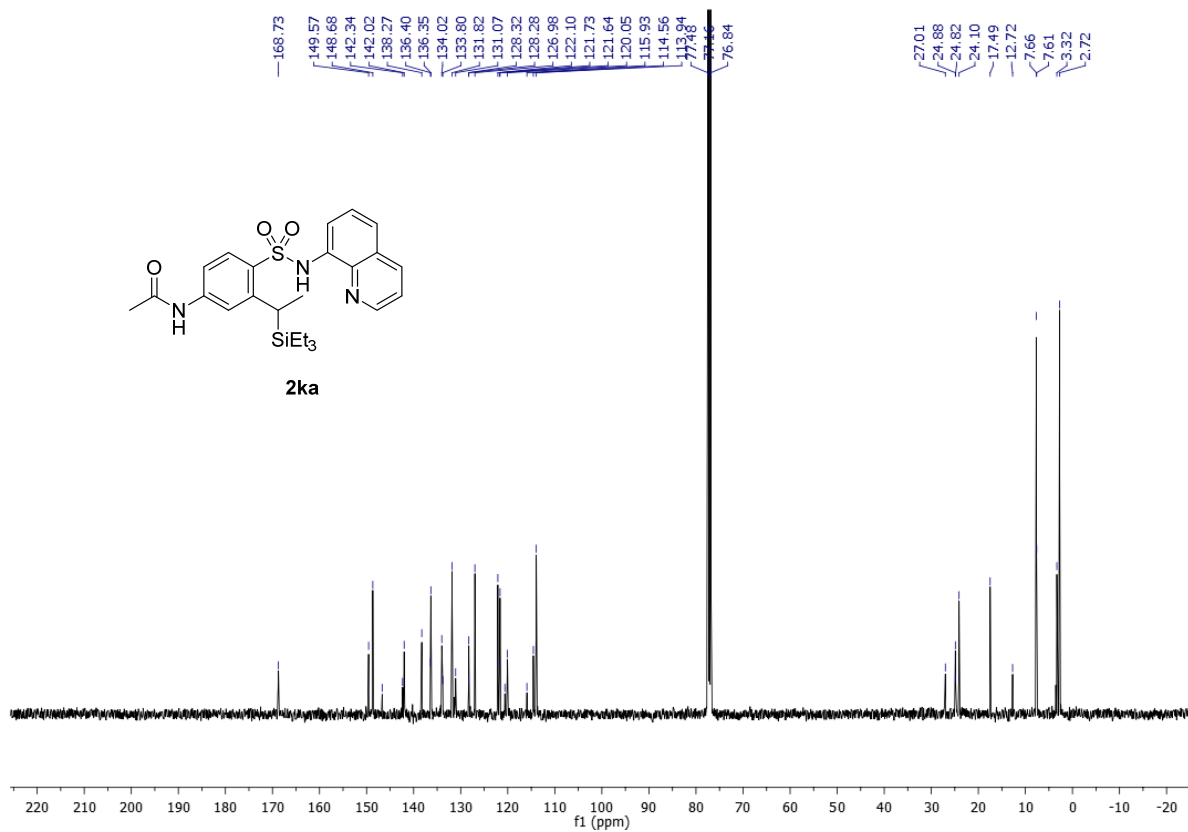


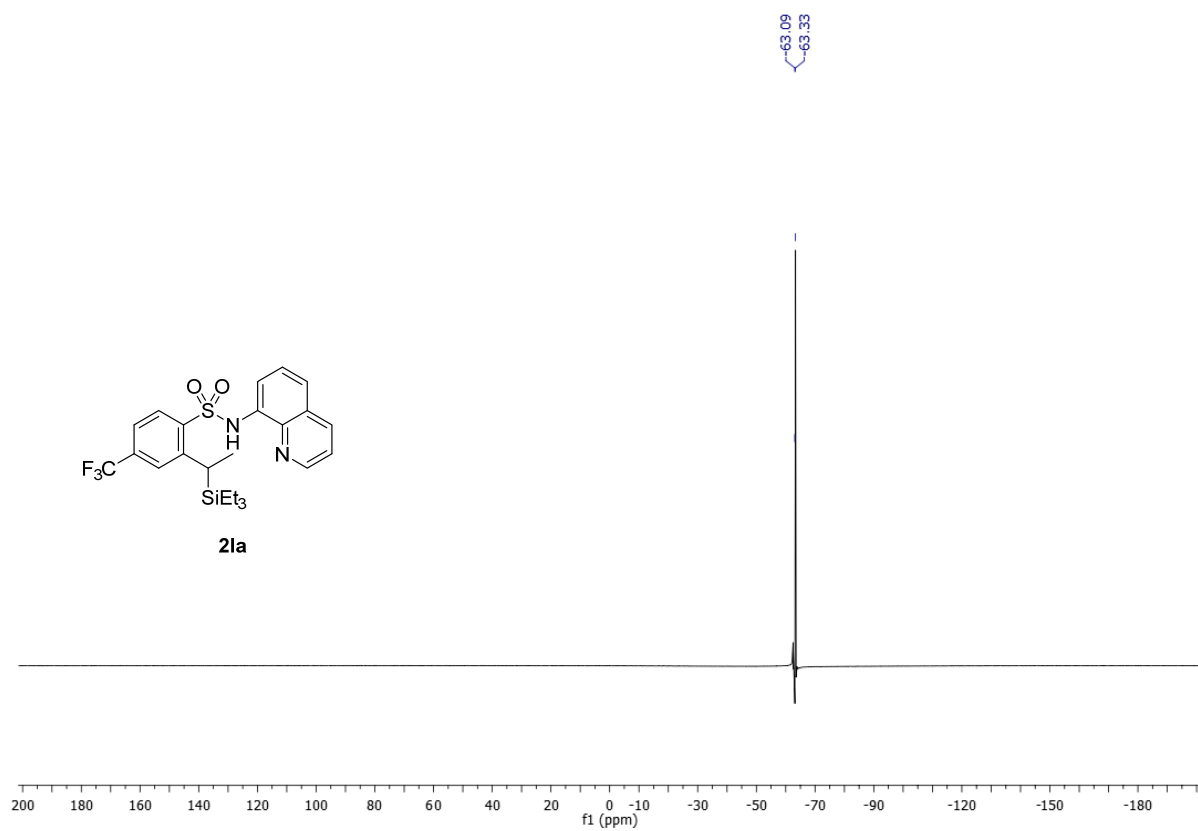
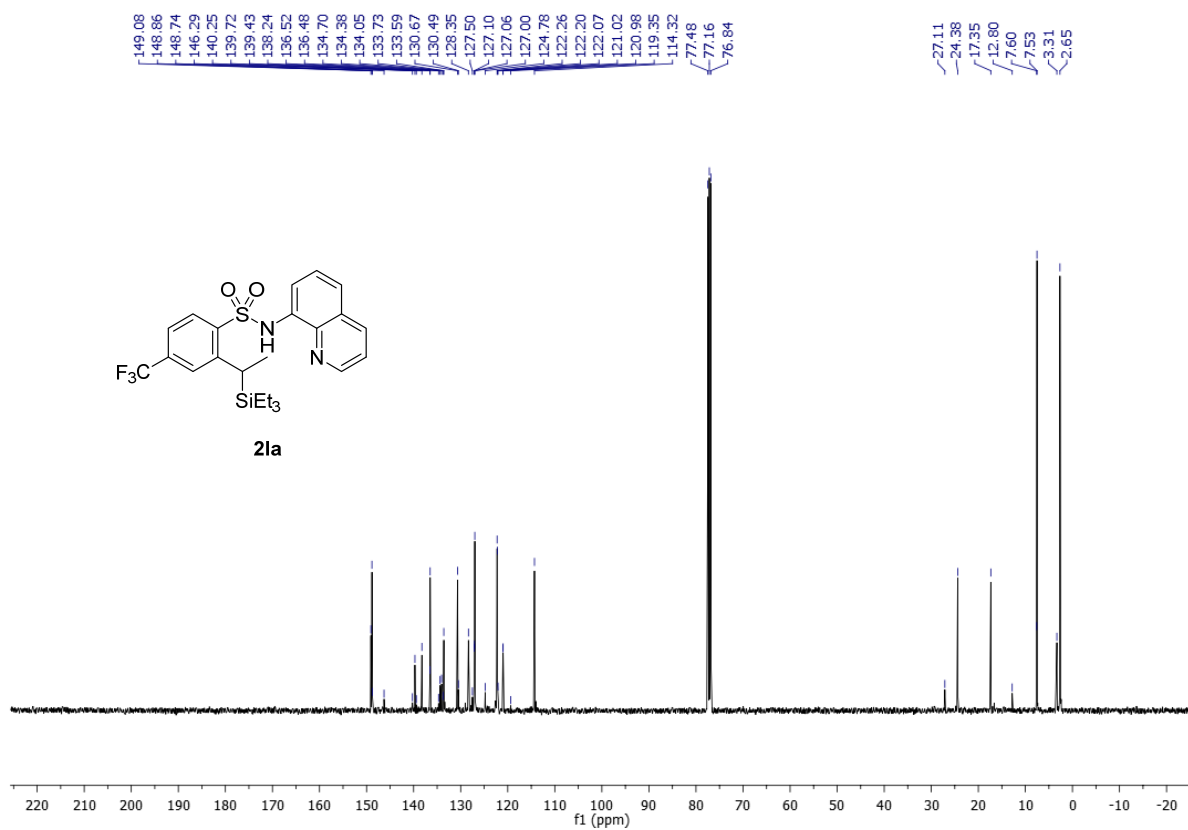


