Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

C3-Selective C-H Thiolation of Quinolines via an *N*-Arylmethyl Activation Strategy

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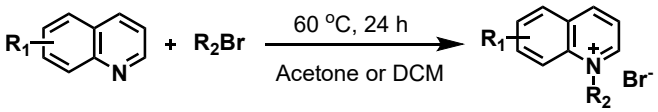
Table of Contents

1. General Information

^{1}H NMR spectra were recorded on Bruker 400 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at Bruker 101 MHz and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). ^{19}F NMR were obtained at Bruker 376 MHZ ($CFCl_3$ as outside standard and low field is positive). GC-MS analysis was recorded on GCMS-QP2020 of SHIMADZU. The NMR yield was determined by ^{19}F NMR using trifluorotoluene as an internal standard. HRMS was recorded on a commercial apparatus (ESI Source, TOF). All reagents were weighed and handled in air at room temperature. All solvents, reagents, and deuterated solvents were purchased from Aladdin, Aldrich, Adamas, and TCI without further purification.

2. Experimental Procedure

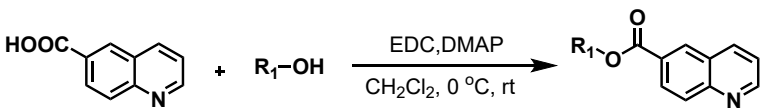
2.1 Synthesis of *N*-heteroarenium Halide Salts.



Method 1: Derivatives of quinoline (3 mmol), alkyl bromide (6 mmol) and acetone (5 mL) were introduced in a flask (50 mL). The resulting mixture was then stirred at 60 ºC for 24 hours. Then, the solvent was removed. The reaction mixture was washed with small amount of diethyl ether and finally dried under vacuum to get the salts (**1a,1ab-1bn**).

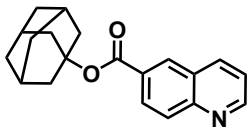
Method 2: Derivatives of quinoline (3 mmol), alkyl bromide (6 mmol) and dichloromethane (DCM, 5-10 mL) were introduced in a flask (50 mL). The resulting mixture was stirred at 60 ºC for 24 hours. Then, the solvent was removed. Finally, the residue was purified by flash chromatography on silica gel with dichloromethane/ethanol to give corresponding quinoline derivatives (**1bo-1bz**).

2.2 Synthesis of Quinoline Derivatives Containing Bioactive Molecules.[1]

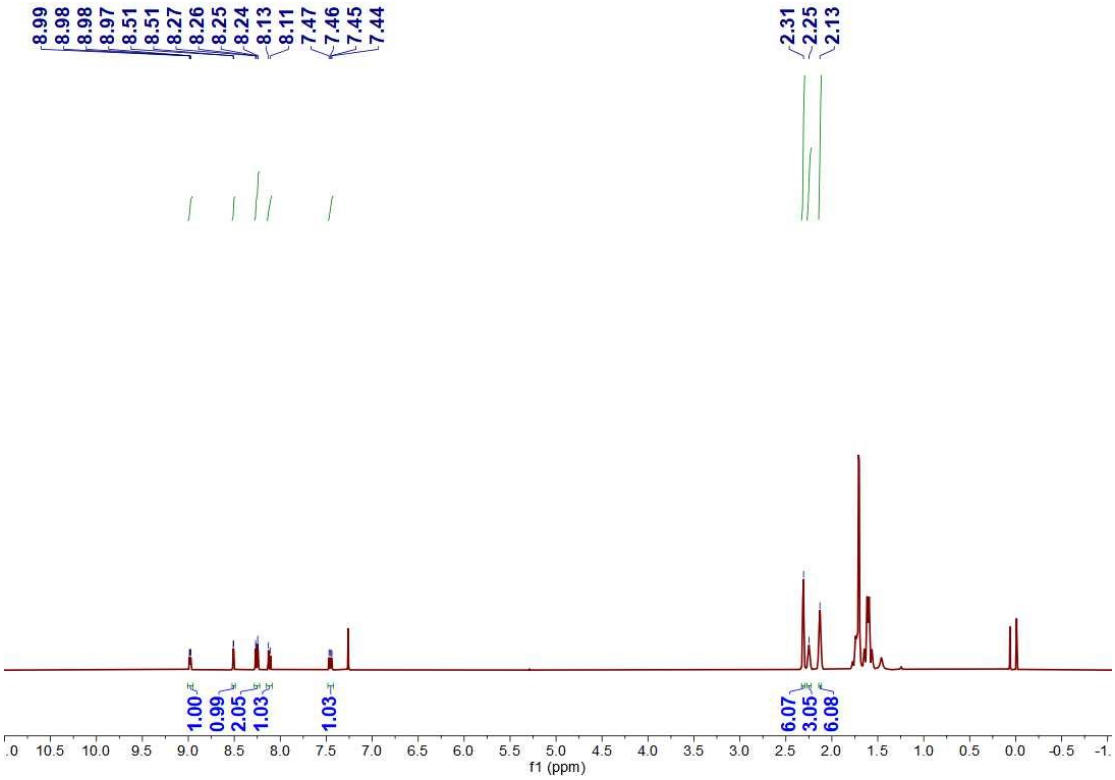


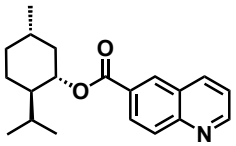
To a suspension of quinoline-6-carboxylic acid (5 mmol) in DCM (10 mL) was added DMAP (4-(dimethylamino)-pyridine, 10 mmol) in one portion at room temperature. The reaction mixture was stirred for 10 min at room temperature. *N*-(3-(Dimethylamino)propyl)-*N*'-ethylcarbodiimide hydrochloride (EDC, 5 mmol) was added at 0 ℃. Then the resultant

suspension was stirred for 10 min at 0 °C. A solution of alcohol (R_3-OH) (4 mmol) in CH_2Cl_2 was added at 0 °C. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 16 h. The solution was diluted by the addition of saturated aqueous NH_4Cl solution and CH_2Cl_2 at room temperature. The organic phase was dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate to give corresponding quinoline derivatives. The product S1, S3 and S4 have been reported in the known literature. [1]



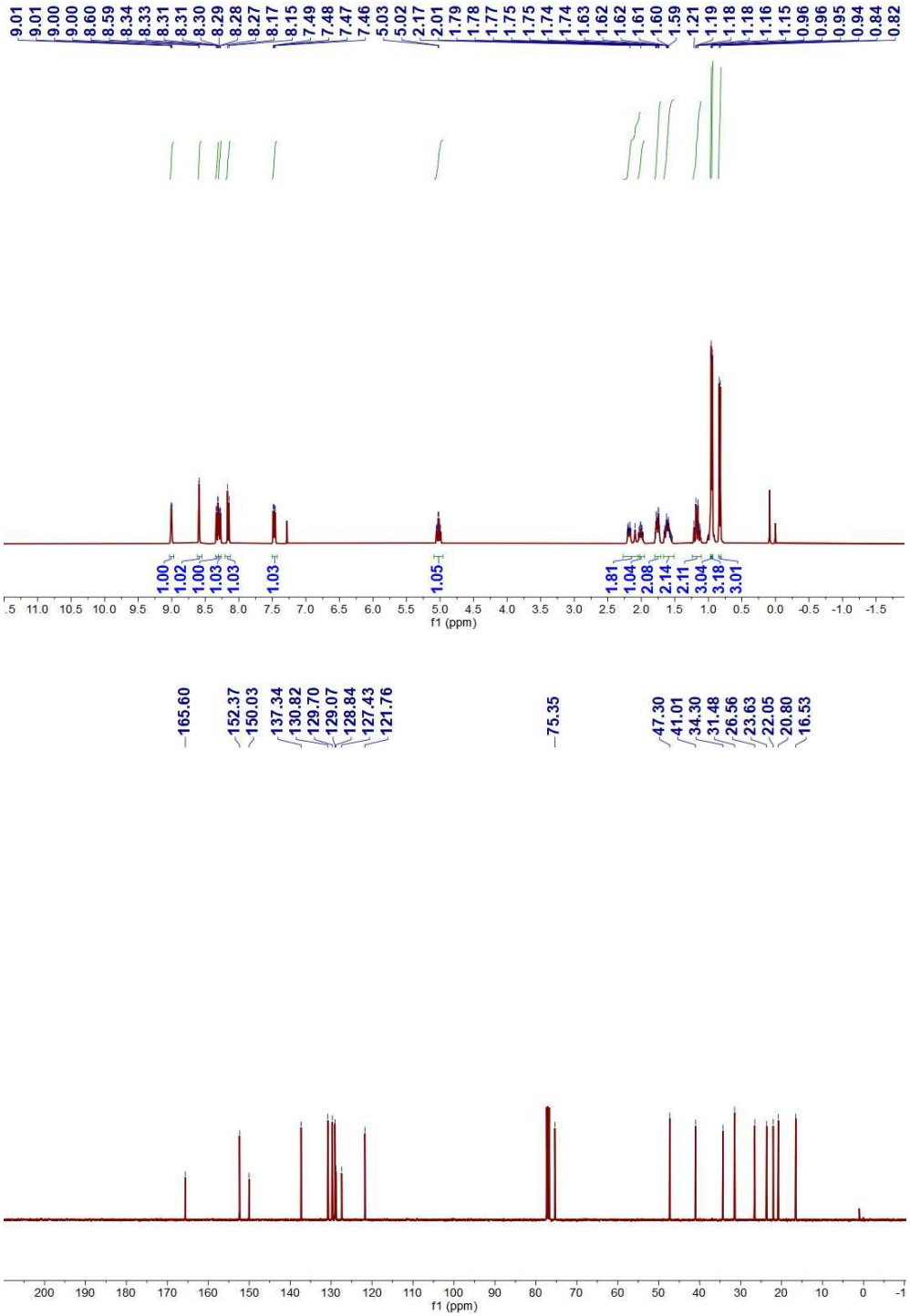
adamantan-1-yl quinoline-6-carboxylate (S1): White solid, 91 % yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.98 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.51 (d, *J* = 1.8 Hz, 1H), 8.25 (dd, *J* = 8.9, 1.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.45 (dd, *J* = 8.3, 4.3 Hz, 1H), 2.31 (s, 6H), 2.25 (s, 3H), 1.78 – 1.68 (m, 6H).

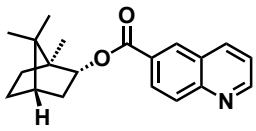




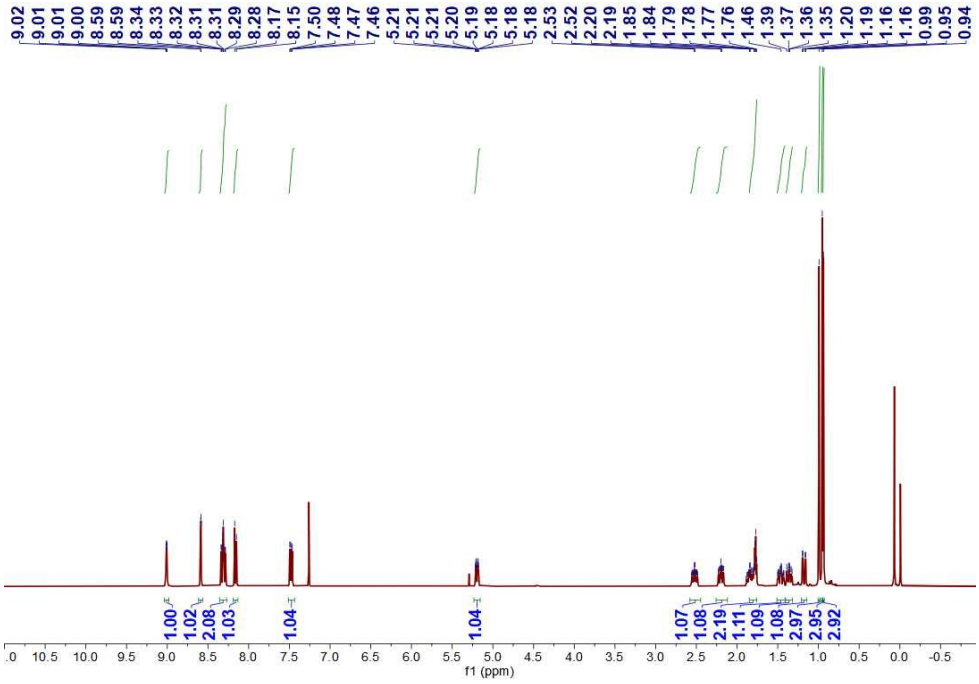
(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl quinoline-6-carboxylate (S2): White solid, 90 % yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.01 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.59 (d, *J* = 1.9 Hz, 1H), 8.32 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.29 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.02 (td, *J* = 10.9, 4.4 Hz, 1H), 2.24 – 2.08 (m, 2H), 2.01 (pd, *J* = 7.0, 2.8 Hz, 1H),

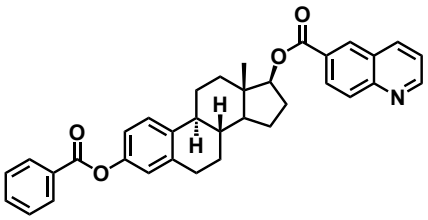
1.82 – 1.70 (m, 2H), 1.68 – 1.51 (m, 2H), 1.29 – 1.07 (m, 2H), 0.96 (d, J = 1.7 Hz, 3H), 0.94 (d, J = 2.1 Hz, 3H), 0.83 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 152.4, 150.0, 137.3, 130.8, 129.7, 129.1, 128.8, 127.4, 121.8, 75.4, 47.3, 41.0, 34.3, 31.5, 26.6, 23.6, 22.1, 20.8, 16.5. HRMS (ESI) m/z: calcd for $C_{20}H_{26}NO_2^+$ $[M+H]^+$: 312.1958. found: 312.1960.



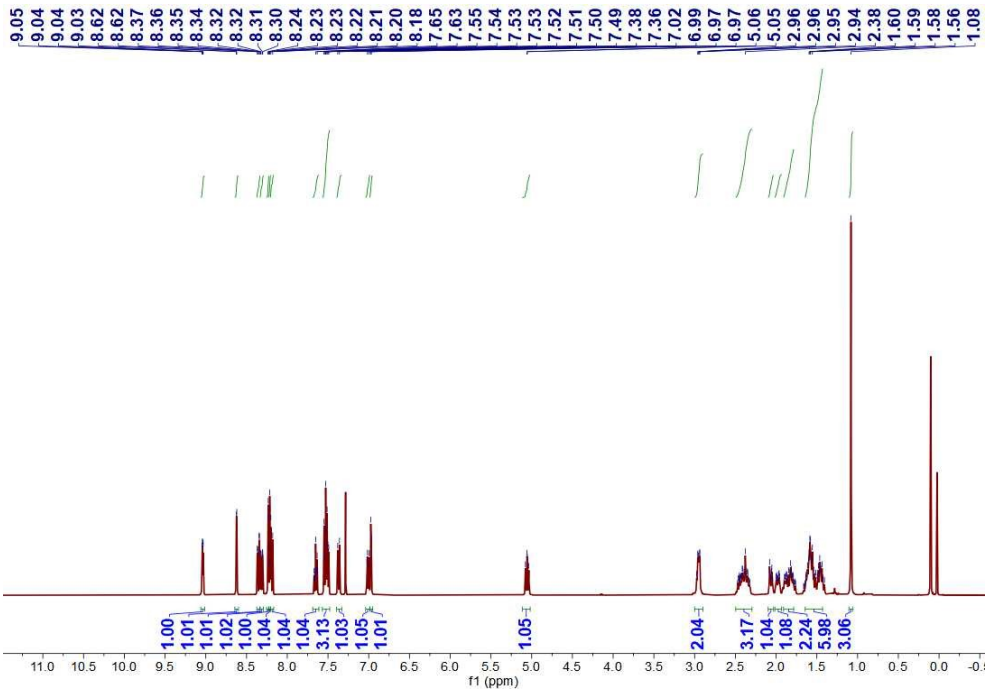


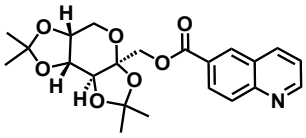
(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl quinoline-6-carboxylate (S3): White solid, 91 % yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.01 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.59 (d, *J* = 1.9 Hz, 1H), 8.31 (ddd, *J* = 10.8, 8.8, 1.9 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.48 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.20 (ddd, *J* = 9.9, 3.5, 2.1 Hz, 1H), 2.70 – 2.42 (m, 1H), 2.20 (ddd, *J* = 13.3, 9.4, 4.4 Hz, 1H), 1.92 – 1.72 (m, 2H), 1.46 (tdd, *J* = 11.9, 4.5, 2.2 Hz, 1H), 1.36 (ddd, *J* = 12.1, 9.4, 4.5 Hz, 1H), 1.18 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.99 (s, 3H), 0.95 (s, 3H), 0.94 (s, 3H).



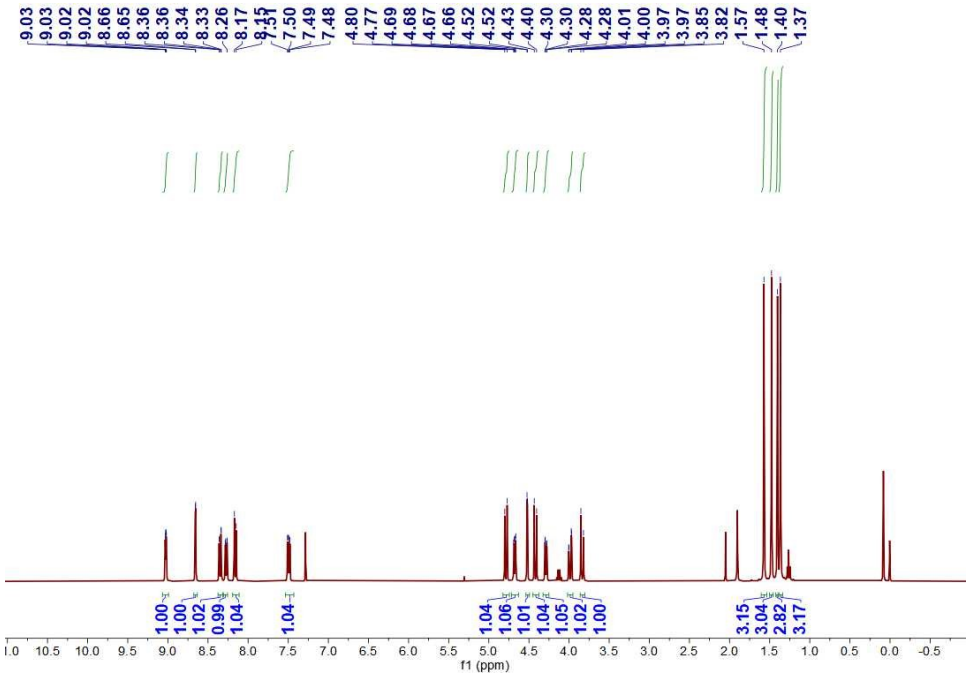


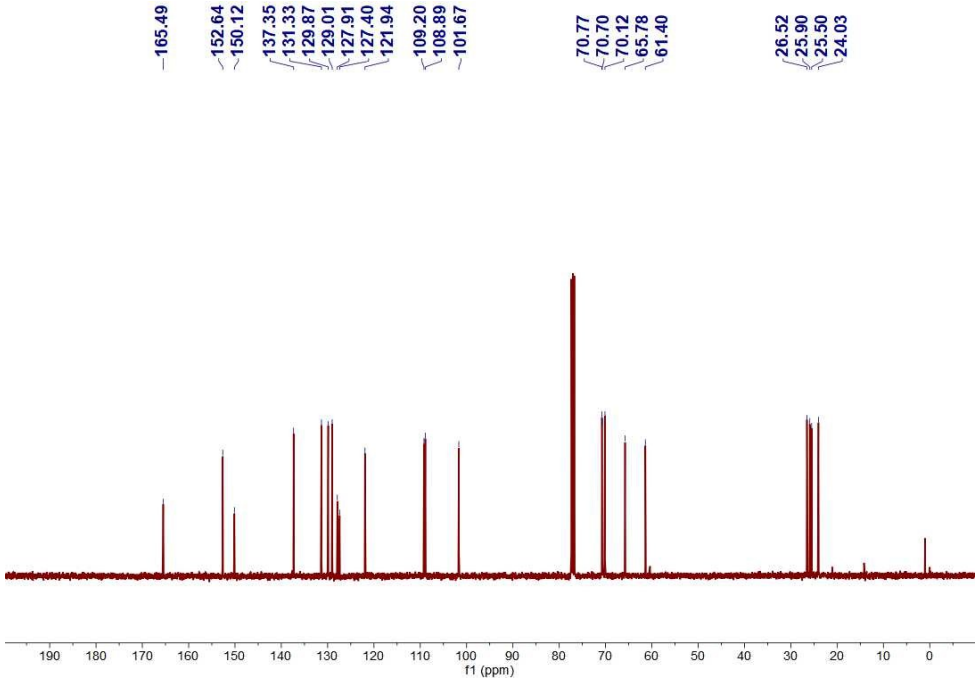
(8R,9S,13S,17S)-3-(benzoyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro - 6H – cyclopenta [a] phenanthrene – 17 - yl quinoline-6-carboxylate (S4): White solid, 95 % yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.04 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.62 (d, *J* = 1.8 Hz, 1H), 8.35 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.31 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.23 (s, 1H), 8.21 (d, *J* = 1.5 Hz, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.58 – 7.45 (m, 3H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.97 (d, *J* = 2.5 Hz, 1H), 5.06 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.02 – 2.88 (m, 2H), 2.53 – 2.28 (m, 3H), 2.12 – 2.03 (m, 1H), 1.98 (ddd, *J* = 9.8, 5.2, 2.7 Hz, 1H), 1.91 – 1.69 (m, 2H), 1.67 – 1.36 (m, 6H), 1.08 (s, 3H).

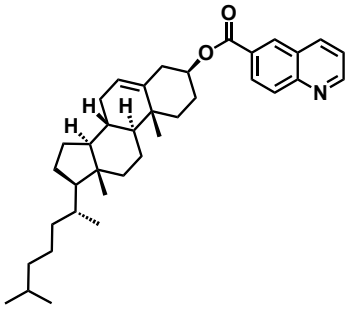




((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl quinoline-6-carboxylate (S5): White solid, 88 % yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.00 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.63 (d, *J* = 1.9 Hz, 1H), 8.32 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.25 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.76 (d, *J* = 11.7 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.50 (d, *J* = 2.6 Hz, 1H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.26 (dd, *J* = 7.9, 1.7 Hz, 1H), 3.96 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.81 (d, *J* = 13.0 Hz, 1H), 1.55 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 152.6, 150.1, 137.4, 131.3, 129.9, 129.0, 127.9, 127.4, 121.9, 109.2, 108.9, 101.7, 70.8, 70.7, 70.1, 65.8, 61.4, 26.5, 25.9, 25.5, 24.0. HRMS (ESI) m/z: calcd for $C_{22}H_{26}NO_7^+$ $[M+H]^+$: 416.1704. found: 416.1708.

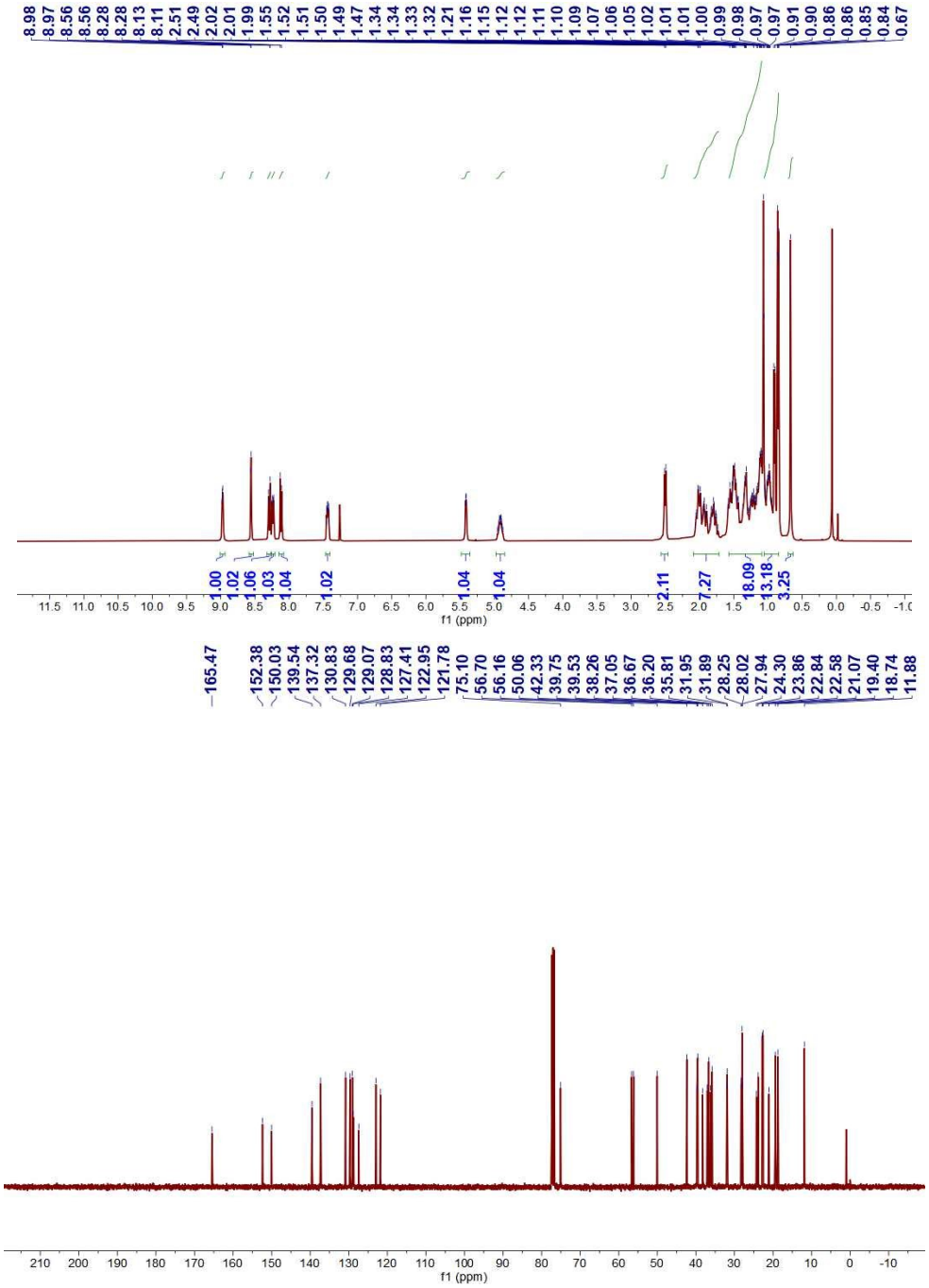




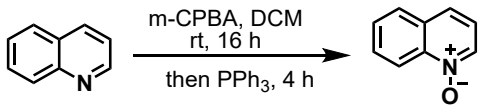


(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-

cyclopenta[a]phenanthren-3-yl quinoline-6-carboxylate (S6)：White solid, 93 % yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.97 (dd, *J* = 4.3, 2.0 Hz, 1H), 8.56 (d, *J* = 2.0 Hz, 1H), 8.29 (dd, *J* = 8.9, 1.8 Hz, 1H), 8.24 (dd, *J* = 8.4, 2.0 Hz, 1H), 8.12 (d, *J* = 8.9 Hz, 1H), 7.52 – 7.38 (m, 1H), 5.42 (d, *J* = 2.7 Hz, 1H), 4.97 – 4.83 (m, 1H), 2.50 (d, *J* = 8.2 Hz, 2H), 2.18 – 1.71 (m, 7H), 1.62 – 1.08 (m, 18H), 1.03 – 0.82 (m, 13H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 152.4, 150.0, 139.5, 137.3, 130.8, 129.7, 129.1, 128.8, 127.4, 122.9, 121.8, 75.1, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.3, 37.1, 36.7, 36.2, 35.8, 31.95, 31.9, 28.3, 28.0, 27.9, 24.3, 23.9, 22.8, 22.6, 21.1, 19.4, 18.7, 11.9. HRMS (ESI) m/z: calcd for $C_{37}H_{52}NO_2^+$ [M+H]$^+$: 542.3993. found: 542.3994.

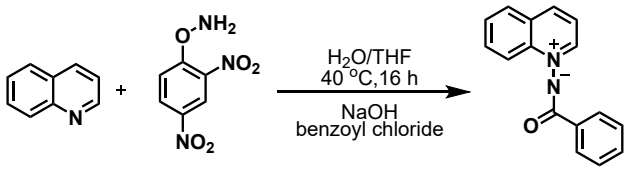


2.3 Synthesis of quinoline 1-oxide 1c. [2]



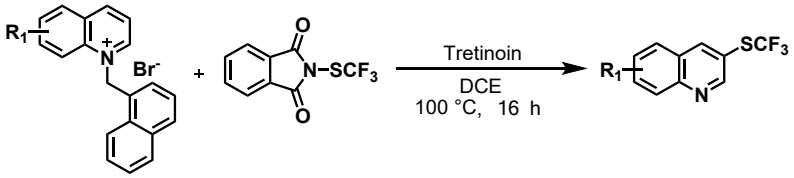
Quinoline (3 mmol), m-CPBA (1 equiv.) and DCM (0.2 M) were introduced in a flask (50 mL). The reaction was allowed to stir for 16 hours at room temperature. PPh_3 (0.5 equiv.) was then added to reduce any unreacted peracid and the mixture was stirred for an additional 4 h. After evaporation, the crude was purified by silica gel column chromatography affording the desired product **1c** in 90% yield.

2.4 Synthesis of benzoyl(quinolin-1-ium-1-yl)amide 1b.[3]



Quinoline (3 mmol) and O-(2,4-dinitrophenyl)hydroxylamine (3.3 mmol) were added to H_2O/THF (1:1 mixture, 2.5 mL). The reaction flask was sealed with a septum, and the resulting suspension was stirred at 40 °C for 16 h. During this period, the reaction mixture turned dark red. The reaction was poured into aqueous NaOH (2.5 N, 15 mL) at room temperature and stirred for 5 min, and then benzoyl chloride (4.6 mmol) was added in one portion. After 5 h, the reaction was diluted with H_2O (12.5 mL) and extracted with $CHCl_3$ (3 × 25 mL). The combined organic phases were washed with NaOH (2.5 N, 12.5 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure affording the **1b**.

2.5 General procedure for the Synthesis of 3a-3r and 5a-10a.



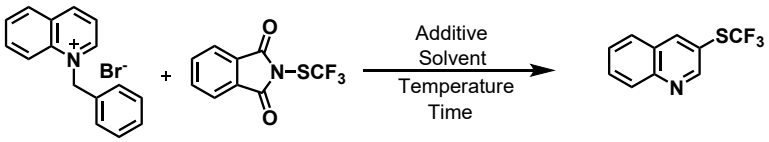
An oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar were charged with corresponding *N*-naphthylmethyl heteroarenium salt (0.10 mmol, 1.0 equiv.), *N*-(trifluoromethylthio)phthalimide (Phth-SCF_3) (0.20 mmol, 2.0 equiv.), Tretinoin (0.05 mmol, 0.5 equiv.) and 1,2-dichloroethane (2 mL) in the air. The resulting solution was stirred at 100 °C (heated by heating plate magnetic stirrer) for 16 h. After cooling to room temperature, the mixture was diluted with dichloromethane and filtered through a short pad of celite, the volatiles were removed under vacuum and the residue was purified by preparative thin layer chromatography (silica gel, petroleum ether/ethyl acetate 20:1 to 10:1) to give pure product.

2.6 General procedure for the Synthesis of 4a-4j and 5b-10b.

An oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar were charged with corresponding *N*-naphthylmethyl heteroarenium salt (0.10 mmol, 1.0 equiv.), *N*-(Phenylthio) phthalimide (Phth-SPh) or *N*-(Cyclohexylthio) phthalimide (Phth-Scy) (0.20 mmol, 2.0 equiv.) and 1,2-dichloroethane (2 mL) in the air. The resulting solution was stirred at 100 °C (heated by heating plate magnetic stirrer) for 8 h. After cooling to room temperature, the mixture was diluted with dichloromethane and filtered through a short pad of celite, the volatiles were removed under vacuum and the residue was purified by preparative thin layer chromatography (silica gel, petroleum ether/ethyl acetate 20:1 to 10:1) to give pure product.

2.7 Optimization Results of the Reaction Conditions for the synthesis of product 3a.

Table S1. Optimization of reaction condition[a, b]



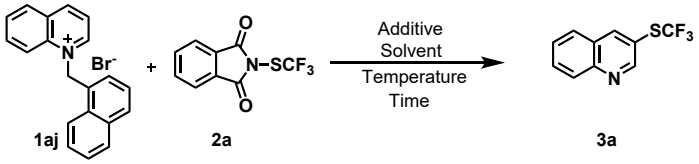
1a **2a** **3a**

Entry	Additive	Solvent	Temperature (°C)	Time (h)	**3a** (%)
1	-	DCE	100	16	40
2	BA	DCE	100	16	47
3	4-^{t}Bu-BA	DCE	100	16	35
4	4-Me_2N-BA	DCE	100	16	57
5	2-CH_3-BA	DCE	100	16	47
6	3,5-Ditert-BA	DCE	100	16	41
7	3,4,5-triethoxy-BA	DCE	100	16	48
8	4-NO_2-BA	DCE	100	16	39
9	4-F-BA	DCE	100	16	42
10	2-CN-BA	DCE	100	16	34
11	Boc-D-proline	DCE	100	16	58
12	Retinoic acid	DCE	100	16	63
13	Citric acid	DCE	100	16	40

14	Piperonylic acid	DCE	100	16	40
15	Abietic acid	DCE	100	16	33
16	Sulindac	DCE	100	16	47
17	Tungstic acid	DCE	100	16	58
18	Nicotinic acid	DCE	100	16	44
19	KO^{t}Bu	DCE	100	16	n.d.

[a] Reaction conditions:**1a** (0.1 mmol), **2a** (0.2 mmol), additive (0.05 mmol), solvent (2.0 mL), [b] yields were determined by ^{19}F-NMR analysis using benzotrifluoride as an internal standard. "–" stands for no addition. "BA" stands for "benzoic". "n.d." stands for no detection.

Table S2. Optimization of reaction condition[a, b]

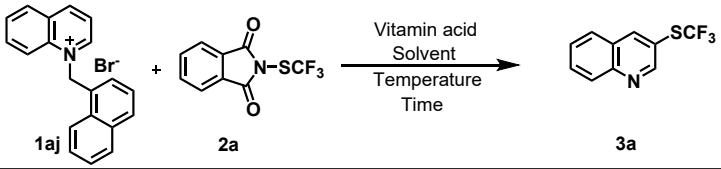


1aj 2a 3a

Entry	Additive	Solvent	Temperature (^{o}C)	Time (h)	**3a** (%)
1	-	DCE	100	16	53
2	BA	DCE	100	16	54
3	4-^{t}Bu-BA	DCE	100	16	30
4	4-Me_2N-BA	DCE	100	16	36
5	2-CH_3-BA	DCE	100	16	40
6	3,5-Ditert-BA	DCE	100	16	45
7	3,4,5-triethoxy-BA	DCE	100	16	45
8	4-NO_2-BA	DCE	100	16	40
9	4-F-BA	DCE	100	16	43
10	2-CN-BA	DCE	100	16	35
11	Boc-D-proline	DCE	100	16	68
12	Retinoic acid	DCE	100	16	75
13	Citric acid	DCE	100	16	50
14	Piperonylic acid	DCE	100	16	50
15	Abietic acid	DCE	100	16	35
16	Sulindac	DCE	100	16	50
17	Tungstic acid	DCE	100	16	56
18	Nicotinic acid	DCE	100	16	40
19	KO^{t}Bu	DCE	100	16	n.d.

[a] Reaction conditions:**1aj** (0.1 mmol), **2a** (0.2 mmol), additive (0.05 mmol), solvent (2.0 mL), [b] yields were determined by ^{19}F-NMR analysis using benzotrifluoride as an internal standard. "–" stands for no addition. "BA" stands for "benzoic". "n.d." stands for no detection.

Table S3. Optimization of reaction condition[a, b]



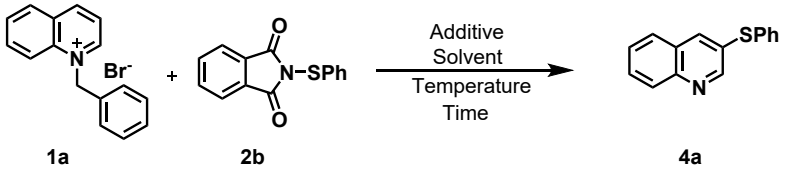
1aj 2a 3a

Entry	Additive	Solvent	Temperature (°C)	Time (h)	**3a** (%)
1	Retinoic acid	DCE	80	16	50
2	Retinoic acid	DCE	60	16	30
3	Retinoic acid	DCE	120	16	70
4	Retinoic acid	DCE	100	14	72
5	Retinoic acid	DCE	100	12	55
6	Retinoic acid	DCE	100	10	45
7	Retinoic acid	DCE	100	14	45
8	Retinoic acid	DCE	100	18	74
9	Retinoic acid	DCE	100	20	75
10	Retinoic acid	DCE	100	22	73
11	Retinoic acid	DBE	100	16	trace
12	Retinoic acid	DCE	100	16	55[c]
13	Retinoic acid	DCE	100	16	50[d]
14	Retinoic acid [e]	DCE	100	16	51
15	Retinoic acid [f]	DCE	100	16	50
16	Retinoic acid [g]	DCE	100	16	70
17	Retinoic acid [h]	DCE	100	16	72

[a] Reaction conditions:**1aj** (0.1 mmol), **2a** (0.2 mmol), retinoic acid (0.05 mmol), solvent (2.0 mL), [b] yields were determined by ^{19}F-NMR analysis using benzotrifluoride as an internal standard. [c] Reaction conditions:**1aj** (0.1 mmol), **2a** (0.2 mmol), retinoic acid (0.05 mmol), DCE (1.0 mL). [d] Reaction conditions:**1aj** (0.1 mmol), **2a** (0.2 mmol), retinoic acid (0.05 mmol), DCE (3.0 mL). [e] Retinoic acid (0.02 mmol). [f] Retinoic acid (0.04 mmol). [g] Retinoic acid (0.08 mmol). [h] Retinoic acid (0.1 mmol). "BA" stands for "benzoic". Reactions cannot proceed using any of these solvents, including: DMA, Acetonitrile, Acetone, Toluene, CH_3OH, EtOH, CH_3Cl, MTBA, Diglyme, 1,4-dioxane, THF.

2.8 Optimization Results of the Reaction Conditions for the synthesis of product 4a.

Table S4. Optimization of reaction condition[a, b]



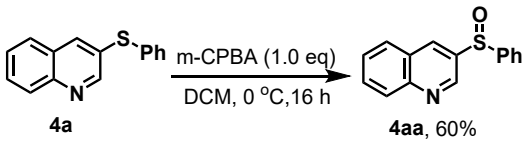
1a 2b 4a

Entry	Additive	Solvent	Temperature (°C)	Time (h)	**4a** (%)
1	-	DCE	100	16	94
2	BA	DCE	100	16	88
3	-	DCE	100	14	93
4	-	DCE	100	12	96
5	-	DCE	100	10	95
6	-	DCE	100	8	95
7	-	DCE	100	6	80
8	-	DCE	100	4	60
9	-	DCE	100	16	42
10	-	DCE	80	8	82
11	-	DMA	100	8	n.d.

[a] Reaction conditions:**1a** (0.1 mmol), **2b** (0.2 mmol), additive (0.05 mmol), solvent (2.0 mL), [b] Isolated yields. "–" stands for no addition, "BA" stands for "benzoic". "n.d." stands for no detection.

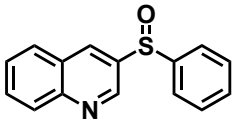
2.9 Useful Transformation and Scale-up Reaction

2.9.1 Synthesis of 4aa and 4ab.

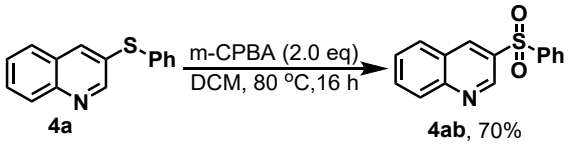


4a **4aa**, 60%

3-(Phenylthio)quinoline **4a** (0.5 mmol, 118.5 mg), m-chloroperoxybenzoic acid (m-CPBA) (1.0 eq, 86.28 mg), and dichloromethane (2.5 mL) were introduced in a Schlenk tube, successively. The resulting mixture was then stirred at 0 °C for 16 h. Then the solvent was removed, the mixture was diluted with dichloromethane and filtered through a short pad of celite, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl) to give pure product (Yield: 75.9 mg, 60%).

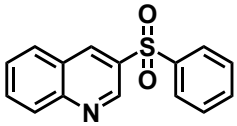


3-(phenylsulfinyl)quinoline (4aa): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 8.62 (d, J = 2.1 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.94 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.81 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.64 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.56 – 7.44 (m, 3H).



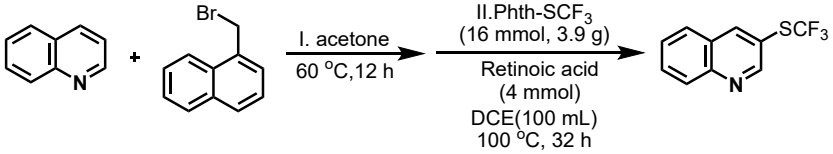
4a **4ab**, 70%

3-(Phenylthio)quinoline **4a** (0.5 mmol, 118.5 mg), m-chloroperoxybenzoic acid (m-CPBA) (2.0 eq, 172.6 mg), and dichloromethane (2.5 mL) were introduced in a Schlenk tube, successively. The resulting mixture was then stirred at 80 °C for 16 h. Then the solvent was removed, the mixture was diluted with dichloromethane and filtered through a short pad of celite, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl) to give pure product (Yield: 94.2 mg, 70%).



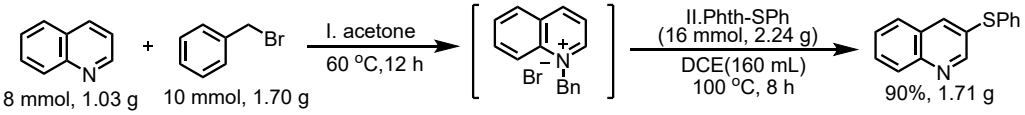
3-(phenylsulfonyl)quinoline (4ab): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (d, *J* = 2.3 Hz, 1H), 8.82 (d, *J* = 2.3 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.09 – 8.01 (m, 2H), 7.97 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.88 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.68 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.54 (t, *J* = 7.4 Hz, 2H).

2.9.2 One-pot gram-scale synthesis of compound 3a



Quinoline (8 mmol, 1.03 g), 1-(bromomethyl) naphthalene (10 mmol, 1.76 g), and toluene (30 mL) were introduced in a Schlenk tube, successively. The resulting mixture was then stirred at 60 °C for 12 h. Then the solvent was removed, and to the reaction was added Phth-SCF_3 (16 mmol, 3.9 g), DCE (160 mL). The reaction was performed at 100 °C for 32 h. After cooling to room temperature, the mixture was diluted with dichloromethane and filtered through a short pad of celite, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl 10:1) to give pure product (Yield: 1.25 g, 68%).

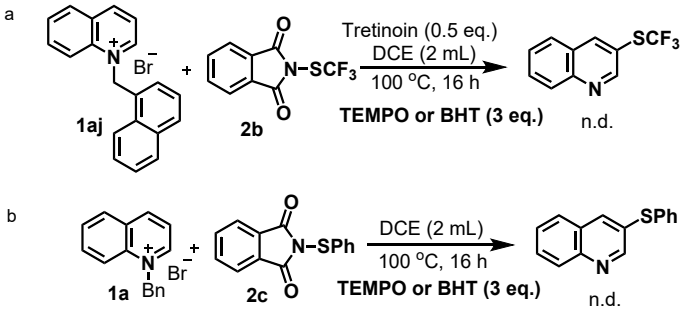
2.9.3 One-pot gram-scale synthesis of compound 4a



Quinoline (8 mmol, 1.03 g), benzyl bromide (10 mmol, 1.70 g), and acetone (30 mL) were introduced in a Schlenk tube, successively. The resulting mixture was then stirred at 60 °C for 12 h. Then the solvent was removed, and to the reaction were added Phth-SPh (16 mmol, 2.24 g), DCE (160 mL). The reaction was performed at 100 °C for 8 h. After cooling to room temperature, the mixture was diluted with dichloromethane and filtered through a short pad of celite, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl 10:1) to give pure product (Yield: 1.71 g, 90%).

2.10. Mechanism studies

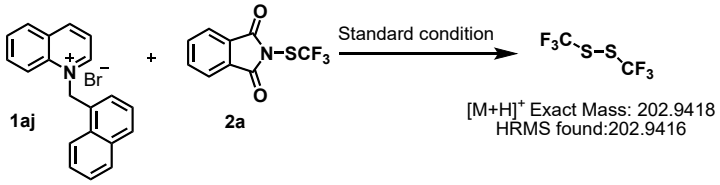
2.10.1 Radical trapping experiment.



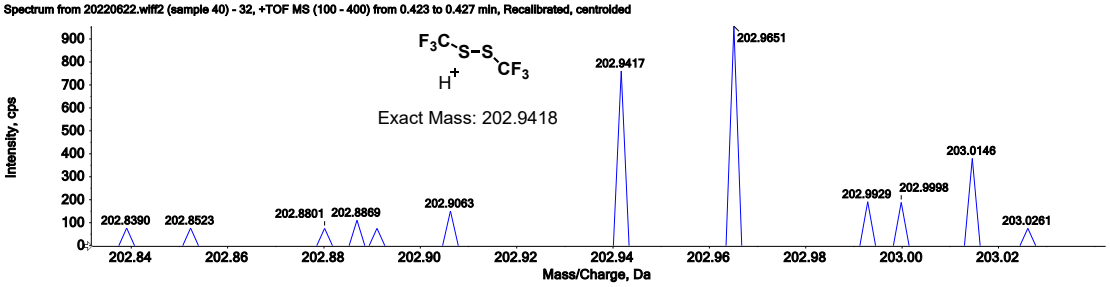
a: The 25 mL Schlenk tube equipped with magnetic stirring bar was charged with **1aj** (0.1 mmol, 34.9 mg), **2b** (0.2 mmol, 49.4 mg), Tretinoin (0.05 mmol), 1,2-Dichloroethane (DCE, 2 mL). Then, 3 times the equivalent of TEMPO (0.3 mmol) or BHT (0.3 mmol) were added to Schlenk tube respectively, each tube was heated at 100℃ for 16 h.