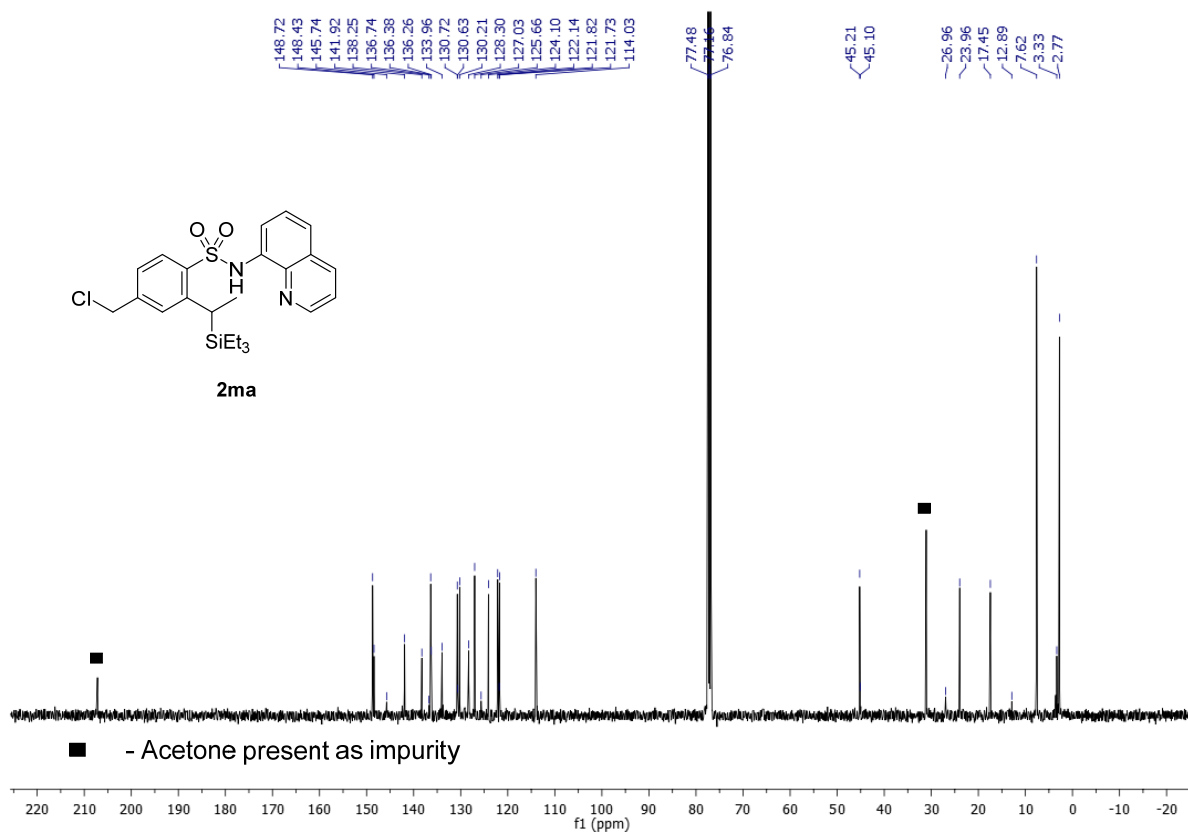
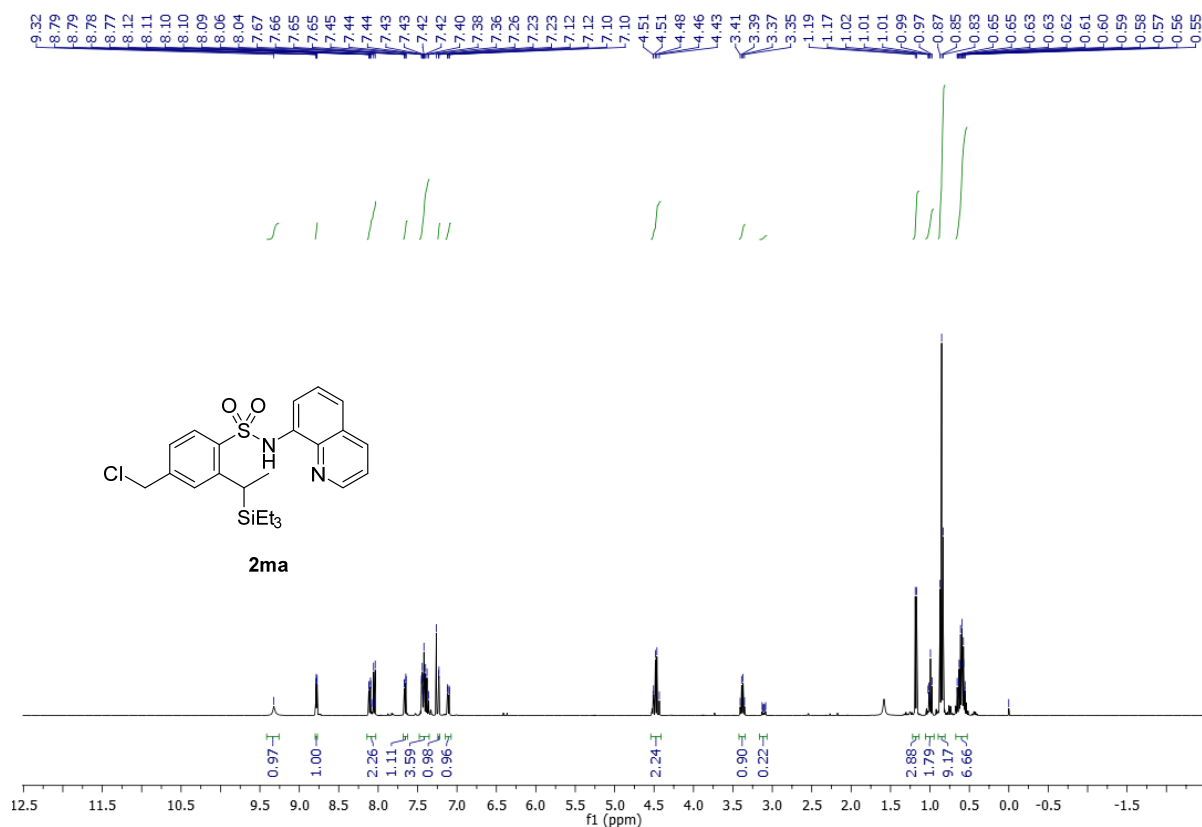


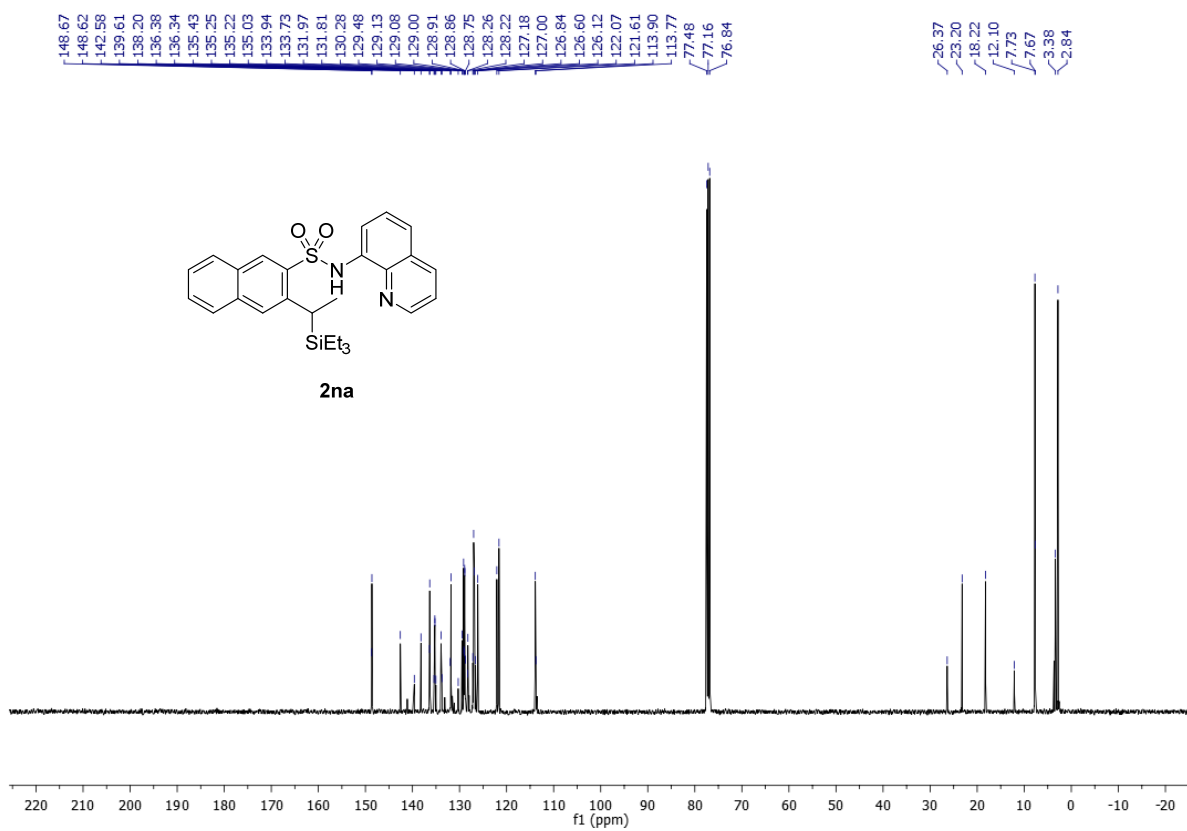
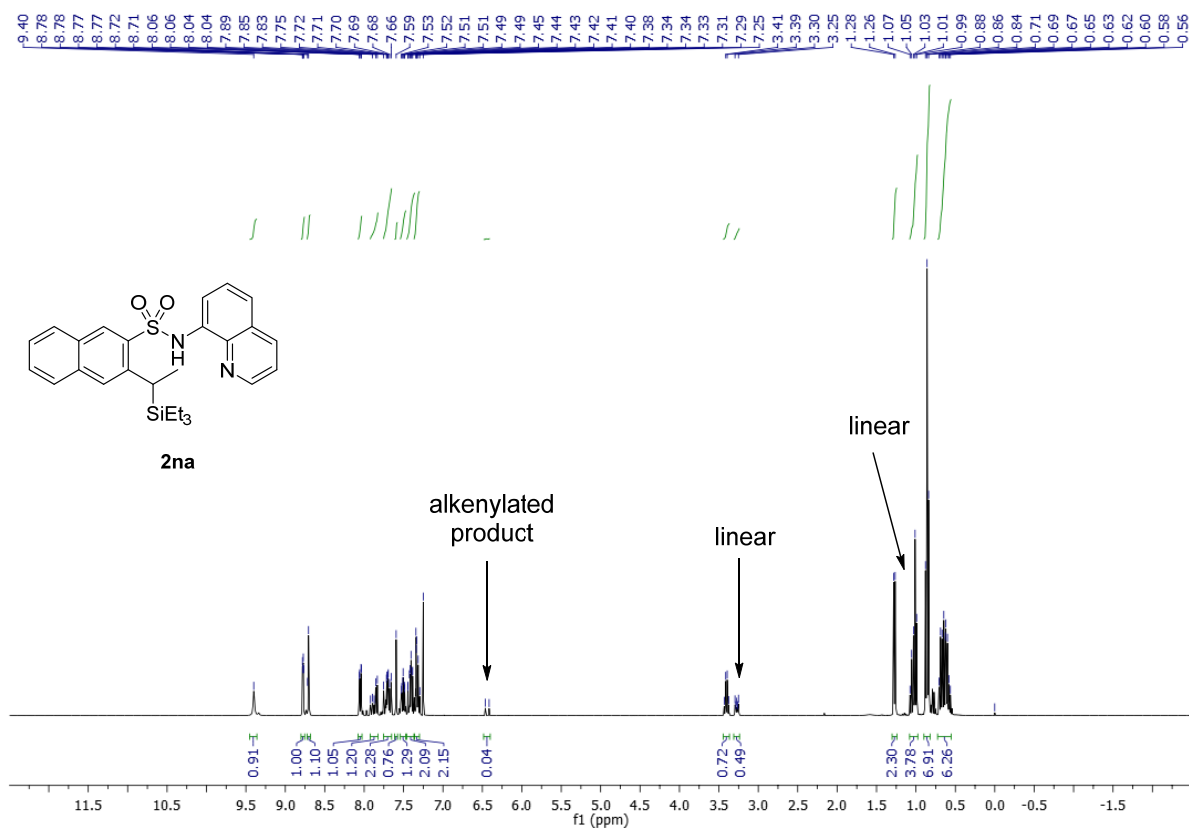


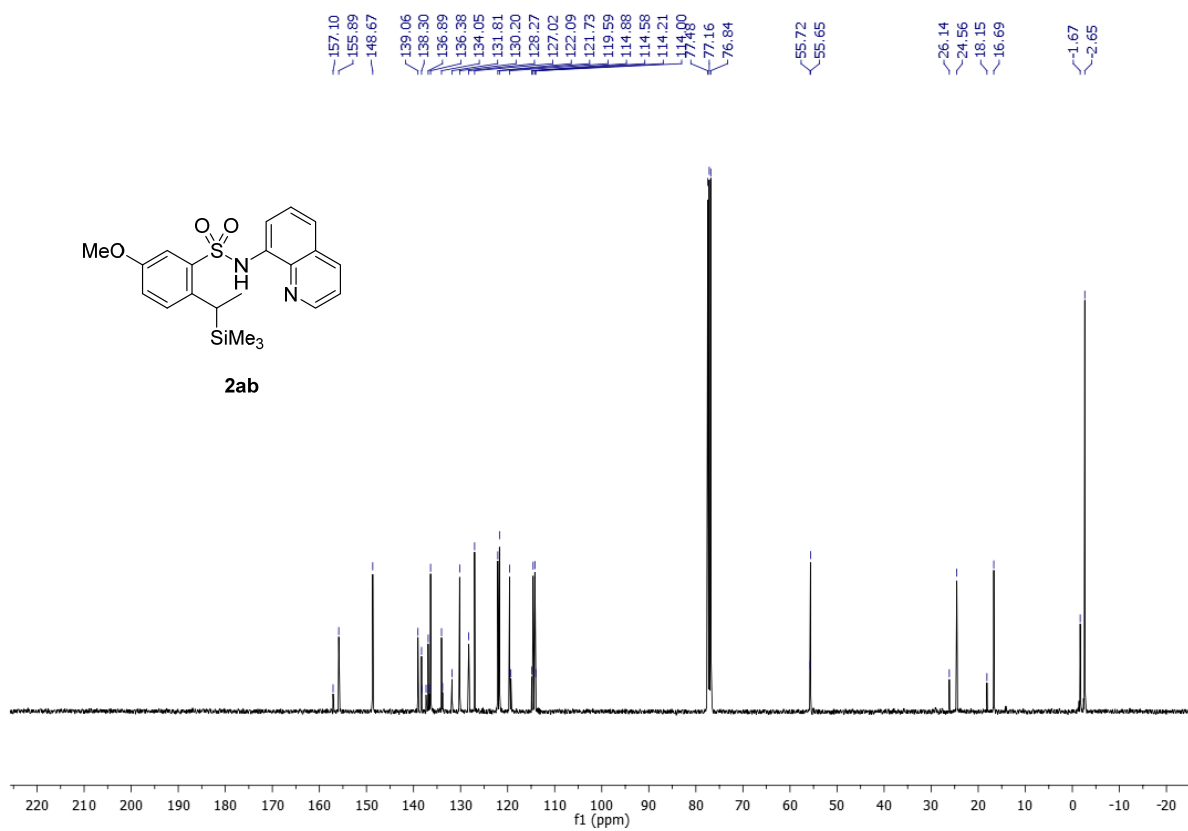