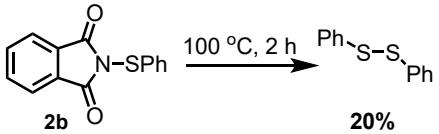
b: The 25 mL Schlenk tube equipped with magnetic stirring bar was charged with **1a** (0.1mmol, 30.0 mg), **2c** (0.2 mmol, 50.1 mg), Tretinoin (0.05 mmol), 1,2-Dichloroethane (DCE, 2 mL). Then, 3 times the equivalent of TEMPO (0.3 mmol) or BHT (0.3 mmol) were added to Schlenk tube respectively, each tube was heated at 100℃ for 16 h.

2.10.2 Proof of radical pathway.

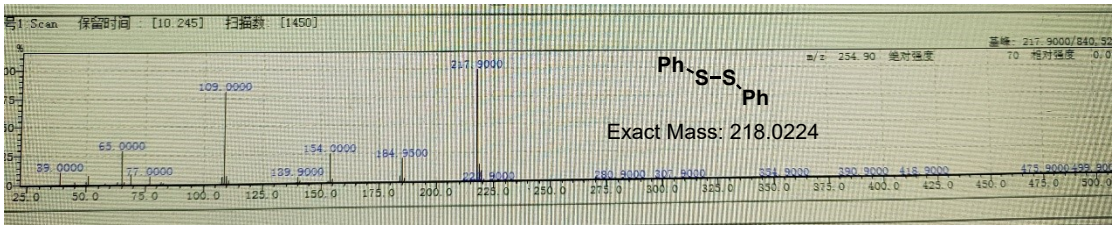


1aj (0.1 mmol), **2a** (0.2 mmol), Retinoic acid (0.05 mmol) were added into 2 mL DCE. The resulting solution was stirred at 100 °C under air for 16 h. Then, the reaction mixture was detected by ESI-HRMS.



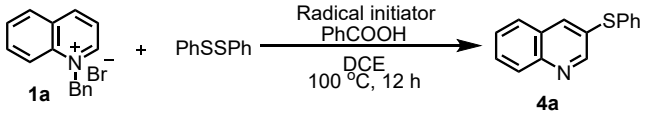


2b (0.2 mmol) was added into 2 mL DCE. The resulting solution was stirred at 100 °C under air for 2 h. Then, the reaction mixture was detected by GC-MS.



2.10.3 Optimization Results of the synthesis of product 4a by diaryldisulfide.

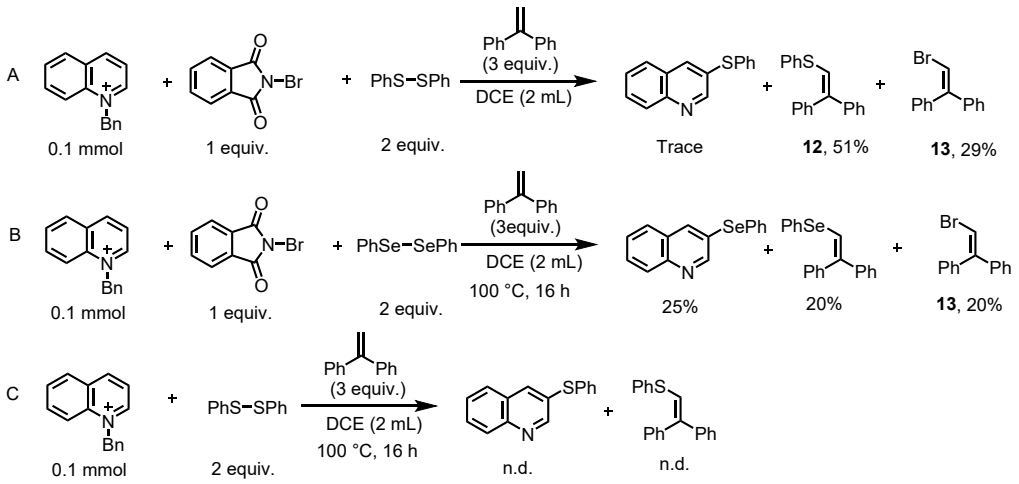
Table S5. Optimization of reaction condition[a,b]



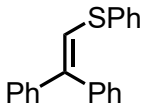
Entry	Radical initiator	**4a** (%)
1	NBS (1 eq)	40
2	NCS (1 eq)	55
3	NIS (1 eq)	50
4	Phth-Br (1 eq)	80
5	Phth-Cl (1 eq)	60
6	Phth-I (1 eq)	55
7	$Na_2S_2O_4$ (1 eq)	10
8	TBHP (1 eq)	12
9	$PhI(OAc)_2$ (1 eq)	15
10	-	n.d.
11	Phth-Br (0.5 eq)	48
12	Phth-Br (0.2 eq)	35

[a] Reaction conditions:**1a** (0.1 mmol), diphenyl disulfide (0.2 mmol), BA (0.05 mmol), DBE (2.0 mL), Radical initiator (0.1 mmol). [b] isolated yields. "–" stands for no addition. "n.d." stands for no detection.

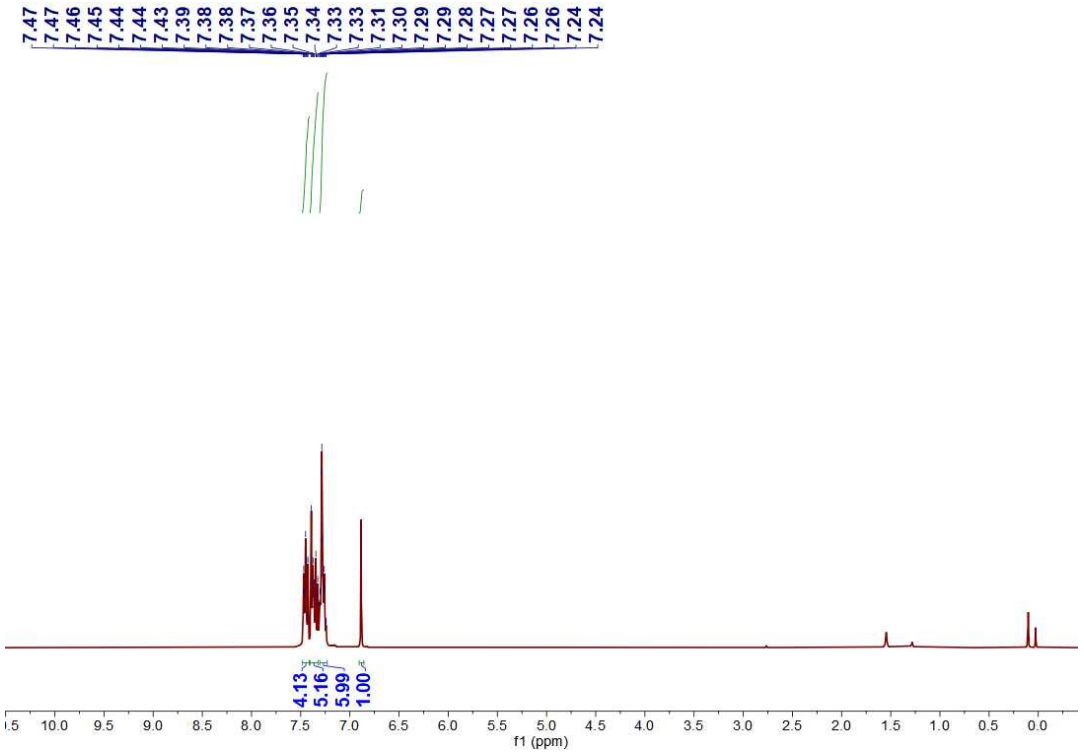
2.10.4 Mechanism research for synthesis of product 4a by diaryldisulfide.

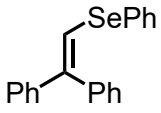


When 3 equiv. of radical scavenger ethene-1,1-diyldibenzene were added to a reaction mixture, the yield of desired product **4a** decreased sharply from 80% to trace, along with 51% product (2,2-diphenylvinyl)(phenyl)sulfane and 29% (2-bromoethene-1,1-diyl)dibenzene which originated from the addition of a thiobenzene radical and bromine radical to the scavenger. The corresponding (2,2-diphenylvinyl)(phenyl)selane was also isolated in 20% yield in the phenylselenylation reaction, while the production of 3-(phenylselanyl)quinoline was decreased from 95% to 20%. Control Experiment C shows that without the addition of the radical initiator Phth-Br, the thiobenzene radical cannot be generated and the desired reaction does not occur. The experimental results show that both thiobenzene radicals and selenobenzene radicals are induced by Phth-Br.

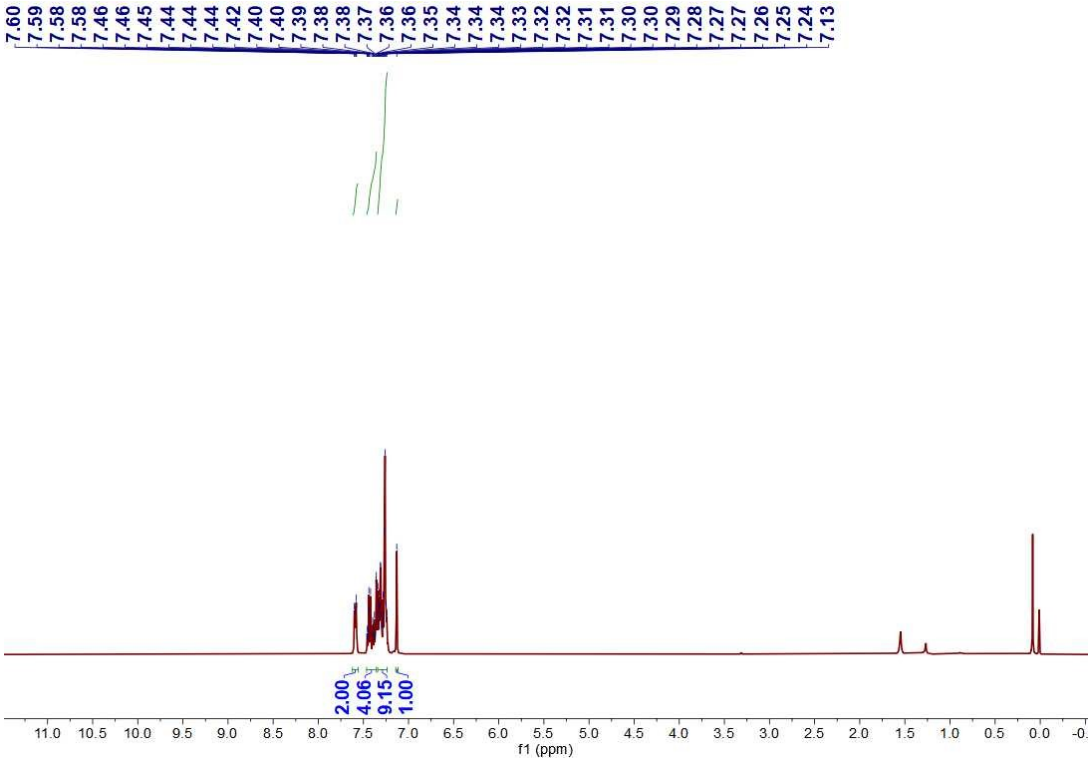


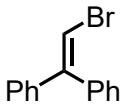
(2,2-diphenylvinyl)(phenyl)sulfane (12)： ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.41 (m, 4H), 7.41 – 7.32 (m, 5H), 7.28 (m, 6H), 6.89 (s, 1H).



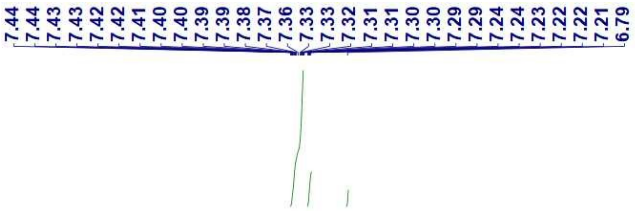


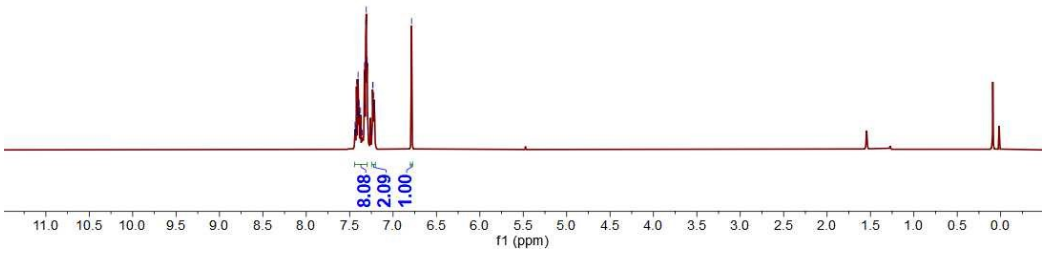
(2,2-diphenylvinyl)(phenyl)sulfane (13): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.47 – 7.37 (m, 4H), 7.37 – 7.23 (m, 9H), 7.13 (s, 1H).



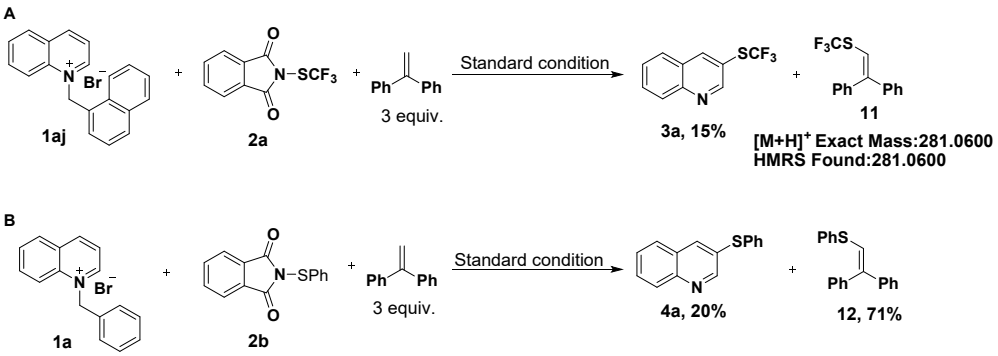


(2-bromoethene-1,1-diyl)dibenzene (13)： ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.28 (m, 8H), 7.23 (m, 2H), 6.79 (s, 1H).



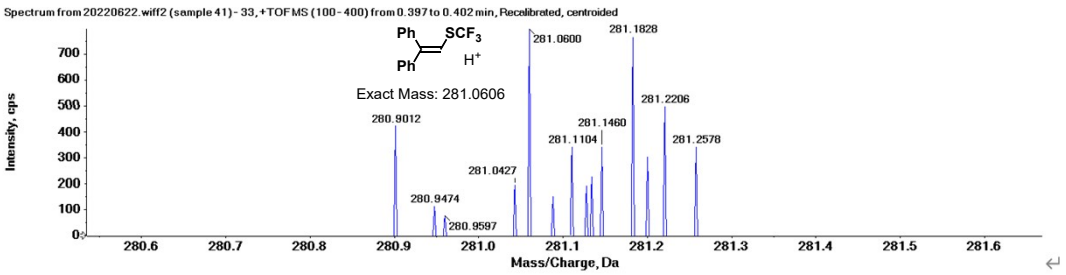


2.10.5 Radical Trapping.

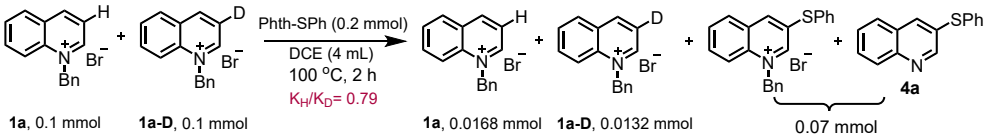


A: **1aj** (0.1 mmol), **2a** (0.2 mmol), Tretinoin (0.05 mmol) and radical scavenger ethene-1,1-diyldibenzene (3.0 equiv) were added into 2 mL DCE. The resulting solution was stirred at 100°C under air for 16 h. Then, the reaction mixture was detected by ESI-HRMS.

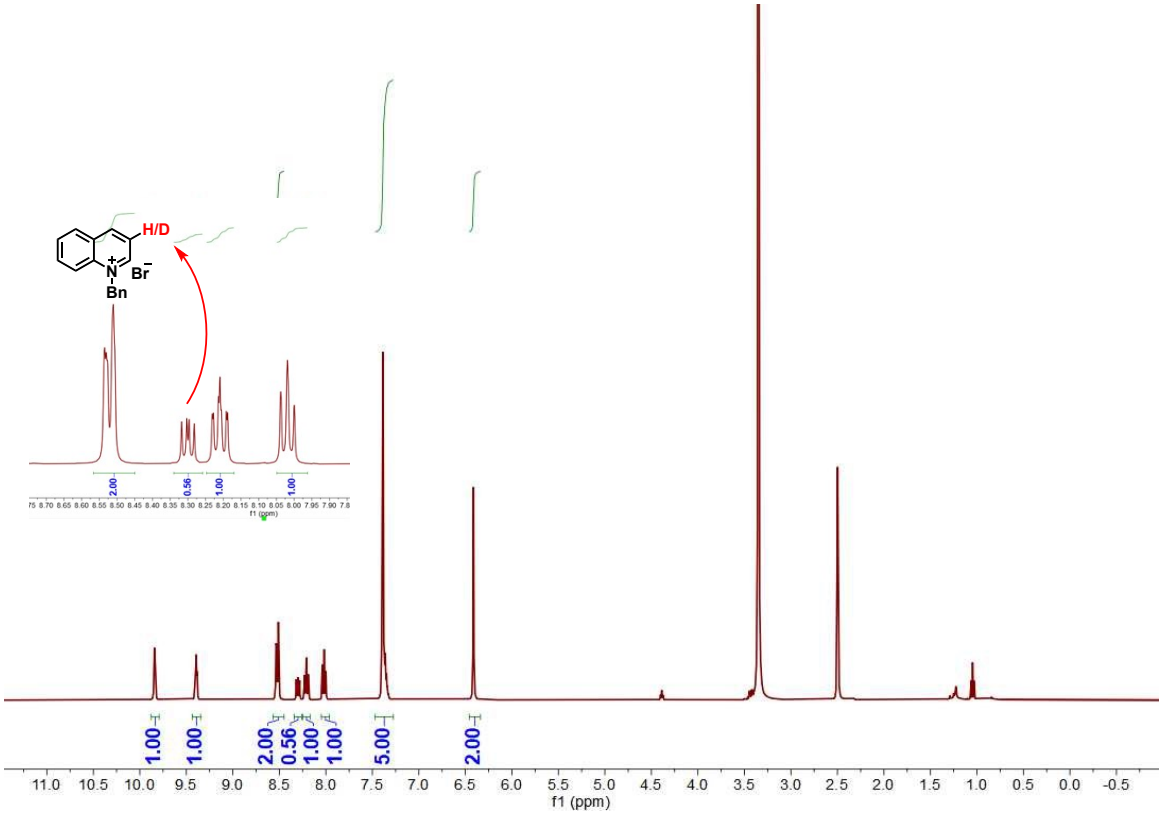
B: **1a** (0.1 mmol), **2b** (0.2 mmol) and radical scavenger ethene-1,1-diyldibenzene (3.0 equiv) were added into 2 mL DCE. The resulting solution was stirred at 100°C under air for 16 h.



2.10.6 H/D kinetic isotope effects study.



An oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar was charged with **1a** (0.1 mmol), **1a-D** (0.1 mol), **2b** (0.2 mmol), DCE (4 mL). The reaction mixture was stirred at 100℃ for 2 h under air. The reaction mixture was filtered and the solvent was evaporated in vacuum. The crude product was purified by flash column chromatography on silica gel using DCM: Methanol=10:1 as eluent to afford the desired products. The KIE value was determined to be kH/kD: [**1a-D**]/[**1a**] = 0.79 based on ^{1}H NMR analysis.



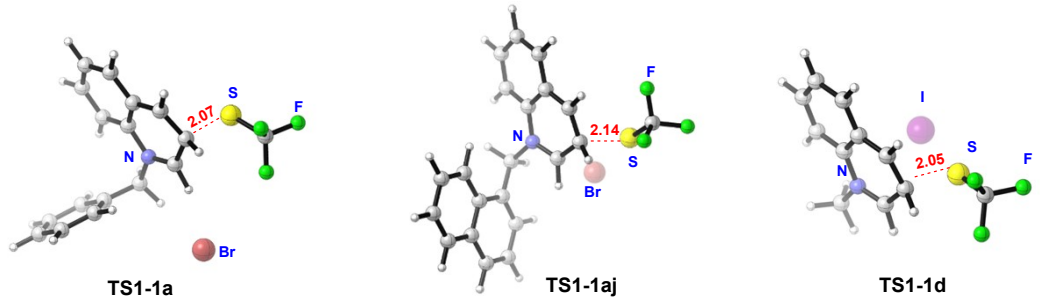
2.11. Computational studies

All calculations were performed using Gaussian 09 program package,[4] employing the B3LYP functional [5] with the 6-311g (d, p) basis set. Geometries were optimized in 1,2-dichloroethane

solvent and characterized by frequency analysis at 373 K. The self-consistent reaction field (SCRF) method based on the universal solvation model SMD[6] was adopted to evaluate the effect of solvent. Dispersion corrections were computed with Grimme's D3 method in structural optimization.[7, 8] The intrinsic reaction coordinate (IRC) path was traced to check the energy profiles connecting each transition state to two associated minima of the proposed mechanism.[9] The global nucleophilicity index (N) of N-benzyl quinolinium was obtained based on the conceptual density functional theory[10], using equation (1):

$$N = E_{HOMO(Nu)}(eV) - E_{HOMO(TCE)}(eV) \quad (1)$$

where $E_{HOMO(Nu)}$ is the HOMO energy of the nucleophile and $E_{HOMO(TCE)}$ corresponds to the HOMO energy of the tetracyanoethylene (TCE) taken as reference. The local nucleophilicity index N_k was defined as $N_k = NP_k^-$, where the atom k nucleophilic Parr functions (P_k^-) was from the Mulliken atomic spin density (ASD) analysis at the radical cation of the corresponding reagent.



TS1-1a TS1-1aj TS1-1d

Figure 1. Optimized geometries of transition states.

Cartesian coordinates and the corresponding energies of all stationary points in this work.

***N*-benzyl quinolinium (1a)**

Zero-point correction = 0.25846 a.u.
Thermal correction to Gibbs Free Energy = 0.19469 a.u.
Sum of electronic and zero-point Energies = -3247.06207 a.u.
Sum of electronic and thermal Free Energies = -3247.12584 a.u.

	X	Y	Z
C	1.10808900	-0.28528900	1.14230200
C	0.04141000	1.38047300	-0.17856500
C	0.76111600	2.38714600	0.52193300
C	1.65051600	2.00357800	1.55812300
C	1.82140200	0.68181800	1.86277800
H	-1.41935400	0.99407100	-1.73458400
H	1.18502700	-1.33392500	1.37018900
C	-0.85286300	1.74251200	-1.20239500
C	0.56734100	3.74124000	0.16553700
H	2.18913500	2.77435900	2.09650900
H	2.50025900	0.35149800	2.63561600
C	-0.30595700	4.08155800	-0.84049900
C	-1.01578100	3.07475900	-1.52177500
H	1.12352800	4.49968100	0.70341000
H	-0.45152300	5.12012300	-1.11053500
H	-1.70567500	3.34658000	-2.31137400
N	0.23967000	0.05555500	0.18639500
C	-4.60999800	-1.49830800	0.57038800

C	-3.67840100	-1.11842500	1.53506500
C	-2.33941400	-0.95085100	1.19008900
C	-1.91990500	-1.15617400	-0.12621500
C	-2.85842200	-1.53005800	-1.09063400
C	-4.19622400	-1.70523900	-0.74403900
H	-5.65156900	-1.62807400	0.84067300
H	-3.99279500	-0.95315400	2.55923700
H	-1.62633300	-0.65482000	1.95082300
H	-2.53986800	-1.68150100	-2.11646000
H	-4.91462500	-1.99567900	-1.50199100
C	-0.46654100	-1.03085100	-0.52489100
H	0.09205400	-1.94081600	-0.30744300
H	-0.36693400	-0.85575200	-1.59465100
Br	3.19036500	-1.86682300	-0.47678300

_N_-methyl quinolinium (1d)

Zero-point correction = 0.17769 a.u.
Thermal correction to Gibbs Free Energy = 0.12352 a.u.
Sum of electronic and zero-point Energies = -7361.40329 a.u.
Sum of electronic and thermal Free Energies = -7361.45746 a.u.

	X	Y	Z
C	-0.14868400	1.65769100	1.11843000
C	-1.70455900	-0.03714100	0.55653300
C	-2.09682600	0.71461600	-0.58769600
C	-1.48270600	1.96176400	-0.83503300
C	-0.51386200	2.42968100	0.01586500
H	-2.01043100	-1.86886000	1.67655600
H	0.61823000	1.98119400	1.80553700
C	-2.30204400	-1.28506300	0.81678300
C	-3.09028700	0.18566400	-1.44644800
H	-1.78141000	2.53232900	-1.70612900
H	-0.00969400	3.37121400	-0.14793400
C	-3.66378300	-1.03256300	-1.18031800
C	-3.26440300	-1.76579300	-0.04388700
H	-3.37944600	0.76362100	-2.31567800
H	-4.42102000	-1.43635500	-1.84061100
H	-3.71953000	-2.72783700	0.15747400
N	-0.72837200	0.48797900	1.38704700
C	-0.26733300	-0.28468100	2.55511000
H	0.49337500	0.29315300	3.07072900
H	0.16394600	-1.22472100	2.21399800
H	-1.10785900	-0.47015600	3.22254900
I	2.48036500	-0.37536800	-0.40871400

_N_-naphthyl quinolinium (1aj)

Zero-point correction = 0.30575 a.u.
Thermal correction to Gibbs Free Energy = 0.23773 a.u.
Sum of electronic and zero-point Energies = -3400.71290 a.u.
Sum of electronic and thermal Free Energies = -3400.78091 a.u.

	X	Y	Z
C	0.65720200	-0.48028500	1.03785600
C	1.82824300	1.09634500	-0.29694800
C	2.68051800	1.38051300	0.80846900
C	2.47449300	0.70090700	2.03530000
C	1.48310700	-0.23309400	2.14127400
H	1.45234900	1.52492000	-2.39405000
H	-0.16997800	-1.16573900	1.09553600
C	2.05786400	1.74115000	-1.52781200
C	3.72132200	2.32411000	0.65289900
H	3.12192000	0.92814000	2.87384100
H	1.31092500	-0.79200000	3.04987200
C	3.92200500	2.95533000	-0.55140000
C	3.08746200	2.65240900	-1.64278500
H	4.35743900	2.53008200	1.50544100
H	4.72189600	3.67611900	-0.66669400
H	3.25397400	3.13863600	-2.59637600
N	0.78737000	0.19536700	-0.10557900
C	-2.01630600	-1.74656000	-0.80140000
C	-1.53050300	-0.45849400	-0.76825700
C	-2.36304100	0.60922800	-0.30789300
C	-3.69500500	0.30494400	0.11923400
C	-4.15591900	-1.03674900	0.06169900
C	-3.33647100	-2.03922800	-0.39087500
H	-0.92404200	2.21629300	-0.56351900
H	-1.35860300	-2.54770400	-1.11751900
C	-1.92539900	1.95847700	-0.24368400
C	-4.52841100	1.35247300	0.58906500
H	-5.16810700	-1.25257700	0.38601800
H	-3.69052900	-3.06269300	-0.42839600
C	-4.07205900	2.64723200	0.64058300
C	-2.75867100	2.95062000	0.21762900
H	-5.53600900	1.10873800	0.90801700
H	-4.71650400	3.43975800	1.00298700
H	-2.40636600	3.97490900	0.25774700
C	-0.12303300	-0.18945700	-1.22771500
H	-0.11619200	0.61528800	-1.95432700
H	0.31413000	-1.08704100	-1.66859000
Br	1.47422000	-3.24434100	-0.06349600

SCF_3 radical

Zero-point correction = 0.01385 a.u.
Thermal correction to Gibbs Free Energy = -0.02427 a.u.
Sum of electronic and zero-point Energies = -735.88749 a.u.
Sum of electronic and thermal Free Energies = -735.92561 a.u.

	X	Y	Z
S	-1.48876900	-0.04078700	0.00131800
C	0.32730500	-0.00386100	0.00018700
F	0.85501900	-0.58106800	1.09019500
F	0.85309100	-0.62522000	-1.06665700
F	0.72038700	1.28137300	-0.02600600

TS1-1d

Zero-point correction = 0.19164 a.u.
Thermal correction to Gibbs Free Energy = 0.12515 a.u.
Sum of electronic and zero-point Energies = -8097.28885 a.u.
Sum of electronic and thermal Free Energies = -8097.35534 a.u.

	X	Y	Z
C	-0.32613900	-0.67760300	1.75051200
C	1.59191800	-1.42437600	0.56416600
C	0.75968600	-2.09180800	-0.38691300
C	-0.62763700	-2.04632000	-0.25623000
C	-1.23619800	-1.19239000	0.73553500
H	3.61037600	-0.91919500	1.13397200
H	-0.72239000	-0.17708600	2.62250700
C	2.97831200	-1.44110600	0.43155900
C	1.39006000	-2.79662200	-1.44718600
H	-1.26163700	-2.59248700	-0.94186300
H	-2.15886400	-1.55685500	1.18060000
C	2.76048500	-2.80734400	-1.56609500
C	3.55542500	-2.12396200	-0.63010400
H	0.76208000	-3.30757300	-2.16659700
H	3.23065500	-3.33605700	-2.38584000
H	4.63292300	-2.12370800	-0.73420500
N	0.97131200	-0.77555200	1.65084900
C	1.81623700	-0.17736400	2.70527000
H	2.45790900	-0.94880200	3.12713200
H	2.40913900	0.61976900	2.26038600
S	-2.00728900	0.47439600	-0.18458500
C	-3.72226400	-0.11944900	-0.17970100
F	-4.48846700	0.77293100	-0.82944400
F	-3.87244000	-1.31251000	-0.79577800
F	-4.23656800	-0.26887700	1.06104200
H	1.16698100	0.23418700	3.47178800
I	1.33826900	2.27570700	-0.40410800

TS1-1a

Zero-point correction = 0.27239 a.u.
Thermal correction to Gibbs Free Energy = 0.19599 a.u.

Sum of electronic and zero-point Energies = -3982.94966 a.u.
Sum of electronic and thermal Free Energies = -3983.02606 a.u.

	X	Y	Z
C	0.53155700	-0.01855600	0.08753200
C	-0.96531800	1.77916900	-0.36349800
C	-0.19432600	2.65186500	0.46572700
C	0.96636700	2.17945900	1.08330500
C	1.47732700	0.87884700	0.73785400
H	-2.67248800	1.60444400	-1.66773600
H	0.73175400	-1.09415400	0.01742300
C	-2.09083600	2.25267900	-1.03188000
C	-0.63862000	3.99137400	0.62593900
H	1.53296300	2.81354400	1.75212500
H	2.08014200	0.38446800	1.49350500
C	-1.75849800	4.44388900	-0.03422800
C	-2.47810000	3.57750300	-0.87314600
H	-0.06163400	4.64946700	1.26413200
H	-2.08281400	5.47003000	0.08583500
H	-3.35321400	3.93697600	-1.39956600
N	-0.58013400	0.42111100	-0.44180500
C	-5.15736700	-1.19634300	1.06682800
C	-3.94479000	-1.14626900	1.75338200
C	-2.75663000	-0.93020900	1.06139600
C	-2.77164100	-0.75377800	-0.32420800
C	-3.98781000	-0.80309400	-1.00769700
C	-5.17602600	-1.02884700	-0.31619200
H	-6.08143300	-1.36644100	1.60718500
H	-3.92292900	-1.28135500	2.82859700
H	-1.81859400	-0.90492600	1.60340500
H	-4.00338300	-0.66496700	-2.08338900
H	-6.11465900	-1.06748700	-0.85685600
C	-1.48737800	-0.56935100	-1.09412600
H	-0.92730600	-1.50879000	-1.12969400
H	-1.67188700	-0.22997300	-2.11193500
Br	0.52875600	-3.48589000	-0.16727000
S	2.92490200	1.12505900	-0.72338100
C	4.23608300	0.15970500	0.07571700
F	4.54826500	0.62920100	1.30226800
F	3.91787600	-1.13560700	0.22754700
F	5.34469800	0.22955600	-0.68071300

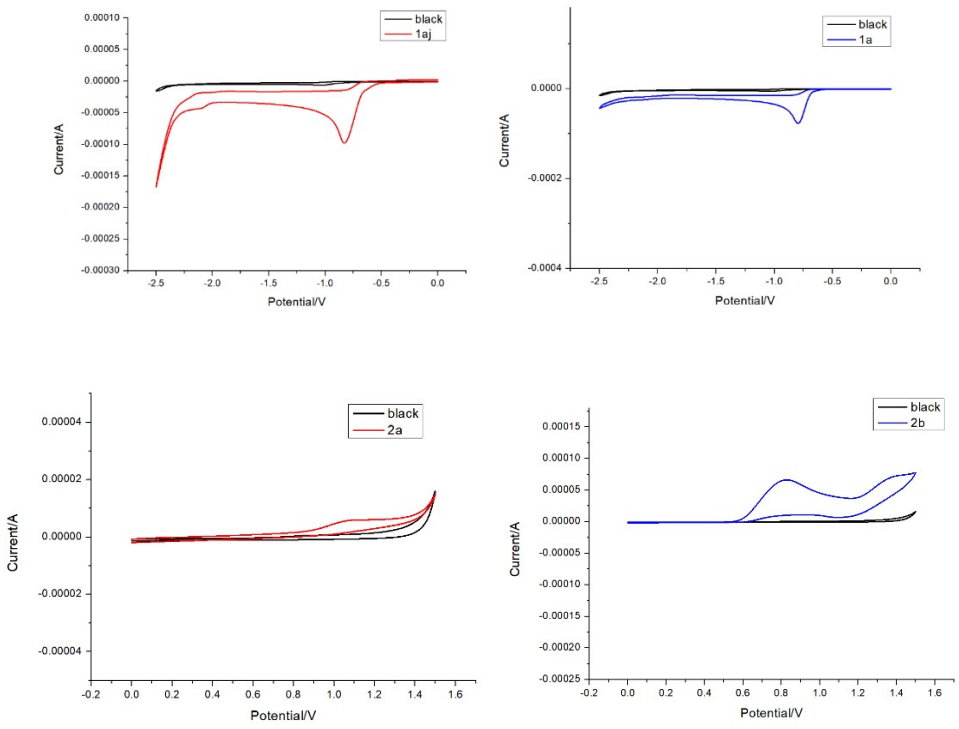
TS1-1aj

Zero-point correction = 0.31940 a.u.
Thermal correction to Gibbs Free Energy = 0.23958 a.u.
Sum of electronic and zero-point Energies = -4136.60197 a.u.
Sum of electronic and thermal Free Energies = -4136.68179 a.u.

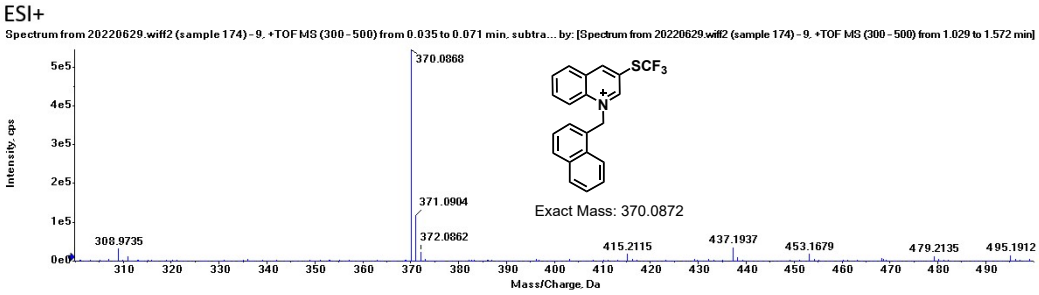
	X	Y	Z
C	-0.11485900	-0.27895100	-0.14029300
C	-0.24747000	1.75229800	1.09164100
C	-1.24202000	2.24686800	0.19314800
C	-1.63623000	1.46675500	-0.89856100
C	-1.23808100	0.09710200	-0.99002400
H	0.82453400	2.12487200	2.93378800
H	0.44530500	-1.17371900	-0.35215200
C	0.10991800	2.49893900	2.21653700
C	-1.79523100	3.53077000	0.43281200
H	-2.30903500	1.87693000	-1.63901500
H	-1.17261900	-0.33472200	-1.98166100
C	-1.42135300	4.26191600	1.53692200
C	-0.47923100	3.73634500	2.43652800
H	-2.53596200	3.90654500	-0.26252400
H	-1.86015800	5.23452300	1.72153900
H	-0.20255400	4.30035400	3.31857200
N	0.37490800	0.53538800	0.76886800
C	2.78466200	-1.98489800	0.81938600
C	2.57807200	-0.63340300	0.65497200
C	3.32029500	0.09163700	-0.32982100
C	4.26934900	-0.61971100	-1.13155100
C	4.45445000	-2.01178300	-0.92251300
C	3.73088800	-2.67925400	0.03242600
H	2.44388600	2.04750600	0.03470100
H	2.18983500	-2.52255100	1.54798400
C	3.15190200	1.48293900	-0.55803900
C	5.00604200	0.08274100	-2.11950300
H	5.17819900	-2.53670000	-1.53635000
H	3.87261100	-3.74255200	0.18548700
C	4.81716800	1.42927000	-2.31538700
C	3.88174400	2.13364400	-1.52526200
H	5.72312900	-0.46696800	-2.71942200
H	5.38425300	1.95566800	-3.07429600
H	3.73927000	3.19644600	-1.68359300
C	1.57872300	0.07205900	1.53017500
H	2.03022900	0.94606800	1.98644700
H	1.19664900	-0.59872900	2.30156300
Br	-0.86422000	-2.40536400	1.91892000
S	-2.89394000	-1.11912200	-0.37598300
C	-3.98067100	-0.59011200	-1.73223000
F	-5.00636700	-1.46137600	-1.83228300
F	-4.53276200	0.63706200	-1.55873800
F	-3.37082800	-0.55102200	-2.94206700

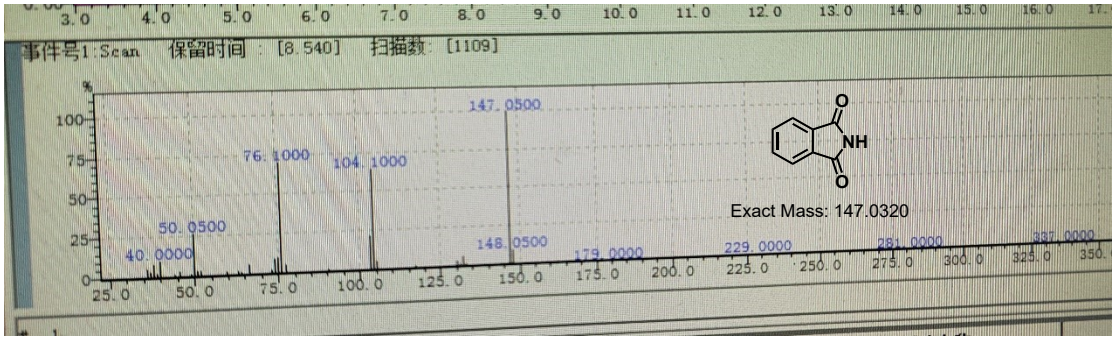
2.12. Cyclic Voltammetry

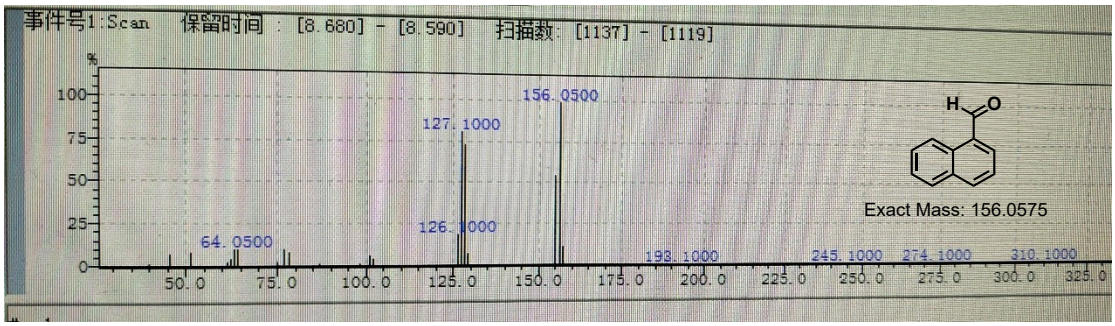
Cyclic voltammetry and square wave voltammetry were performed on an ALS/CHI 660C/680C electrochemical analyzer. The measurements were conducted in 0.1M n-Bu_4NPF_6/DMA using a glassy carbon-disk working electrode; Pt disk as counter electrode; Ag/AgCl as reference electrode, at 0.05 V/s scan rate.

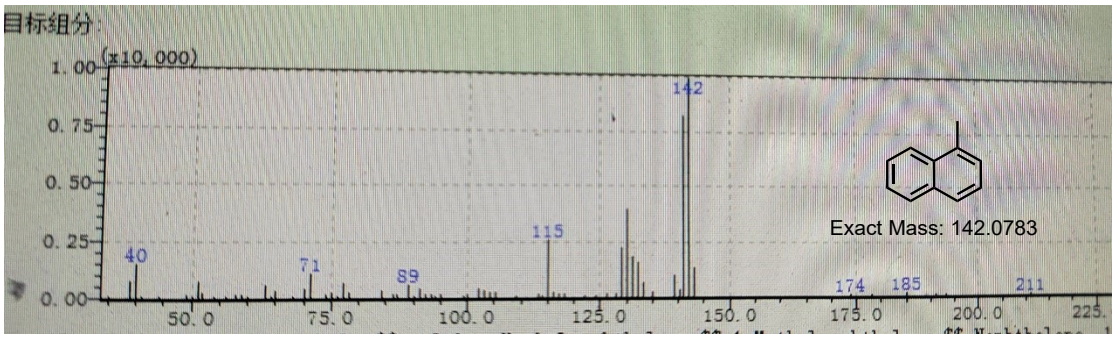


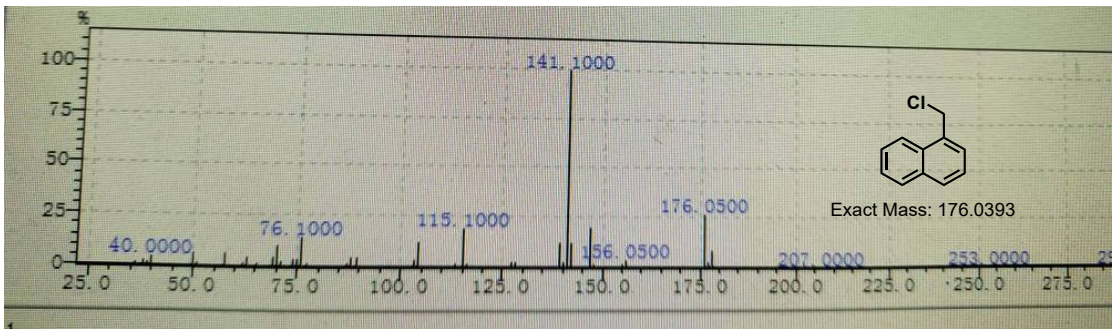
2.13. Additional evidence for mechanism studies via HMRS and GCMS.





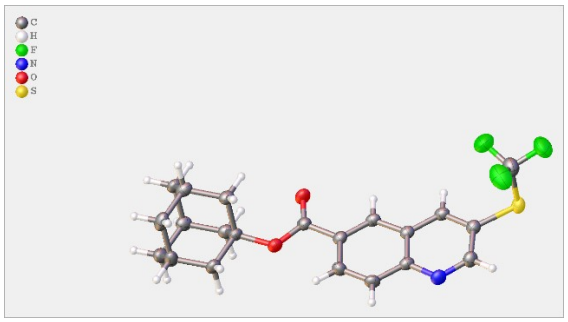






2.14. X-Ray crystallographic data.

2.14.1 Figure S2 Crystallographic structure of 5a



Crystal data and structure refinement for **5a** (CCDC 2223432)

Bond precision: C-C = 0.0053 A Wavelength=0.71073

Cell: a=9.4973(11) b=7.3472(9) c=26.515(3)

alpha=90 beta=94.680(4) gamma=90

Temperature: 150 K

	Calculated	Reported
Volume	1844.0(4)	1844.0(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H20 F3 N O2 S	C21 H20 F3 N O2 S
Sum formula	C21 H20 F3 N O2 S	C21 H20 F3 N O2 S
Mr	407.44	407.44
Dx,g cm-3	1.468	1.468
Z	4	4
Mu (mm-1)	0.222	0.222
F000	848.0	848.0
F000’	848.98	
h,k,lmax	11,8,31	11,8,31
Nref	3250	3227
Tmin,Tmax	0.951,0.987	0.560,0.746
Tmin’	0.942	

Correction method= # Reported T Limits: Tmin=0.560 Tmax=0.746

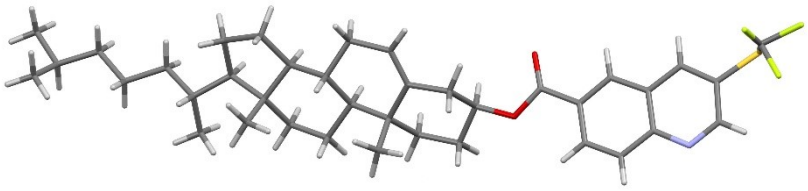
AbsCorr = MULTI-SCAN

Data completeness= 0.993 Theta(max)= 24.999

R(reflections)= 0.0696(2498) wR2(reflections)=0.1733(3227)

S = 1.072 Npar= 253

2.14.2 Figure S2 Crystallographic structure of 10a



Crystal data and structure refinement for **10a** (CCDC 2225455)

Bond precision: C-C = 0.0058 A Wavelength=1.54178

Cell:	a=11.5054(7) alpha=84.517(3)	b=11.8944(8) beta=75.634(2)	c=13.0322(8) gamma=89.507(2)
Temperature: 173 K			

	Calculated	Reported
Volume	1719.57(19)	1719.57(19)
Space group	P 1	P 1
Hall group	P 1	P 1
Moiety formula	C38 H50 F3 N O2 S	2(C38 H50 F3 N O2 S)
Sum formula	C38 H50 F3 N O2 S	C76 H100 F6 N2 O4 S2
Mr	641.85	1283.69
Dx,g cm-3	1.240	1.240
Z	2	1
Mu (mm-1)	1.244	1.244
F000	688.0	688.0
F000’	690.66	
h,k,lmax	13,14,15	13,14,15
Nref	12630[6315]	12295
Tmin,Tmax	0.752,0.830	0.753,0.905
Tmin’	0.542	

Correction method=#Reported T Limits: Tmin=0.753 Tmax=0.905

AbsCorr = NUMERICAL

Data completeness= 1.95/0.97 Theta(max)= 68.389

R(reflections)= 0.0472(11622) wR2(reflections)=0.1327(12295)

S = 1.036 Npar= 880

3.References.