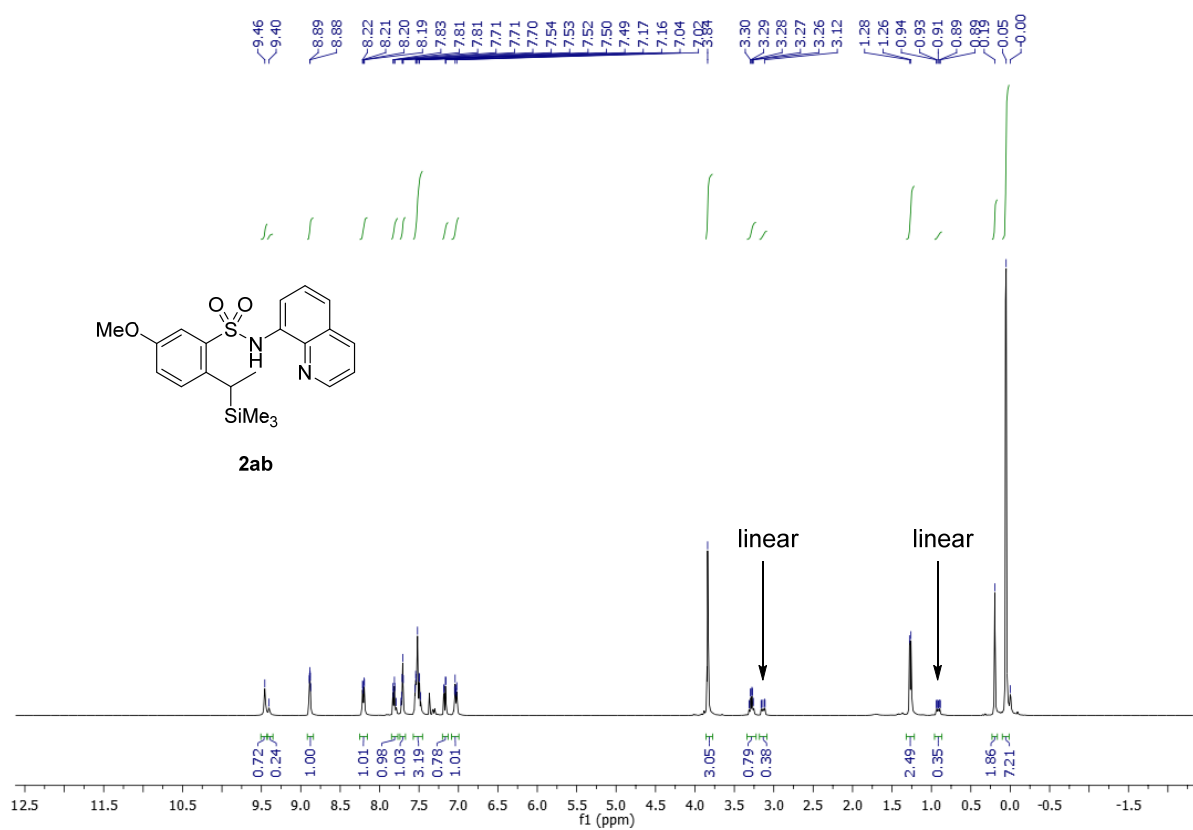


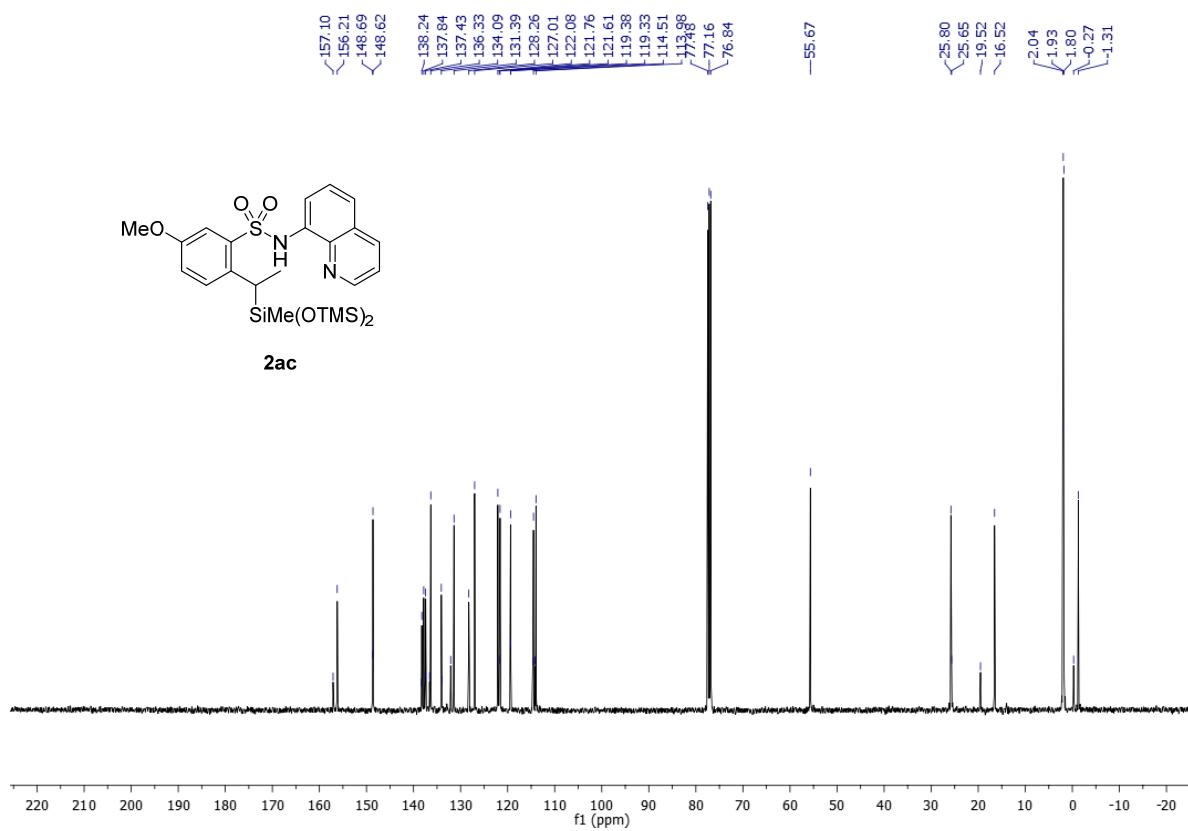
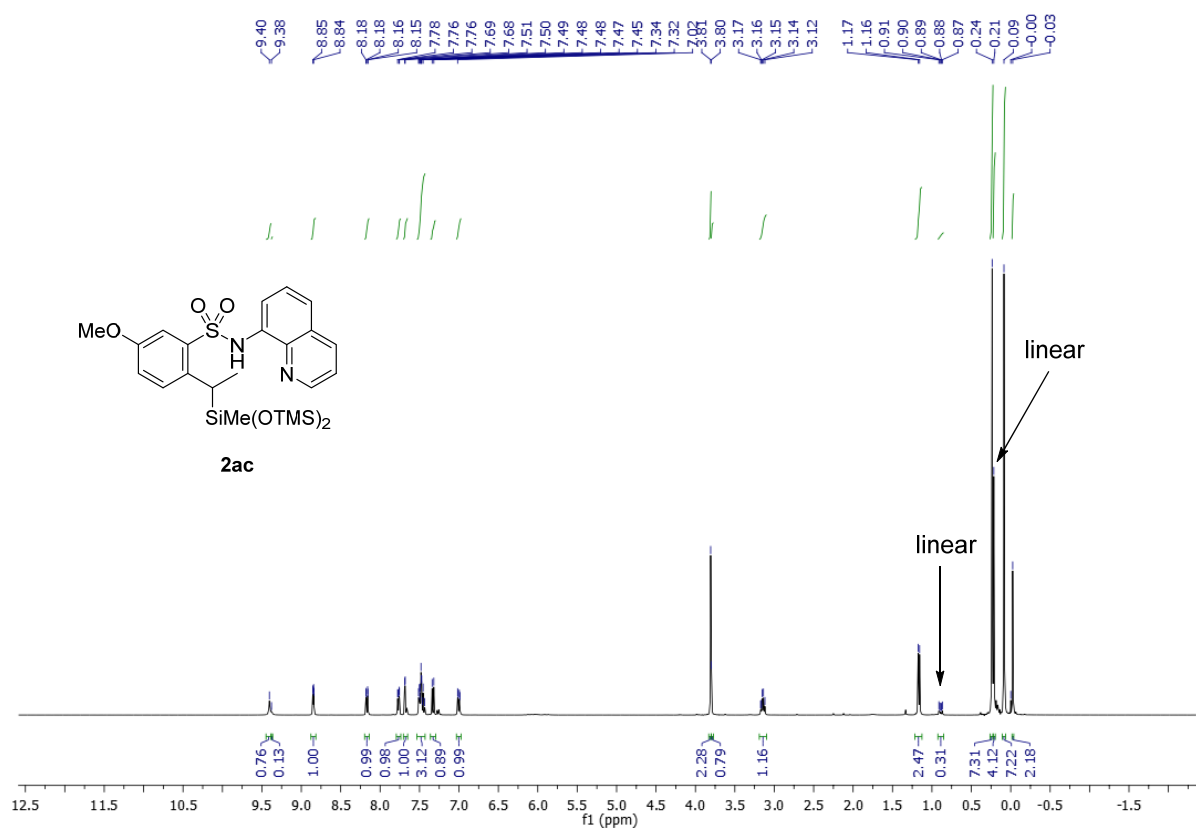