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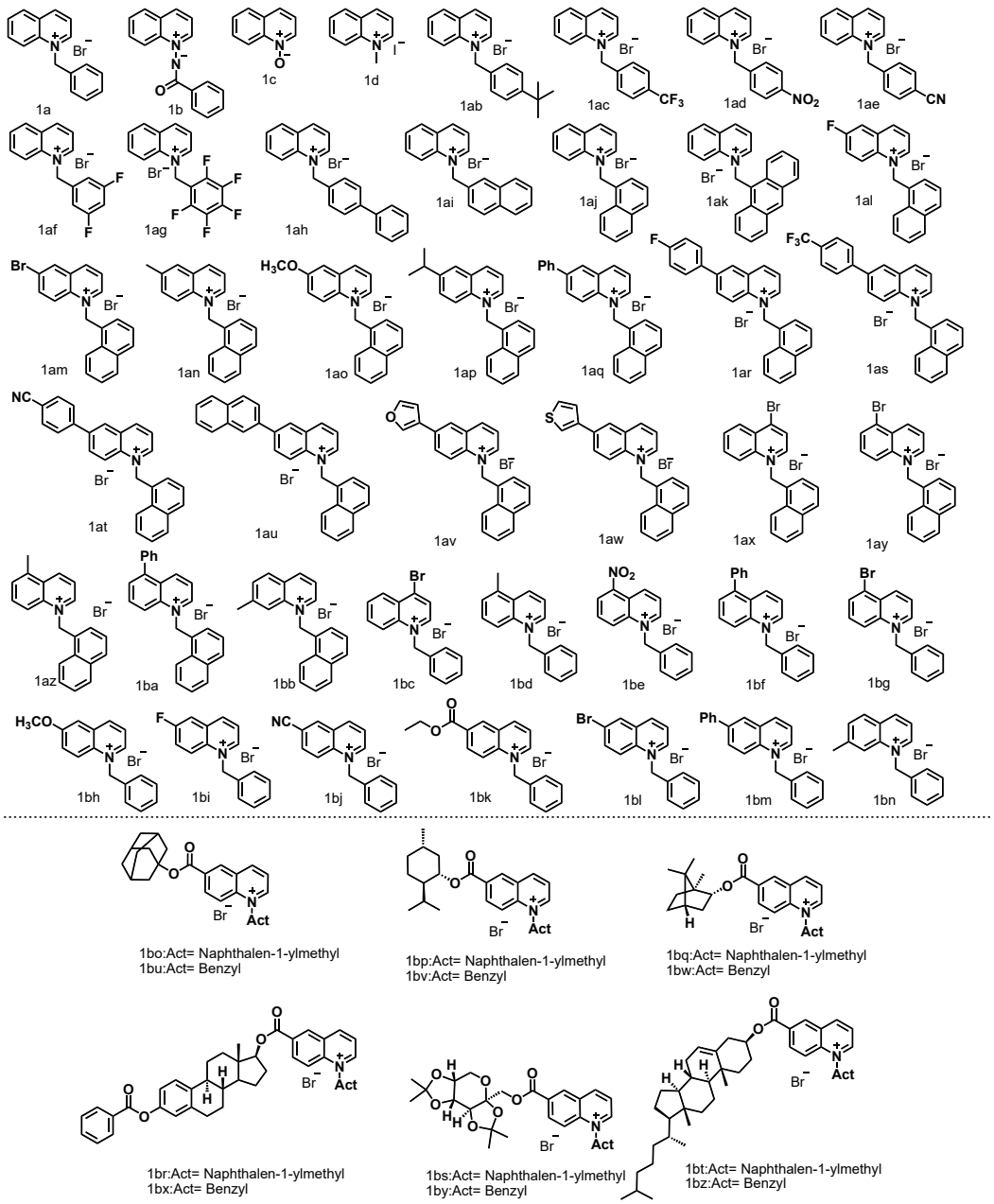
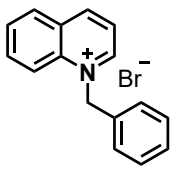
4.Characterization Data

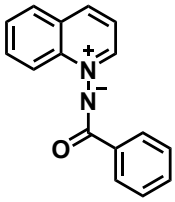
Characterization data for raw materials



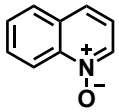
1a, 1b, 1c, 1d, 1ae, 1ag, 1ah, 1ai, 1bg, 1bh, 1bi, 1bj, 1bl and **1bn** have been reported in the known literature.



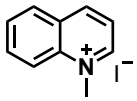
1-benzylquinolin-1-ium bromide (1a): White solid (807.4 mg, 90 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.81 (dd, J = 5.8, 1.5 Hz, 1H), 9.40 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 8.2 Hz, 2H), 8.31 (dd, J = 8.4, 5.8 Hz, 1H), 8.22 (ddd, J = 8.8, 7.0, 1.5 Hz, 1H), 8.02 (ddd, J = 8.1, 6.9, 0.8 Hz, 1H), 7.46 – 7.27 (m, 5H), 6.41 (s, 2H).



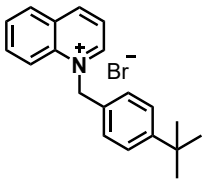
***N*-Benzoyliminoquinolinium ylide (1b):** Brown solid (595.4 mg, 80 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.23 (d, *J* = 5.9 Hz, 1H), 8.82 (d, *J* = 8.9 Hz, 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 8.36 – 8.25 (m, 2H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.92 (ddd, *J* = 8.8, 6.9, 1.5 Hz, 1H), 7.78 (td, *J* = 7.6, 7.0, 1.1 Hz, 1H), 7.70 (dd, *J* = 8.4, 5.9 Hz, 1H), 7.47 (dd, *J* = 5.2, 2.0 Hz, 3H).



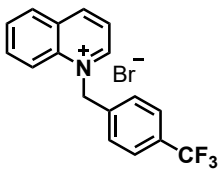
Quinoline *N*-oxide (1c): White solid (409.0 mg, 94 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 8.8 Hz, 1H), 8.53 (d, *J* = 6.0 Hz, 1H), 7.86 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.75 (ddd, *J* = 8.8, 5.3, 3.8 Hz, 2H), 7.64 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 7.29 (dd, J = 8.5, 6.0 Hz, 1H).



1-methylquinolin-1-ium Iodide (1d): White solid (257.4 mg, 95 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.53 (s, 1H), 9.30 (d, *J* = 8.3 Hz, 1H), 8.56 – 8.46 (m, 2H), 8.30 (ddt, *J* = 8.3, 7.0, 1.3 Hz, 1H), 8.17 (s, 1H), 8.07 (dd, *J* = 8.2, 7.0 Hz, 1H), 4.66 (s, 2H).

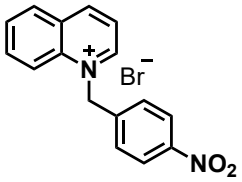


1-(4-(tert-butyl)benzyl)quinolin-1-ium bromide (1ab): White solid (852.2 mg, 80 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.81 (dd, *J* = 5.9, 1.5 Hz, 1H), 9.40 (dt, *J* = 8.4, 1.2 Hz, 1H), 8.75 – 8.56 (m, 1H), 8.53 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.31 (dd, *J* = 8.4, 5.8 Hz, 1H), 8.24 (ddd, *J* = 8.9, 7.0, 1.5 Hz, 1H), 8.04 (ddd, *J* = 8.0, 7.0, 0.9 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.37 (s, 2H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.8, 150.8, 148.6, 138.0, 136.3, 131.4, 131.3, 130.5, 130.4, 127.7, 126.3, 122.9, 119.8, 60.0, 34.8, 31.4. HRMS (ESI) m/z: calcd for $C_{20}H_{22}N^+$: 276.1747; found: 276.1746.

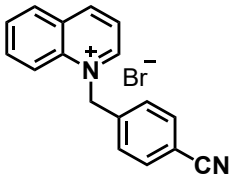


1-(4-(trifluoromethyl)benzyl)quinolin-1-ium bromide (1ac): White solid (935.8 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.83 (dd, *J* = 5.9, 1.4 Hz, 1H), 9.44 (d, *J* = 8.3 Hz, 1H), 8.54 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.46 (d, *J* = 9.0 Hz, 1H), 8.34 (dd, *J* = 8.4, 5.8 Hz, 1H), 8.22 (ddd, *J* = 8.7, 6.9, 1.5 Hz,

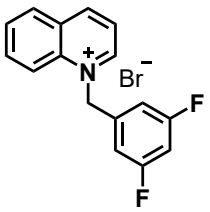
1H), 8.04 (t, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.3, 149.0, 138.9, 138.0, 136.5, 131.5, 130.6, 130.4, 129.6 (q, *J* = 32.2 Hz), 128.5, 126.4 (q, *J* = 3.8 Hz), 124.9 (d, *J* = 257.3 Hz), 123.0, 119.5, 59.8. HRMS (ESI) m/z: calcd for $C_{17}H_{13}F_3N^+$: 288.0995; found: 288.0994.



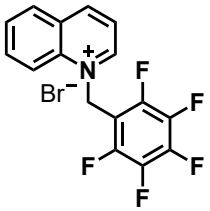
1-(4-nitrobenzyl)quinolin-1-ium bromide (1ad): Yellow solid (675.9 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.84 (dd, *J* = 5.8, 1.5 Hz, 1H), 9.45 (dt, *J* = 8.4, 1.1 Hz, 1H), 8.55 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.42 (d, *J* = 8.9 Hz, 1H), 8.35 (dd, *J* = 8.4, 5.8 Hz, 1H), 8.26 – 8.16 (m, 3H), 8.04 (ddd, *J* = 8.0, 6.9, 0.9 Hz, 1H), 7.71 – 7.51 (m, 2H), 6.59 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.5, 149.1, 148.0, 141.7, 138.0, 136.5, 131.5, 130.6, 130.5, 129.0, 124.6, 123.1, 119.6, 59.6. HRMS (ESI) m/z: calcd for $C_{16}H_{13}N_2O_2^+$: 265.0972; found: 265.0972.



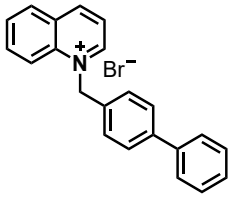
1-(4-cyanobenzyl)quinolin-1-ium bromide (1ae): Yellow solid (777.6 mg, 80 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.82 (d, *J* = 5.8 Hz, 1H), 9.44 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.55 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.49 – 8.37 (m, 1H), 8.33 (dd, *J* = 8.4, 5.8 Hz, 1H), 8.21 (ddd, *J* = 8.8, 7.0, 1.5 Hz, 1H), 8.04 (ddd, *J* = 8.1, 7.0, 0.9 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 6.53 (s, 2H).



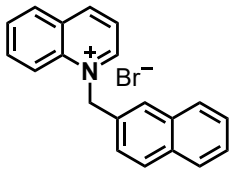
1-(3,5-difluorobenzyl)quinolin-1-ium bromide (1af): White solid (660.7 mg, 86 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.77 (dd, *J* = 5.8, 1.4 Hz, 1H), 9.41 (dt, *J* = 8.4, 1.1 Hz, 1H), 8.54 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.45 (dd, *J* = 8.9, 1.0 Hz, 1H), 8.30 (dd, *J* = 8.4, 5.8 Hz, 1H), 8.23 (ddd, *J* = 8.8, 7.0, 1.5 Hz, 1H), 8.04 (ddd, *J* = 8.0, 7.0, 0.9 Hz, 1H), 7.36 – 7.12 (m, 3H), 6.41 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.1 (dd, *J* = 247.4, 13.3 Hz), 151.5, 148.9, 138.5 (t, *J* = 9.9 Hz), 138.0, 136.34, 131.4, 130.47, 130.45, 123.2, 119.5, 111.6 (dd, *J* = 19.1, 2.9 Hz), 104.9 (t, *J* = 25.8 Hz), 59.31. HRMS (ESI) m/z: calcd for $C_{16}H_{12}F_2N^+$: 256.0932; found: 256.0931.



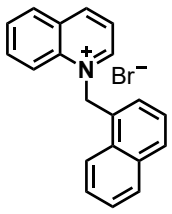
1-((perfluorophenyl)methyl)quinolin-1-ium bromide (1ag): White solid (736.7 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.68 – 9.62 (m, 1H), 9.43 (d, J = 8.3 Hz, 1H), 8.56 (dd, J = 8.3, 1.5 Hz, 1H), 8.50 (d, J = 8.9 Hz, 1H), 8.35 (ddd, J = 8.9, 7.1, 1.6 Hz, 1H), 8.26 (dd, J = 8.3, 5.9 Hz, 1H), 8.10 (ddd, J = 8.0, 7.0, 0.9 Hz, 1H), 6.57 (s, 2H).



1-([1,1'-biphenyl]-4-ylmethyl)quinolin-1-ium bromide (1ah): White solid (956.2 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.83 (dt, J = 4.1, 2.1 Hz, 1H), 9.41 (d, J = 7.9 Hz, 1H), 8.59 (d, J = 9.0 Hz, 1H), 8.53 (dd, J = 8.2, 1.5 Hz, 1H), 8.32 (dd, J = 8.4, 5.8 Hz, 1H), 8.24 (ddd, J = 8.8, 7.0, 1.5 Hz, 1H), 8.04 (ddd, J = 8.0, 7.0, 0.9 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.63 (dd, J = 8.2, 1.2 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.39 – 7.34 (m, 1H), 6.44 (s, 2H).

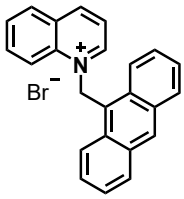


1-(naphthalen-2-ylmethyl)quinolin-1-ium bromide (1ai): White solid (686.5 mg, 89 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.86 (dd, J = 5.9, 1.4 Hz, 1H), 9.43 (dd, J = 8.2, 1.3 Hz, 1H), 8.58 (d, J = 9.0 Hz, 1H), 8.53 (dd, J = 8.2, 1.5 Hz, 1H), 8.34 (dd, J = 8.4, 5.8 Hz, 1H), 8.20 (ddd, J = 8.8, 7.0, 1.5 Hz, 1H), 8.01 (ddd, J = 8.0, 6.9, 0.8 Hz, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.88 – 7.81 (m, 1H), 7.58 – 7.48 (m, 3H), 6.57 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.0, 148.7, 138.1, 136.3, 133.1, 131.9, 131.4, 130.5, 130.4, 129.4, 128.4, 128.2, 127.33, 127.30, 127.0, 125.3, 123.0, 119.8, 60.6. HRMS (ESI) m/z: calcd for $C_{20}H_{16}N^+$: 257.1199; found: 257.1199.

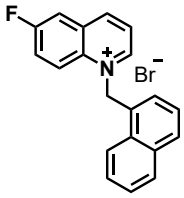


1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1aj): White solid (594.2 mg, 90 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.52 (d, J = 5.8 Hz, 1H), 9.47 (d, J = 8.3 Hz, 1H), 8.60 (dd, J = 8.3, 1.5 Hz, 1H), 8.43 (d, J = 8.9 Hz, 1H), 8.28 (dd, J = 8.4, 5.8 Hz, 1H), 8.21 (ddd, J = 8.9, 7.0, 1.5 Hz, 2H),

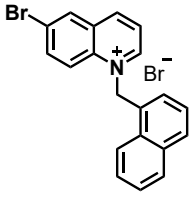
8.12 – 8.04 (m, 2H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.70 (dddd, *J* = 16.4, 8.1, 6.9, 1.4 Hz, 2H), 7.40 (dd, *J* = 8.3, 7.2 Hz, 1H), 6.91 (s, 2H), 6.79 (dd, *J* = 7.2, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.5, 148.9, 138.7, 136.4, 133.8, 131.4, 130.6, 130.4, 129.8, 129.7, 129.4, 127.8, 127.2, 126.1, 125.3, 123.5, 123.1, 119.8, 58.3. HRMS (ESI) m/z: calcd for $C_{20}H_{16}N^+$: 257.1199; found: 257.1198.



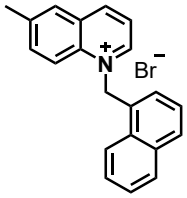
1-(anthracen-9-ylmethyl)quinolin-1-ium bromide (1ak): White solid (672.3 mg, 70 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.29 (dd, *J* = 18.4, 8.6 Hz, 2H), 9.03 (s, 1H), 8.62 (s, 1H), 8.52 (ddd, *J* = 8.8, 7.1, 1.5 Hz, 1H), 8.38 – 8.29 (m, 3H), 8.29 – 8.18 (m, 3H), 7.81 (dd, *J* = 8.3, 5.9 Hz, 1H), 7.72 – 7.57 (m, 4H), 7.22 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.0, 146.5, 139.5, 136.1, 132.3, 131.9, 131.7, 131.1, 130.7, 130.3, 130.1, 128.7, 126.3, 123.9, 122.8, 120.7, 120.3, 53.2. HRMS (ESI) m/z: calcd for $C_{24}H_{18}N^+$: 320.1434; found: 320.1433.



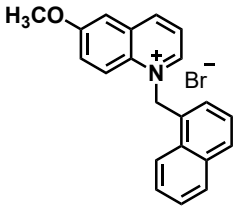
6-fluoro-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1al): White solid (734.7 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 – 9.42 (m, 1H), 9.39 (d, *J* = 8.5 Hz, 1H), 8.57 (dd, *J* = 9.8, 4.4 Hz, 1H), 8.48 (dd, *J* = 8.6, 2.8 Hz, 1H), 8.30 (dd, *J* = 8.5, 5.8 Hz, 1H), 8.24 – 8.15 (m, 2H), 8.10 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.77 – 7.65 (m, 2H), 7.42 (dd, *J* = 8.3, 7.1 Hz, 1H), 6.91 (s, 2H), 6.84 (d, *J* = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.4 (d, *J* = 252.2 Hz), 150.2, 148.2 (d, *J* = 5.1 Hz), 136.0, 133.8, 131.9 (d, *J* = 11.1 Hz), 130.4, 129.9, 129.6, 129.4, 127.8, 127.3, 126.1, 126.0 (d, *J* = 26.5 Hz), 125.6. 124.1, 123.5, 123.4 (d, *J* = 9.8 Hz), 114.7 (d, *J* = 23.1 Hz), 58.8. HRMS (ESI) m/z: calcd for $C_{20}H_{15}FN^+$: 288.1183; found: 288.1185.



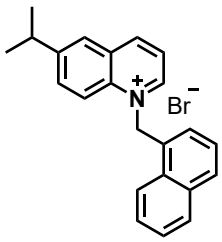
6-bromo-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1am): White solid (866.6 mg, 83 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (d, *J* = 5.8 Hz, 1H), 9.36 (d, *J* = 8.4 Hz, 1H), 8.92 (d, *J* = 2.1 Hz, 1H), 8.39 (d, *J* = 9.5 Hz, 1H), 8.38 – 8.27 (m, 2H), 8.22 – 8.15 (m, 1H), 8.08 (dd, *J* = 7.7, 1.8 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.42 (s, 1H), 6.88 (s, 2H), 6.81 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.0, 147.9, 138.8, 137.8, 133.8, 133.0, 131.6, 130.4, 129.8, 129.6, 129.4, 127.8, 127.3, 126.1, 125.5, 124.3, 123.8, 123.5, 122.1, 58.7. HRMS (ESI) m/z: calcd for $C_{20}H_{15}BrN^+$: 348.0382; found: 348.0385.



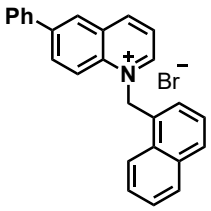
6-methyl-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1an): White solid (724.5 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.45 (dd, J = 5.9, 1.4 Hz, 1H), 9.34 (d, J = 8.3 Hz, 1H), 8.38 – 8.30 (m, 2H), 8.28 – 8.18 (m, 2H), 8.12 – 8.01 (m, 2H), 8.00 (d, J = 8.3 Hz, 1H), 7.71 (dddd, J = 17.6, 8.0, 6.9, 1.4 Hz, 2H), 7.39 (dd, J = 8.3, 7.2 Hz, 1H), 6.89 (s, 2H), 6.72 (dd, J = 7.2, 1.1 Hz, 1H), 3.35 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.5, 148.0, 141.0, 138.4, 137.3, 133.8, 130.5, 130.3, 123.0, 129.7, 129.6, 129.4, 127.8, 127.2, 126.1, 125.0, 123.5, 123.1, 119.5, 58.3, 21.3. HRMS (ESI) m/z: calcd for $C_{21}H_{18}N^{+}$: 284.1434; found: 284.1434.



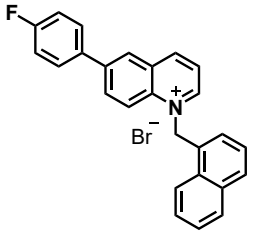
6-methoxy-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1ao): White solid (632.6 mg, 87 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (t, J = 4.7 Hz, 1H), 9.29 (d, J = 7.7 Hz, 1H), 8.33 (d, J = 9.7 Hz, 1H), 8.22 (dd, J = 8.4, 5.9 Hz, 2H), 8.08 (dd, J = 7.9, 1.6 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.84 (dd, J = 9.6, 2.9 Hz, 1H), 7.71 (dddd, J = 17.5, 8.0, 6.9, 1.4 Hz, 2H), 7.40 (dd, J = 8.3, 7.2 Hz, 1H), 6.88 (d, J = 2.5 Hz, 2H), 6.73 (dd, J = 7.2, 1.1 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.6, 146.9, 134.4, 133.8, 132.5, 130.3, 130.0, 129.7, 129.3, 128.5, 127.8, 127.2, 126.1, 125.0, 123.5, 123.4, 121.5, 108.9, 58.4, 56.9. HRMS (ESI) m/z: calcd for $C_{21}H_{18}NO^{+}$: 300.1383; found: 300.1384.



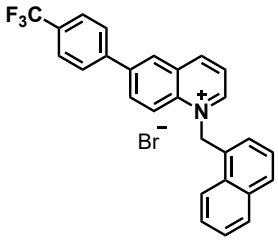
6-isopropyl-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1ap): White solid (824.1 mg, 88 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.46 (d, J = 4.5 Hz, 1H), 9.39 (d, J = 8.3 Hz, 1H), 8.44 (d, J = 2.0 Hz, 1H), 8.36 (d, J = 9.2 Hz, 1H), 8.29 – 8.21 (m, 2H), 8.18 (dd, J = 9.2, 2.1 Hz, 1H), 8.09 (dd, J = 7.9, 1.7 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.71 (dddd, J = 17.2, 8.1, 6.9, 1.4 Hz, 2H), 7.41 (dd, J = 8.3, 7.1 Hz, 1H), 6.90 (s, 2H), 6.80 (dd, J = 7.1, 1.2 Hz, 1H), 1.34 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.1, 149.5, 148.3, 137.5, 136.3, 133.8, 130.7, 130.4, 129.9, 129.7, 129.4, 127.8, 127.2, 126.1, 125.3, 123.5, 123.1, 119.7, 58.2, 33.7, 23.7. HRMS (ESI) m/z: calcd for $C_{23}H_{22}N^{+}$: 312.1747; found: 312.1746.



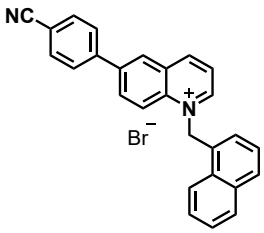
1-(naphthalen-1-ylmethyl)-6-phenylquinolin-1-ium bromide (1aq): White solid (346.1 mg, 89 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (dd, J = 10.4, 7.0 Hz, 2H), 8.94 (d, J = 2.2 Hz, 1H), 8.57 (dd, J = 9.3, 2.2 Hz, 1H), 8.49 (d, J = 9.3 Hz, 1H), 8.30 (dd, J = 8.4, 5.8 Hz, 1H), 8.25 (d, J = 8.3 Hz, 1H), 8.09 (dd, J = 8.0, 1.6 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.94 (dd, J = 7.3, 1.8 Hz, 2H), 7.78 – 7.65 (m, 2H), 7.60 (dd, J = 8.3, 6.8 Hz, 2H), 7.56 – 7.48 (m, 1H), 7.46 – 7.37 (m, 1H), 6.94 (s, 2H), 6.83 (d, J = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.2, 148.9, 141.6, 138.1, 137.6, 135.2, 133.8, 131.0, 130.4, 129.91, 129.89, 129.73, 129.66, 129.4, 128.0, 127.9, 127.8, 127.3, 126.1, 125.3, 123.5, 120.5, 58.4. HRMS (ESI) m/z: calcd for $C_{26}H_{20}N^+$: 346.1590; found: 346.1595.



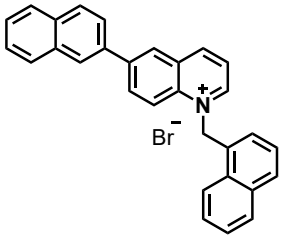
6-(4-fluorophenyl)-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1ar): White solid (928.6 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.47 (d, J = 8.9 Hz, 2H), 9.01 – 8.81 (m, 1H), 8.59 – 8.51 (m, 1H), 8.48 (d, J = 9.3 Hz, 1H), 8.30 (dd, J = 8.4, 5.7 Hz, 1H), 8.27 – 8.20 (m, 1H), 8.15 – 8.05 (m, 1H), 8.00 (dd, J = 8.5, 5.7 Hz, 3H), 7.82 – 7.61 (m, 2H), 7.42 (tdd, J = 9.1, 7.0, 2.5 Hz, 3H), 6.96 (s, 2H), 6.82 (d, J = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.32 (d, J = 246.9 Hz), 150.3, 148.8, 140.5, 138.0, 135.0, 134.1, 133.8, 130.9, 130.4, 130.2, 130.1, 129.9, 129.7, 129.4, 127.9, 127.8, 127.3, 126.1, 125.3, 123.6, 123.5, 120.5, 116.9, 116.7, 58.4. HRMS (ESI) m/z: calcd for $C_{26}H_{19}FN^+$: 364.1496; found: 364.1500.



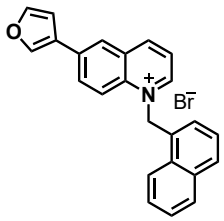
1-(naphthalen-1-ylmethyl)-6-(4-(trifluoromethyl)phenyl)quinolin-1-ium bromide (1as): White solid (1031.2 mg, 83 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.67 – 9.42 (m, 2H), 9.13 – 8.99 (m, 1H), 8.62 (d, J = 9.3 Hz, 1H), 8.55 (d, J = 9.3 Hz, 1H), 8.39 – 8.30 (m, 1H), 8.26 (dd, J = 8.4, 4.8 Hz, 1H), 8.18 (d, J = 8.1 Hz, 2H), 8.10 (dd, J = 7.9, 1.6 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.99 – 7.92 (m, 2H), 7.80 – 7.64 (m, 2H), 7.43 (t, J = 7.7 Hz, 1H), 6.98 (s, 2H), 6.85 (d, J = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.7, 149.1, 141.6, 139.9, 138.5, 135.1, 133.8, 130.8, 130.4, 129.9, 129.8, 129.7 (q, J = 30.3 Hz), 129.4, 129.1, 128.8, 127.8, 127.3, 126.7 (q, J = 4.1 Hz), 126.1, 125.3, 124.6 (q, J = 273.71 Hz), 123.8, 123.5, 120.7, 58.5. HRMS (ESI) m/z: calcd for $C_{27}H_{19}F_3N^+$: 414.1464; found: 414.1466.



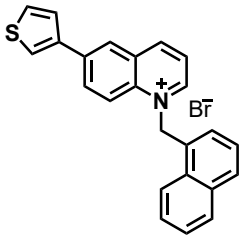
6-(4-cyanophenyl)-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide(1at): White solid (946.4 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.46 (dd, J = 16.6, 7.4 Hz, 2H), 9.01 – 8.76 (m, 1H), 8.55 (d, J = 9.3 Hz, 1H), 8.48 (d, J = 9.3 Hz, 1H), 8.30 (ddd, J = 8.5, 5.7, 2.8 Hz, 1H), 8.24 (dd, J = 8.7, 3.4 Hz, 1H), 8.09 (dd, J = 8.0, 1.6 Hz, 1H), 8.00 (ddd, J = 8.8, 4.7, 2.0 Hz, 3H), 7.80 – 7.53 (m, 2H), 7.50 – 7.31 (m, 3H), 6.93 (s, 2H), 6.82 (d, J = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.5, 162.1, 150.2, 148.8, 140.5, 138.0, 135.0, 134.0, 133.8, 130.9, 130.3, 130.2, 130.1, 129.9, 129.7, 129.4, 127.9, 127.8, 127.3, 126.1, 125.3, 123.6, 123.5, 120.5, 116.9, 116.7, 58.4. HRMS (ESI) m/z: calcd for $C_{27}H_{19}N_2^+$: 371.1543; found: 371.1543.



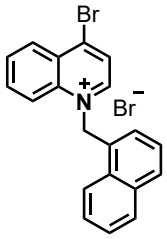
1-(naphthalen-1-ylmethyl)-6-(naphthalen-2-yl)quinolin-1-ium bromide (1au)：White solid (974.9 mg, 82 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.58 – 9.54 (m, 1H), 9.52 (d, J = 8.4 Hz, 1H), 8.76 (d, J = 2.0 Hz, 1H), 8.58 (d, J = 9.2 Hz, 1H), 8.39 – 8.31 (m, 2H), 8.28 (d, J = 8.3 Hz, 1H), 8.11 (ddd, J = 8.3, 4.0, 1.3 Hz, 3H), 8.05 (d, J = 8.3 Hz, 1H), 7.85 – 7.67 (m, 4H), 7.66 – 7.52 (m, 3H), 7.47 (dd, J = 8.3, 7.1 Hz, 1H), 6.99 (s, 2H), 6.93 (d, J = 6.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.5, 148.9, 141.9, 138.2 (d, J = 3.1 Hz), 137.0, 133.9, 133.8, 131.4, 130.9, 130.7, 130.4, 129.83, 129.81, 129.5, 129.4, 129.2, 128.4, 127.8, 127.6, 127.3, 126.9, 126.2, 125.4, 125.1, 123.5, 119.9, 58.5. HRMS (ESI) m/z: calcd for $C_{30}H_{22}N^+$: 396.1747; found: 396.1748.



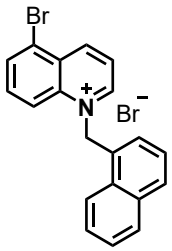
6-(furan-2-yl)-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1av): White solid (836.9 mg, 83 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.42 (d, J = 5.8 Hz, 1H), 9.33 (d, J = 8.3 Hz, 1H), 8.82 (d, J = 2.0 Hz, 1H), 8.56 (s, 1H), 8.50 (dd, J = 9.3, 2.0 Hz, 1H), 8.44 (d, J = 9.3 Hz, 1H), 8.35 – 8.19 (m, 2H), 8.10 (dd, J = 7.9, 1.7 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.91 (s, 1H), 7.72 (dddd, J = 17.3, 8.0, 6.9, 1.4 Hz, 2H), 7.42 (dd, J = 8.3, 7.2 Hz, 1H), 7.24 (d, J = 1.9 Hz, 1H), 6.91 (s, 2H), 6.88 – 6.71 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.5, 148.1, 145.8, 142.5, 137.8, 134.3, 134.1, 133.8, 131.1, 130.4, 129.8, 129.77, 129.4, 127.8, 127.2, 126.1, 125.9, 125.5, 124.3, 123.6, 123.5, 120.4, 109.1, 58.3. HRMS (ESI) m/z: calcd for $C_{24}H_{18}NO^+$: 336.1383; found: 336.1385.



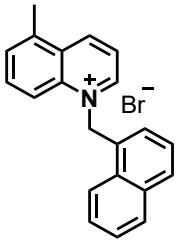
1-(naphthalen-1-ylmethyl)-6-(thiophen-2-yl)quinolin-1-ium bromide (1aw): White solid (866.2 mg, 82 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.44 (s, 1H), 9.38 (d, J = 8.4 Hz, 1H), 9.05 – 8.88 (m, 1H), 8.62 (dd, J = 9.3, 2.1 Hz, 1H), 8.45 (d, J = 9.3 Hz, 1H), 8.33 (dd, J = 2.9, 1.4 Hz, 1H), 8.29 – 8.19 (m, 2H), 8.10 (dd, J = 8.0, 1.6 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.90 – 7.77 (m, 2H), 7.76 – 7.65 (m, 2H), 7.42 (t, J = 7.7 Hz, 1H), 6.92 (s, 2H), 6.85 (d, J = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.7, 148.4, 139.0, 137.8, 136.6, 134.7, 133.8, 131.1, 130.4, 129.9, 129.8, 129.4, 128.8, 127.8, 127.2, 126.7, 126.6, 126.1, 125.4, 125.3, 123.5, 120.4, 58.3. HRMS (ESI) m/z: calcd for $C_{24}H_{18}NS^{+}$: 352.1154; found: 352.1155.



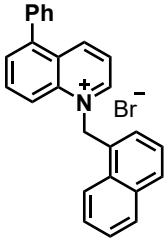
4-bromo-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1ax): White solid (887.4 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (d, J = 5.6 Hz, 1H), 9.42 (d, J = 8.4 Hz, 1H), 8.57 (dd, J = 9.8, 4.3 Hz, 1H), 8.53 – 8.42 (m, 1H), 8.31 (dd, J = 8.4, 5.8 Hz, 1H), 8.25 – 8.16 (m, 2H), 8.09 (dd, J = 7.7, 1.9 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.77 – 7.61 (m, 2H), 7.42 (t, J = 7.8 Hz, 1H), 6.93 (s, 2H), 6.90 – 6.78 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.2, 148.2, 136.0, 133.8, 132.0, 131.9, 130.4, 129.9, 129.6, 129.4, 127.8, 127.3, 126.1, 125.9, 125.6, 124.1, 123.6, 123.4, 123.3, 58.8. HRMS (ESI) m/z: calcd for $C_{20}H_{15}BrN^{+}$: 348.0382; found: 348.0383.



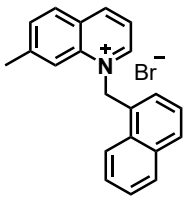
5-bromo-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1ay): White solid (887.2 mg, 84 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.57 (d, J = 5.9 Hz, 1H), 9.52 (d, J = 8.7 Hz, 1H), 8.47 (dd, J = 14.5, 8.3 Hz, 2H), 8.37 (dd, J = 8.7, 5.8 Hz, 1H), 8.21 (dd, J = 8.0, 1.6 Hz, 1H), 8.14 – 8.06 (m, 2H), 8.02 (d, J = 8.2 Hz, 1H), 7.77 – 7.65 (m, 2H), 7.41 (dd, J = 8.3, 7.2 Hz, 1H), 6.93 (s, 2H), 6.88 – 6.82 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.4, 147.6, 140.1, 136.6, 134.7, 133.8, 130.3, 129.8, 129.6, 129.4, 129.3, 127.8, 127.3, 126.1, 125.6, 124.6, 124.5, 123.6, 120.1, 59.1. HRMS (ESI) m/z: calcd for $C_{20}H_{15}BrN^{+}$: 348.0382; found: 348.0384.



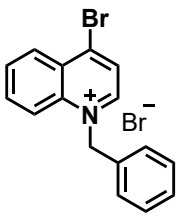
5-methyl-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1az): White solid (724.6 mg, 85 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 – 9.08 (m, 2H), 7.88 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.67 (dd, *J* = 9.0, 7.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.30 (dddd, *J* = 18.2, 8.0, 6.9, 1.4 Hz, 2H), 6.98 (dd, *J* = 8.3, 7.2 Hz, 1H), 6.51 (s, 2H), 6.31 (d, *J* = 7.1 Hz, 1H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.7, 144.1, 144.0, 140.9, 138.5, 135.6, 135.0, 134.8, 134.5, 134.4, 134.1, 132.5, 132.0, 130.8, 129.7, 128.2, 127.3, 127.2, 122.4, 63.4, 24.0. HRMS (ESI) m/z: calcd for $C_{21}H_{18}N^+$: 284.1434; found: 284.1431.



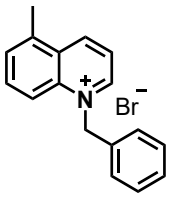
1-(naphthalen-1-ylmethyl)-5-phenylquinolin-1-ium bromide (1ba)： White solid (913.9 mg, 88 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.57 (s, 1H), 9.12 (d, *J* = 8.6 Hz, 1H), 8.47 (d, *J* = 9.0 Hz, 1H), 8.24 (ddd, *J* = 12.9, 8.9, 6.6 Hz, 3H), 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.03 (dd, *J* = 7.7, 2.9 Hz, 2H), 7.80 – 7.49 (m, 7H), 7.43 (dd, *J* = 8.3, 7.2 Hz, 1H), 6.97 (s, 2H), 6.84 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.5, 146.7, 142.9, 139.3, 137.2, 135.8, 133.8, 131.1, 130.8, 130.3, 129.9, 129.7, 129.5, 129.39, 129.36, 128.7, 127.8, 127.3, 126.1, 125.2, 123.5, 123.3, 119.2, 58.9. HRMS (ESI) m/z: calcd for $C_{26}H_{20}N^+$: 346.1590; found: 346.1591.



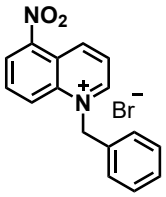
7-methyl-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1bb): White solid (740.0 mg, 90 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.50 – 9.17 (m, 2H), 8.49 (d, *J* = 8.5 Hz, 1H), 8.39 (s, 1H), 8.23 – 8.13 (m, 2H), 8.13 – 8.06 (m, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.94 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.77 – 7.60 (m, 2H), 7.42 (dd, *J* = 8.3, 7.2 Hz, 1H), 6.86 (s, 2H), 6.83 – 6.70 (m, 1H), 3.35 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.7, 148.33, 148.32, 139.2, 133.8, 132.6, 130.9, 130.5, 129.8, 129.8, 129.3, 128.7, 127.7, 127.2, 126.1, 125.4, 123.6, 122.1, 118.4, 58.0, 22.7. HRMS (ESI) m/z: calcd for $C_{21}H_{18}N^+$: 284.1434; found: 284.1433.



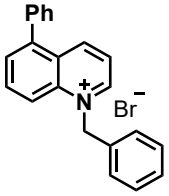
1-benzyl-4-bromoquinolin-1-ium bromide (1bc): White solid (786.8 mg, 88 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.88 (dd, J = 5.8, 1.5 Hz, 1H), 9.46 (d, J = 8.7 Hz, 1H), 8.56 (d, J = 9.0 Hz, 1H), 8.48 – 8.35 (m, 2H), 8.10 (dd, J = 9.0, 7.7 Hz, 1H), 7.58 – 7.21 (m, 5H), 6.45 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.8, 147.3, 139.3, 136.4, 134.6, 134.1, 129.6, 129.38, 129.36, 127.8, 124.5, 124.4, 119.9, 61.0. HRMS (ESI) m/z: calcd for $C_{16}H_{13}BrN^+$: 298.0226; found: 298.0225.



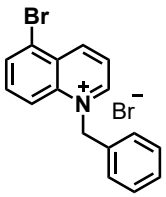
1-benzyl-5-methylquinolin-1-ium bromide (1bd): White solid (632.1 mg, 90 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.79 (dd, J = 5.9, 1.5 Hz, 1H), 9.29 (d, J = 8.5 Hz, 1H), 8.45 (d, J = 9.1 Hz, 1H), 8.37 – 8.20 (m, 2H), 8.06 (dd, J = 9.2, 2.0 Hz, 1H), 7.58 – 7.28 (m, 5H), 6.42 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.8, 147.7, 140.9, 138.2, 136.5, 134.5, 130.5, 129.7, 129.6, 129.2, 127.8, 122.9, 119.6, 60.2, 21.3. HRMS (ESI) m/z: calcd for $C_{17}H_{16}N^+$: 234.1277; found: 234.1278.



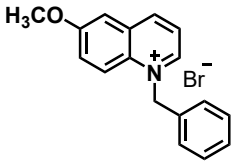
1-benzyl-5-nitroquinolin-1-ium bromide (1be): Yellow solid (887.4 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.99 (d, J = 5.8 Hz, 1H), 9.62 (d, J = 9.0 Hz, 1H), 8.93 (d, J = 9.1 Hz, 1H), 8.74 (d, J = 7.7 Hz, 1H), 8.52 (dd, J = 9.0, 5.7 Hz, 1H), 8.37 (dd, J = 9.1, 7.8 Hz, 1H), 7.64 – 7.35 (m, 5H), 6.52 (s, 2H).



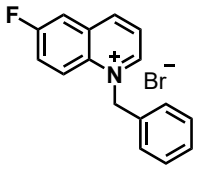
1-benzyl-5-phenylquinolin-1-ium bromide (1bf)：Yellow solid (755.1 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.87 (dd, J = 5.8, 1.4 Hz, 1H), 9.04 (d, J = 8.7 Hz, 1H), 8.70 – 8.54 (m, 1H), 8.39 – 8.19 (m, 2H), 7.97 (dd, J = 7.3, 0.8 Hz, 1H), 7.75 – 7.55 (m, 5H), 7.52 – 7.19 (m, 5H), 6.49 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.9, 146.4, 143.0, 138.6, 137.2, 135.6, 134.4, 131.0, 130.7, 129.6, 129.5, 129.4, 129.3, 128.8, 127.8, 123.1, 119.2, 60.8. HRMS (ESI) m/z: calcd for $C_{22}H_{18}N^+$: 296.1434; found: 296.1433.



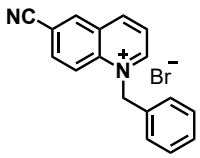
1-benzyl-5-bromoquinolin-1-ium bromide (1bg): White solid (886.2 mg, 88 % yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.87 (d, J = 18.9 Hz, 1H), 9.46 (d, J = 8.7 Hz, 1H), 8.56 (t, J = 8.2 Hz, 1H), 8.40 (dt, J = 8.3, 3.2 Hz, 2H), 8.10 (dd, J = 9.0, 7.7 Hz, 1H), 7.49 – 7.29 (m, 5H), 6.44 (d, J = 11.5 Hz, 2H).



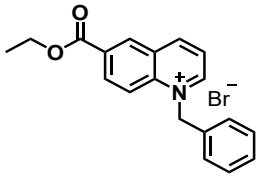
1-benzyl-6-methoxyquinolin-1-ium bromide (1bh): White solid (839.0 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.64 (d, J = 5.8 Hz, 1H), 9.23 (d, J = 8.4 Hz, 1H), 8.45 (d, J = 9.7 Hz, 1H), 8.25 (dd, J = 8.5, 5.8 Hz, 1H), 7.97 (d, J = 2.9 Hz, 1H), 7.85 (dd, J = 9.7, 2.9 Hz, 1H), 7.60 – 7.25 (m, 5H), 6.39 (s, 2H), 3.98 (s, 3H).



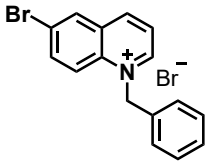
1-benzyl-6-fluoroquinolin-1-ium bromide (1bi): White solid (792.0 mg, 83 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 – 9.75 (m, 1H), 9.36 (d, J = 8.5 Hz, 1H), 8.65 (dd, J = 9.8, 4.4 Hz, 1H), 8.43 (dd, J = 8.5, 2.9 Hz, 1H), 8.36 (dd, J = 8.4, 5.7 Hz, 1H), 8.19 (ddd, J = 9.7, 8.1, 3.0 Hz, 1H), 7.60 – 7.23 (m, 5H), 6.44 (s, 2H).



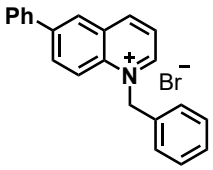
1-benzyl-6-cyanoquinolin-1-ium bromide (1bj): White solid (886.2 mg, 85 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.99 – 9.91 (m, 1H), 9.45 (d, J = 8.4 Hz, 1H), 9.21 (s, 1H), 8.85 – 8.64 (m, 1H), 8.54 (dd, J = 9.2, 1.9 Hz, 1H), 8.49 – 8.41 (m, 1H), 7.48 – 7.28 (m, 5H), 6.45 (d, J = 2.4 Hz, 2H).



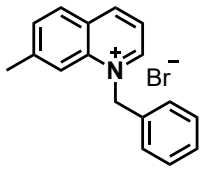
1-benzyl-6-(ethoxycarbonyl)quinolin-1-ium bromide (1bk): White solid (771.2 mg, 88 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.95 (dd, J = 5.9, 1.5 Hz, 1H), 9.61 (d, J = 8.3 Hz, 1H), 9.16 (d, J = 1.9 Hz, 1H), 8.68 (d, J = 9.3 Hz, 1H), 8.56 (dd, J = 9.3, 2.0 Hz, 1H), 8.42 (dd, J = 8.4, 5.8 Hz, 1H), 7.56 – 7.27 (m, 5H), 6.46 (s, 2H), 4.43 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.5, 152.7, 149.9, 139.8, 134.6, 134.1, 133.2, 131.0, 130.2, 129.6, 129.3, 127.9, 124.0, 120.8, 62.4, 60.6, 14.6. HRMS (ESI) m/z: calcd for $C_{19}H_{18}NO_2^+$: 292.1332; found: 292.1331.



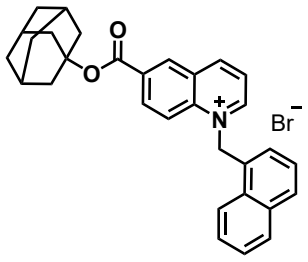
1-benzyl-6-bromoquinolin-1-ium bromide (1bl): White solid (937.5 mg, 83 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.85 (d, J = 1.8 Hz, 1H), 9.33 (d, J = 8.3 Hz, 1H), 8.87 (d, J = 2.3 Hz, 1H), 8.48 (d, J = 9.5 Hz, 1H), 8.42 – 8.11 (m, 2H), 7.40 (d, J = 4.4 Hz, 5H), 6.42 (s, 2H).



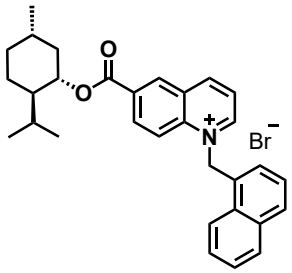
1-benzyl-6-phenylquinolin-1-ium bromide (1bm): White solid (732.3 mg, 83 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 – 9.60 (m, 1H), 9.41 (d, J = 8.5 Hz, 1H), 8.87 (s, 1H), 8.64 – 8.51 (m, 2H), 8.45 – 8.18 (m, 1H), 8.00 – 7.81 (m, 2H), 7.59 (td, J = 8.4, 7.7, 2.0 Hz, 2H), 7.51 (td, J = 6.9, 6.3, 1.5 Hz, 1H), 7.46 – 7.28 (m, 5H), 6.44 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.6, 148.6, 141.5, 137.5, 137.4, 135.0, 134.0, 131.0, 129.8, 129.6, 129.3, 128.1, 127.9, 127.8, 123.4, 120.5, 60.4. HRMS (ESI) m/z: calcd for $C_{22}H_{18}N^+$: 296.1434; found: 296.1433.