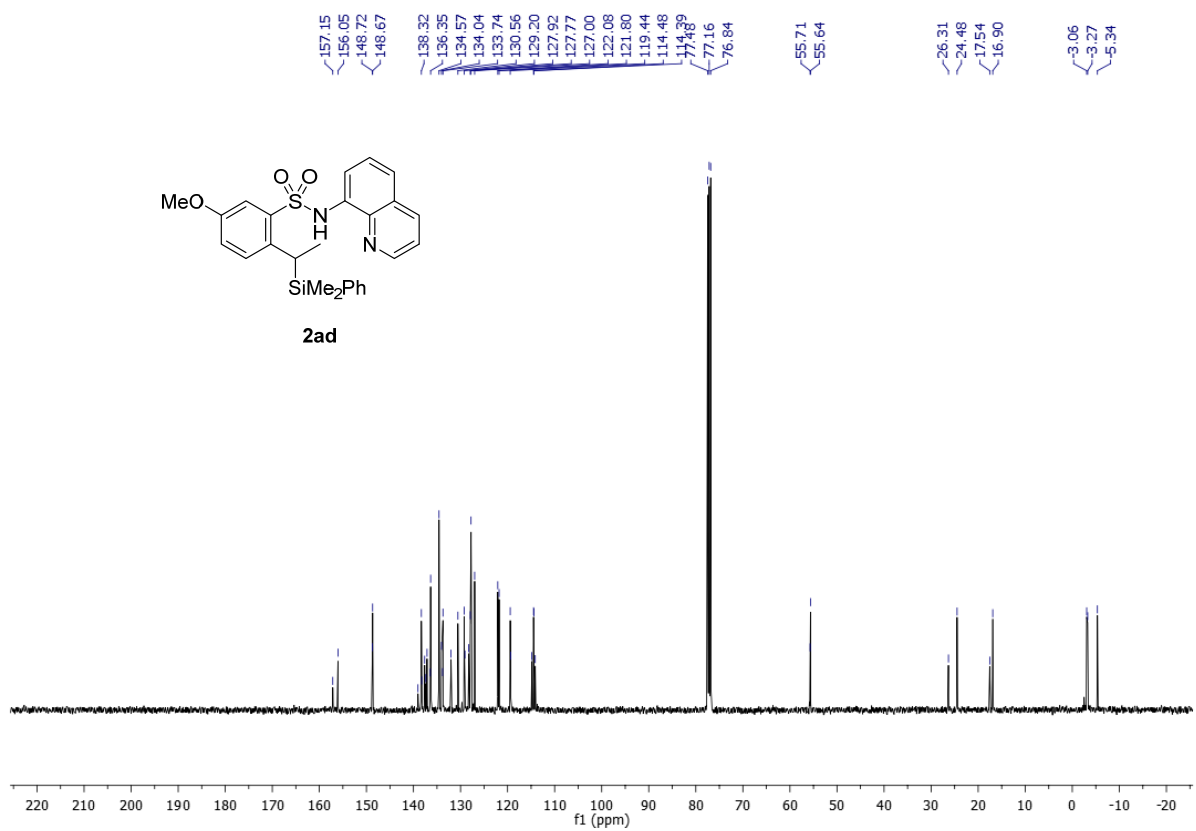
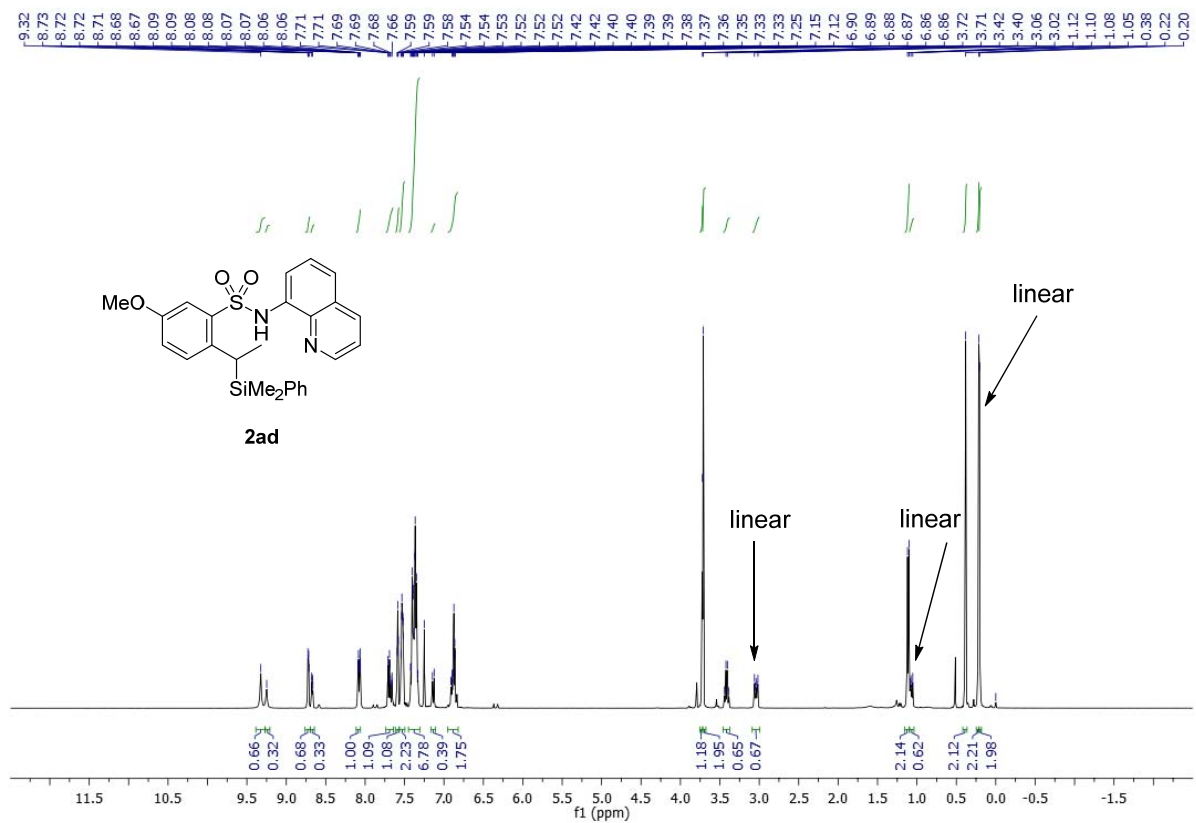


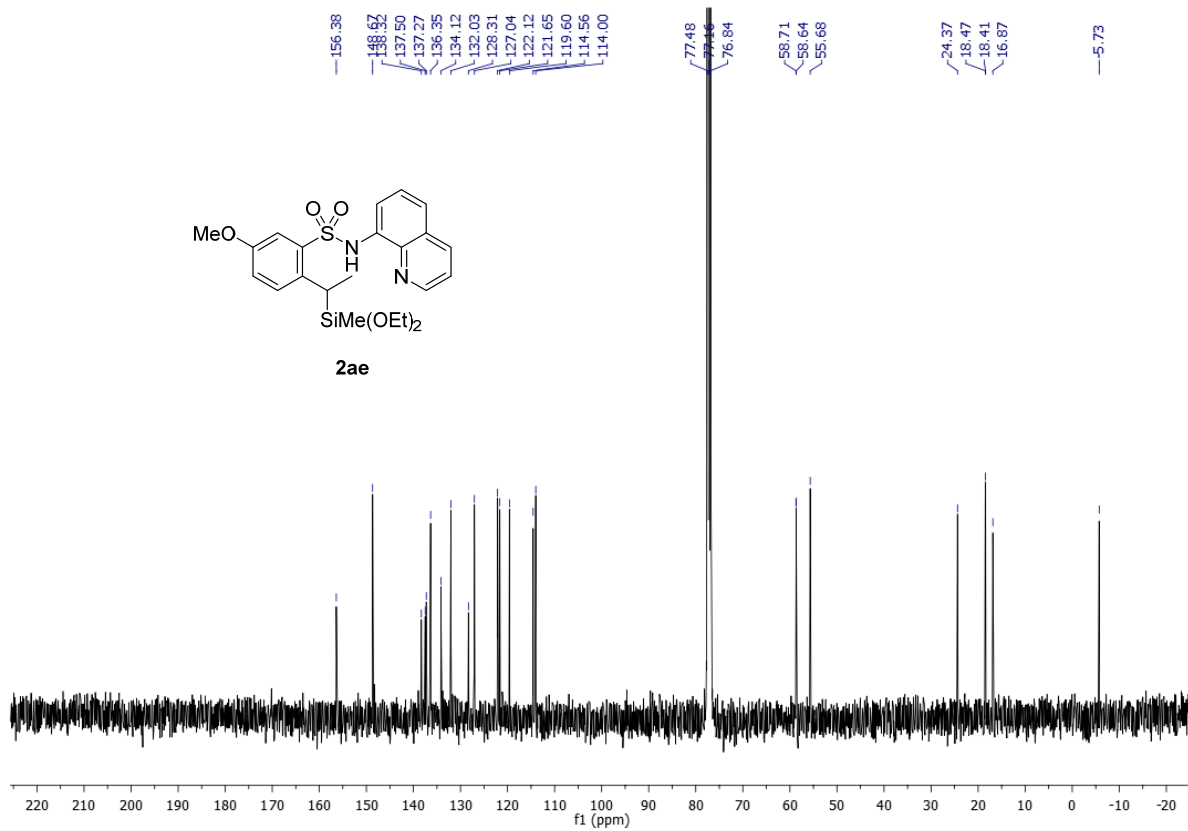
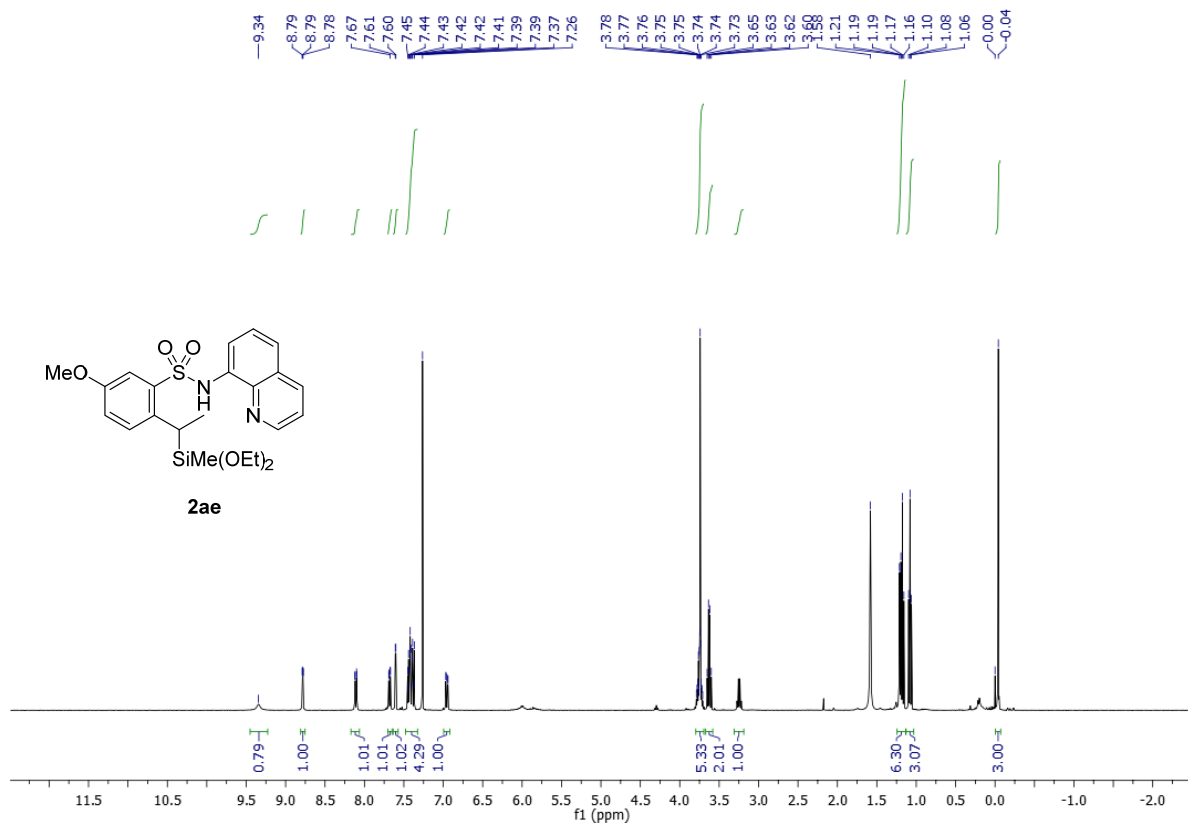


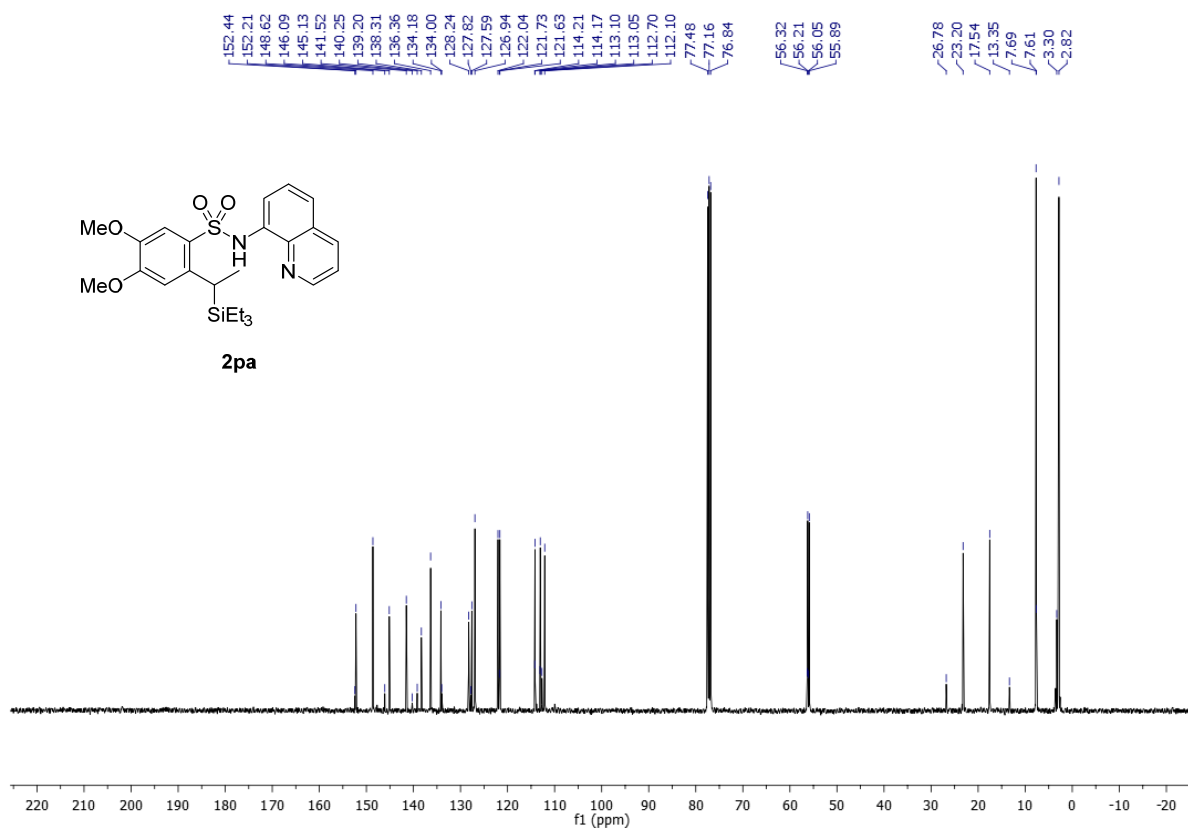
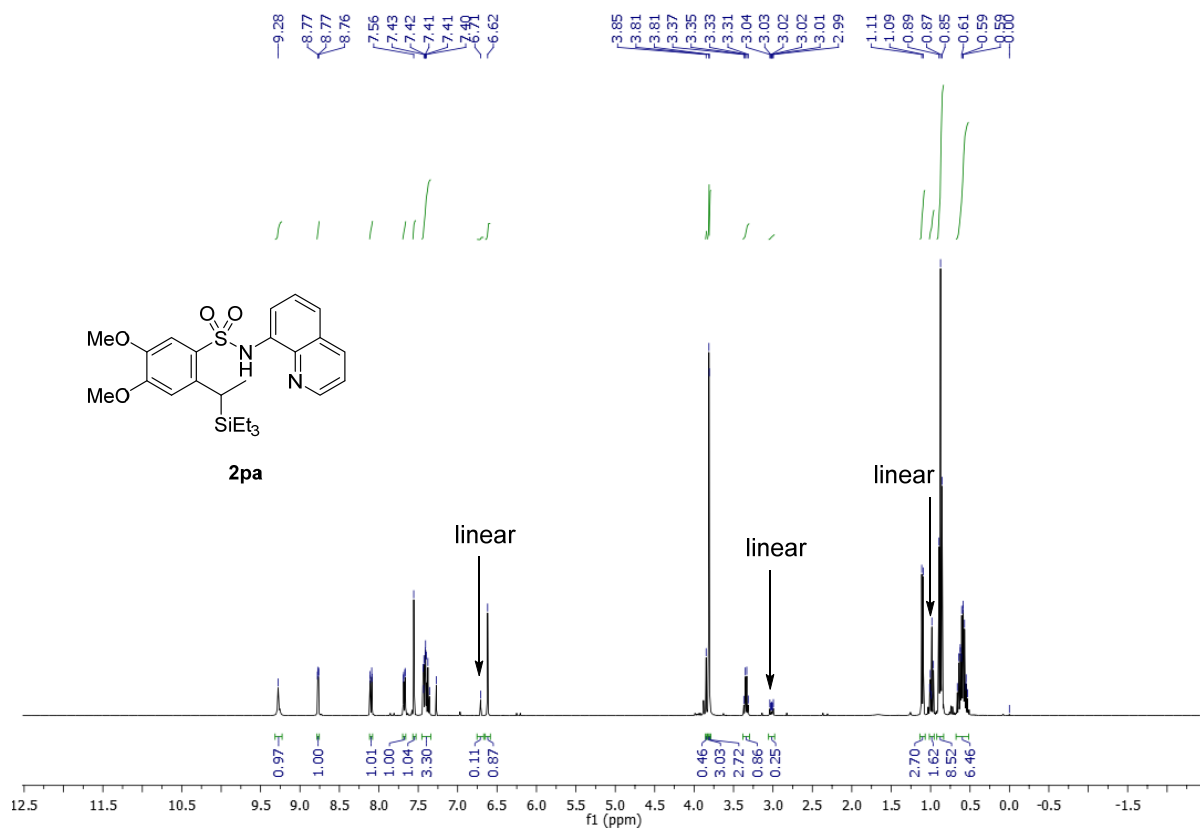