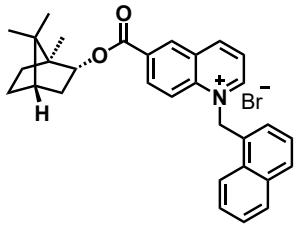
1-benzyl-7-methylquinolin-1-ium bromide (1bn): White solid (886.3 mg, 88 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.71 (d, J = 6.1 Hz, 1H), 9.33 (d, J = 7.4 Hz, 1H), 8.54 – 8.33 (m, 2H), 8.21 (dd, J = 8.3, 5.8 Hz, 1H), 7.88 (dd, J = 8.5, 1.3 Hz, 1H), 7.60 – 7.09 (m, 5H), 6.37 (s, 2H), 3.35 (s, 3H).



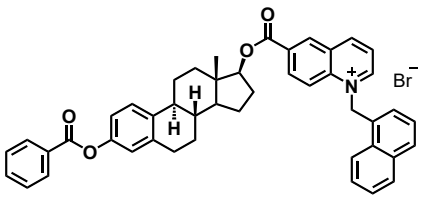
6-((adamantan-1-yloxy)carbonyl)-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1bo)： White solid (1210.2 mg, 88 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (d, J = 7.2 Hz, 1H), 9.61 (dd, J = 5.9, 1.4 Hz, 1H), 9.14 (d, J = 1.6 Hz, 1H), 8.57 – 8.46 (m, 2H), 8.37 (dd, J = 8.4, 5.8 Hz, 1H), 8.22 (dd, J = 8.2, 1.4 Hz, 1H), 8.09 (dd, J = 7.9, 1.7 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.71 (dddd, J = 16.4, 8.0, 6.9, 1.4 Hz, 2H), 7.39 (dd, J = 8.3, 7.2 Hz, 1H), 6.94 (s, 2H), 6.79 (dd, J = 7.2, 1.1 Hz, 1H), 2.26 (s, 6H), 2.22 (s, 3H), 1.69 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.3, 152.2, 150.3, 140.5, 134.8, 133.8, 133.0, 132.5, 130.3, 130.1, 129.7, 129.6, 129.3, 127.8, 127.2, 126.1, 125.3, 124.0, 123.5, 120.7, 82.8, 58.7, 41.3, 36.0, 30.8. HRMS (ESI) m/z: calcd for $C_{31}H_{30}NO_2^+$: 448.2271; found: 448.2275.



6-((((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)-1-(naphthalen-1-ylmethyl) quinoline-1-ium bromide (1bp)：White solid (1193.8 mg, 88 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.73 – 9.50 (m, 2H), 9.22 (d, J = 1.4 Hz, 1H), 8.56 (d, J = 1.7 Hz, 2H), 8.38 (tt, J = 6.1, 2.6 Hz, 1H), 8.22 (dd, J = 8.4, 3.0 Hz, 1H), 8.12 – 8.04 (m, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.79 – 7.59 (m, 2H), 7.43 – 7.28 (m, 1H), 6.95 (s, 2H), 6.80 (d, J = 6.6 Hz, 1H), 4.97 (td, J = 10.8, 4.4 Hz, 1H), 2.06 (dd, J = 12.3, 4.0 Hz, 1H), 1.91 (ddq, J = 9.7, 7.0, 3.4, 2.7 Hz, 1H), 1.71 (d, J = 12.2 Hz, 2H), 1.64 – 1.47 (m, 2H), 1.16 (dq, J = 19.6, 12.7, 12.3 Hz, 2H), 0.91 (dt, J = 12.0, 4.5 Hz, 7H), 0.76 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.1, 152.4, 150.3, 140.6, 134.7, 133.8, 133.2, 131.1, 130.3, 130.2, 129.8, 129.6, 129.3, 127.8, 127.2, 126.1, 125.4, 124.1, 123.5, 120.9, 76.0, 58.7, 47.1, 34.1, 31.3, 26.6, 23.6, 22.3, 21.0, 16.9. HRMS (ESI) m/z: calcd for $C_{31}H_{34}NO_2^+$: 452.2584; found: 452.2586.

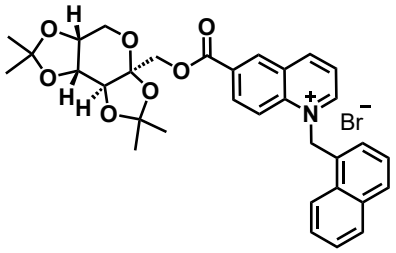


1-(naphthalen-1-ylmethyl)-6-((((1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl)quinolin-1-ium bromide (1bq)：White solid (1121.1 mg, 83 % yield).^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (s, 1H), 9.63 (dd, J = 6.0, 1.5 Hz, 1H), 9.23 (d, J = 1.9 Hz, 1H), 8.64 – 8.49 (m, 2H), 8.38 (dd, J = 8.4, 5.8 Hz, 1H), 8.29 – 8.14 (m, 1H), 8.09 (dd, J = 7.9, 1.6 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.71 (dddd, J = 17.5, 8.1, 6.9, 1.4 Hz, 2H), 7.39 (dd, J = 8.3, 7.2 Hz, 1H), 6.94 (s, 2H), 6.87 – 6.74 (m, 1H), 5.14 (ddd, J = 9.9, 3.5, 1.9 Hz, 1H), 2.44 (tt, J = 9.9, 4.1 Hz, 1H), 2.16 (ddd, J = 13.0, 9.0, 3.8 Hz, 1H), 1.85 – 1.67 (m, 2H), 1.37 (dddd, J = 32.5, 13.1, 7.0, 3.1 Hz, 1H), 1.17 (dd, J = 13.7, 3.5 Hz, 1H), 0.95 (s, 3H), 0.91 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.7, 152.4, 150.4, 140.5, 134.8, 133.8, 133.1, 131.3, 130.3, 130.2, 129.8, 129.7, 129.4, 127.8, 127.3, 126.1, 125.3, 124.1, 123.5, 120.9, 81.6, 58.7, 49.3, 48.1, 44.8, 36.7, 28.1, 27.4, 20.0, 19.1, 13.9. HRMS (ESI) m/z: calcd for $C_{31}H_{32}NO_2^+$: 450.2428; found: 450.2430.

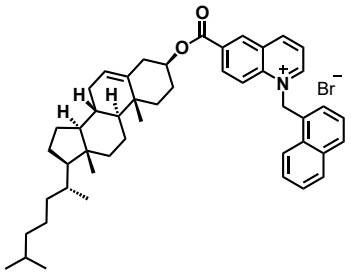


6-((((8R,9S,13S,17S)-3-(benzoyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)oxy)carbonyl)-1-(naphthalen-1-ylmethyl)quinolin-1-ium

bromide (1br)： White solid (1612.8 mg, 80 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.70 (d, J = 8.4 Hz, 1H), 9.61 (dd, J = 5.8, 1.4 Hz, 1H), 9.23 (d, J = 1.8 Hz, 1H), 8.68 – 8.50 (m, 2H), 8.38 (dd, J = 8.3, 5.7 Hz, 1H), 8.23 (d, J = 8.1 Hz, 1H), 8.17 – 8.06 (m, 3H), 8.02 (d, J = 8.4 Hz, 1H), 7.84 – 7.65 (m, 3H), 7.61 (t, J = 7.8 Hz, 2H), 7.44 – 7.30 (m, 2H), 7.02 (dd, J = 8.4, 2.6 Hz, 1H), 6.99 – 6.91 (m, 3H), 6.82 (d, J = 7.2 Hz, 1H), 4.98 (t, J = 8.3 Hz, 1H), 2.93 – 2.72 (m, 2H), 2.41 – 2.18 (m, 3H), 1.97 – 1.83 (m, 2H), 1.83 – 1.67 (m, 2H), 1.62 – 1.29 (m, 6H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.2, 164.5, 152.4, 150.4, 148.9, 140.6, 138.3, 137.9, 134.8, 134.5, 133.8, 133.2, 131.2, 130.3, 130.22, 130.17, 129.8, 129.6, 129.5, 129.45, 129.4, 127.8, 127.3, 126.9, 126.1, 125.4, 124.1, 123.5, 122.0, 120.9, 119.4, 84.4, 58.7, 49.4, 43.8, 43.5, 38.3, 36.8, 29.4, 27.8, 27.0, 26.2, 23.4, 12.6. HRMS (ESI) m/z: calcd for $C_{46}H_{42}NO_4^+$: 672.3108; found: 672.3110.

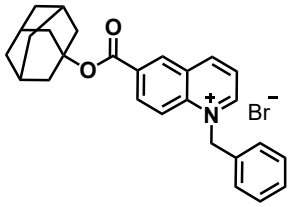


1-(naphthalen-1-ylmethyl)-6-((((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methoxy)carbonyl)quinolin-1-ium bromide (1bs)： White solid (1385.0 mg, 83 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.71 – 9.62 (m, 1H), 9.60 – 9.49 (m, 1H), 9.29 (s, 1H), 8.64 (dd, J = 9.3, 1.9 Hz, 1H), 8.58 (dd, J = 9.4, 1.9 Hz, 1H), 8.36 (qd, J = 5.3, 2.4 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 8.13 – 8.07 (m, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.79 – 7.62 (m, 2H), 7.41 (dd, J = 8.3, 7.2 Hz, 1H), 6.93 (s, 2H), 6.87 (d, J = 7.2 Hz, 1H), 4.75 (d, J = 11.6 Hz, 1H), 4.66 (dd, J = 7.9, 2.6 Hz, 1H), 4.58 (t, J = 2.1 Hz, 1H), 4.29 (dd, J = 10.1, 4.5 Hz, 2H), 3.81 (dd, J = 13.1, 1.9 Hz, 1H), 3.66 (d, J = 13.0 Hz, 1H), 1.46 (s, 3H), 1.34 (s, 3H), 1.28 (d, J = 8.3 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.0, 152.4, 150.2, 140.7, 134.9, 133.8, 133.6, 130.6, 130.5, 130.1, 129.9, 129.4, 127.8, 127.3, 126.1, 125.8, 124.2, 123.6, 120.9, 108.8, 108.6, 101.4, 70.4, 69.7, 66.2, 61.2, 58.7, 26.7, 26.2, 25.7, 24.4. HRMS (ESI) m/z: calcd for $C_{33}H_{34}NO_7^+$: 556.2330; found: 556.2331.

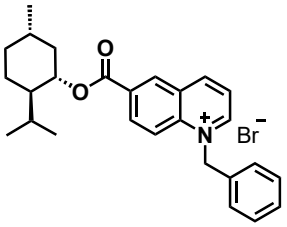


6-((((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)carbonyl)-1-(naphthalen-1-ylmethyl)quinolin-1-ium bromide (1bt)： White solid (1801.7 mg, 88 % yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 10.25 (d, J = 5.8 Hz, 1H), 9.18 (d, J = 8.3 Hz, 1H), 8.89 (d, J = 1.8 Hz, 1H), 8.54 (dd, J = 9.3, 1.9 Hz, 1H), 8.36 (d, J = 9.3 Hz, 1H), 8.27 (ddd, J = 8.4, 4.3, 2.1 Hz, 1H), 8.13 – 8.06 (m, 1H), 7.91 (dd, J = 7.6, 1.9 Hz, 1H), 7.84 (d, J = 8.3 Hz, 1H), 7.66 –

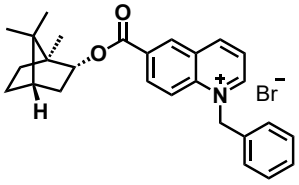
7.52 (m, 2H), 7.29 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.13 (s, 2H), 7.01 (d, *J* = 7.2 Hz, 1H), 5.58 – 5.26 (m, 1H), 4.92 (tq, *J* = 10.8, 4.8 Hz, 1H), 2.68 – 2.33 (m, 2H), 2.19 – 1.89 (m, 4H), 1.85 – 1.70 (m, 3H), 1.66 – 0.97 (m, 22H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2, 148.6, 140.1, 139.1, 135.5, 133.8, 132.6, 132.3, 130.2, 130.1, 129.4, 129.3, 128.0, 127.9, 126.9, 126.0, 125.4, 123.5, 123.4, 122.9, 122.3, 119.7, 56.7, 56.2, 50.0, 42.3, 39.7, 39.5, 38.3, 38.1, 36.9, 36.6, 36.2, 35.8, 31.9, 31.86, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 19.3, 18.7. HRMS (ESI) m/z: calcd for $C_{48}H_{60}NO_2^+$: 682.4619; found: 682.4622.



6-((adamantan-1-yloxy)carbonyl)-1-benzylquinolin-1-ium bromide (1bu)：White solid (979.0 mg, 82 % yield). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.90 (d, *J* = 5.9 Hz, 1H), 9.58 (d, *J* = 8.4 Hz, 1H), 9.07 (s, 1H), 8.63 (d, *J* = 9.4 Hz, 1H), 8.57 – 8.46 (m, 1H), 8.40 (dd, *J* = 8.4, 5.8 Hz, 1H), 7.40 (m, 5H), 6.44 (s, 2H), 2.34 – 2.09 (m, 9H), 1.68 (s, 6H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 163.2, 152.6, 150.0, 139.7, 134.6, 134.1, 133.0, 132.4, 130.2, 129.6, 129.3, 127.9, 123.9, 120.7, 82.7, 60.6, 41.3, 36.0, 30.8. HRMS (ESI) m/z: calcd for $C_{27}H_{28}NO_2^+$: 398.2115; found: 398.2116.

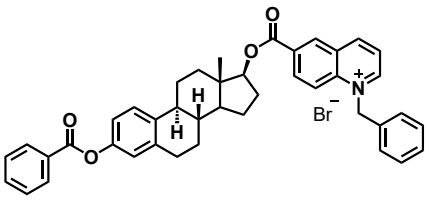


1-benzyl-6-((((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)quinolin-1-ium (1bv): White solid (1061.8 mg, 88 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.82 (d, *J* = 4.4 Hz, 1H), 9.18 (d, *J* = 8.3 Hz, 1H), 8.85 (d, *J* = 1.8 Hz, 1H), 8.73 (d, *J* = 9.3 Hz, 1H), 8.63 (dd, *J* = 9.3, 1.8 Hz, 1H), 8.38 (dd, *J* = 8.4, 5.8 Hz, 1H), 7.46 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.33 – 7.15 (m, 3H), 6.88 (s, 2H), 5.01 (td, *J* = 10.9, 4.4 Hz, 1H), 2.10 (m, 2H), 1.90 (pd, *J* = 6.9, 2.7 Hz, 1H), 1.76 (m, 2H), 1.59 (m, 2H), 1.24 – 1.06 (m, 2H), 0.93 (t, *J* = 7.0 Hz, 6H), 0.77 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4, 152.4, 148.6, 139.8, 135.3, 132.8, 132.4, 132.2, 129.6, 129.4, 129.2, 127.7, 123.6, 120.5, 61.4, 47.1, 40.8, 34.1, 31.5, 26.4, 23.4, 21.9, 20.8, 16.3. HRMS (ESI) m/z: calcd for $C_{27}H_{32}NO_2^+$: 402.2428; found: 402.2427.

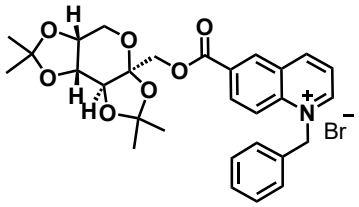


1-benzyl-6-((((1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl)quinolin-1-ium bromide (1bw)：White solid (1044.5 mg, 87 % yield). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.95 (d, *J* = 1.8 Hz, 1H), 9.66 (d, *J* = 8.4 Hz, 1H), 9.17 (d, *J* = 1.9 Hz, 1H), 8.67 (d, *J* = 9.4 Hz, 1H), 8.59 (dd, *J*

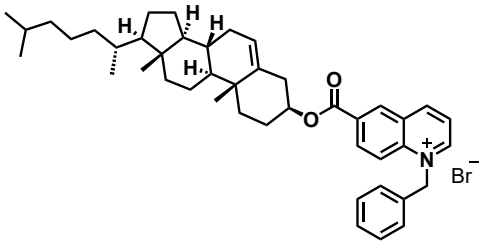
= 9.3, 1.9 Hz, 1H), 8.43 (dd, *J* = 8.4, 5.8 Hz, 1H), 7.52 – 7.28 (m, 5H), 6.46 (s, 2H), 5.13 (ddd, *J* = 9.9, 3.5, 1.9 Hz, 1H), 2.43 (ddt, *J* = 13.9, 10.0, 4.0 Hz, 1H), 2.16 (ddd, *J* = 13.1, 9.1, 4.0 Hz, 1H), 1.91 – 1.68 (m, 2H), 1.37 (dddd, *J* = 32.5, 13.4, 7.0, 3.4 Hz, 2H), 1.16 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.94 (s, 3H), 0.90 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.6, 152.8, 150.1, 139.8, 134.6, 134.2, 133.2, 131.2, 130.2, 129.6, 129.3, 127.9, 123.9, 120.9, 81.6, 60.7, 49.3, 48.1, 44.8, 36.7, 28.1, 27.4, 19.9, 19.1, 13.9. HRMS (ESI) m/z: calcd for $C_{27}H_{30}NO_2^+$: 400.2271; found: 400.2275.



6-((((8R,9S,13S,17S)-3-(benzoyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)oxy)carbonyl)-1-benzylquinolin-1-ium bromide (1bx): White solid (1643.9 mg, 88 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.93 (dd, *J* = 5.9, 1.5 Hz, 1H), 9.63 (d, *J* = 8.4 Hz, 1H), 9.16 (d, *J* = 1.9 Hz, 1H), 8.67 (d, *J* = 9.4 Hz, 1H), 8.59 (dd, *J* = 9.3, 2.0 Hz, 1H), 8.43 (dt, *J* = 8.5, 6.0 Hz, 1H), 8.20 – 8.04 (m, 2H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.45 – 7.27 (m, 6H), 7.04 – 6.92 (m, 2H), 6.46 (s, 2H), 4.95 (t, *J* = 8.2 Hz, 1H), 2.96 – 2.76 (m, 2H), 2.42 – 2.20 (m, 3H), 2.03 – 1.83 (m, 2H), 1.74 (m, 2H), 1.44 (m, 6H), 1.00 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.2, 164.4, 152.8, 150.1, 148.9, 142.5, 139.9, 138.3, 137.9, 134.6, 134.1, 133.2, 131.1, 130.2, 129.6, 129.5, 129.4, 128.5, 127.9, 126.9, 123.9, 122.0, 120.9, 119.4, 108.5, 84.4, 60.7, 49.4, 43.8, 43.5, 38.3, 36.8, 29.4, 27.8, 26.9, 26.1, 23.4, 12.6. HRMS (ESI) m/z: calcd for $C_{42}H_{40}NO_2^+$: 622.2952; found: 622.6953.



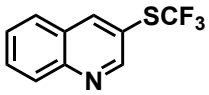
1-benzyl-6-((((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis ([1,3] dioxolo) [4,5-b:4',5'-d] pyran-3a-yl) methoxy) carbonyl) quinolin-1-ium bromide (1by): White solid (1245.2 mg, 82 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.78 (d, *J* = 5.7 Hz, 1H), 9.18 (d, *J* = 8.3 Hz, 1H), 8.91 (d, *J* = 1.8 Hz, 1H), 8.70 (d, *J* = 9.4 Hz, 1H), 8.63 (dd, *J* = 9.3, 1.9 Hz, 1H), 8.39 (dd, *J* = 8.4, 5.7 Hz, 1H), 7.44 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.32 – 7.17 (m, 3H), 6.82 (s, 2H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.64 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.39 (dd, *J* = 7.1, 4.5 Hz, 2H), 4.25 (dd, *J* = 7.8, 1.7 Hz, 1H), 3.92 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.78 (d, *J* = 13.0 Hz, 1H), 1.52 (s, 3H), 1.41 (s, 3H), 1.33 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4, 152.8, 148.6, 139.8, 135.2, 132.8, 132.7, 129.5, 129.4, 129.3, 127.7, 123.8, 120.6, 109.2, 108.9, 101.3, 70.8, 70.6, 69.9, 67.1, 61.4, 26.4, 25.9, 25.4, 24.0. HRMS (ESI) m/z: calcd for $C_{29}H_{32}NO_7^+$: 506.2173; found: 506.2175.



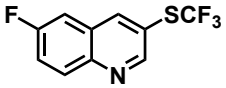
1-benzyl-6-((((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)carbonyl)quinolin-1-ium bromide (1bz): White solid (1423.0 mg, 75 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.85 (s, 1H), 9.15 (dd, *J* = 8.4, 3.6 Hz, 1H), 8.85 (d, *J* = 1.8 Hz, 1H), 8.79 – 8.56 (m, 2H), 8.31 (dd, *J* = 8.4, 5.8 Hz, 1H), 7.57 – 7.36 (m, 2H), 7.30 – 7.15 (m, 3H), 6.85 (s, 2H), 5.51 – 5.34 (m, 1H), 4.91 (t, *J* = 5.5 Hz, 1H), 2.67 – 2.34 (m, 2H), 2.11 – 1.89 (m, 4H), 1.87 – 1.65 (m, 3H), 1.64 – 0.93 (m, 22H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.7, 1.8 Hz, 6H), 0.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2, 154.7, 149.6, 139.8, 139.1, 135.4, 132.7, 132.4, 129.6, 129.5, 129.4, 127.7, 125.7, 123.4, 123.3, 120.1, 61.3, 56.7, 56.2, 50.0, 42.3, 39.7, 39.5, 38.1, 36.9, 36.6, 36.2, 35.8, 31.9, 31.86, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.6, 21.1, 19.3, 18.7, 11.9. HRMS (ESI) m/z: calcd for $C_{44}H_{58}NO_2^+$: 632.4422; found: 632.4464.

Characterization data for products

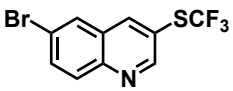
3a, 4j, 4k, 4l, 4n, 4o, 4q, 4aa, 4ab have been reported in the known literature.



3-((trifluoromethyl)thio) quinoline (3a): White solid (17.2 mg, 75 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.07 (d, *J* = 2.2 Hz, 1H), 8.56 (d, *J* = 2.2 Hz, 1H), 8.19 (dq, *J* = 8.5, 0.9 Hz, 1H), 7.98 – 7.79 (m, 2H), 7.68 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H).

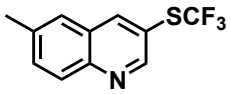


6-fluoro-3-((trifluoromethyl)thio) quinoline (3b): White solid (17.4mg, 70 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.02 (d, *J* = 2.1 Hz, 1H), 8.51 (d, *J* = 2.1 Hz, 1H), 8.19 (dd, *J* = 9.3, 5.2 Hz, 1H), 7.73 – 7.59 (m, 1H), 7.52 (dd, *J* = 8.4, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.3, 159.8, 153.8 (d, *J* = 2.8 Hz), 145.6, 143.8 (d, *J* = 5.5 Hz), 132.2 (d, *J* = 9.2 Hz), 128.5 (q, *J*= 310.07 Hz),122.0 (d, *J* = 25.8 Hz), 119.5, 111.1 (d, *J* = 22.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.06, -110.78. HRMS (ESI) m/z: calcd for $C_{10}H_6F_4NS^+$ [M+H]$^+$: 248.0152. found: 248.0151.

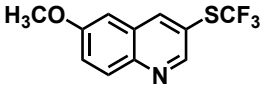


6-bromo-3-((trifluoromethyl)thio) quinoline (3c): White solid (18.4 mg, 60 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.09 – 8.99 (m, 1H), 8.44 (d, *J* = 2.2 Hz, 1H), 8.07 – 8.01 (m, 2H), 7.90 (dd, *J* = 9.0, 2.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 147.0, 143.4, 135.1, 131.3,

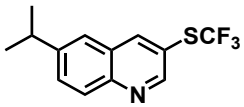
130.6, 130.0, 128.8 (q, *J*= 306.2 Hz), 127.6, 121.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.06. HRMS (ESI) m/z: calcd for $C_{10}H_6BrF_3NS^+$ $[M+H]^+$: 307.9351. found: 307.9352.



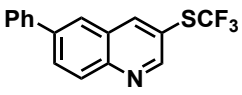
6-methyl-3-((trifluoromethyl)thio) quinoline (3d): White solid (18.1 mg, 74 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.43 (d, *J* = 2.1 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.66 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.63 (s, 1H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.7, 147.1, 144.1, 137.9, 134.0, 129.2 (q, *J*= 308.05 Hz), 129.2, 127.7, 126.8, 118.2, 21.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.41. HRMS (ESI) m/z: calcd for $C_{11}H_9F_3NS^+$ $[M+H]^+$: 244.0402. found: 244.0405.



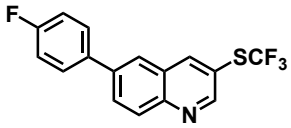
6-methoxy-3-((trifluoromethyl)thio)quinoline (3e): White solid (18.2 mg, 70 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.88 (d, *J* = 2.0 Hz, 1H), 8.41 (d, *J* = 2.1 Hz, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.47 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.10 (d, *J* = 2.8 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6, 152.1, 144.7, 143.2, 130.9, 129.1 (q, J= 305.2 Hz), 124.7, 118.6, 105.1, 55.7.^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.32. HRMS (ESI) m/z: calcd for $C_{11}H_9F_3NOS^+$ $[M+H]^+$: 260.0351. found: 260.0352.



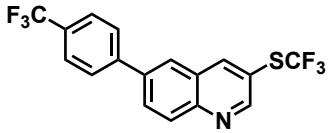
6-isopropyl-3-((trifluoromethyl)thio)quinoline (3f): White solid (16.3 mg, 60 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.00 (s, 1H), 8.50 (d, *J* = 2.1 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.77 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 3.16 (p, *J* = 6.9 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.8, 148.7, 147.4, 144.4, 131.8, 129.3, 129.2 (q, *J*= 288.1 Hz), 127.9, 124.1, 118.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.43. HRMS (ESI) m/z: calcd for $C_{13}H_{13}F_3NOS^+$ $[M+H]^+$:272.0715. found: 272.0715.



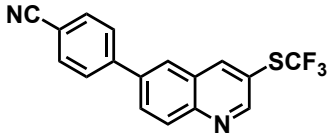
6-phenyl-3-((trifluoromethyl)thio)quinoline (3g)： White solid (22.0 mg, 72 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.03 (s, 1H), 8.57 (d, *J* = 2.1 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.10 (dd, *J* = 8.7, 2.1 Hz, 1H), 8.04 (d, *J* = 2.1 Hz, 1H), 7.72 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.52 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.49 – 7.39 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.5, 147.8, 144.8, 140.7, 139.6, 131.5, 130.8, 129.9, 129.1, 129.0 (q, *J*= 310.2 Hz), 128.2, 127.5, 125.6, 118.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.26. HRMS (ESI) m/z: calcd for $C_{16}H_{11}F_3NS^+$ $[M+H]^+$:306.0559. found: 306.0560.



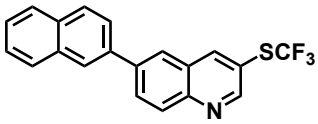
6-(4-fluorophenyl)-3-((trifluoromethyl)thio) quinoline (3h): White solid (27.5 mg, 85 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.06 (d, *J* = 2.2 Hz, 1H), 8.60 (d, *J* = 2.2 Hz, 1H), 8.32 – 8.23 (m, 1H), 8.12 – 8.02 (m, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.0 (d, *J* = 248.2 Hz), 154.5, 147.7, 144.7, 139.7, 135.8 (d, *J* = 3.3 Hz), 131.3, 130.1, 129.4 (q, *J* = 259.7 Hz), 129.1 (d, *J* = 8.2 Hz), 128.0, 127.7, 125.5, 116.1 (d, *J* = 21.6 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.24, -114.01. HRMS (ESI) m/z: calcd for $C_{16}H_{10}F_4NS^+$ $[M+H]^+$:324.0465. found: 324.0465.



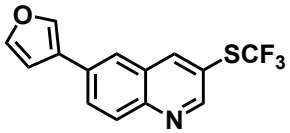
6-(4-(trifluoromethyl)phenyl)-3-((trifluoromethyl)thio)quinoline (3i): White solid (33.2 mg, 89 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.06 (d, *J* = 2.2 Hz, 1H), 8.60 (d, *J* = 2.2 Hz, 1H), 8.32 – 8.23 (m, 1H), 8.13 – 8.05 (m, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.9, 148.0, 144.8, 143.2, 139.2, 131.1, 130.6 (q, *J* = 32.6 Hz), 130.4, 129.3 (q, *J* = 274.4 Hz), 127.9, 127.8, 127.6, 126.2, 126.1 (q, *J* = 3.8 Hz), 124.1 (d, *J* = 272.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.18, -62.54. HRMS (ESI) m/z: calcd for $C_{17}H_{10}F_6NS^+$ $[M+H]^+$:374.0433. found: 374.0434.



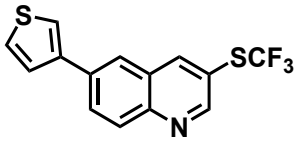
4-(3-((trifluoromethyl)thio)quinolin-6-yl)benzonitrile (3j): White solid (26.5 mg, 80 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.03 (d, *J* = 2.2 Hz, 1H), 8.56 (d, *J* = 2.2 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.04 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.99 (d, *J* = 2.1 Hz, 1H), 7.73 – 7.62 (m, 2H), 7.21 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2, 161.8, 154.5, 147.7, 144.7, 139.7, 135.8 (d, *J* = 3.3 Hz), 131.2, 130.1, 129.2, 129.1, 129.07 (q, *J* = 274.4 Hz), 125.4, 116.2, 115.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.06. HRMS (ESI) m/z: calcd for $C_{17}H_{10}F_3N_2S^+$ $[M+H]^+$:331.0511. found: 331.0512.



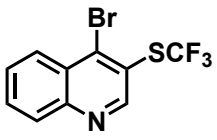
6-(naphthalen-2-yl)-3-((trifluoromethyl)thio) quinoline (3k): White solid (23.5 mg, 66 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.09 (d, *J* = 2.2 Hz, 1H), 8.58 (d, *J* = 2.1 Hz, 1H), 8.35 – 8.23 (m, 1H), 8.08 – 7.91 (m, 4H), 7.91 – 7.80 (m, 1H), 7.66 – 7.40 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.7, 147.7, 144.7, 140.65, 138.6, 134.3, 133.8, 133.6, 131.4, 129.5 (q, J= 262.6Hz), 129.3, 128.6, 128.5, 127.9, 127.7, 127.4, 126.6, 126.1, 125.5, 125.4. HRMS (ESI) m/z: calcd for $C_{20}H_{13}F_3NS^+$ $[M+H]^+$:356.0715. found: 356.0716.



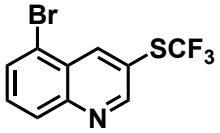
6-(furan-3-yl)-3-((trifluoromethyl)thio) quinoline (3l): White solid (19.2 mg, 65 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.99 (s, 1H), 8.51 (d, *J* = 2.1 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.97 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.56 (t, *J* = 1.7 Hz, 1H), 6.84 (dd, *J* = 1.9, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.1, 147.7, 144.4, 144.36, 139.6, 134.1, 132.1, 130.3, 130.0, 129.2 (q, *J*= 310.67 Hz), 128.2, 125.4, 123.6, 108.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.38. HRMS (ESI) m/z: calcd for $C_{14}H_9F_3NOS^+$ $[M+H]^+$:296.0351. found: 296.0357.



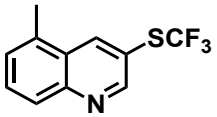
6-(thiophen-3-yl)-3-((trifluoromethyl)thio) quinoline (3m): White solid (23.1 mg, 74 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.02 (d, *J* = 2.2 Hz, 1H), 8.56 (d, *J* = 2.2 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 8.12 (dd, *J* = 8.8, 2.1 Hz, 1H), 8.06 (d, *J* = 2.0 Hz, 1H), 7.67 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.55 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.51 (dd, *J* = 5.0, 2.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.3, 147.697, 144.6, 140.8, 135.2, 130.9, 130.0, 129.2 (d, *J* = 308.8 Hz), 128.2, 127.1, 126.2, 124.4, 122.0, 118.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.38. HRMS (ESI) m/z: calcd for $C_{14}H_9F_3NS_2^+$ $[M+H]^+$:312.0123. found: 312.0125.



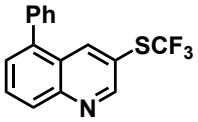
4-bromo-3-((trifluoromethyl)thio) quinoline (3n): White solid (6.47 mg, 21 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.08 (s, 1H), 8.92 (s, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.1, 149.2, 143.9, 131.8, 131.6, 130.6, 129.5, 129.1 (q, *J*= 308.2 Hz), 122.0, 120.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.06. HRMS (ESI) m/z: calcd for $C_{10}H_6BrF_3NS^+$ $[M+H]^+$:307.9351. found: 307.9353.



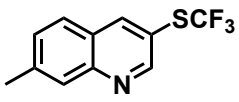
5-bromo-3-((trifluoromethyl)thio)quinoline (3o)： White solid (7.7 mg, 25 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.08 (d, *J* = 2.2 Hz, 1H), 8.92 (d, *J* = 2.1 Hz, 1H), 8.16 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.95 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.71 (dd, *J* = 8.5, 7.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.14, 149.19, 143.97, 131.80, 131.58, 129.49, 129.06 (q, *J*= 310.4 Hz)127.43, 122.02, 120.10. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.96. HRMS (ESI) m/z: calcd for $C_{10}H_6BrF_3NS^+$ $[M+H]^+$:307.9351. found: 307.9355.



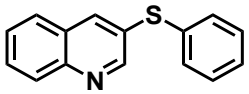
5-methyl-3-((trifluoromethyl)thio)quinoline (3p): White solid (6.1 mg, 25 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.07 (s, 1H), 8.70 (d, *J* = 2.1 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.84 – 7.66 (m, 1H), 7.50 (d, *J* = 7.1 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.2, 148.8, 141.4, 135.2, 131.4, 129.2 (q, *J*= 311.1 Hz), 128.3, 127.8, 127.3, 117.9, 18.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.41. HRMS (ESI) m/z: calcd for $C_{11}H_9F_3NS^+$ $[M+H]^+$:244.0402. found: 244.0403.



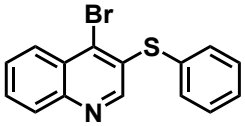
5-phenyl-3-((trifluoromethyl)thio)quinoline (3q): White solid (15.3 mg, 50 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.05 (d, *J* = 2.1 Hz, 1H), 8.59 (d, *J* = 2.1 Hz, 1H), 8.18 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.88 (dd, *J* = 8.5, 7.1 Hz, 1H), 7.61 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.59 – 7.40 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.4, 148.7, 143.3, 141.0, 138.4, 131.1, 129.9, 129.0 (q, *J*= 310.2 Hz),128.9, 128.8, 128.4, 128.2, 126.4, 118.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.38. HRMS (ESI) m/z: calcd for $C_{16}H_{11}F_3NS^+$ $[M+H]^+$: 306.0559. found: 306.0560.



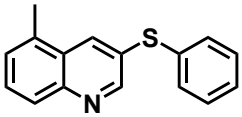
7-methyl-3-((trifluoromethyl)thio)quinoline (3r): White solid (10.7 mg, 44 % yield).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.99 (d, *J* = 2.2 Hz, 1H), 8.47 (d, *J* = 2.2 Hz, 1H), 7.93 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.48 (dd, *J* = 8.4, 1.7 Hz, 1H), 2.61 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.7, 148.7, 144.5, 142.5, 130.1, 129.2 (q, *J*= 308.1 Hz), 128.5, 127.7, 125.9, 117.2, 22.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.41. HRMS (ESI) m/z: calcd for $C_{11}H_9F_3NS^+$ $[M+H]^+$:244.0402. found: 244.0403.



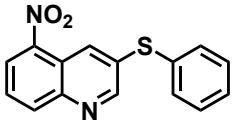
3-(phenylthio)quinoline (4a): White solid (22.5 mg, 95 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 8.08 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.76 – 7.64 (m, 2H), 7.54 (td, *J* = 7.2, 6.7, 1.1 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.27 (m, 3H).



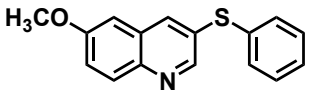
4-bromo-3-(phenylthio)quinoline (4b)： White solid (23.7 mg, 75 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 2.2 Hz, 1H), 8.42 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.83 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.54 (dd, *J* = 8.5, 7.5 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.43 – 7.34 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.2, 147.2, 135.3, 133.2, 132.6, 132.1, 131.0, 129.7, 129.5, 129.2, 128.3, 127.7, 121.2. HRMS (ESI) m/z: calcd for $C_{15}H_{11}BrNS^{+}$ $[M+H]^{+}$:315.9790. found: 315.9791.



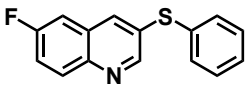
5-methyl-3-(phenylthio)quinoline (4c): White solid (24.2 mg, 96 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 2.2 Hz, 1H), 8.31 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.59 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.35 – 7.27 (m, 3H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.1, 147.0, 134.9, 134.6, 134.2, 130.8, 129.48, 129.46, 129.1, 127.8, 127.6, 127.5, 18.5. HRMS (ESI) m/z: calcd for $C_{16}H_{14}NS^{+}$ $[M+H]^{+}$:252.0841. found: 252.0842.



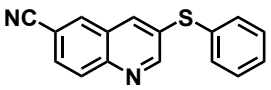
5-nitro-3-(phenylthio)quinoline (4d): White solid (20.7 mg, 73 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (d, *J* = 2.2 Hz, 1H), 8.73 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.35 (ddd, *J* = 8.4, 4.9, 1.2 Hz, 2H), 7.71 (dd, *J* = 8.4, 7.7 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.49 – 7.40 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.5, 146.2, 144.5, 136.7, 136.4, 133.6, 131.1, 130.1, 129.3, 129.2, 126.8, 125.4, 121.3. HRMS (ESI) m/z: calcd for $C_{15}H_{11}N_2O_2S^{+}$ $[M+H]^{+}$:283.0536. found: 283.0535.



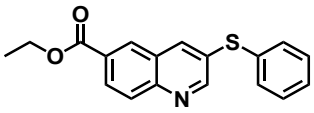
6-methoxy-3-(phenylthio)quinoline (4e): White solid (26.5 mg, 99 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 2.2 Hz, 1H), 8.00 – 7.88 (m, 2H), 7.44 – 7.37 (m, 2H), 7.37 – 7.27 (m, 4H), 6.94 (d, *J* = 2.8 Hz, 1H). 3.90 (s, 3H) ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.3, 149.5, 142.8, 135.8, 134.4, 131.4, 130.7, 130.4, 129.5, 129.4, 127.7, 122.4, 104.7, 55.6. HRMS (ESI) m/z: calcd for $C_{16}H_{14}NOS^+$ $[M+H]^+$:268.0791. found: 268.0798.



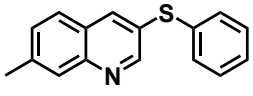
6-fluoro-3-(phenylthio)quinoline (4f): White solid (23.0 mg, 90 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 2.3 Hz, 1H), 8.05 (dd, *J* = 9.2, 5.3 Hz, 1H), 7.90 (d, *J* = 2.3 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.44 – 7.33 (m, 5H), 7.29 (dd, *J* = 8.8, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.9 (d, *J* = 249.2 Hz), 150.8 (d, *J* = 2.8 Hz), 143.6, 134.9 (d, *J* = 5.4 Hz), 133.2, 132.2, 132.1, 131.8 (d, *J* = 9.4 Hz), 129.7, 128.9 (d, *J* = 9.9 Hz), 128.3, 119.5 (d, *J* = 25.9 Hz), 110.2 (d, *J* = 22.1 Hz). HRMS (ESI) m/z: calcd for $C_{15}H_{11}FNS^+$ $[M+H]^+$:256.0591. found: 256.0593.



3-(phenylthio)quinoline-6-carbonitrile (4g): White solid (17.6 mg, 67 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 8.07 (d, *J* = 1.8 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.81 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.47 – 7.43 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5, 147.0, 134.4, 134.1, 133.2, 133.1, 131.7, 130.8, 130.0, 129.8, 129.0, 127.6, 118.4, 111.1. HRMS (ESI) m/z: calcd for $C_{16}H_{11}N_2S^+$ $[M+H]^+$:263.0637. found: 263.0635.

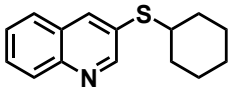


ethyl 3-(phenylthio)quinoline-6-carboxylate (4h): White solid (22.6 mg, 73 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.85 (d, *J* = 2.3 Hz, 1H), 8.43 (d, *J* = 1.9 Hz, 1H), 8.25 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.09 (d, *J* = 8.8, 1H), 8.04 (d, *J* = 2.3, 1H), 7.50 – 7.43 (m, 2H), 7.41 – 7.33 (m, 3H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 153.4, 148.2, 136.7, 133.1, 132.3, 132.1, 130.1, 129.8, 129.6, 129.1, 128.9, 128.4, 127.5, 61.5, 14.4. HRMS (ESI) m/z: calcd for $C_{18}H_{16}NO_2S^+$ $[M+H]^+$:310.0896. found: 310.0898.

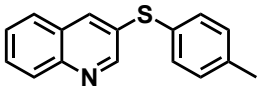


7-methyl-3-(phenylthio)quinoline (4i): White solid (22.2 mg, 88 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79 (d, *J* = 2.3 Hz, 1H), 8.07 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.86 (s, 1H), 7.61 (d, *J* = 8.3

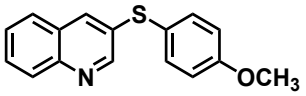
Hz, 1H), 7.42 – 7.25 (m, 6H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.6, 147.0, 140.2, 137.7, 135.0, 130.8, 129.6, 129.4, 128.5, 128.3, 127.4, 126.9, 126.3, 21.9. HRMS (ESI) m/z: calcd for $C_{16}H_{14}NS^+$ $[M+H]^+$:252.0841. found: 252.0842.



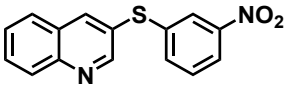
3-(cyclohexylthio)quinoline (4j): White solid (9.4 mg, 40 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 8.17 (d, *J* = 1.4 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 3.20 (tt, *J* = 10.6, 3.7 Hz, 1H), 2.06 – 1.95 (m, 2H), 1.84 – 1.77 (m, 2H), 1.66 – 1.57 (m, 1H), 1.45 – 1.23 (m, 5H).



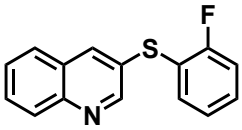
3-(p-tolylthio)quinoline (4k)： White solid (10.0 mg, 40 % yield). White solid (33.2 mg, 89 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 2.3 Hz, 1H), 8.06 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.97 (dd, *J* = 2.3, 0.8 Hz, 1H), 7.73 – 7.59 (m, 2H), 7.52 (td, *J* = 7.2, 1.2 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H).



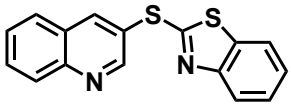
3-((4-methoxyphenyl)thio)quinoline (4l)： White solid (9.4 mg, 35 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 2.3 Hz, 1H), 8.07 – 7.99 (m, 1H), 7.83 (d, *J* = 1.1 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.57 – 7.41 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H).



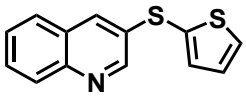
3-((3-nitrophenyl)thio)quinoline (4m): White solid (11.9 mg, 42 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.88 (d, *J* = 2.2 Hz, 1H), 8.31 (dd, *J* = 2.3, 0.8 Hz, 1H), 8.21 – 8.11 (m, 2H), 8.07 (ddd, *J* = 8.1, 2.2, 1.0 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.62 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.56 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.1, 147.4, 140.4, 138.9, 134.8, 130.9, 130.1, 129.5, 128.3, 127.8, 127.6, 126.6, 123.9, 122.2, 121.8. HRMS (ESI) m/z: calcd for $C_{15}H_{11}N_2O_2S^+$ $[M+H]^+$:283.0836. found: 283.0838.



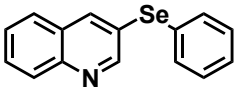
3-((2-fluorophenyl)thio)quinoline (4n): White solid (11.5 mg, 45 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 8.23 – 7.87 (m, 2H), 7.76 – 7.64 (m, 2H), 7.55 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.40 – 7.30 (m, 2H), 7.18 – 7.07 (m, 2H).



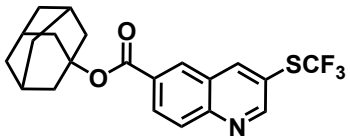
2-(quinolin-3-ylthio)benzo[d]thiazole (4o): White solid (19.1 mg, 65 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.11 (d, *J* = 2.3 Hz, 1H), 8.59 (d, *J* = 2.2 Hz, 1H), 8.26 – 8.15 (m, 1H), 7.94 – 7.78 (m, 3H), 7.73 – 7.58 (m, 2H), 7.43 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H).



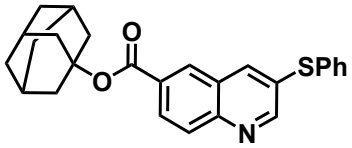
3-(thiophen-2-ylthio)quinoline (4p): White solid (11.5 mg, 47 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (d, *J* = 2.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 2.3 Hz, 1H), 7.77 – 7.58 (m, 2H), 7.58 – 7.47 (m, 2H), 7.40 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.14 (dd, *J* = 5.4, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.6, 146.4, 136.4, 133.5, 132.4, 131.8, 129.8, 129.3, 129.28, 128.2, 128.16, 127.3, 127.2. HRMS (ESI) m/z: calcd for $C_{13}H_{10}NS_2^+$ $[M+H]^+$:244.0249. found: 244.0250.



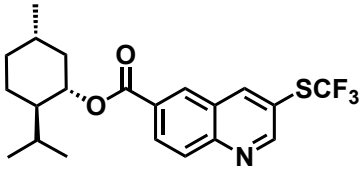
3-(phenylselanyl)quinoline (4q)： White solid (27.1 mg, 95 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.92 (d, *J* = 2.1 Hz, 1H), 8.25 (d, *J* = 2.2 Hz, 1H), 8.13 – 8.01 (m, 1H), 7.82 – 7.65 (m, 2H), 7.59 – 7.48 (m, 3H), 7.34 – 7.26 (m, 3H).



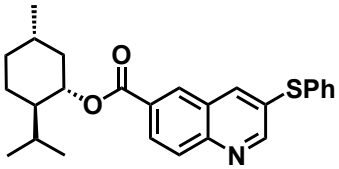
adamantan-1-yl 3-((trifluoromethyl)thio)quinoline-6-carboxylate (5a): White solid (24.5 mg, 60 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.10 (d, *J* = 2.3 Hz, 1H), 8.63 (d, *J* = 2.2 Hz, 1H), 8.55 (d, *J* = 1.9 Hz, 1H), 8.37 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 2.31 (s, 6H), 2.26 (s, 3H), 1.74 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3, 156.2, 149.9, 145.8, 131.4, 131.3, 130.6, 129.6, 129.3 (q, *J*= 248.6 Hz), 127.6, 126.9, 82.2, 41.5, 36.2, 30.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.17. HRMS calculated for $C_{21}H_{21}F_3NO_2S^+$ $[M+H]^+$= 408.1240; found: 408.1241.



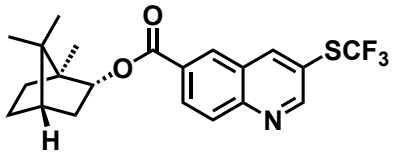
adamantan-1-yl 3-(phenylthio)quinoline-6-carboxylate (5b): White solid (41.2 mg, 99 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (d, *J* = 2.3 Hz, 1H), 8.36 (d, *J* = 1.8 Hz, 1H), 8.21 (dd, *J* = 8.9, 1.9 Hz, 1H), 8.06 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.40 – 7.30 (m, 3H), 2.29 (s, 6H), 2.24 (s, 3H), 1.78 – 1.63 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.7, 153.4, 148.1, 137.1, 133.4, 132.1, 131.6, 130.8, 129.8, 129.7, 129.3, 129.1, 128.2, 127.4, 81.8, 41.4, 36.2, 30.9. HRMS calculated for $C_{26}H_{26}NO_2S^+$ $[M+H]^+$= 416.1679; found: 416.1680.



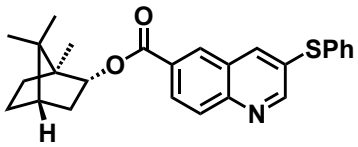
(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 3-((trifluoromethyl)thio)quinoline-6-carboxylate (6a): White solid (27.6 mg, 67 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.11 (d, *J* = 2.2 Hz, 1H), 8.64 (dd, *J* = 12.1, 2.1 Hz, 2H), 8.42 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 5.03 (td, *J* = 10.9, 4.4 Hz, 1H), 2.21 – 2.13 (m, 1H), 1.98 (pd, *J* = 6.9, 2.8 Hz, 1H), 1.82 – 1.73 (m, 2H), 1.61 (ddt, *J* = 14.3, 11.2, 5.4 Hz, 3H), 1.21 – 1.09 (m, 2H), 0.95 (dd, *J* = 6.8, 3.0 Hz, 6H), 0.82 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0, 156.4, 150.0, 145.8, 131.2, 130.9, 130.4, 130.1, 129.8, 129.4 (q, *J*= 253.5 Hz), 127.0, 47.3, 40.9, 34.3, 31.5, 26.6, 23.6, 22.0, 20.8, 16.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.12. HRMS calculated for $C_{21}H_{25}F_3NO_2S^+$ $[M+H]^+$= 412.1553; found: 412.1556.



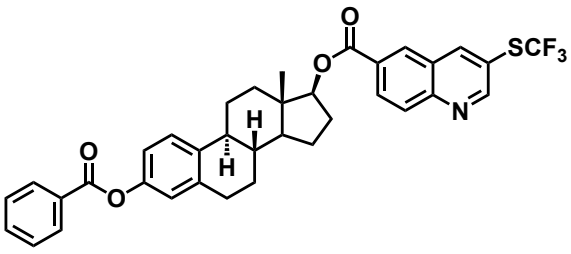
(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 3 - (phenylthio) quinoline – 6 - carboxylate (6b): White solid (30.7 mg, 73 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 8.43 (d, *J* = 1.9 Hz, 1H), 8.26 (dd, *J* = 8.7, 1.9 Hz, 1H), 8.13 – 8.03 (m, 2H), 7.48 – 7.42 (m, 2H), 7.40 – 7.28 (m, 3H), 5.00 (td, *J* = 10.9, 4.4 Hz, 1H), 2.20 – 2.06 (m, 1H), 1.97 (td, *J* = 7.0, 2.8 Hz, 1H), 1.82 – 1.46 (m, 5H), 1.24 – 1.06 (m, 2H), 0.94 (d, *J* = 4.7 Hz, 3H), 0.93 (d, *J* = 5.3 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 153.4, 148.1, 136.9, 133.2, 132.2, 131.9, 130.0, 129.7, 129.5, 129.48, 129.0, 128.3, 127.5, 75.4, 47.3, 41.0, 34.3, 31.5, 26.5, 23.6, 22.0, 20.8, 16.5. HRMS calculated for $C_{26}H_{30}NO_2S^+$ $[M+H]^+$= 420.1992; found: 420.1995.



(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-((trifluoromethyl)thio) quinoline-6-carboxylate (7a): White solid (15.2 mg, 37 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 8.67 (d, *J* = 2.2 Hz, 1H), 8.62 (d, *J* = 1.9 Hz, 1H), 8.43 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 5.30 – 5.11 (m, 1H), 2.59 – 2.44 (m, 1H), 2.22 – 2.14 (m, 1H), 1.95 – 1.74 (m, 2H), 1.52 – 1.42 (m, 1H), 1.36 (ddd, *J* = 12.1, 9.4, 4.3 Hz, 1H), 1.18 (dd, *J* = 13.9, 3.5 Hz, 1H), 1.00 (s, 3H), 0.96 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 163.7, 156.4, 150.0, 145.8, 134.9, 131.2, 130.8, 130.2, 129.9, 128.4 (q, *J*= 278.76 Hz)，81.5, 49.2, 48.0, 44.9, 36.9, 28.1, 27.5, 19.7, 18.9, 13.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.09. HRMS calculated for $C_{21}H_{23}F_3NO_2S^+$ $[M+H]^+$= 410.1396; found: 410.1397.

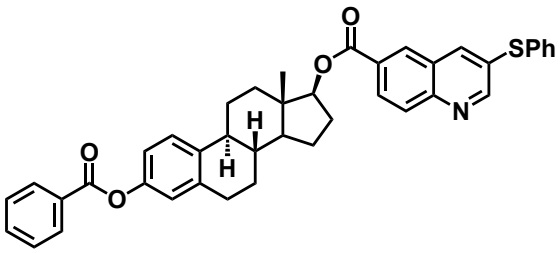


(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3 - (phenylthio) quinoline -6-carboxylate (7b): White solid (50.3 mg, 97 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.86 (d, *J* = 2.3 Hz, 1H), 8.44 (d, *J* = 1.9 Hz, 1H), 8.27 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.45 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.41 – 7.29 (m, 3H), 5.18 (ddd, *J* = 10.0, 3.5, 2.1 Hz, 1H), 2.60 – 2.37 (m, 1H), 2.16 (ddd, *J* = 13.3, 9.4, 4.4 Hz, 1H), 1.92 – 1.66 (m, 2H), 1.50 – 1.40 (m, 1H), 1.34 (ddd, *J* = 12.1, 9.4, 4.4 Hz, 1H), 1.16 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.98 (s, 3H), 0.94 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 153.6, 148.2, 137.1, 133.3, 132.1, 131.8, 130.0, 129.7, 129.6, 129.5, 128.9, 128.3, 127.5, 81.2, 49.2, 47.9, 45.0, 36.9, 28.1, 27.5, 19.7, 18.9, 13.7. HRMS calculated for $C_{26}H_{28}NO_2S^+$ $[M+H]^+$= 518.1835; found: 518.1837.

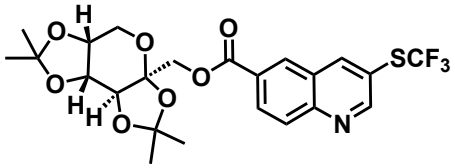


(8R,9S,13S,17S)-3-(benzoyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl 3-((trifluoromethyl)thio)quinoline-6-carboxylate (8a): White solid (33.5 mg, 53 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (d, *J* = 2.3 Hz, 1H), 8.64 (dd, *J* = 11.6, 2.0 Hz, 2H), 8.43 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.24 – 8.20 (m, 2H), 8.19 (d, *J* = 1.5 Hz, 1H), 7.69 – 7.58 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* =

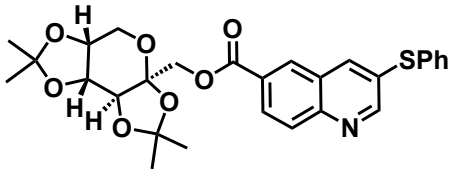
8.4, 2.6 Hz, 1H), 6.95 (d, *J* = 2.5 Hz, 1H), 5.04 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.15 – 2.72 (m, 2H), 2.51 – 2.29 (m, 3H), 2.08 – 1.91 (m, 1H), 2.00 – 1.93 (m, 1H), 1.91 – 1.72 (m, 2H), 1.59 – 1.38 (m, 6H), 1.06 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 156.5, 148.8, 145.8, 138.2, 137.9, 137.8, 137.5, 133.5, 131.2, 130.9, 130.2, 129.99, 129.9, 129.7, 129.3 (q, *J*= 250.48 Hz), 128.5, 127.0, 126.5, 121.7, 118.8, 83.9, 49.9, 44.0, 43.5, 38.3, 37.0, 29.6, 27.8, 27.1, 26.1, 23.4, 12.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.08. HRMS calculated for $C_{36}H_{33}F_3NO_4S^+$ $[M+H]^+$= 632.2077; found: 632.2078.



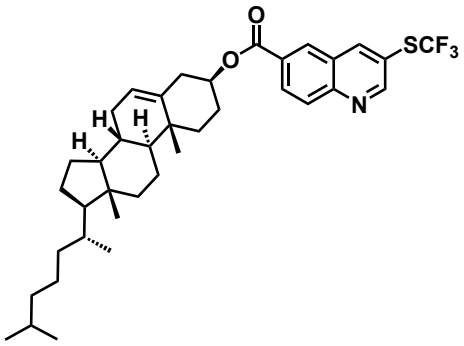
(8R,9S,13S,17S)-3-(benzoyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-deca hydro-6H-cyclopenta[a]phenanthren-17-yl-3-(phenylthio)quinoline-6-car boxylate (8b)： White solid (32.0 mg, 50 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.87 (d, *J* = 2.3 Hz, 1H), 8.44 (d, *J* = 1.9 Hz, 1H), 8.27 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.23 – 8.17 (m, 2H), 8.14 – 8.06 (m, 2H), 7.69 – 7.60 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.42 – 7.30 (m, 4H), 7.04 – 6.88 (m, 2H), 5.01 (dd, *J* = 9.2, 7.7 Hz, 1H), 2.96 – 2.81 (m, 2H), 2.52 – 2.23 (m, 3H), 2.12 – 1.97 (m, 1H), 1.98 – 1.91 (m, 1H), 1.90 – 1.67 (m, 2H), 1.64 – 1.35 (m, 6H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 165.5, 153.6, 148.8, 138.2, 137.8, 136.9, 133.5, 133.2, 132.2, 130.2, 130.1, 129.8, 129.7, 129.6, 128.9, 128.5, 128.3, 126.5, 121.7, 118.7, 83.7, 49.9, 44.0, 43.4, 38.3, 37.0, 29.6, 27.8, 27.1, 26.1, 23.4, 12.5. HRMS calculated for $C_{41}H_{38}NO_4S^+$ $[M+H]^+$= 640.2516; found: 640.2520.



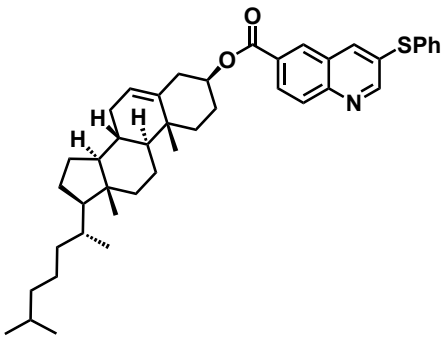
((3aS,5aR,8aR,8bS)-2,2-dimethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 3-((trifluoromethyl)thio)quinoline-6-carboxylate (9a): White solid (42.3 mg, 82 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.15 (s, 1H), 8.71 (d, *J* = 1.9 Hz, 1H), 8.64 (d, *J* = 2.1 Hz, 1H), 8.47 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 4.80 (d, *J* = 11.8 Hz, 1H), 4.69 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.51 (d, *J* = 2.6 Hz, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.31 (dd, *J* = 7.9, 1.8 Hz, 1H), 4.00 (dd, *J* = 13.1, 1.9 Hz, 1H), 3.85 (d, *J* = 13.0 Hz, 1H), 1.59 (s, 3H), 1.49 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (201 MHz, Chloroform-*d*) δ 164.9, 156.6, 150.1, 145.7, 131.4, 131.4, 131.1, 130.0, 129.2, 127.6 (q, *J*= 259.29 Hz), 119.6, 109.2, 108.9, 101.6, 70.8, 70.7, 70.1, 66.2, 61.4, 26.5, 25.9, 25.5, 24.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.12. HRMS calculated for $C_{23}H_{25}F_3NO_7S^+$ $[M+H]^+$= 516.1298; found: 516.1290.



((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 3-(phenylthio)quinoline-6-carboxylate (9b)： White solid (30.6 mg, 58 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 8.47 (d, *J* = 1.9 Hz, 1H), 8.27 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 2.2 Hz, 1H), 7.55 – 7.43 (m, 2H), 7.44 – 7.34 (m, 3H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.47 (d, *J* = 2.6 Hz, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.27 (dd, *J* = 8.0, 1.7 Hz, 1H), 3.96 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.81 (d, *J* = 13.0 Hz, 1H), 1.55 (s, 3H), 1.45 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 153.5, 148.2, 136.4, 132.8, 130.5, 129.8, 129.7, 128.9, 128.6, 128.5, 127.4, 109.2, 108.9, 101.6, 70.8, 70.7, 70.1, 65.9, 61.4, 26.5, 25.9, 25.5, 24.0. HRMS calculated for $C_{28}H_{30}NO_7S^+$ $[M+H]^+$= 527.1737; found: 527.1738.



(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-((trifluoromethyl)thio)quinoline-6-carboxylate (10a): White solid (57.8 mg, 90 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.11 (s, 1H), 8.63 (dd, *J* = 5.1, 2.1 Hz, 2H), 8.42 (dd, *J* = 8.9, 1.9 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 5.45 (d, *J* = 5.0 Hz, 1H), 5.09 – 4.72 (m, 1H), 2.64 – 2.38 (m, 2H), 2.12 – 1.69 (m, 7H), 1.69 – 1.16 (m, 18H), 1.09 (s, 3H), 1.06 – 1.01 (m, 1H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 1.8 Hz, 3H), 0.86 (d, *J* = 1.8 Hz, 3H), 0.70 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 156.3, 150.0, 149.9, 145.7, 139.4, 131.2, 130.9, 130.1, 129.8, 129.5 (q, *J*= 254.5 Hz),127.0, 123.1, 75.5, 56.7, 56.2, 50.1, 42.3, 39.7, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 31.96, 31.9, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 18.7, 11.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.12. HRMS calculated for $C_{38}H_{51}F_3NO_2S^+$ $[M+H]^+$= 642.3587; found: 642.3591.

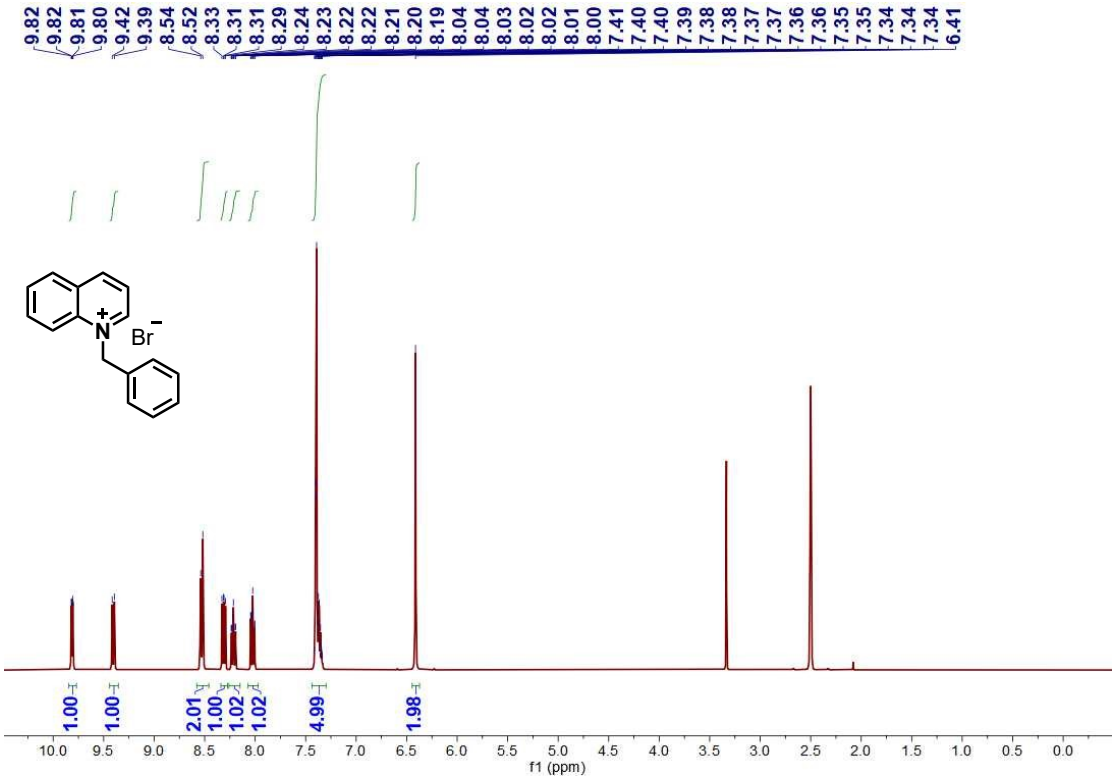


(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-(phenylthio)quinoline-6-carboxylate (10b)：

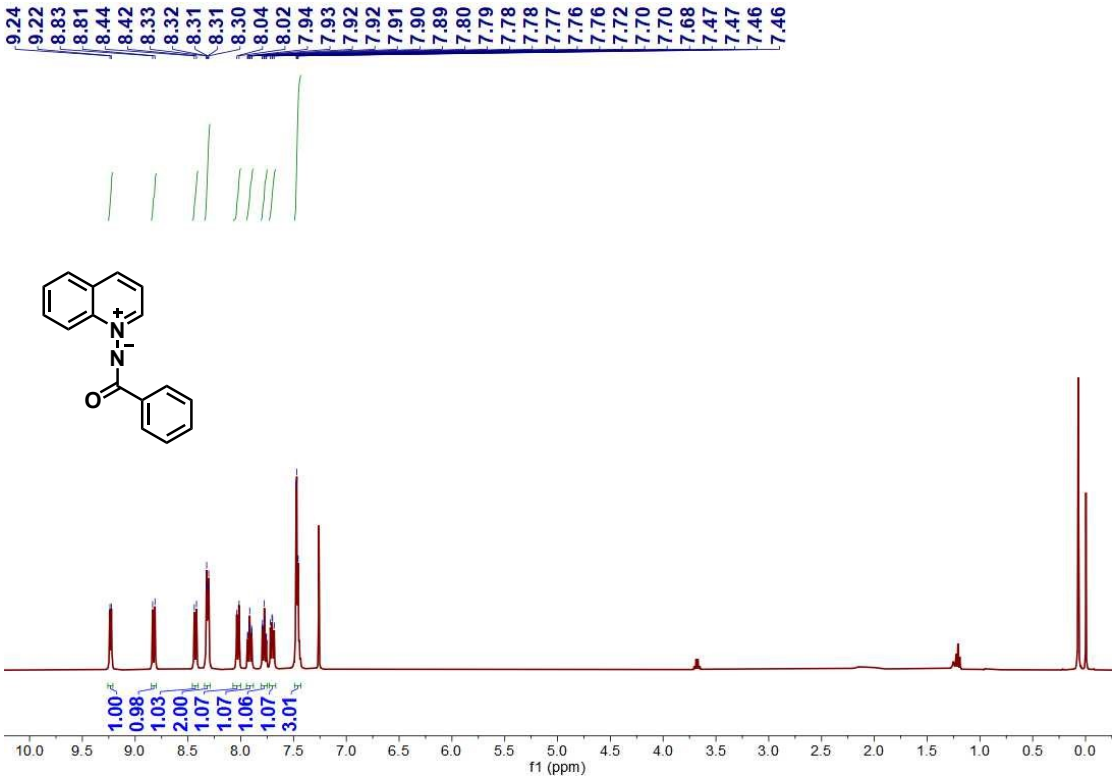
White solid (39.7 mg, 61 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 8.42 (d, *J* = 1.9 Hz, 1H), 8.26 (dd, *J* = 8.7, 1.9 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 2.3 Hz, 1H), 7.46 (dd, *J* = 7.9, 1.9 Hz, 2H), 7.41 – 7.34 (m, 3H), 5.52 – 5.25 (m, 1H), 5.01 – 4.78 (m, 1H), 2.50 (d, *J* = 7.9 Hz, 2H), 2.17 – 1.71 (m, 7H), 1.68 – 1.10 (m, 18H), 1.08 (s, 3H), 1.04 – 0.97 (m, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 1.8 Hz, 3H), 0.86 (d, *J* = 1.8 Hz, 3H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 153.4, 139.5, 136.7, 133.1, 132.3, 131.9, 130.5, 130.4, 130.0, 129.8, 129.5, 128.9, 128.4, 127.5, 122.9, 75.2, 56.7, 56.1, 50.1, 42.3, 39.7, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 31.95, 31.9, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 18.7, 11.9. HRMS calculated for $C_{43}H_{56}NO_2S^+$ $[M+H]^+$= 650.4026; found: 650.4027.