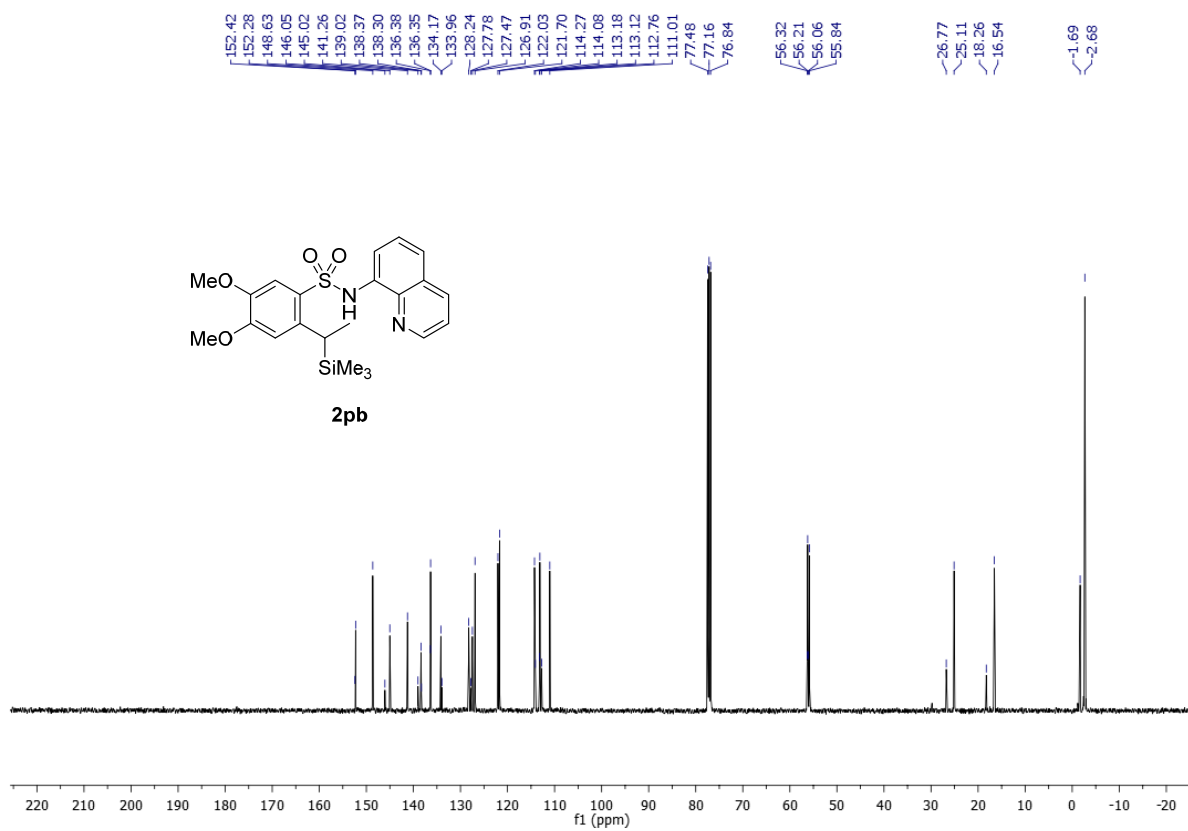
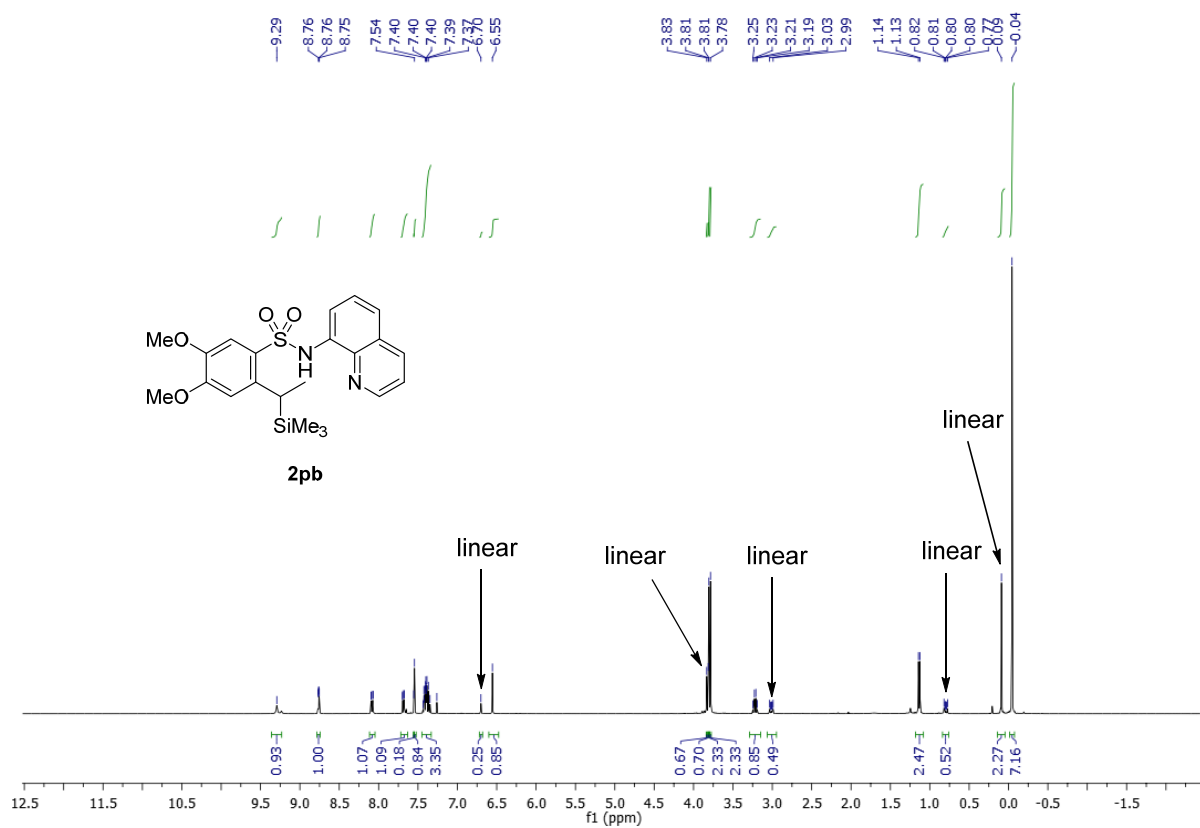


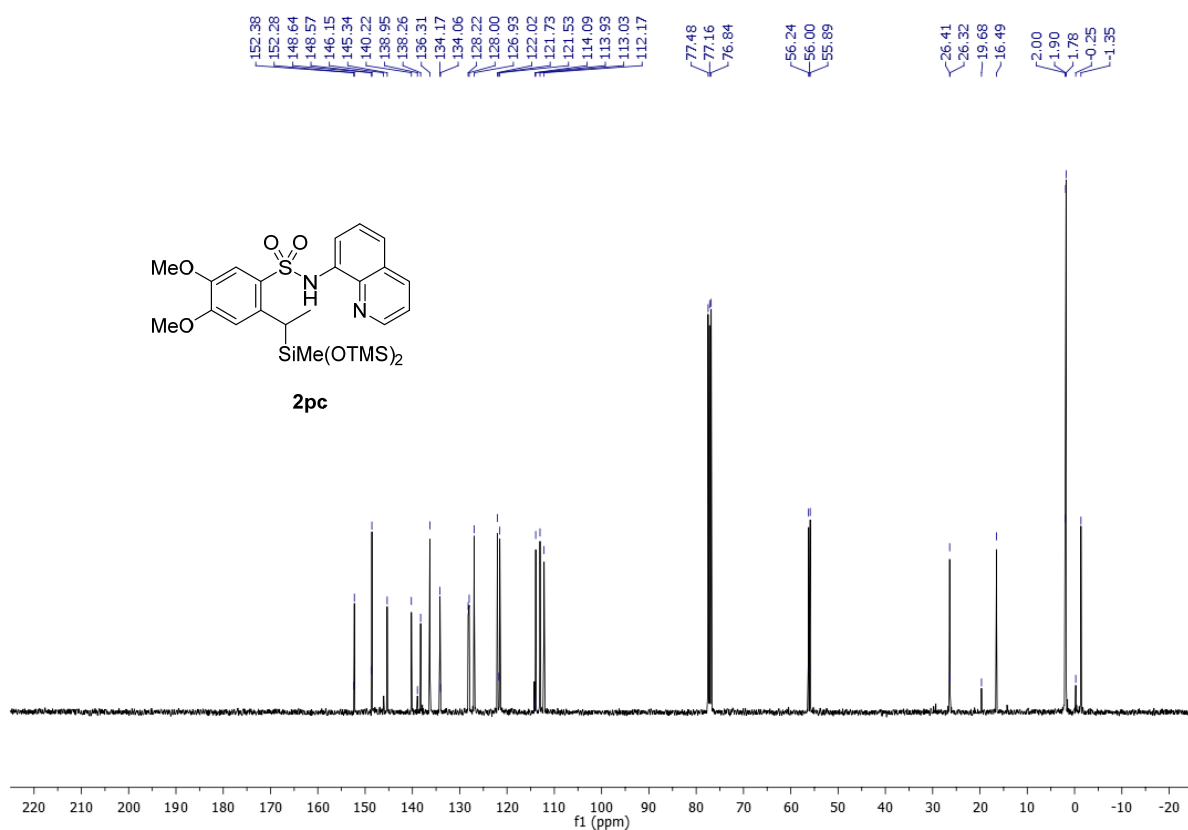
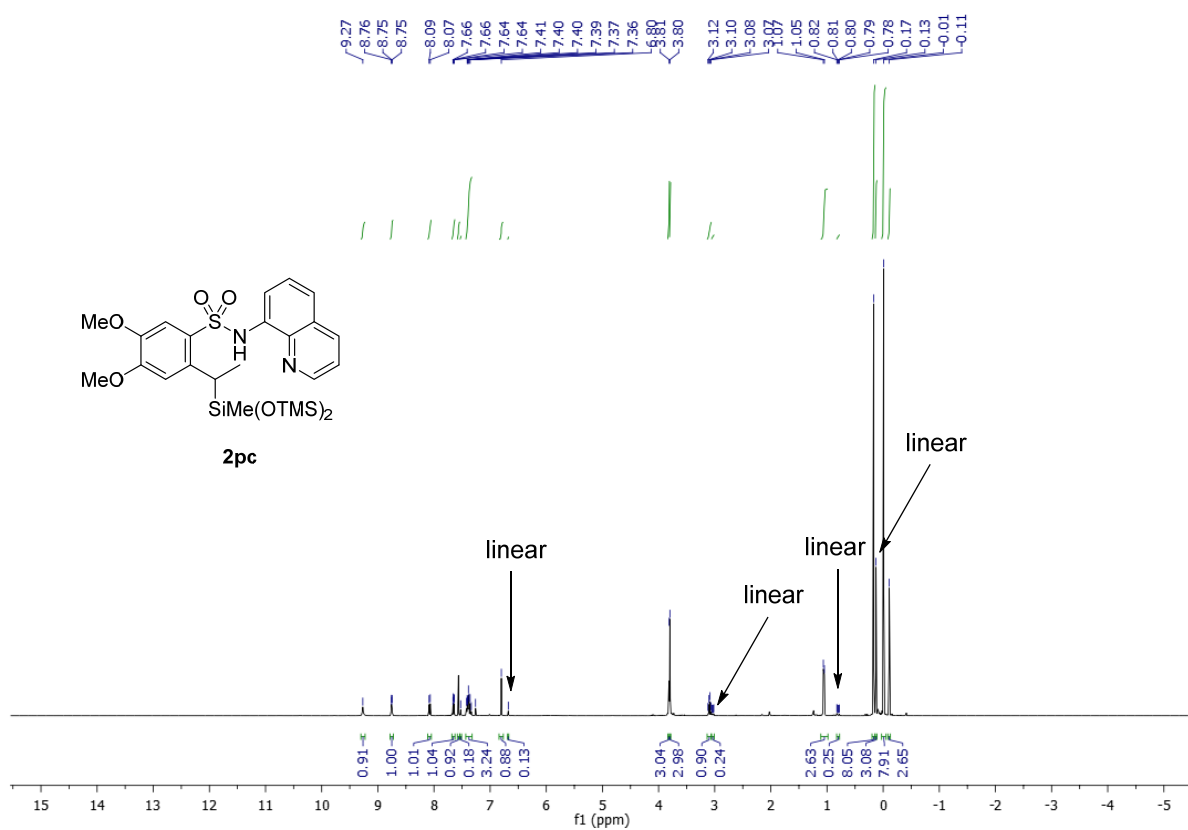












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