5. Spectra

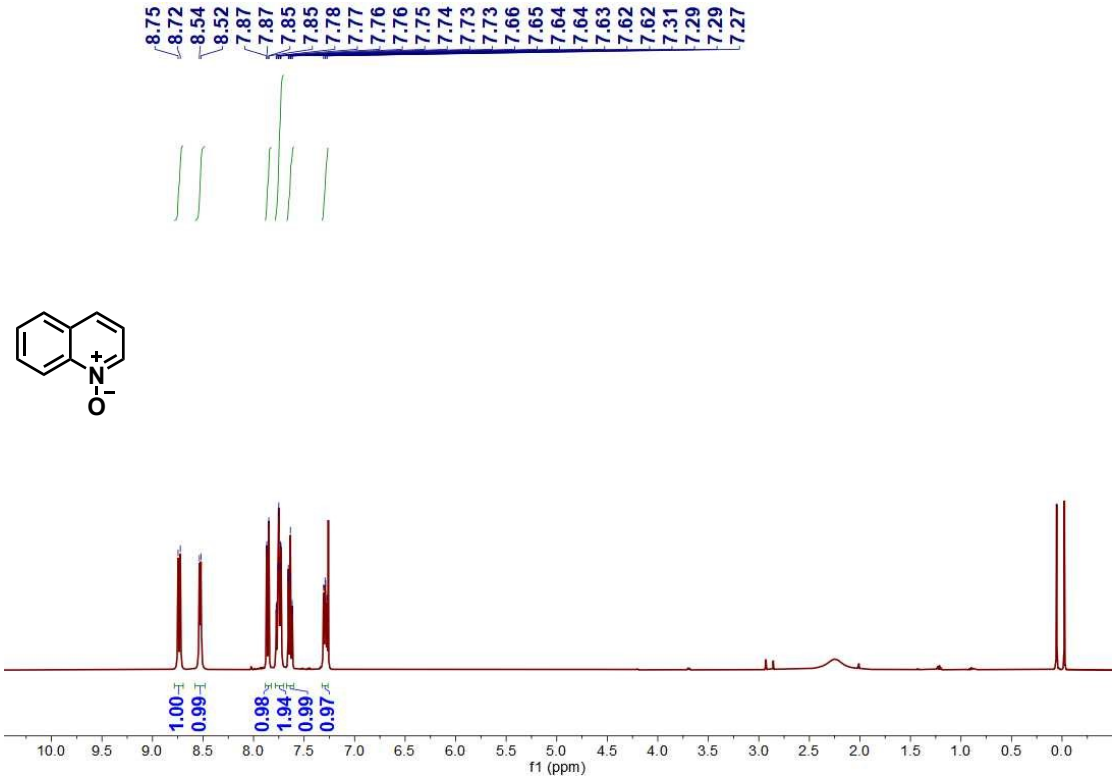
^{1}H NMR of **1a**



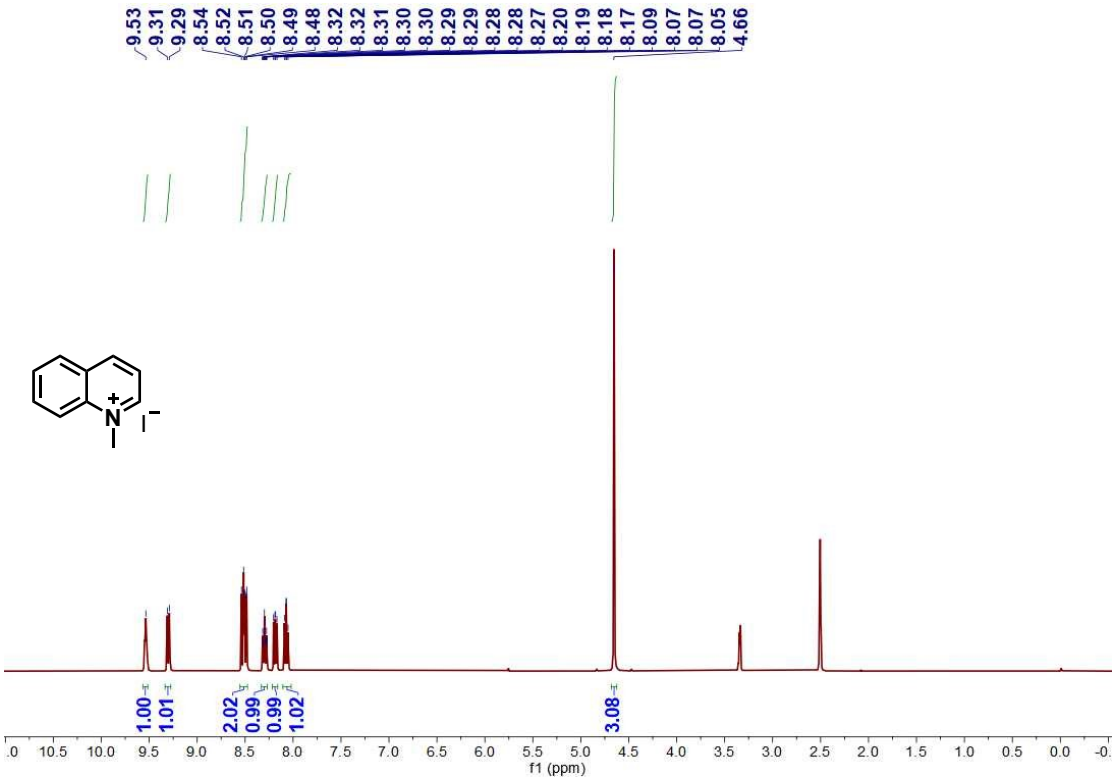
^{1}H NMR of **1b**



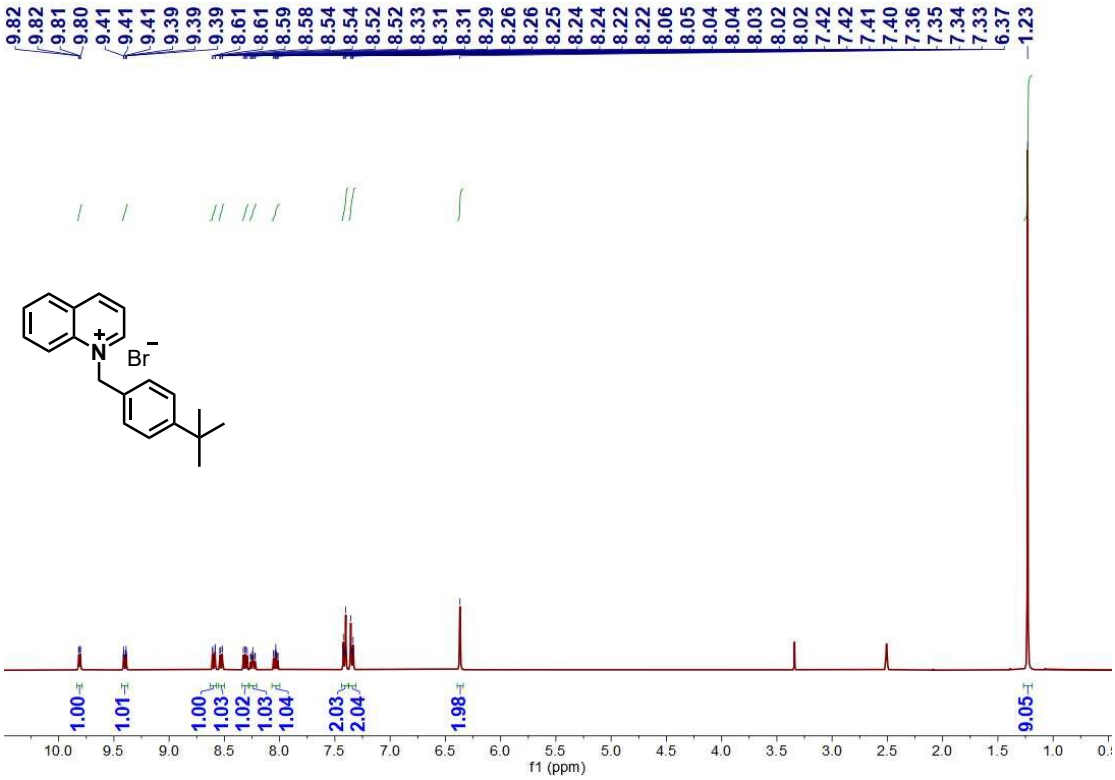
^{1}H NMR of **1c**

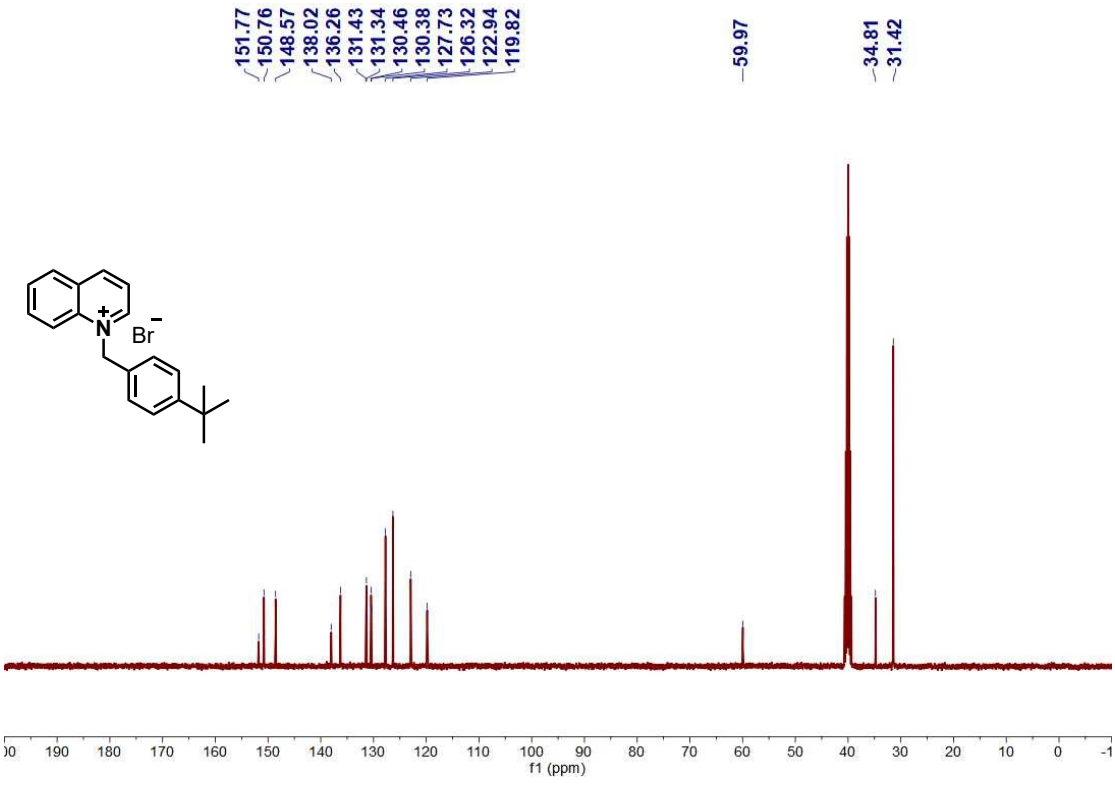


^{1}H NMR of **1d**

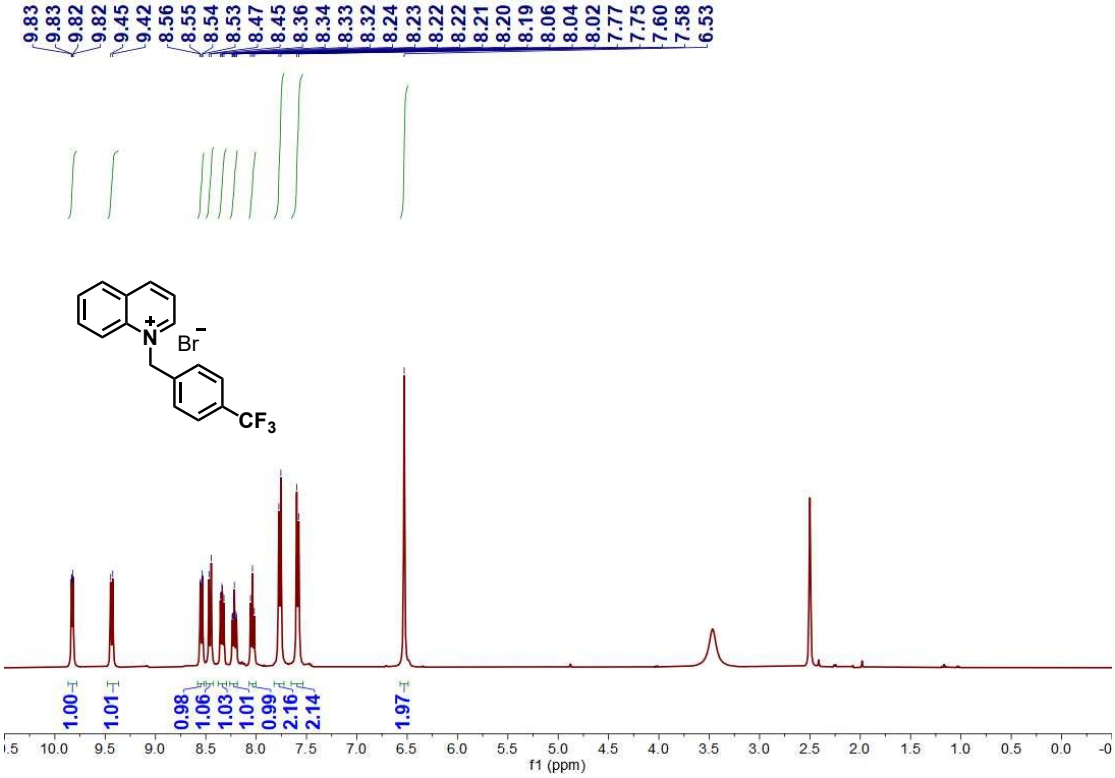


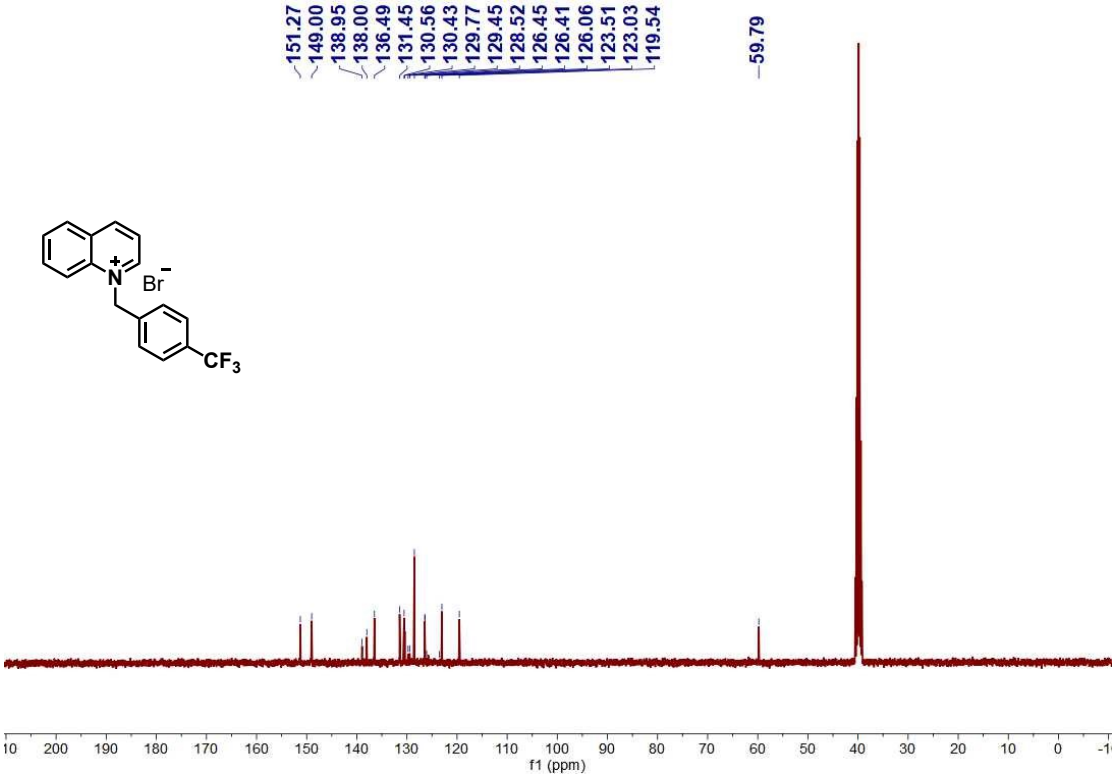
^{1}H NMR and ^{13}C NMR of **1ab**



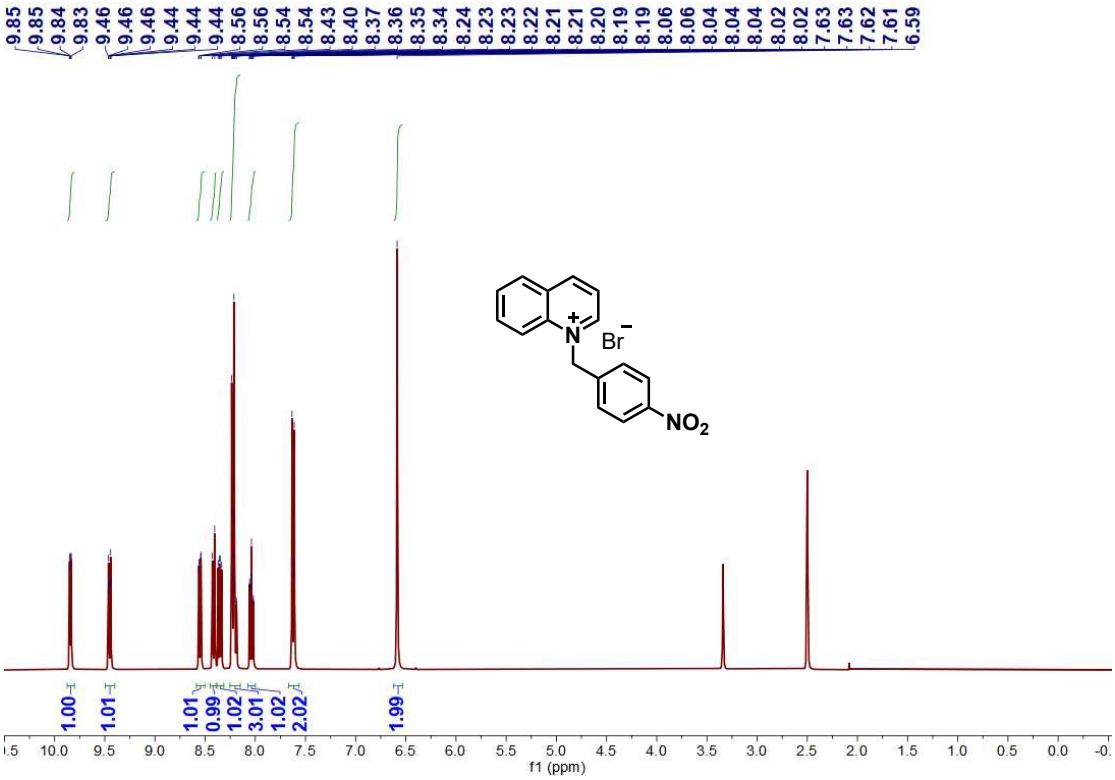


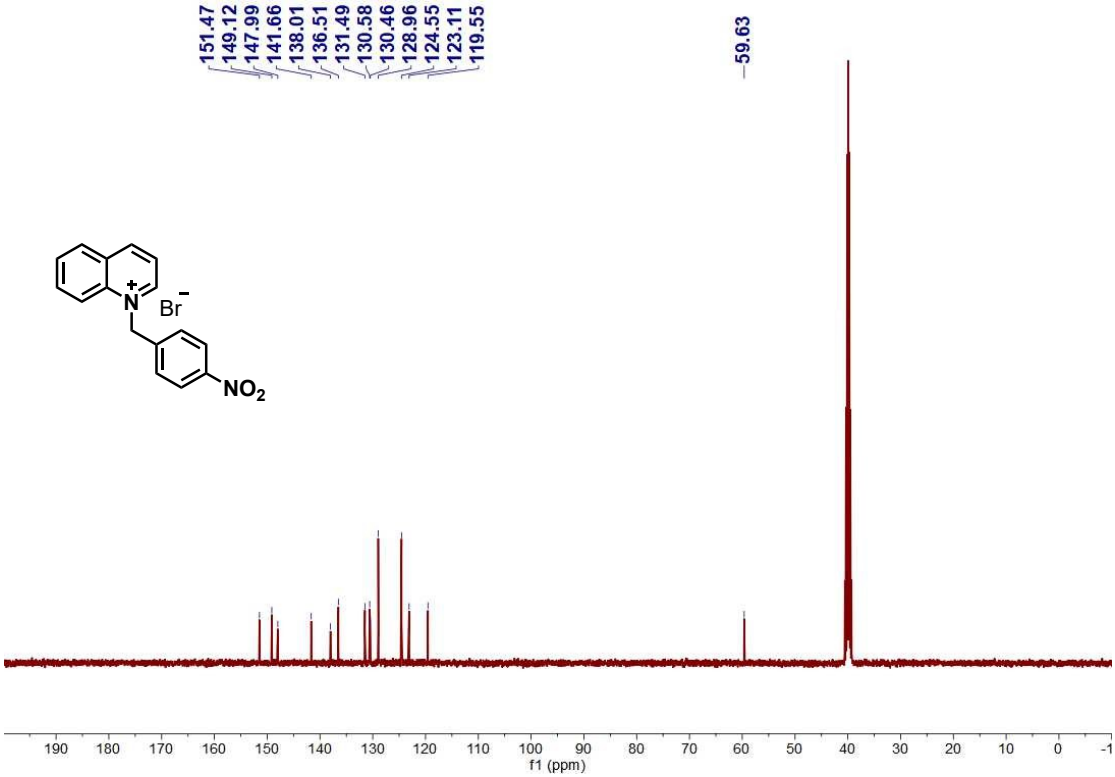
^{1}H NMR and ^{13}C NMR of **1ac**



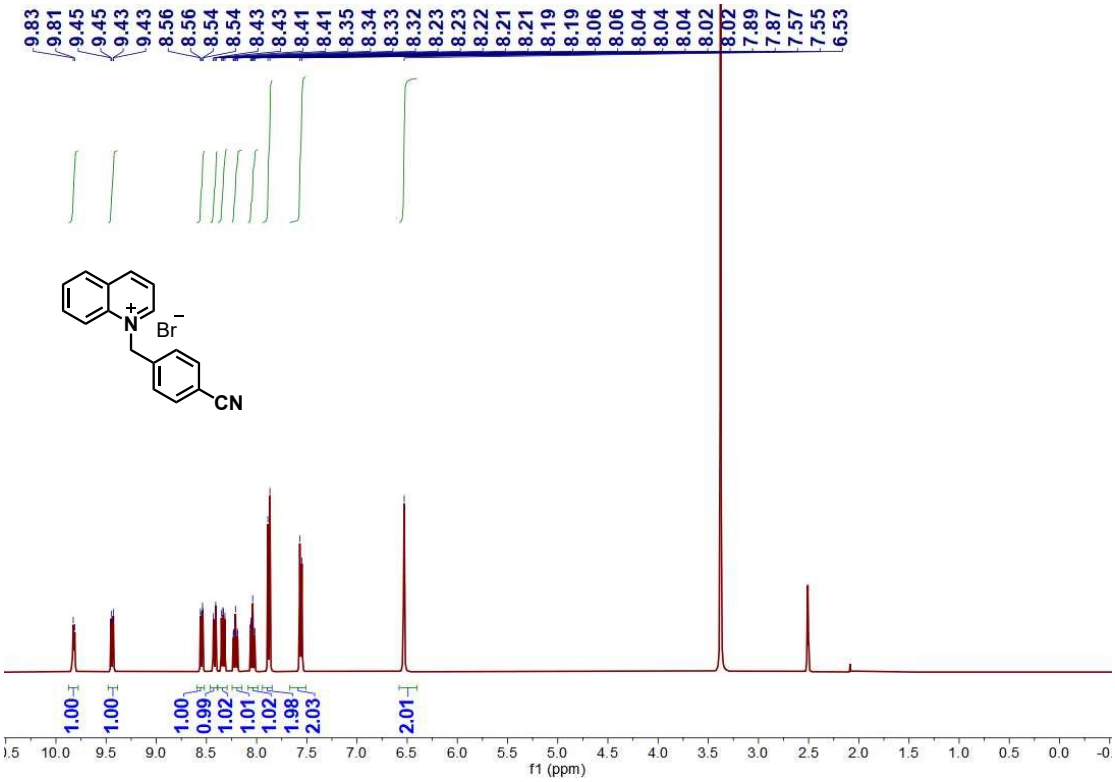


^{1}H NMR and ^{13}C NMR of **1ad**

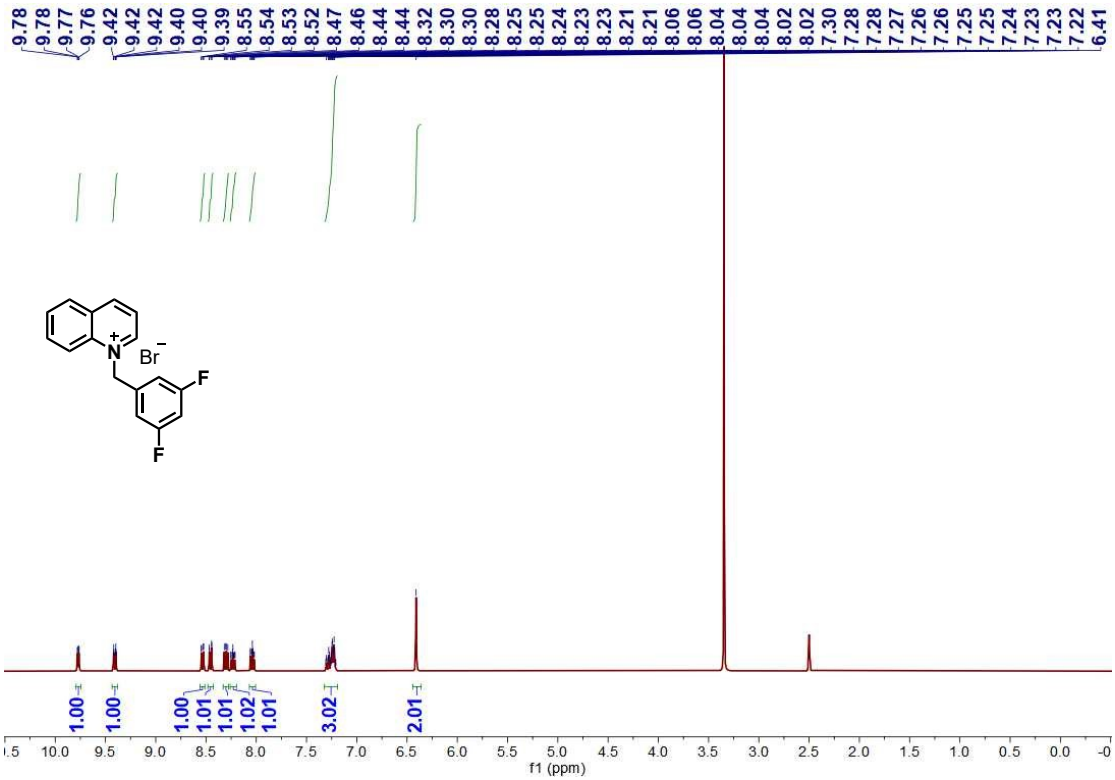


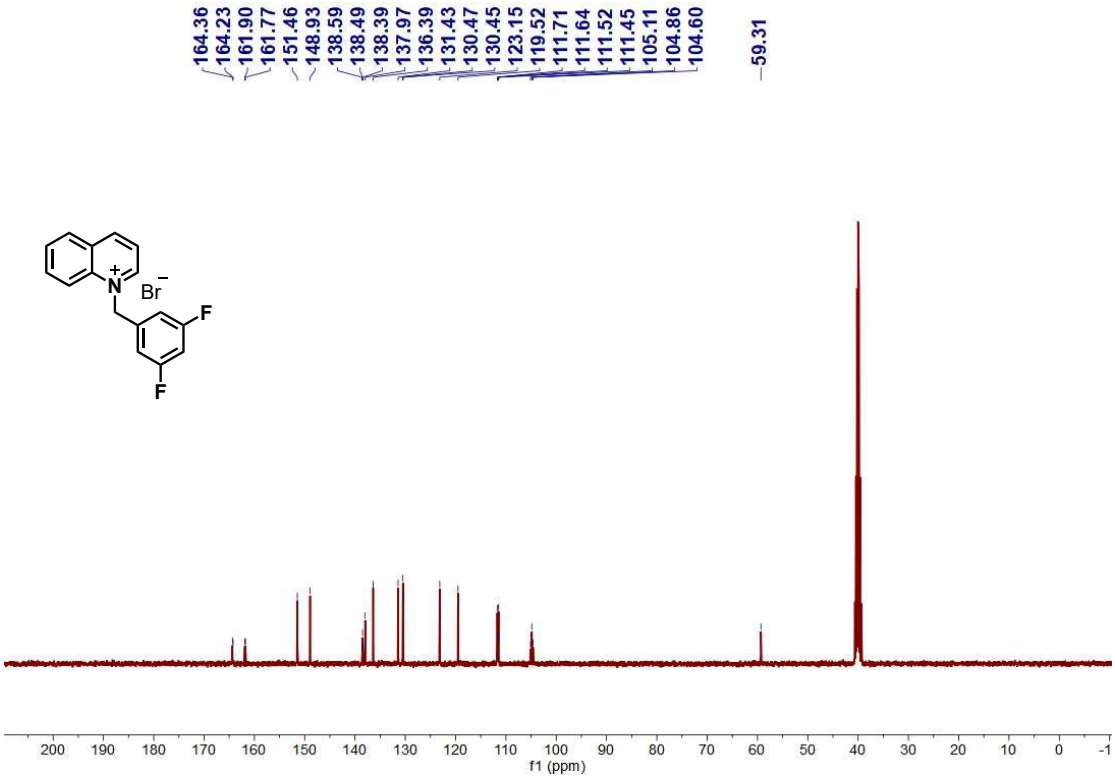


^{1}H NMR of **1ae**

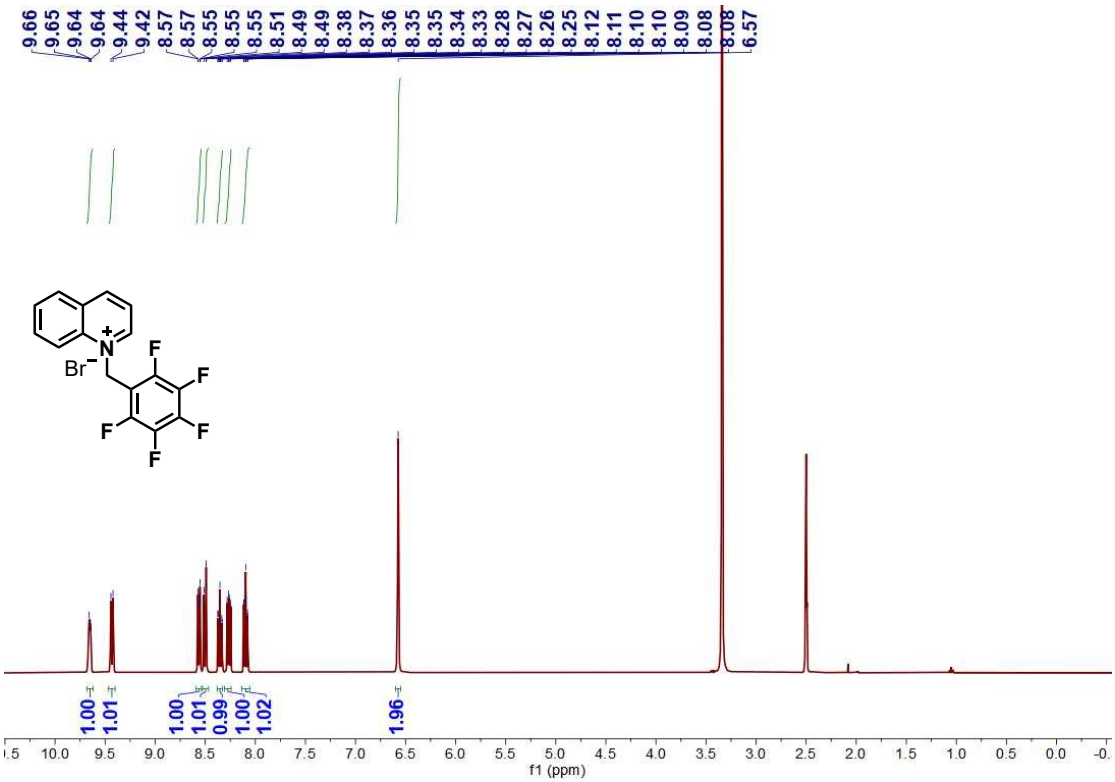


^{1}H NMR and ^{13}C NMR of **1af**

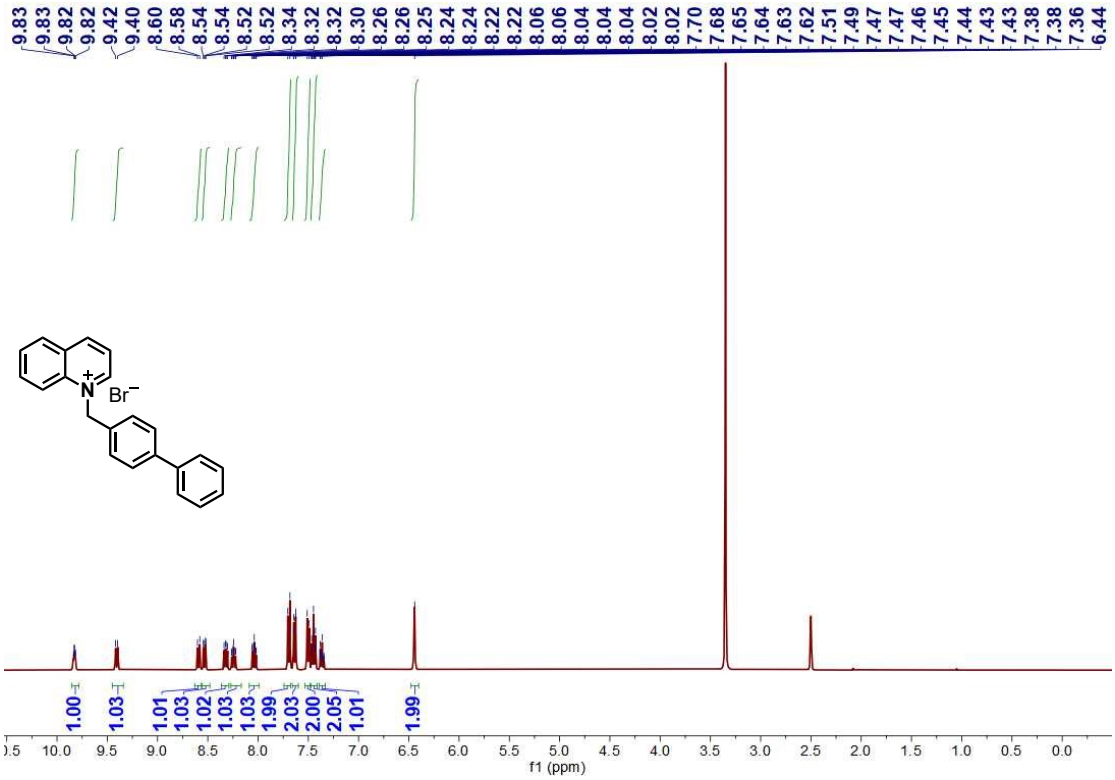



164.36
164.23
161.90
161.77
151.46
148.93
138.59
138.49
138.39
137.97
136.39
131.43
130.47
130.45
123.15
119.52
111.71
111.64
111.52
111.45
105.11
104.86
104.60
59.31
Br
F
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

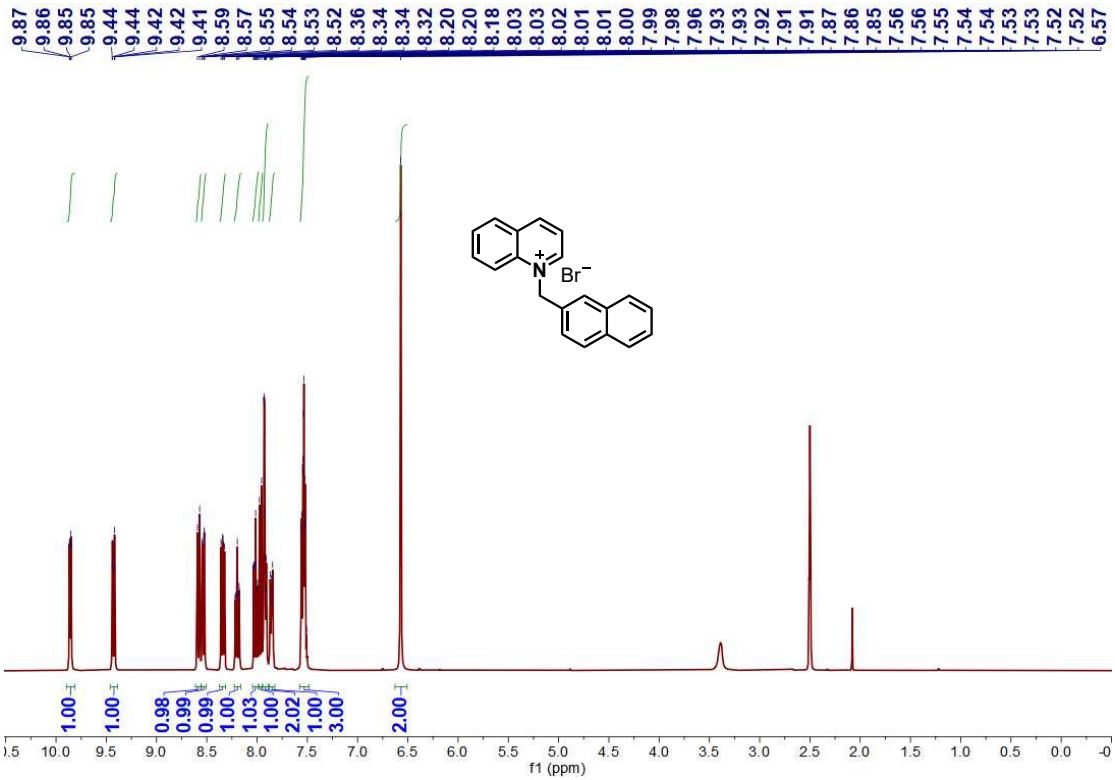
^{1}H NMR of **1ag**

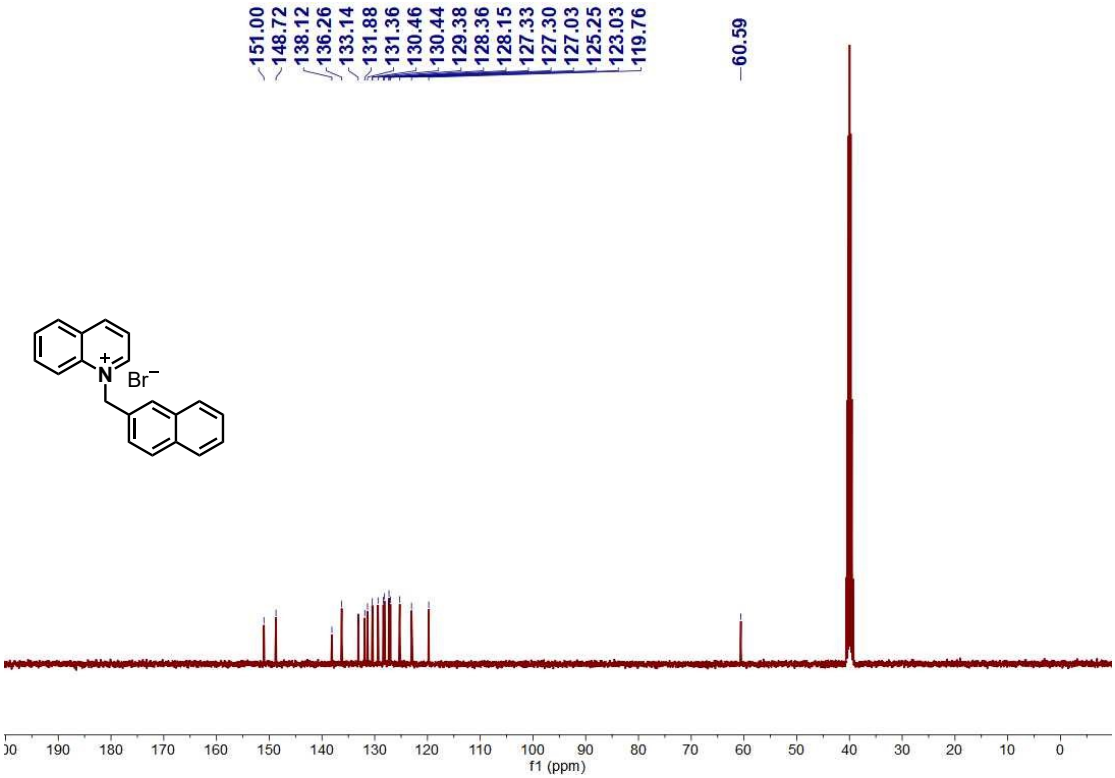

9.66
9.65
9.64
9.64
9.44
9.42
8.57
8.57
8.55
8.55
8.55
8.51
8.49
8.49
8.38
8.37
8.36
8.35
8.35
8.34
8.33
8.28
8.27
8.26
8.25
8.12
8.11
8.10
8.10
8.09
8.08
8.08
6.57
Br
F
F
F
F
F
1.00
1.01
1.00
1.01
0.99
1.00
1.02
1.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{1}H NMR and ^{13}C NMR of **1ah**

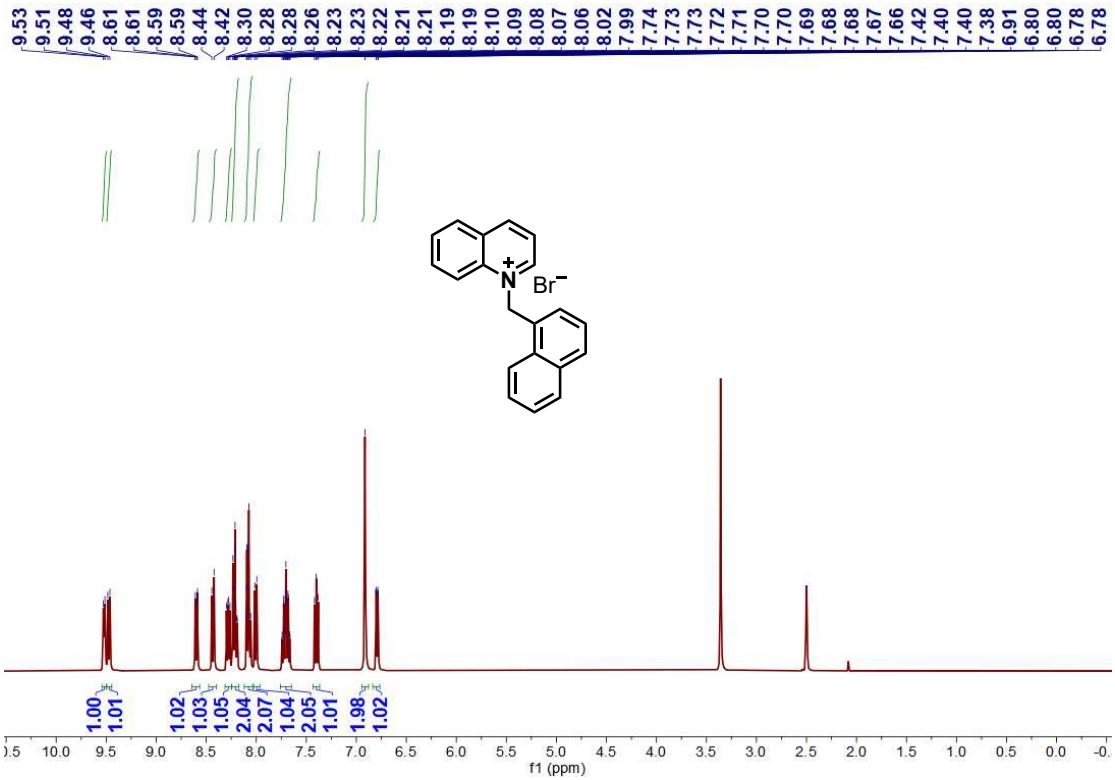


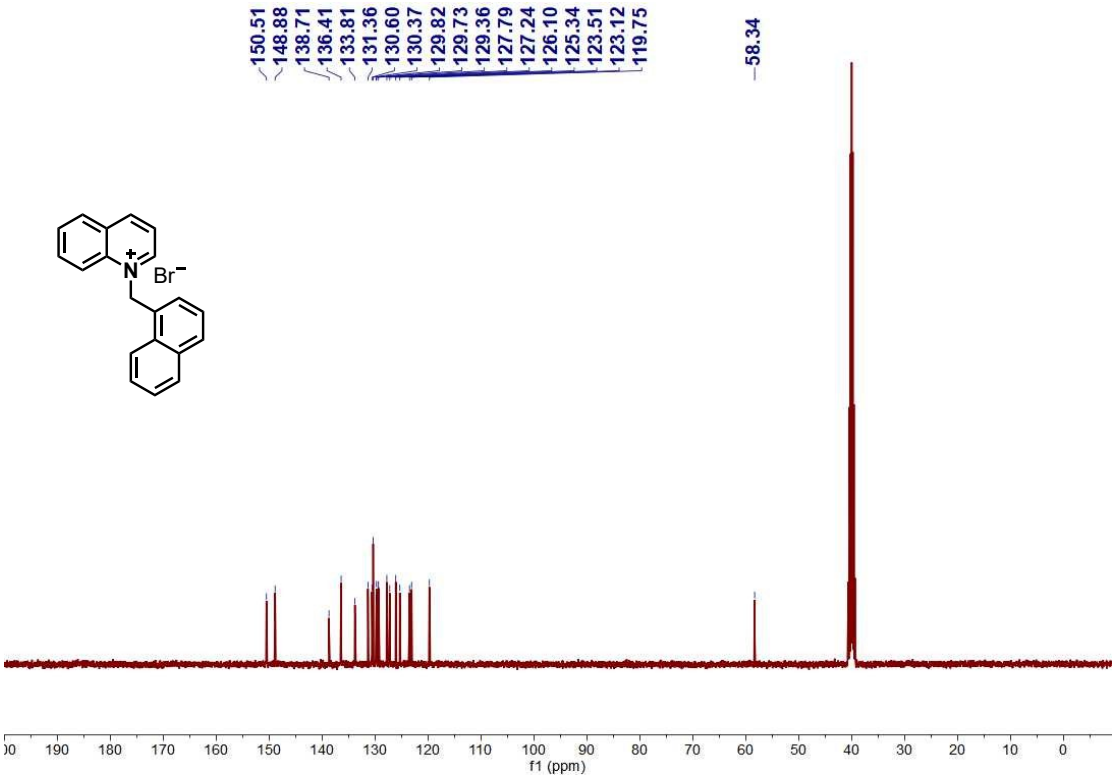
^{1}H NMR and ^{13}C NMR of **1ai**



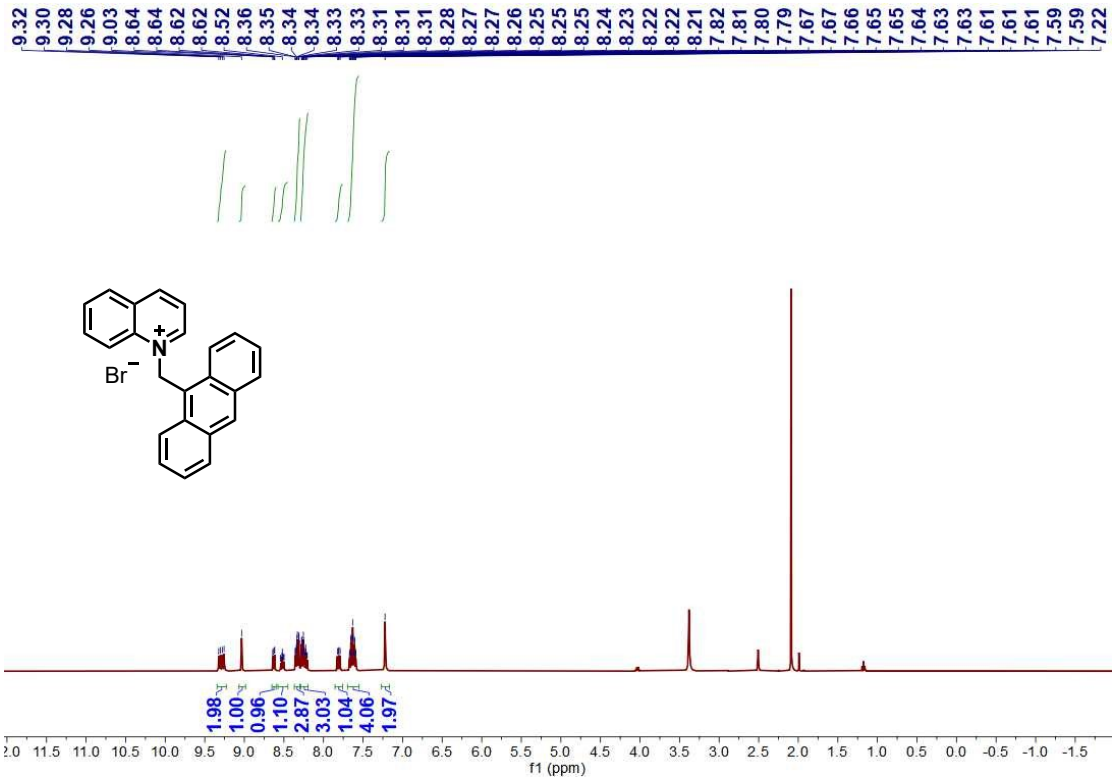


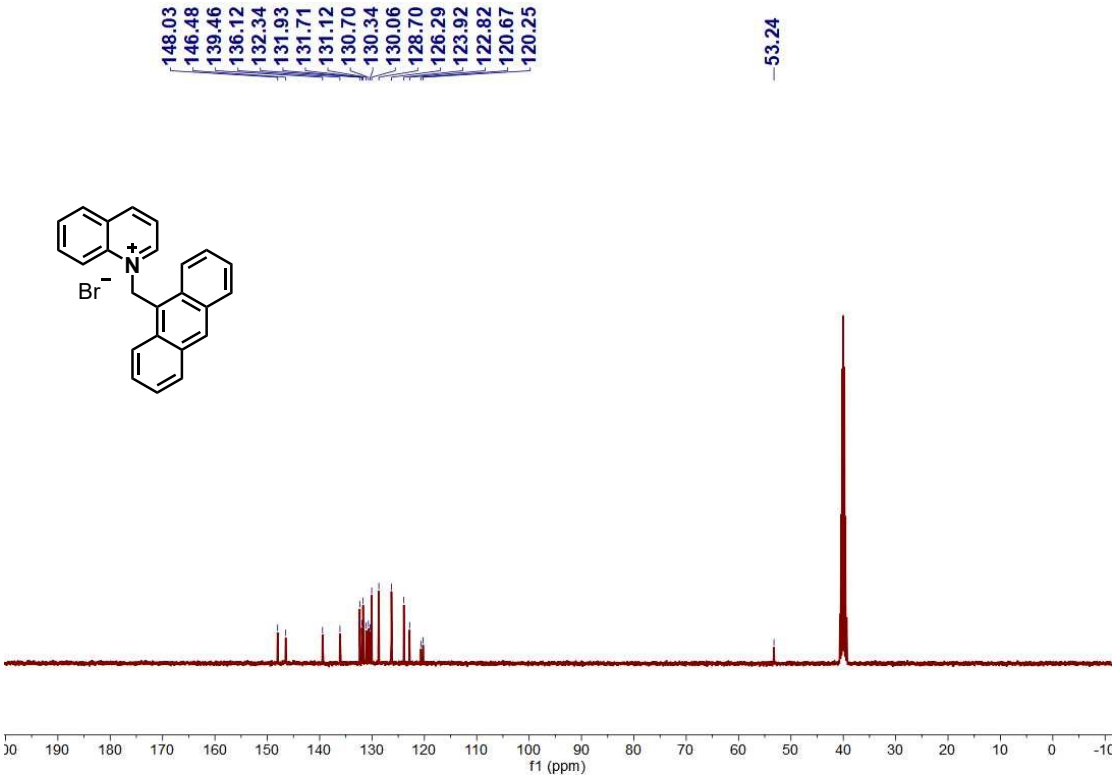
^{1}H NMR and ^{13}C NMR of **1aj**



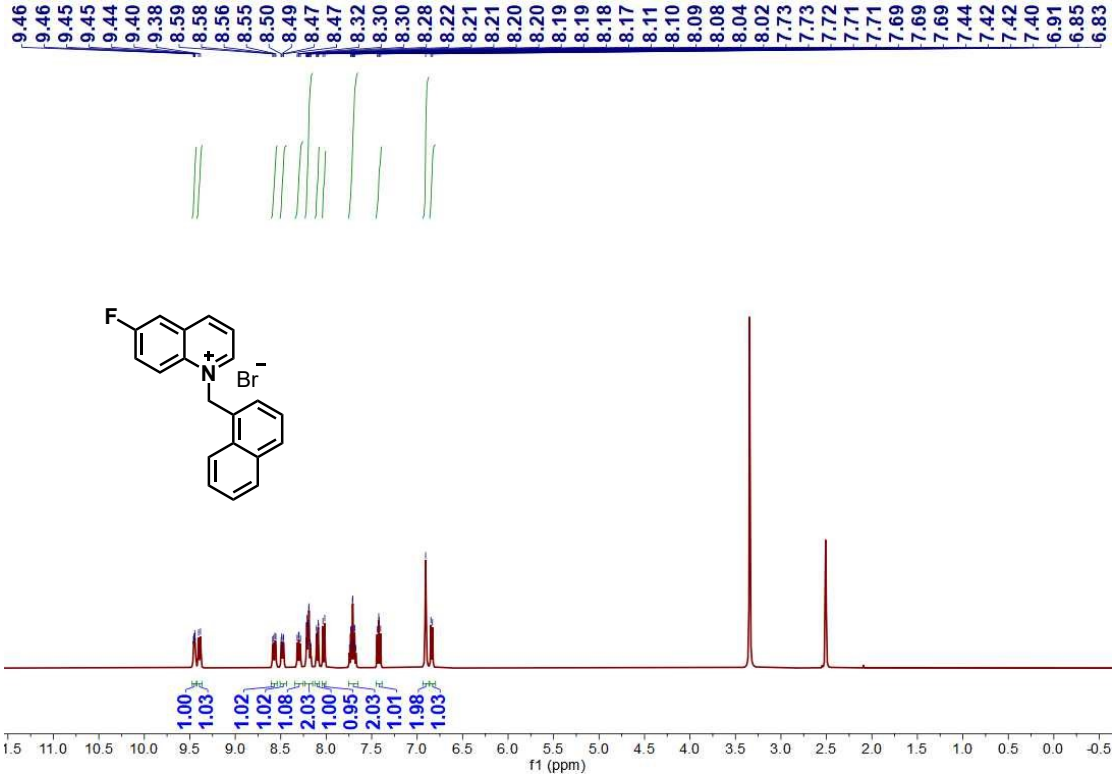


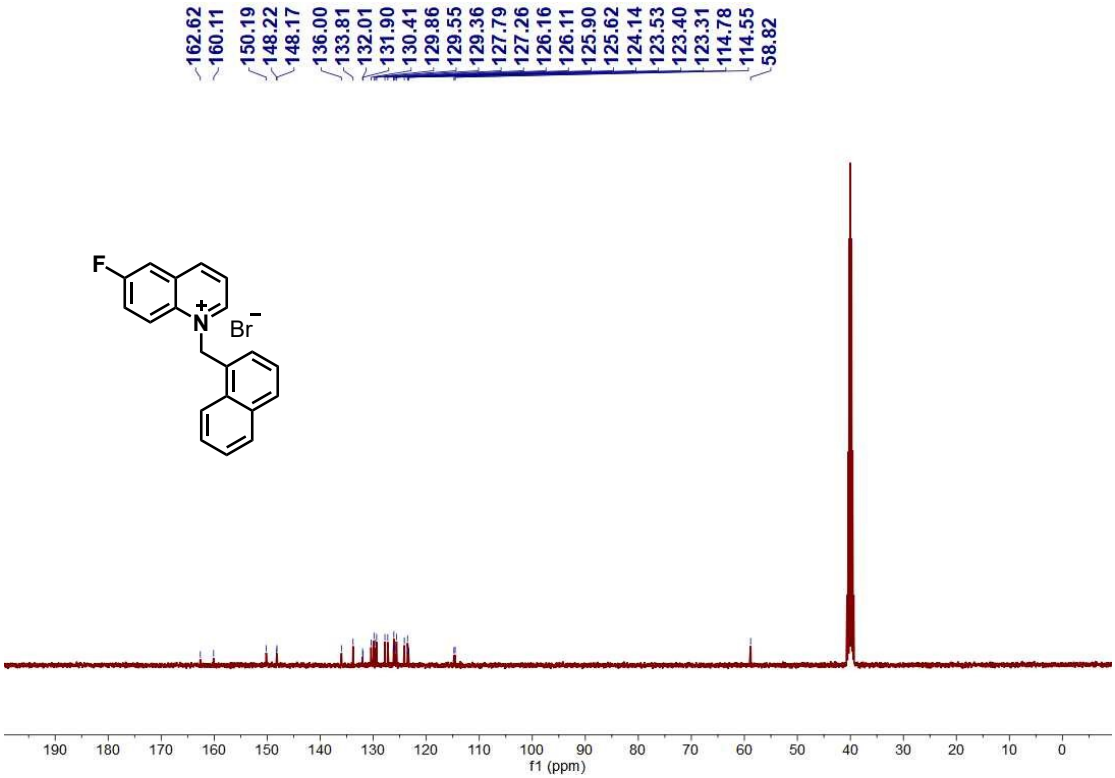
^{1}H NMR and ^{13}C NMR of **1ak**



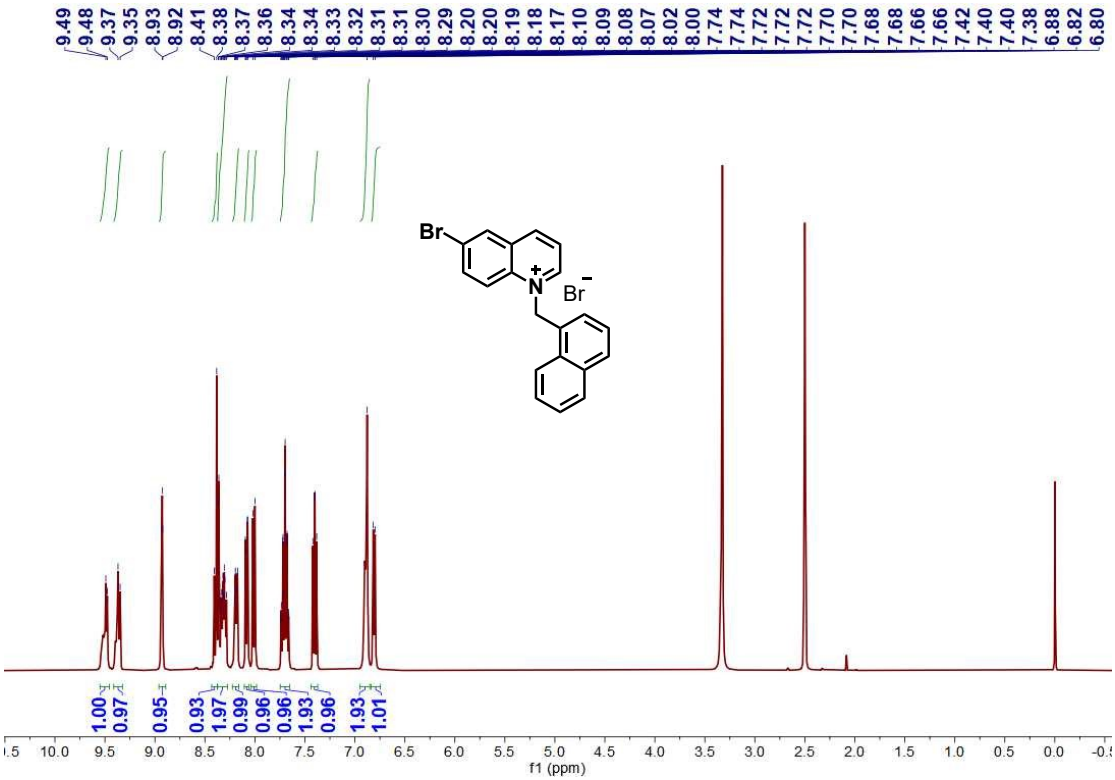


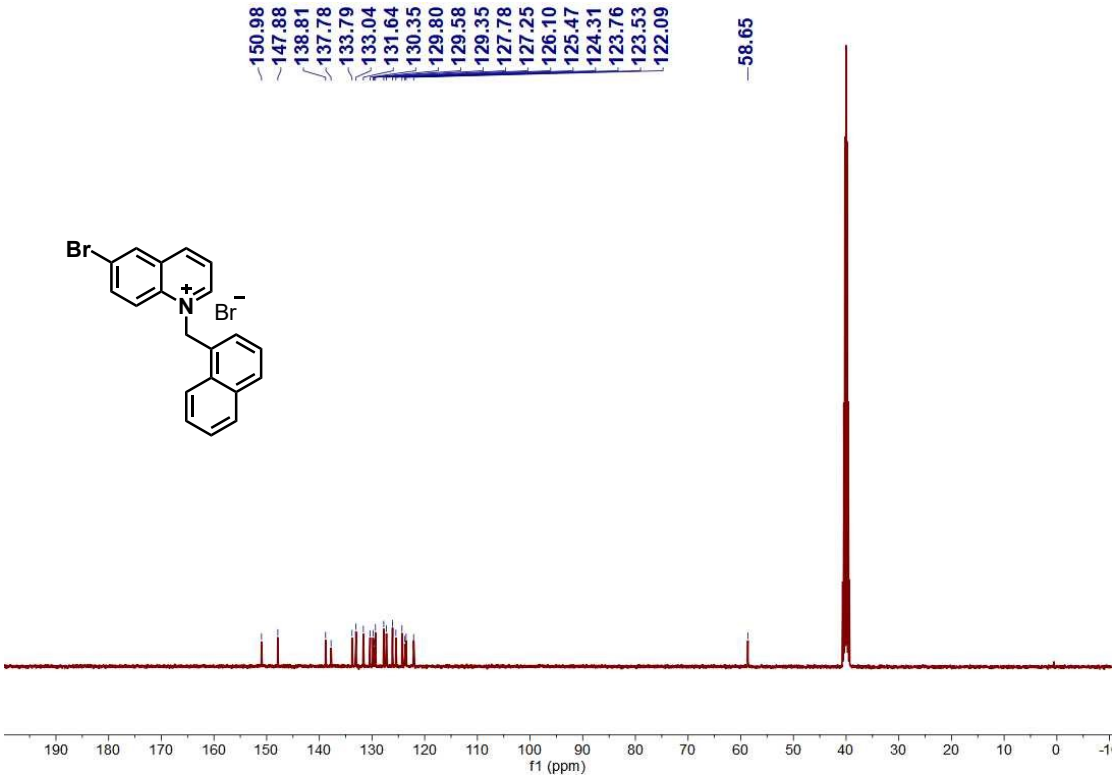
^{1}H NMR and ^{13}C NMR of **1al**



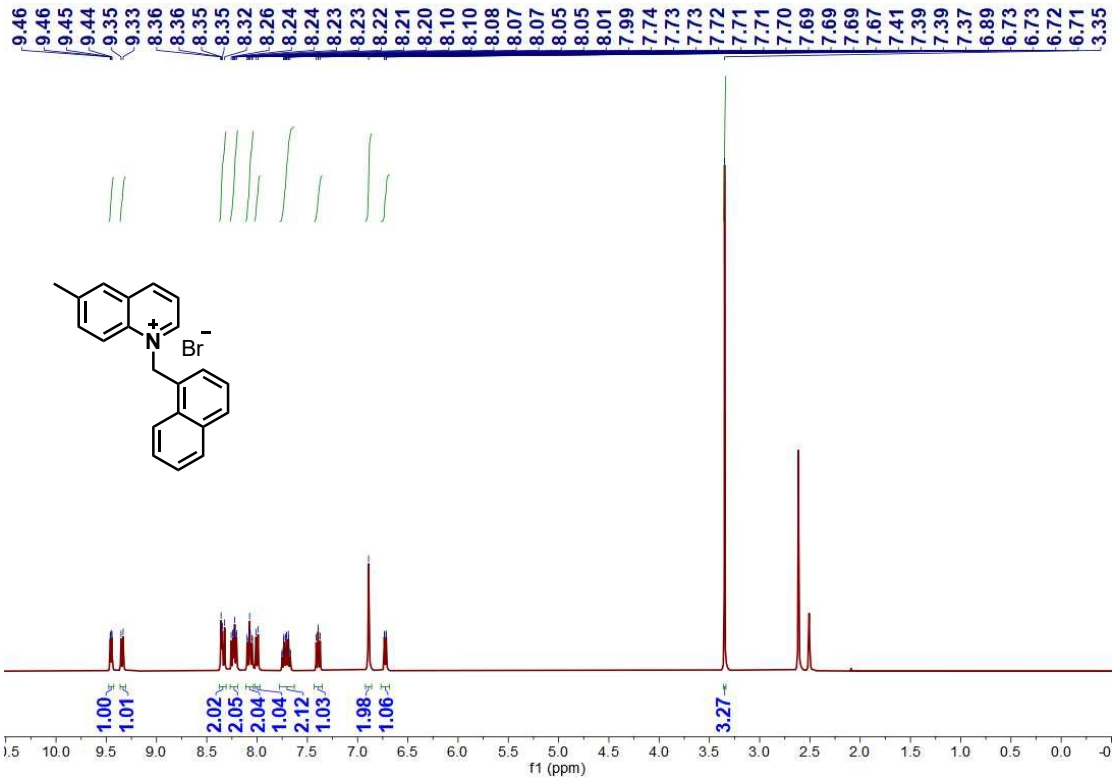


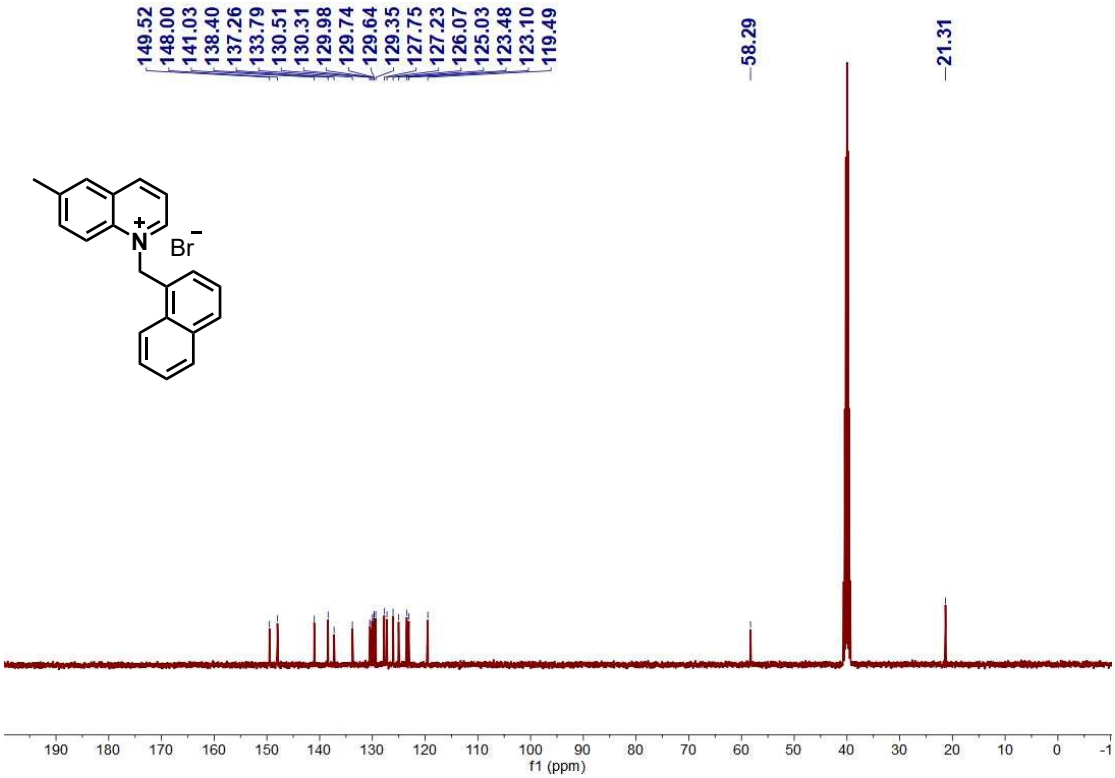
^{1}H NMR and ^{13}C NMR of **1am**



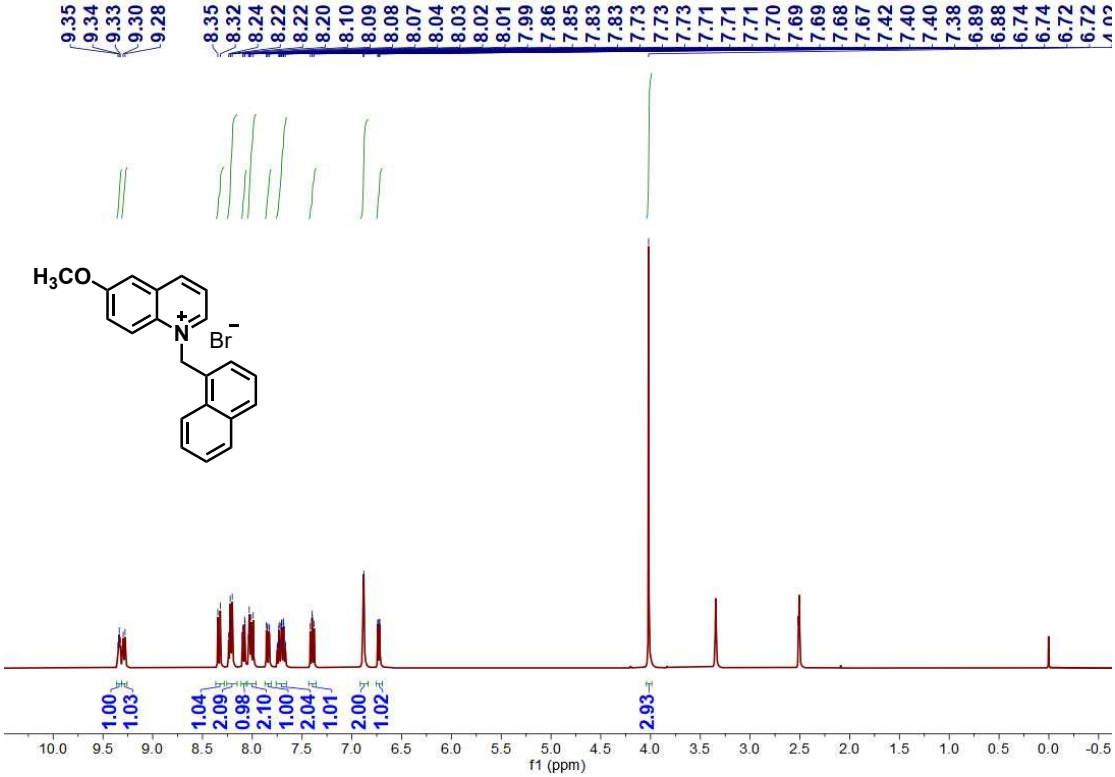


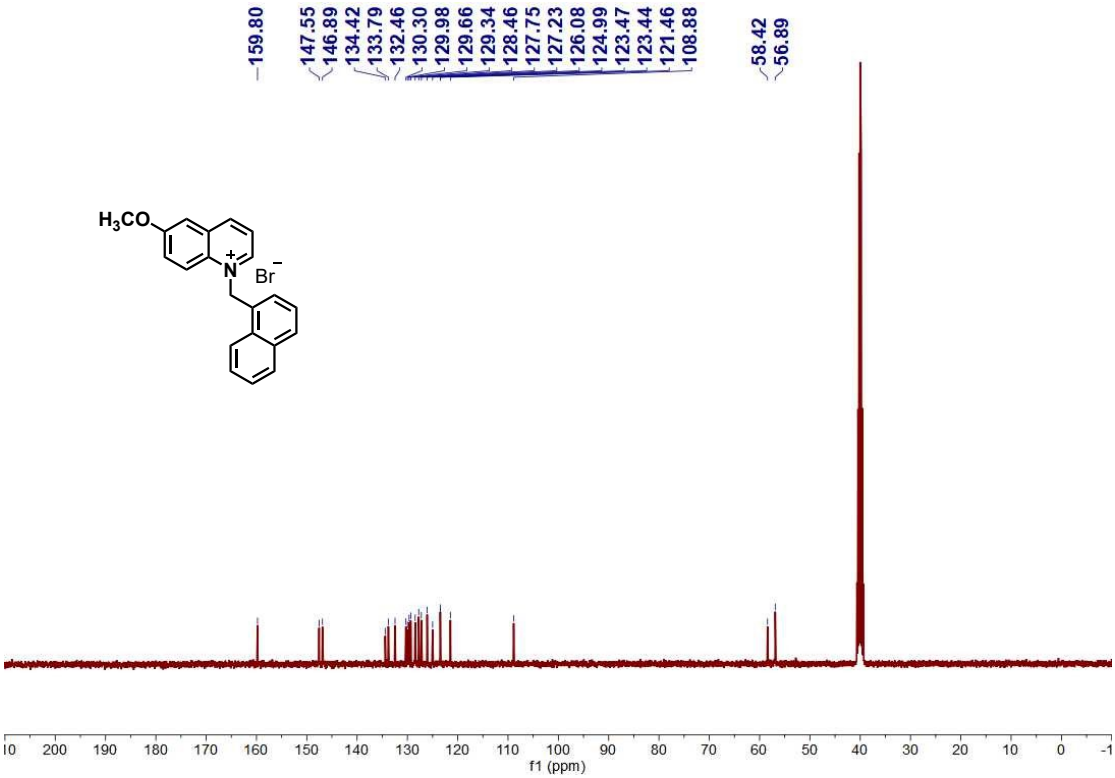
^{1}H NMR and ^{13}C NMR of **1an**



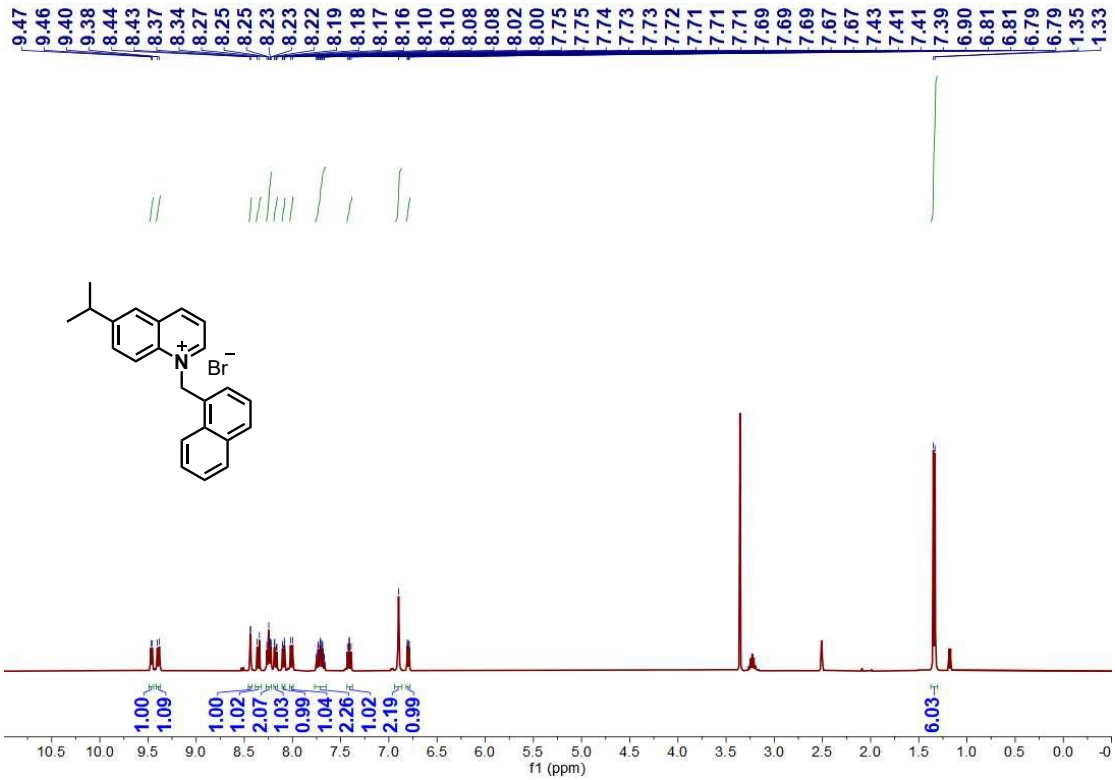


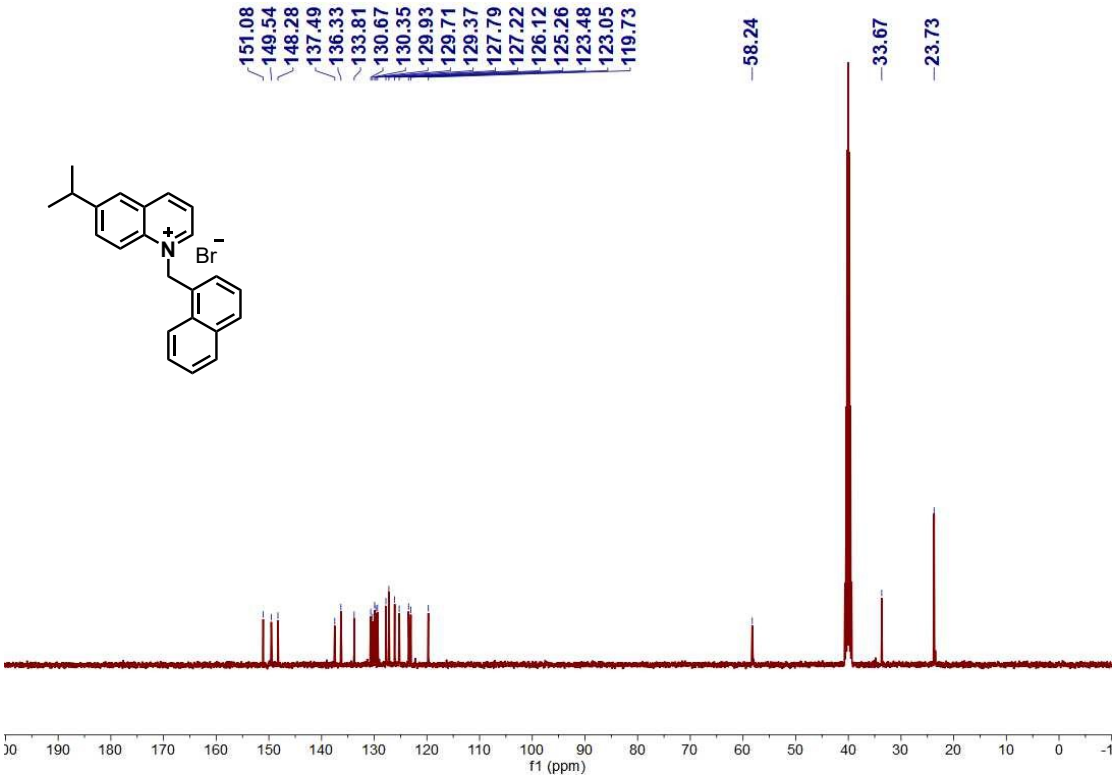
^{1}H NMR and ^{13}C NMR of **1ao**



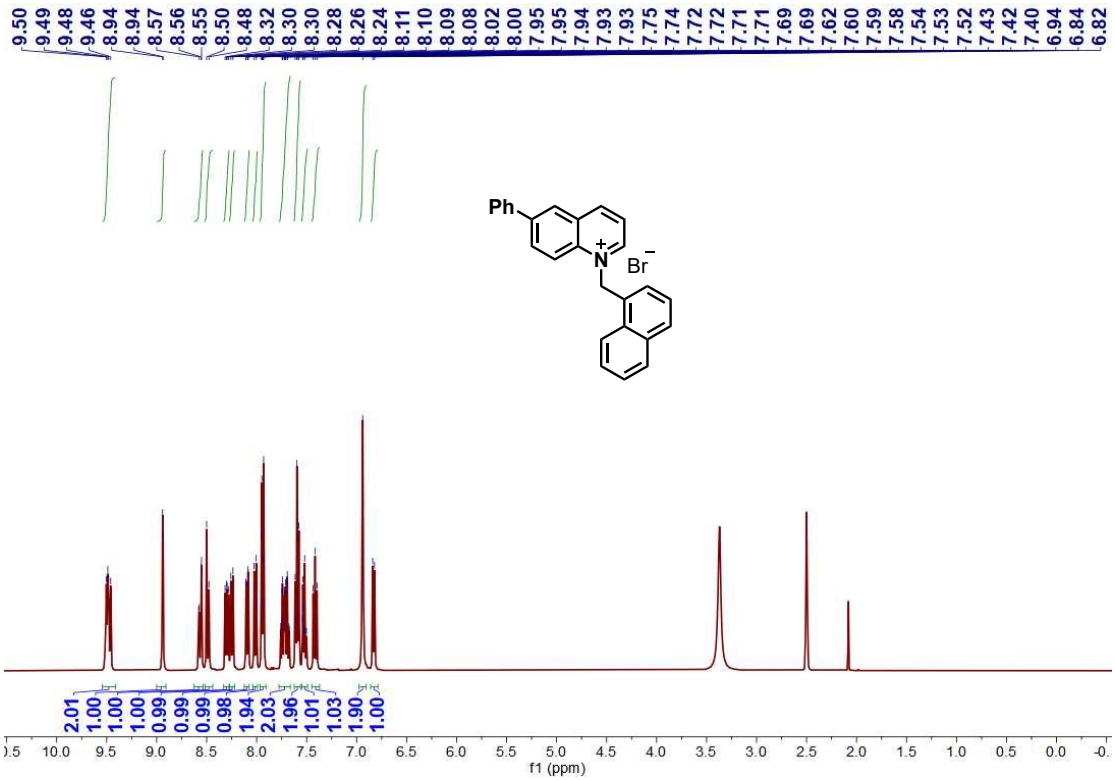


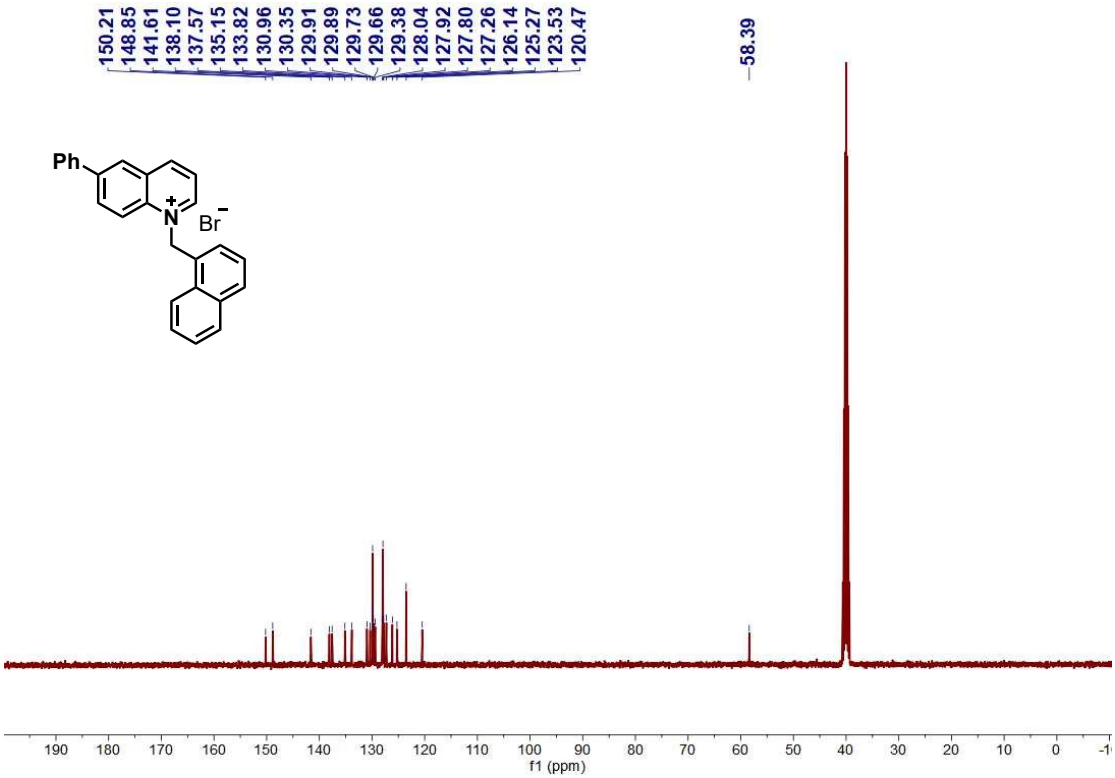
^{1}H NMR and ^{13}C NMR of **1ap**



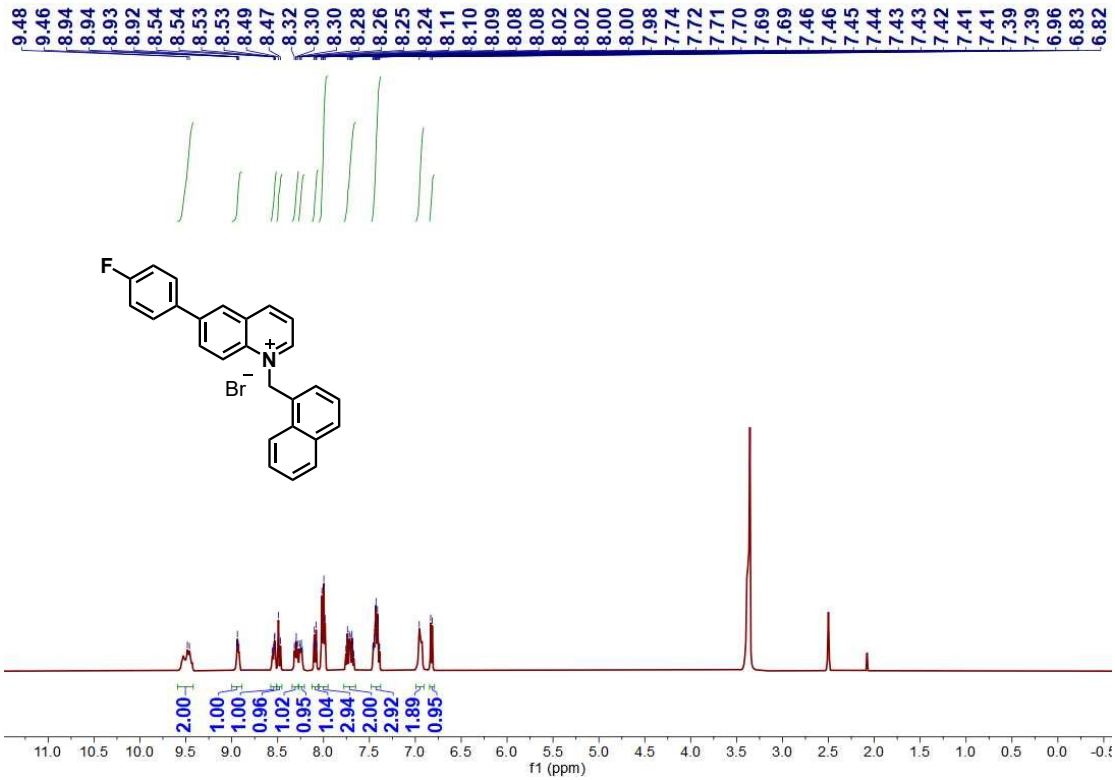


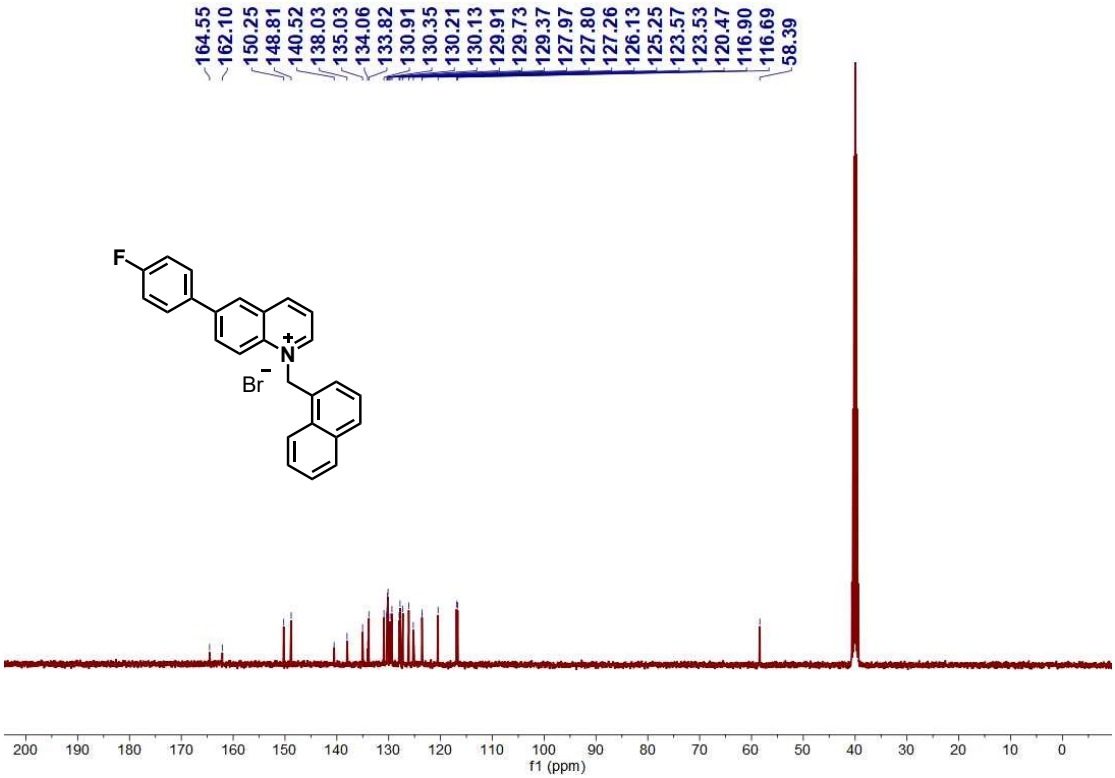
^{1}H NMR and ^{13}C NMR of **1aq**



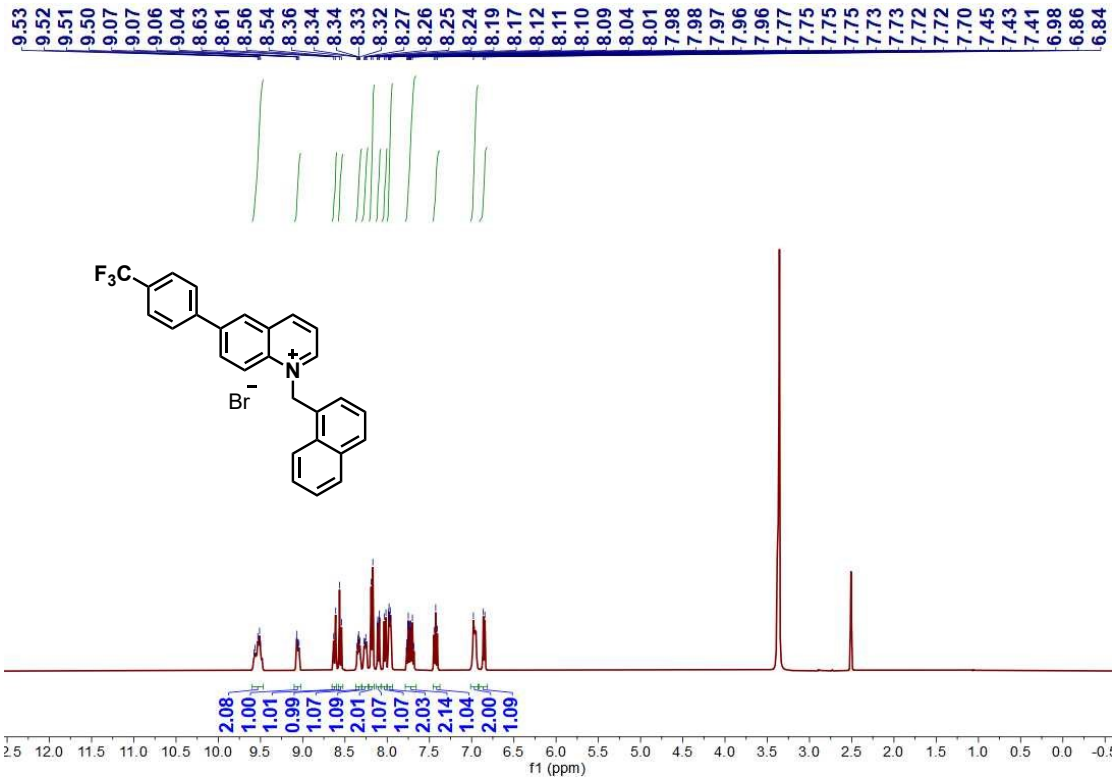


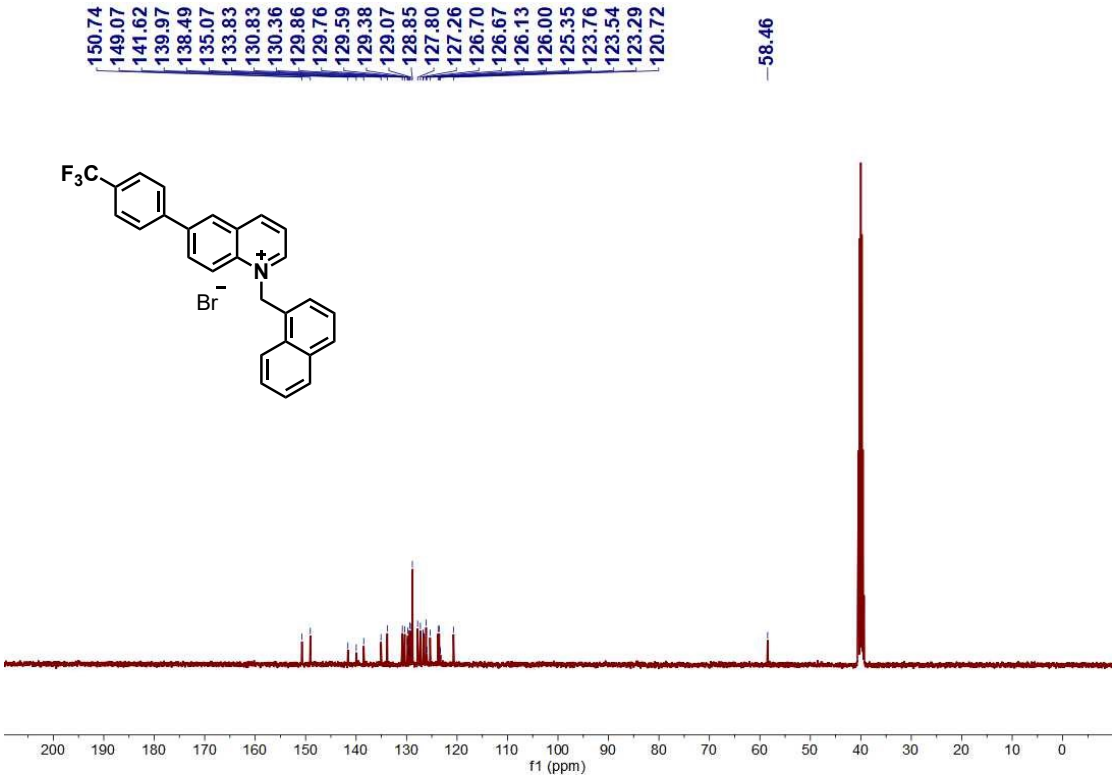
^{1}H NMR and ^{13}C NMR of **1ar**



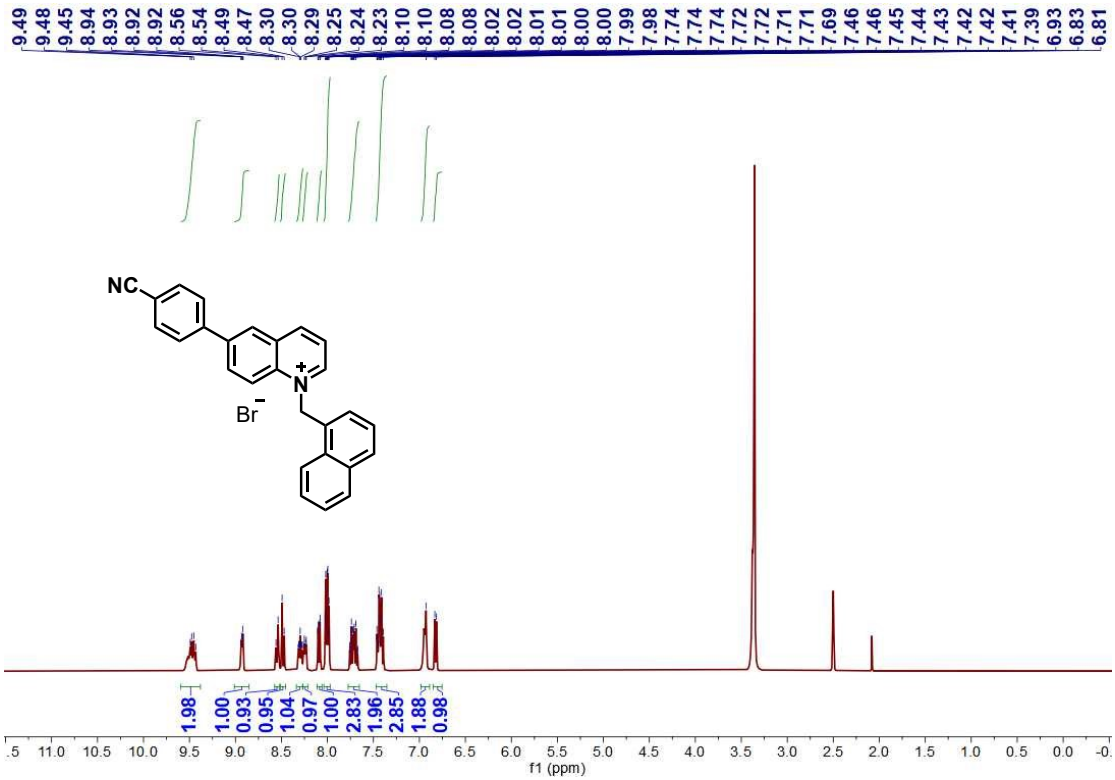


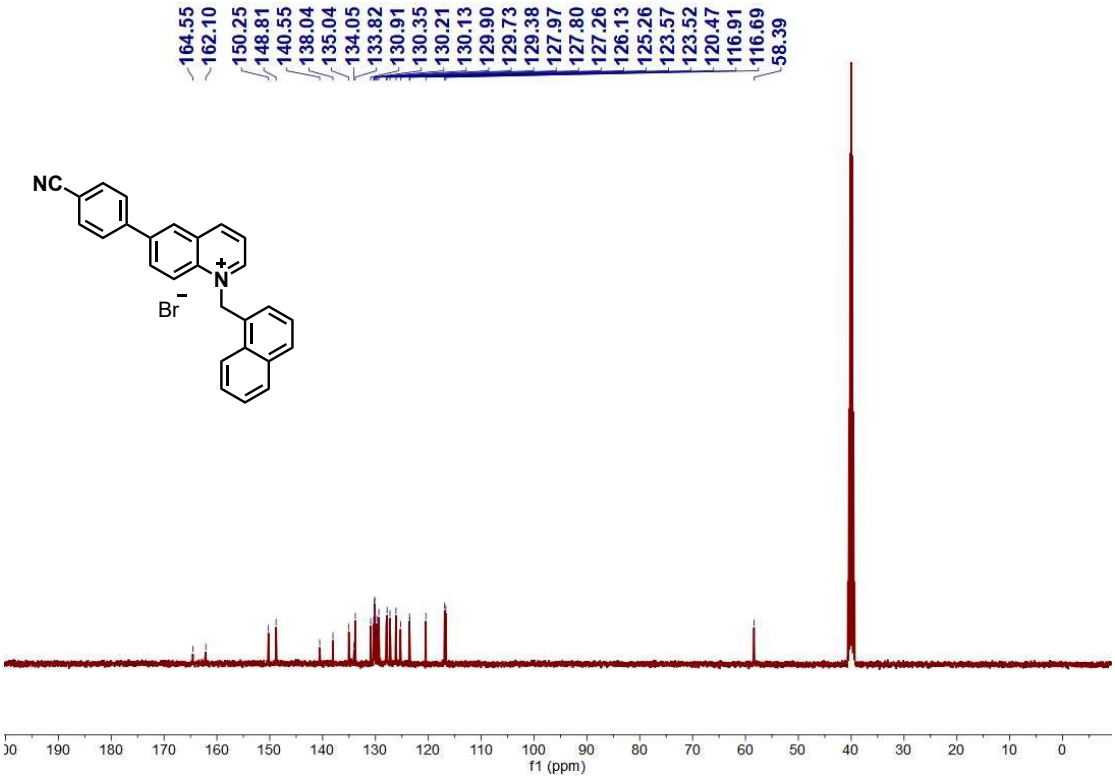
^{1}H NMR and ^{13}C NMR of **1as**



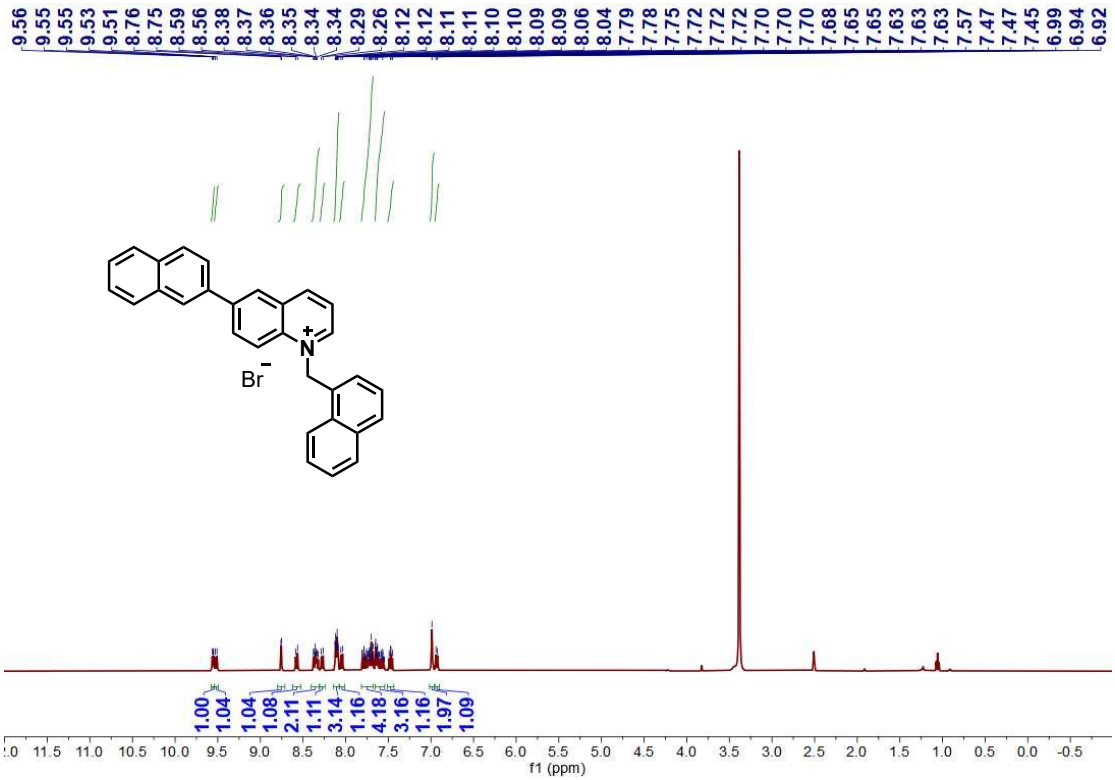


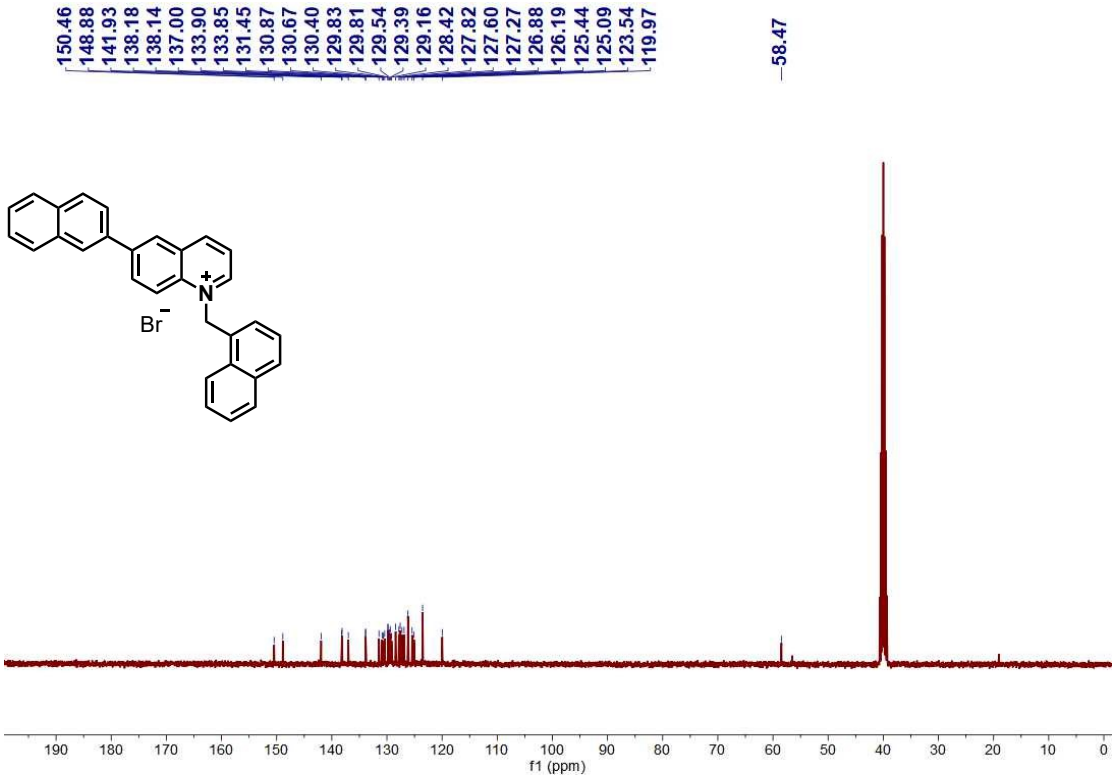
^{1}H NMR and ^{13}C NMR of **1at**



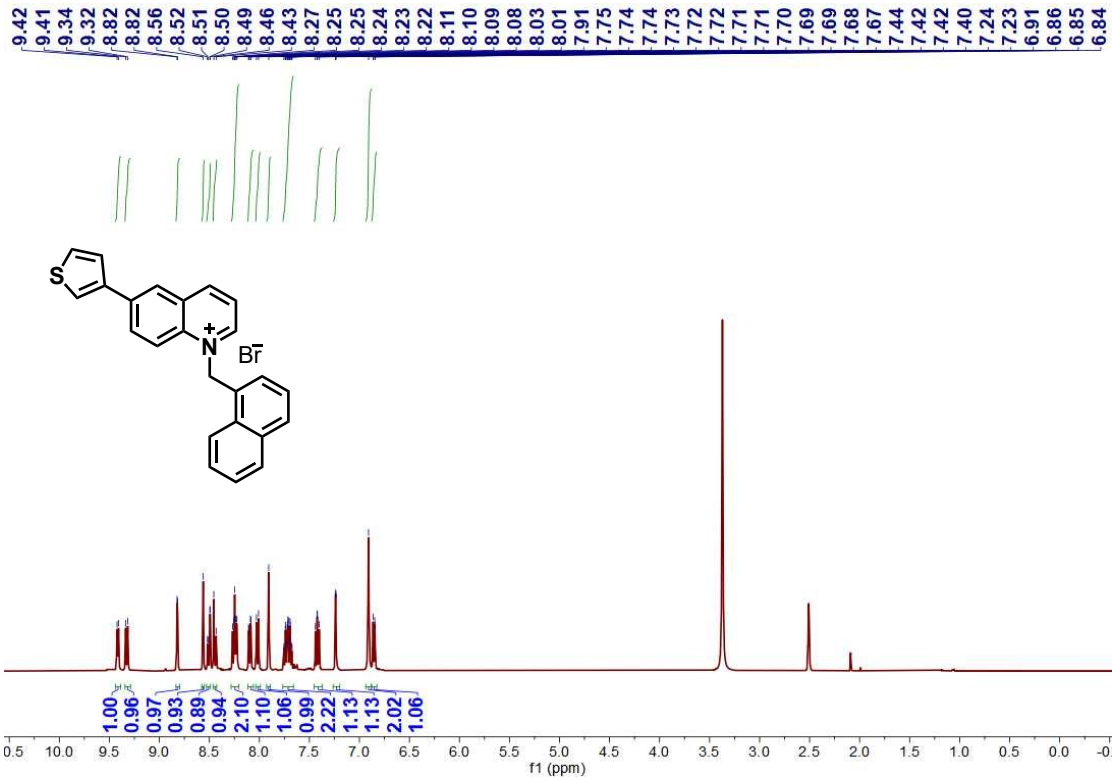


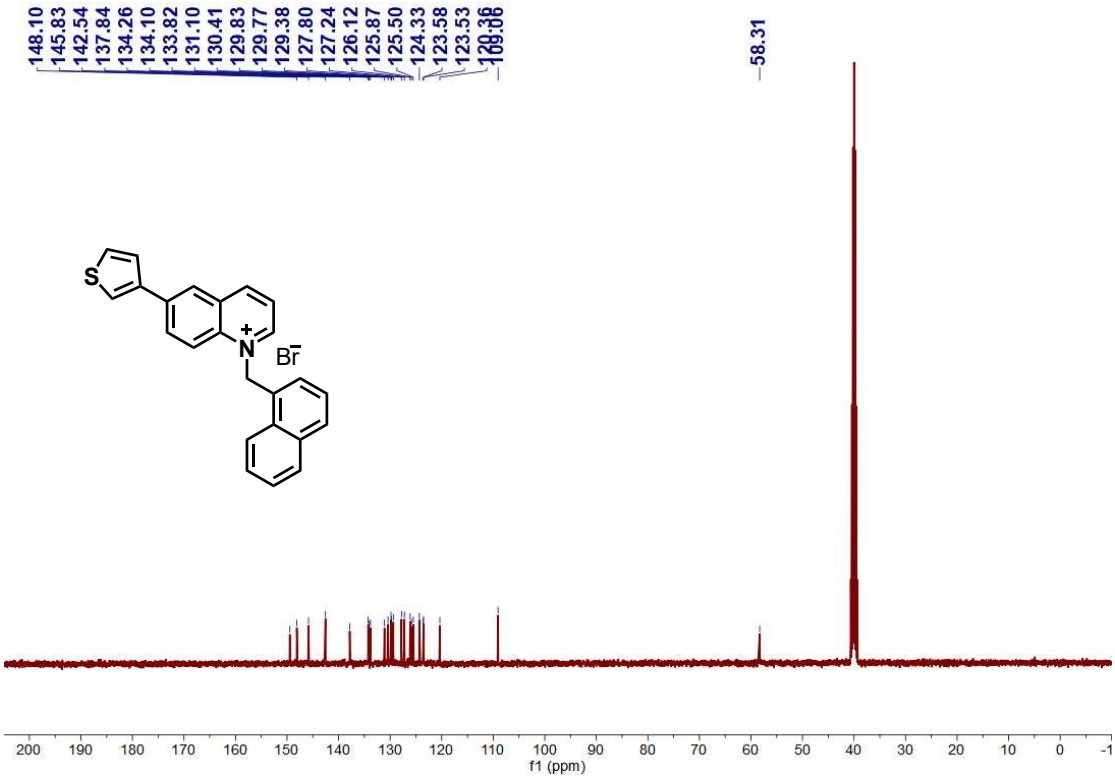
^{1}H NMR and ^{13}C NMR of **1au**



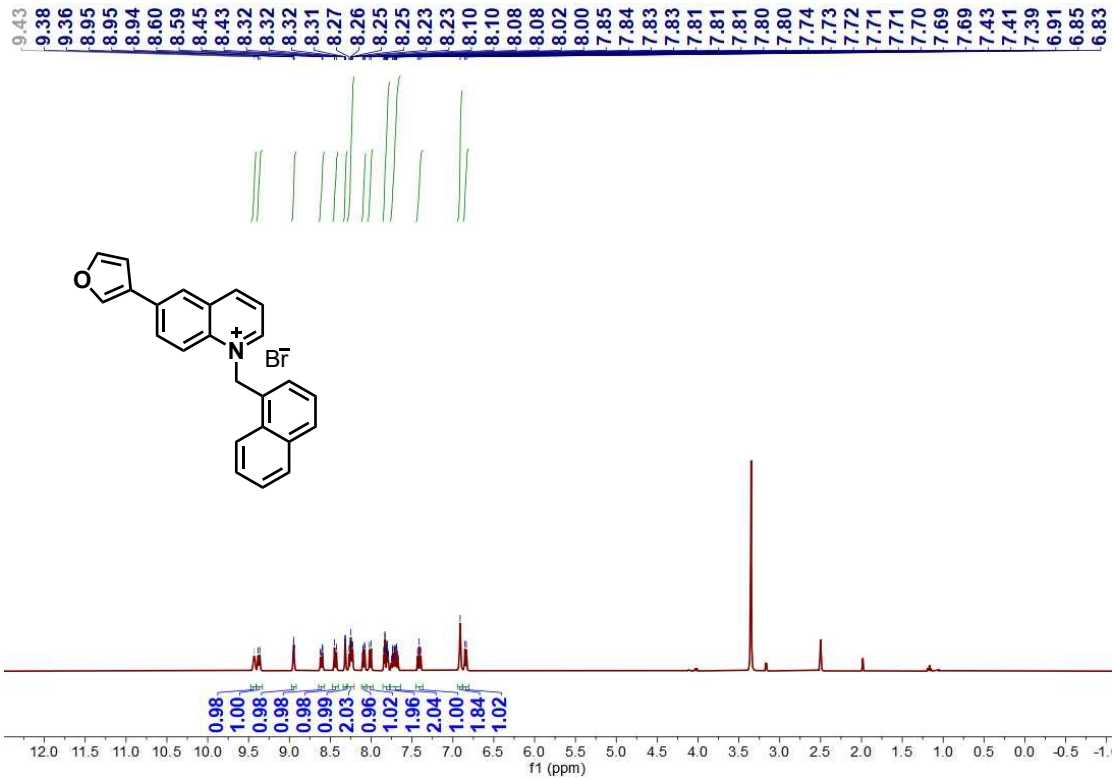


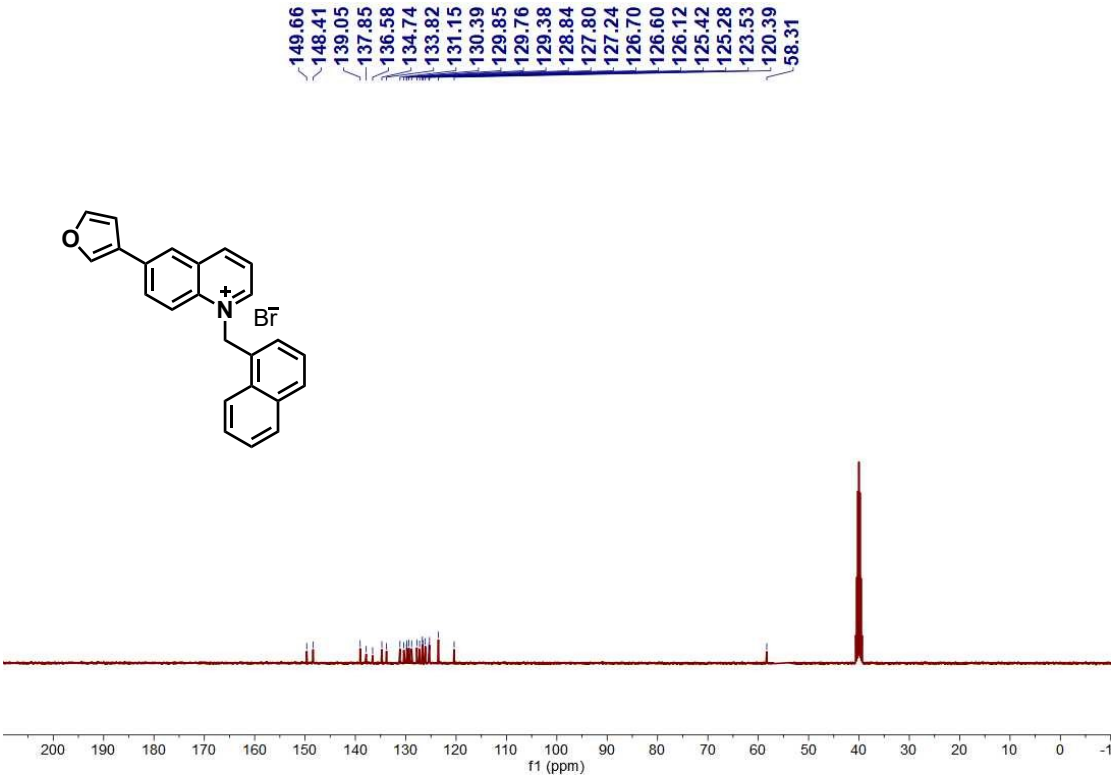
^{1}H NMR and ^{13}C NMR of **1av**



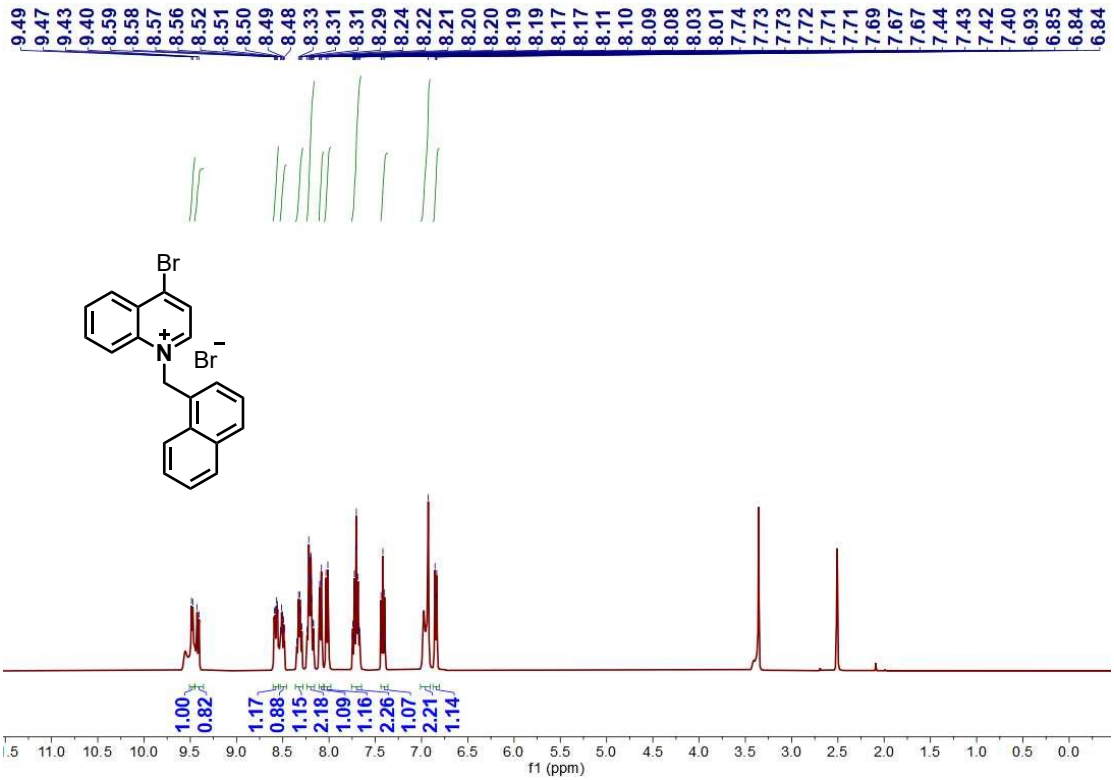


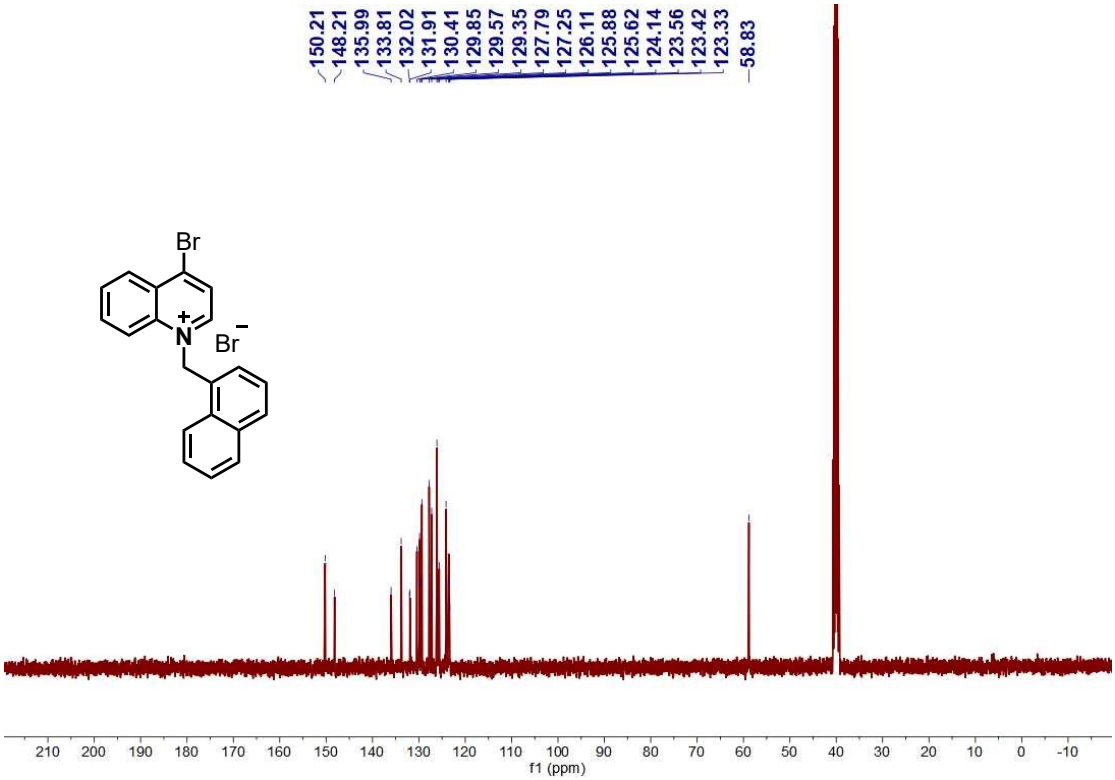
^{1}H NMR and ^{13}C NMR of **1aw**



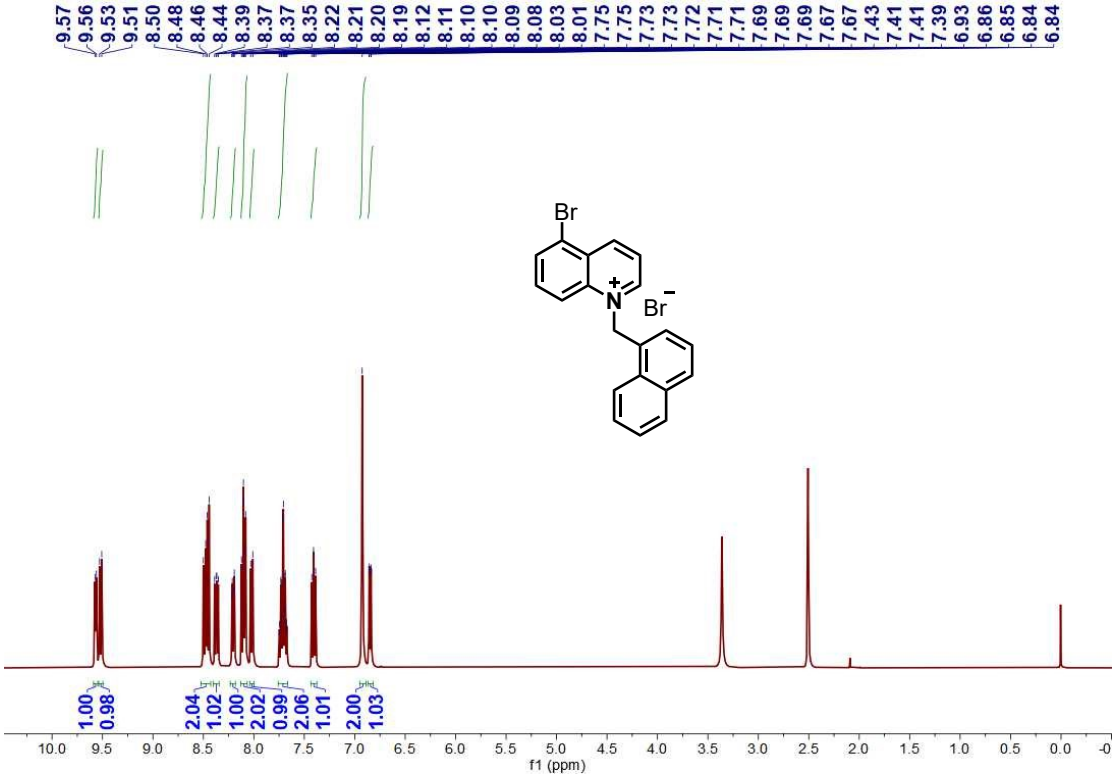


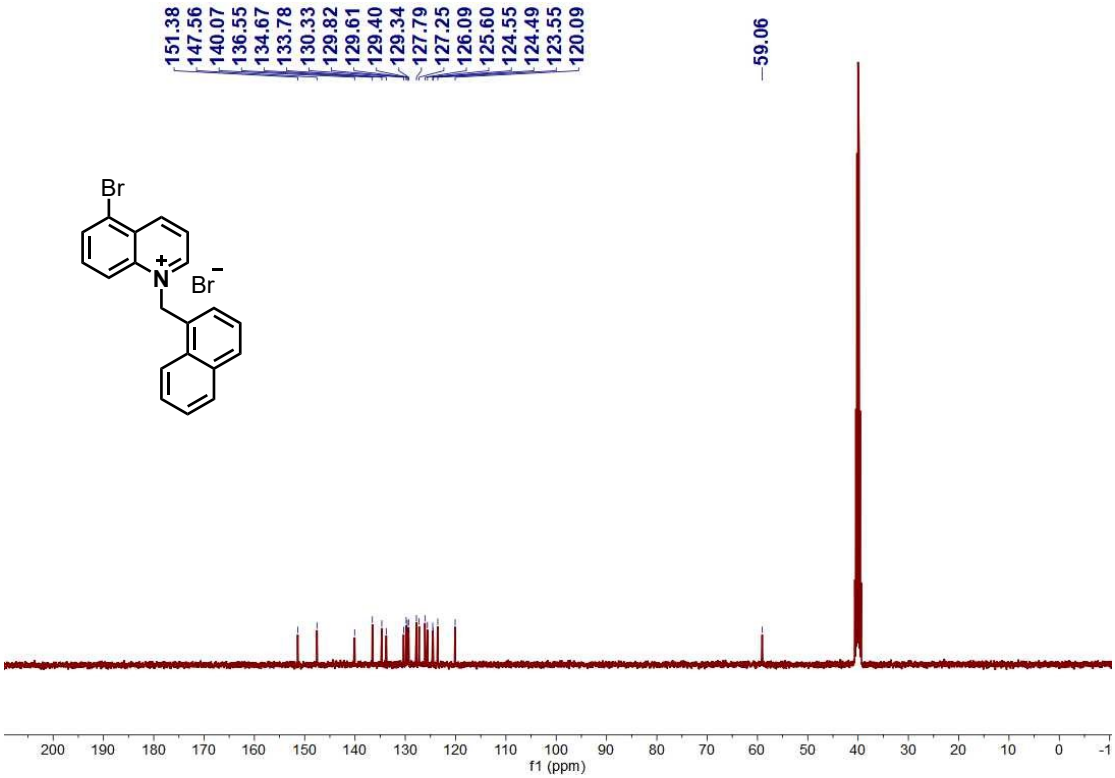
^{1}H NMR and ^{13}C NMR of **1ax**



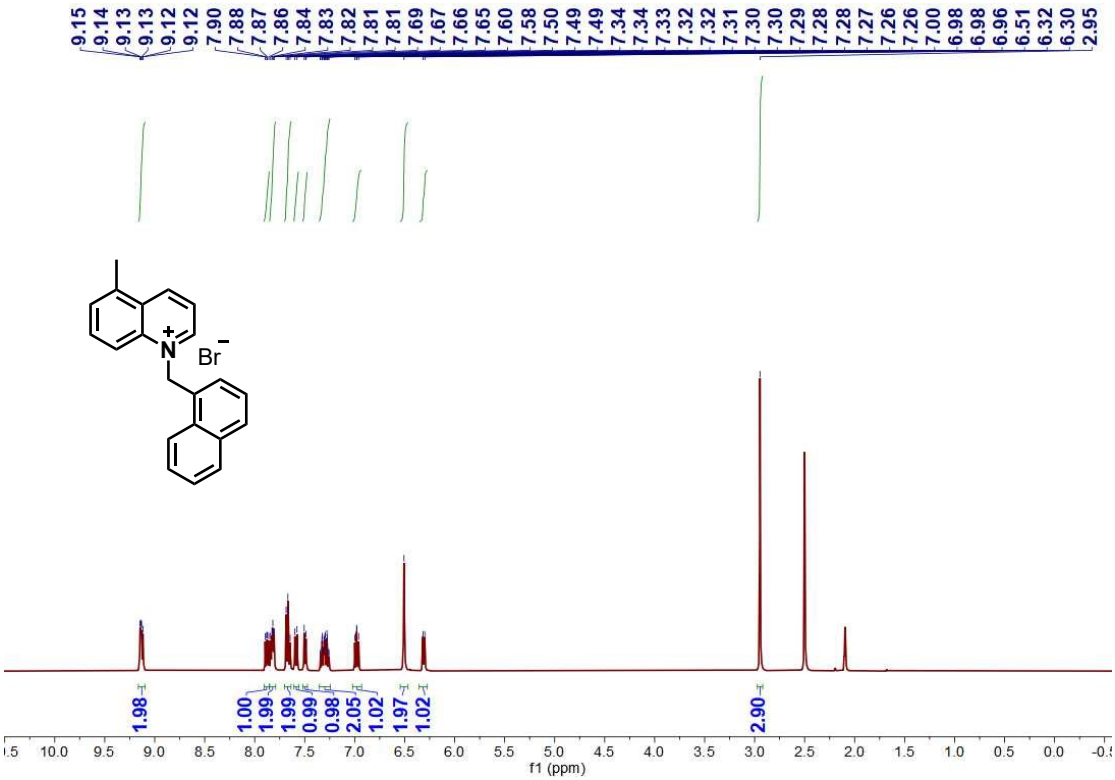


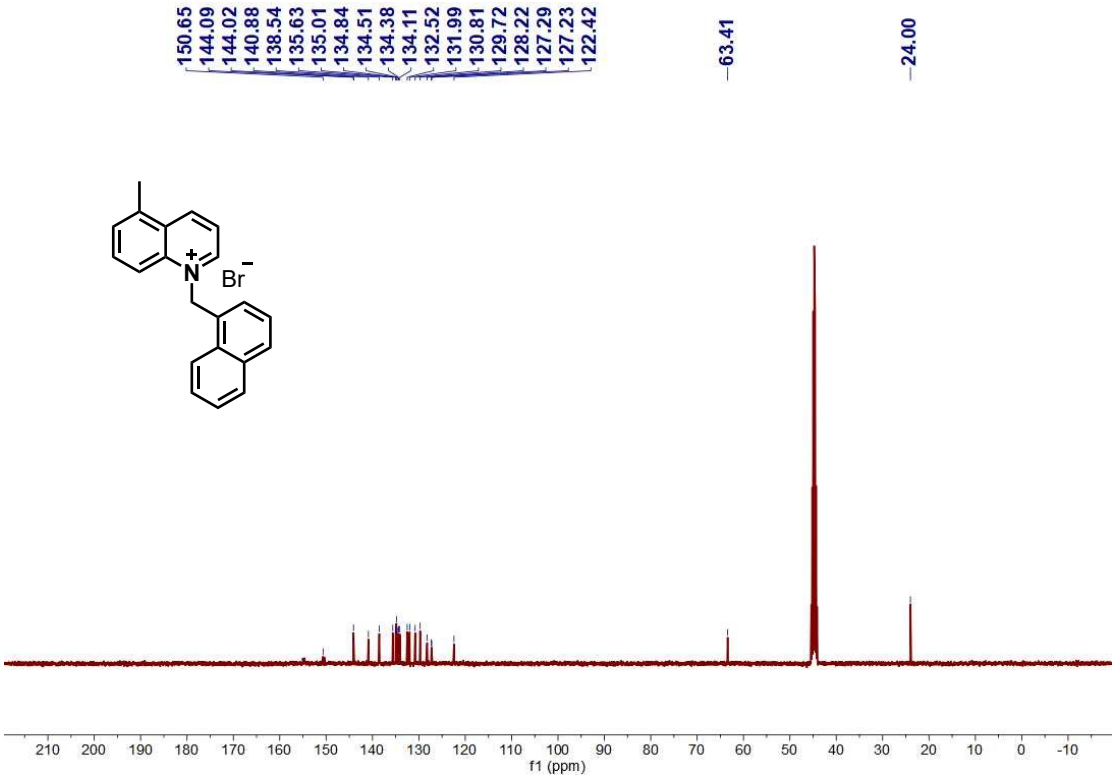
^{1}H NMR and ^{13}C NMR of **1ay**



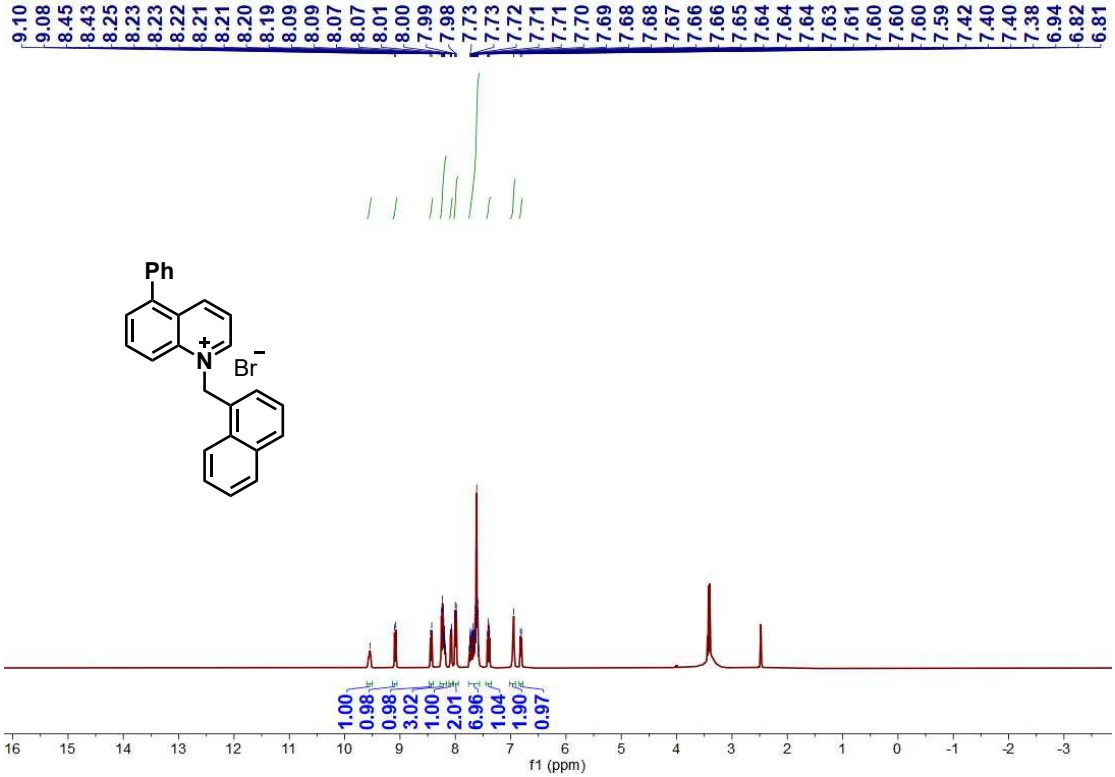


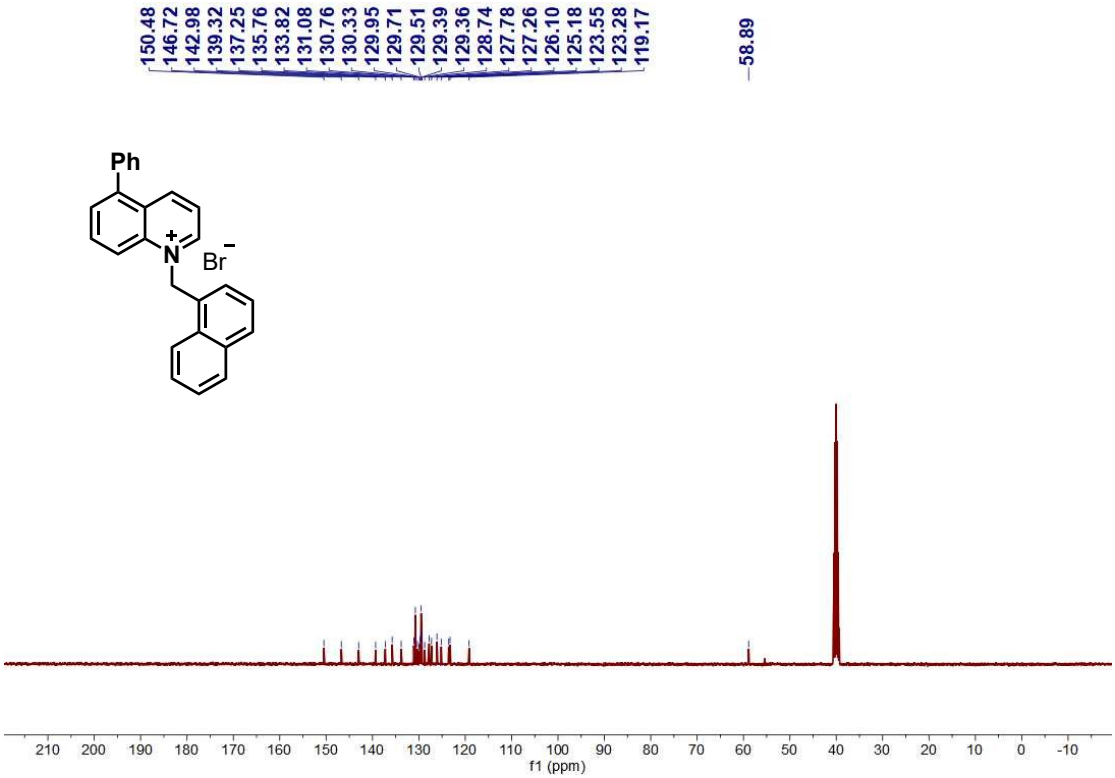
^{1}H NMR and ^{13}C NMR of **1az**



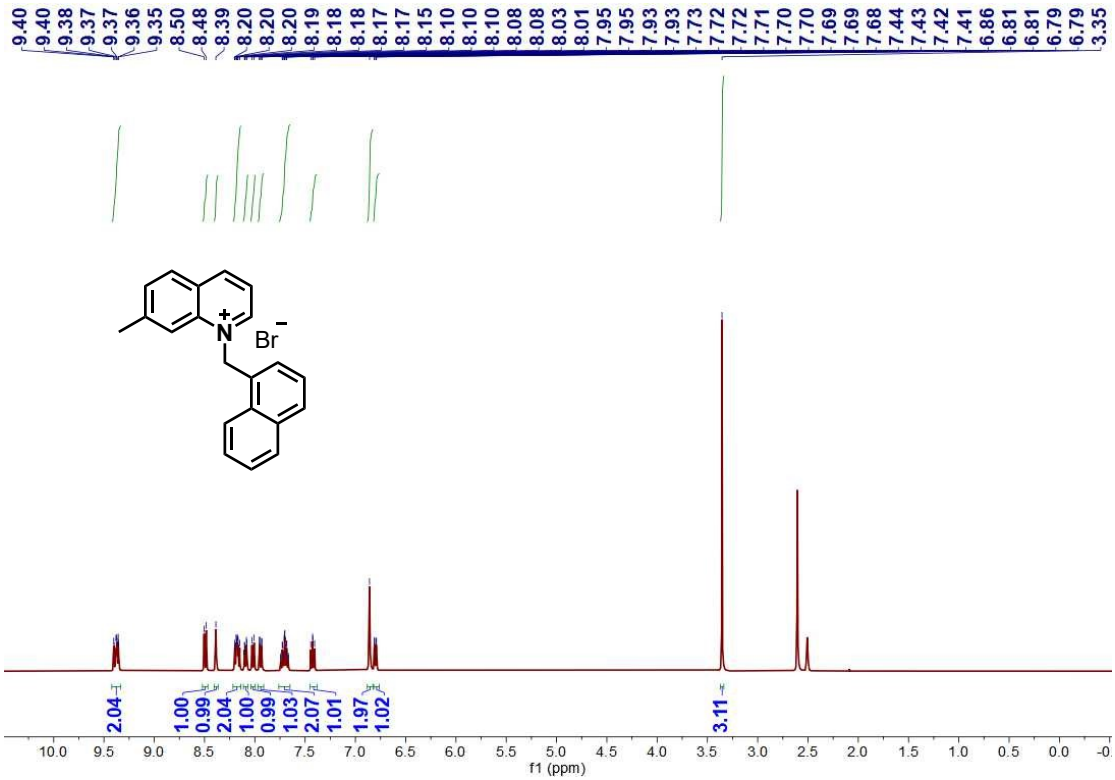


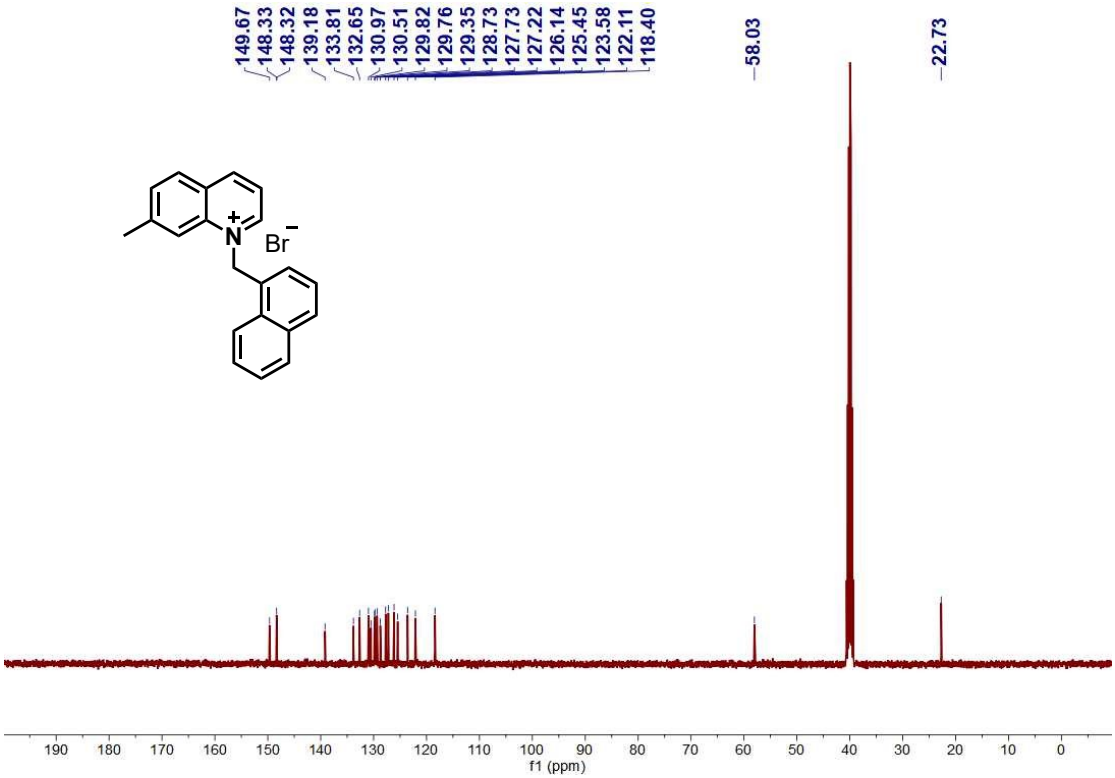
^{1}H NMR and ^{13}C NMR of **1ba**



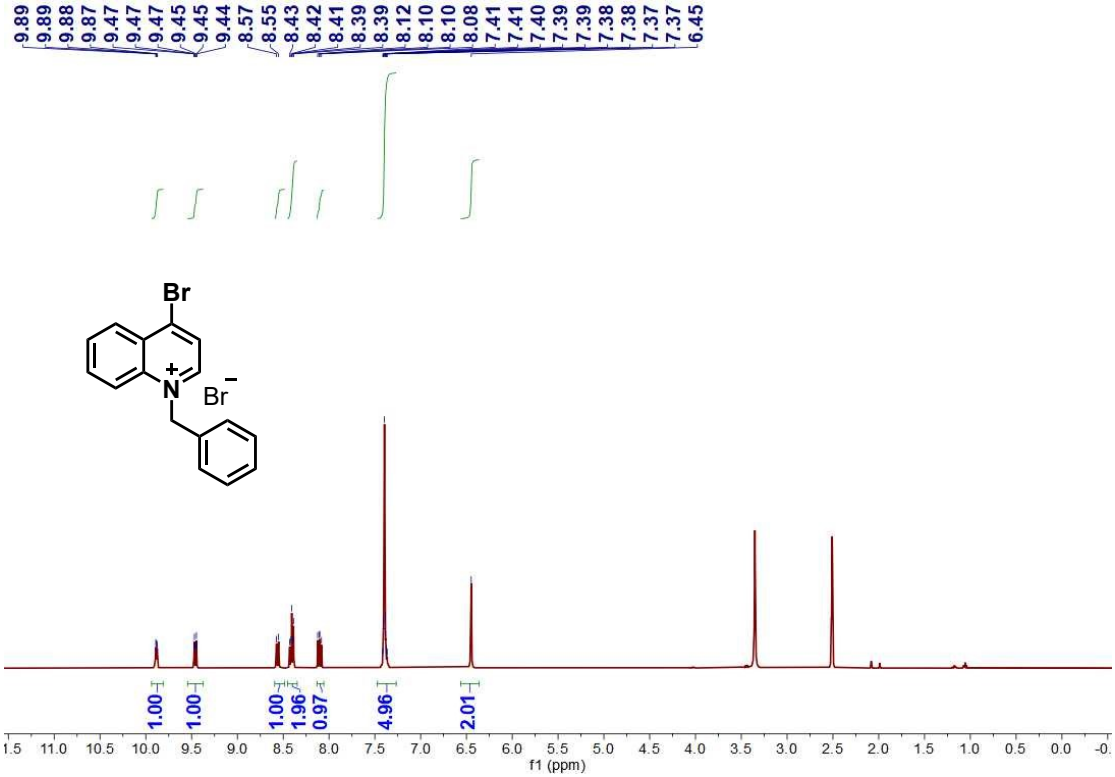


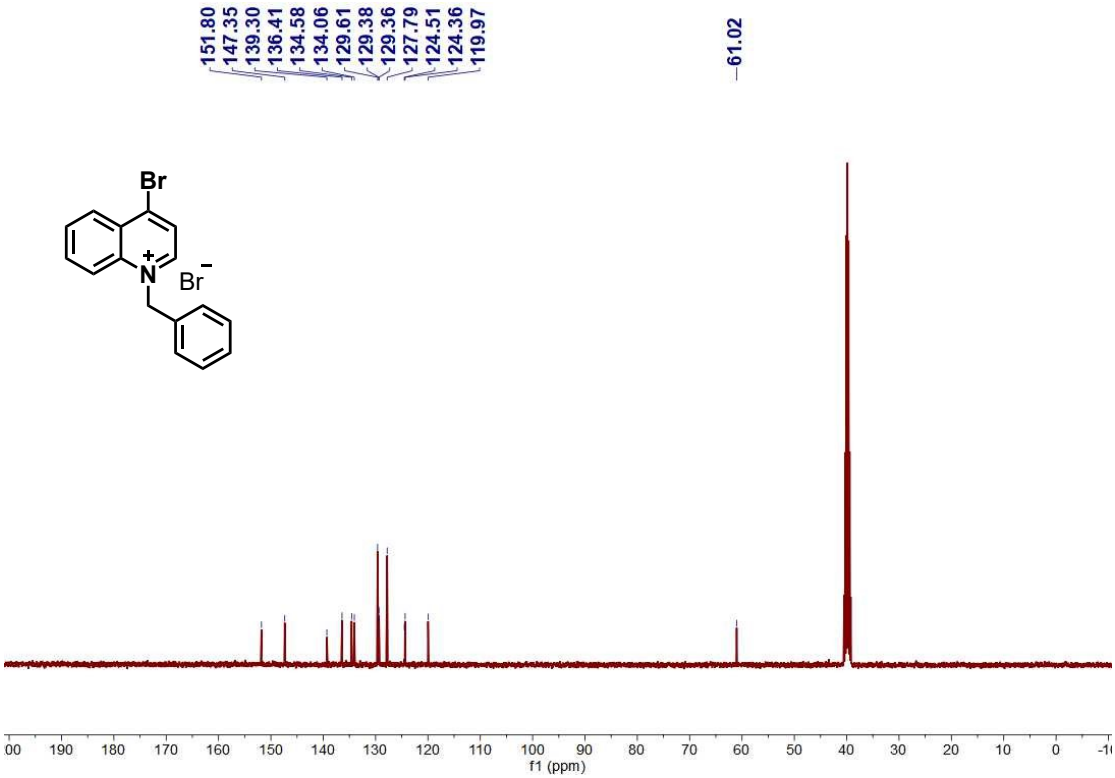
^{1}H NMR and ^{13}C NMR of **1bb**



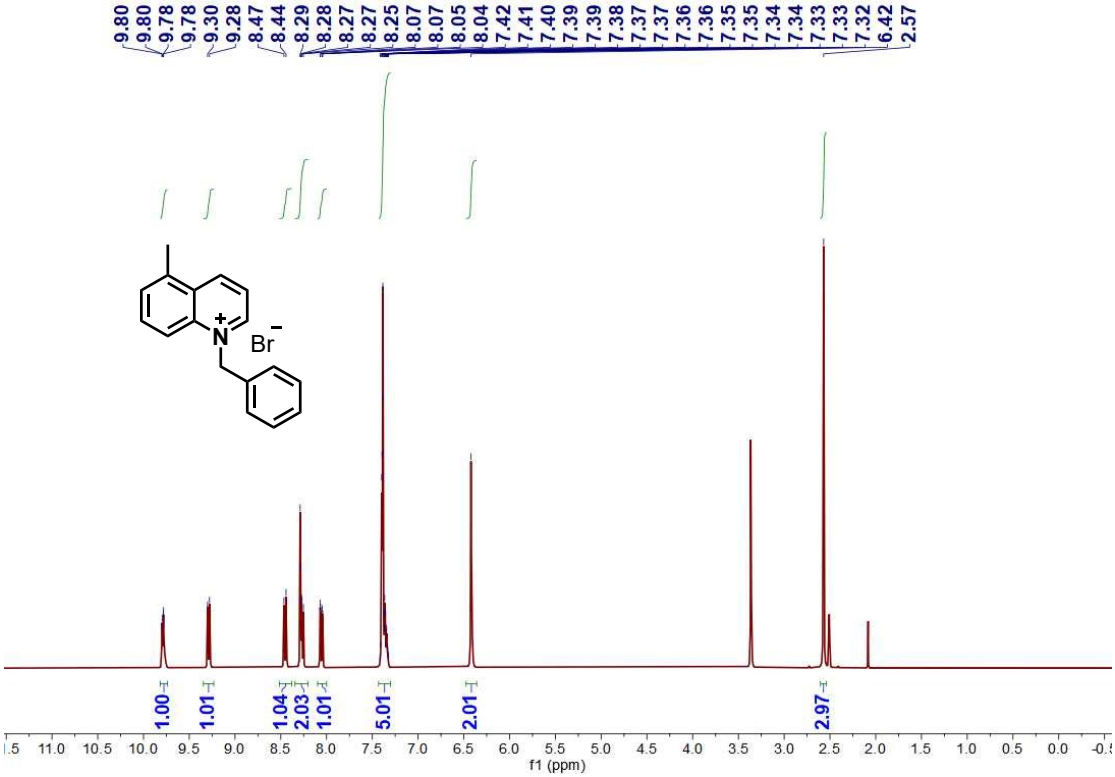


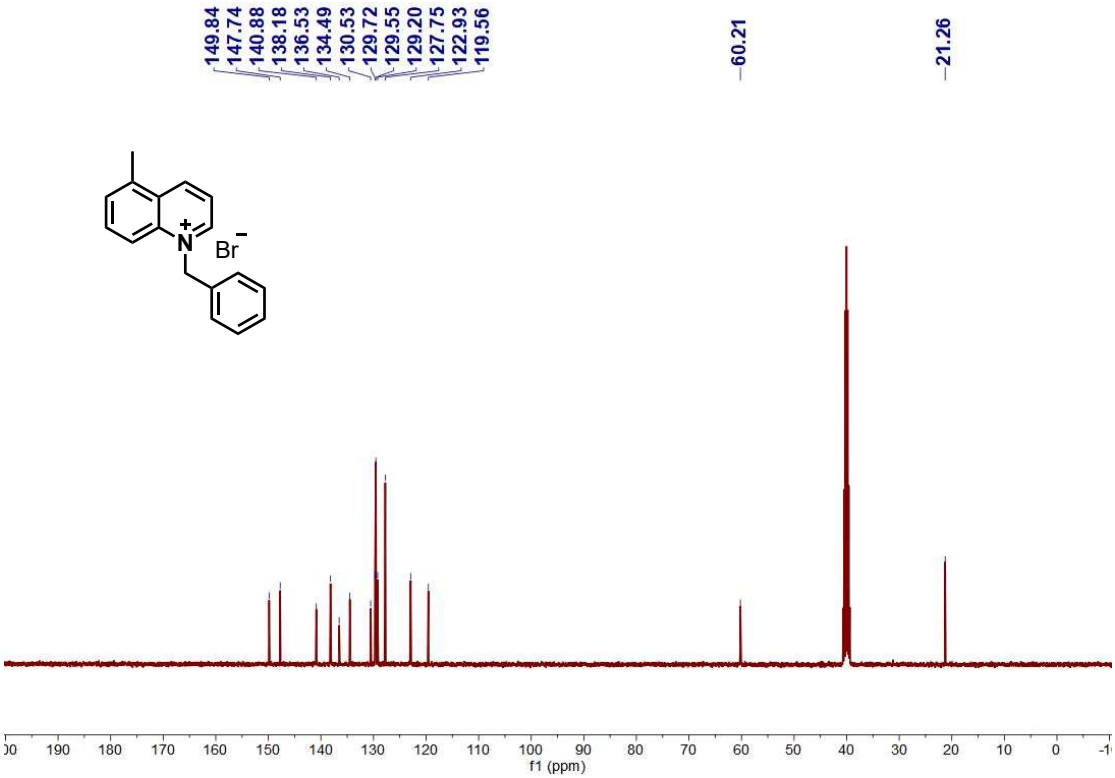
^{1}H NMR and ^{13}C NMR of **1bc**



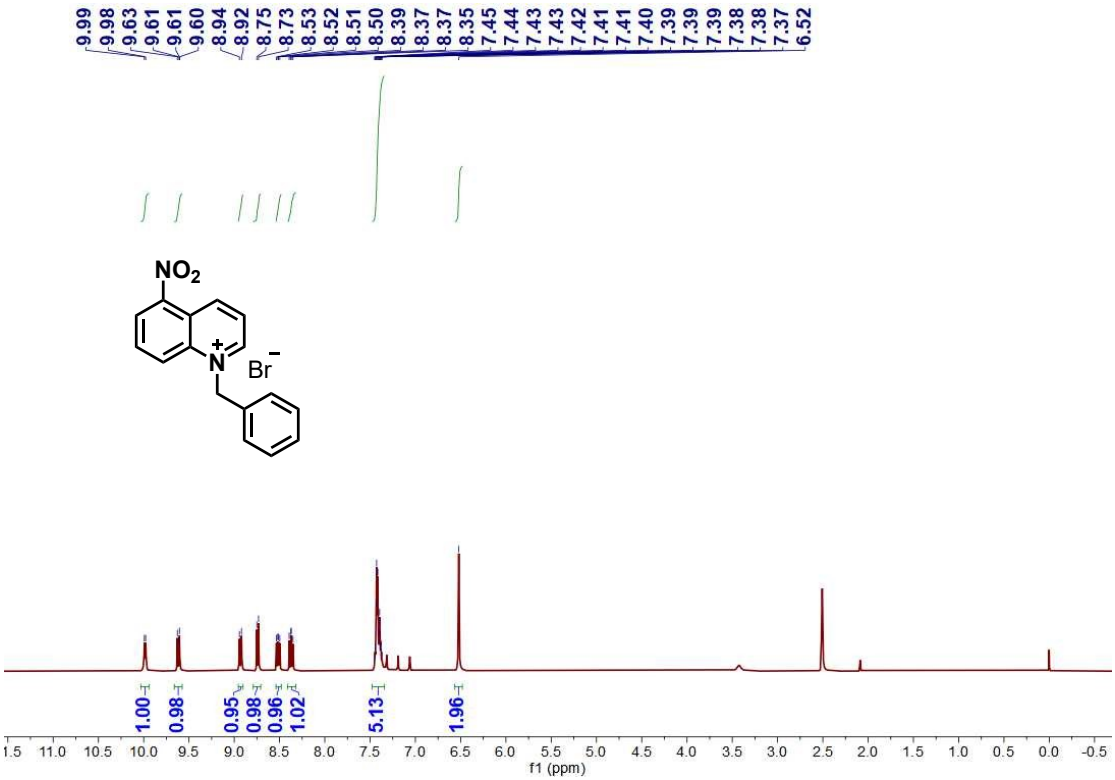


^{1}H NMR and ^{13}C NMR of **1bd**

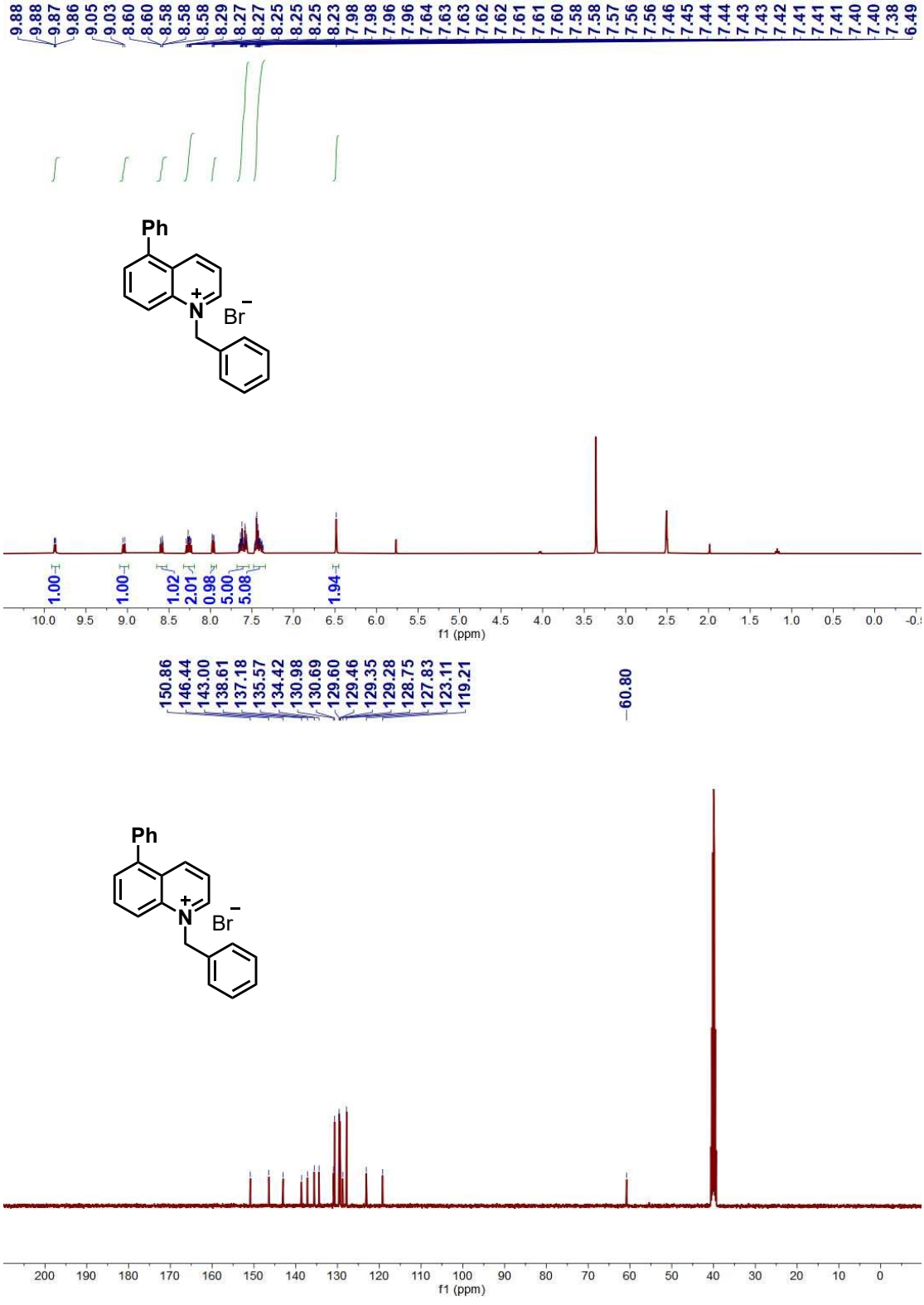



149.84
147.74
140.88
138.18
136.53
134.49
130.53
129.72
129.55
129.20
127.75
122.93
119.56
60.21
21.26
Br
f1 (ppm)

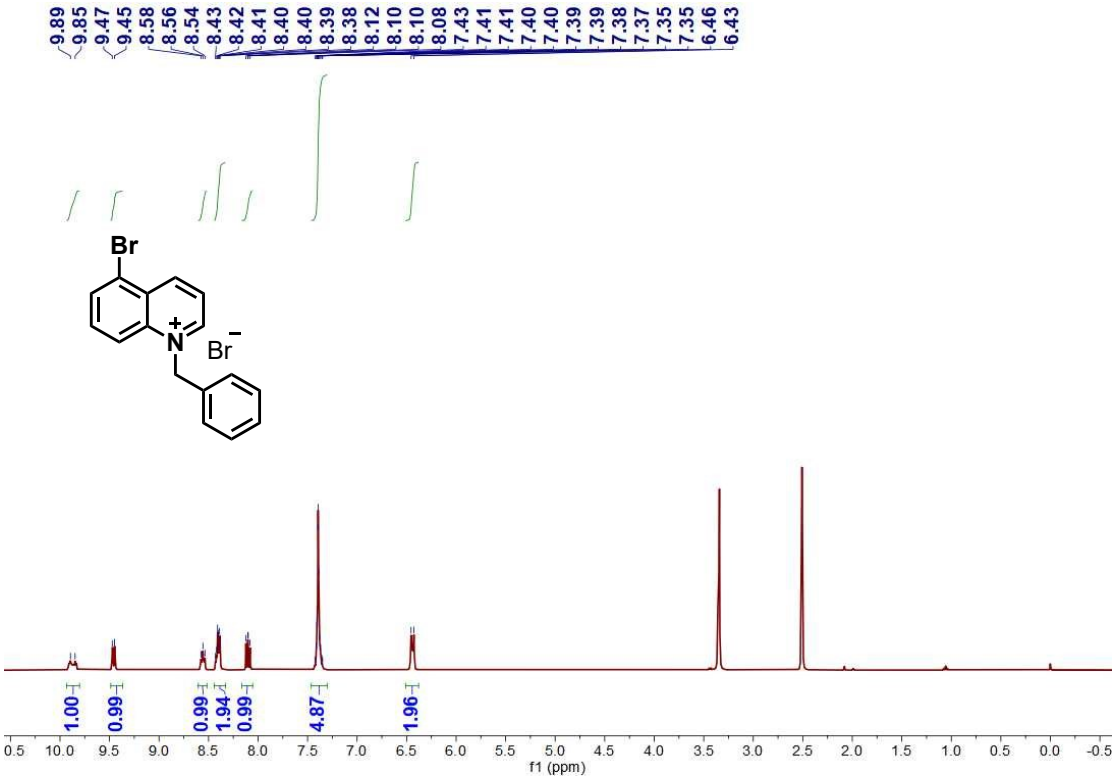
^{1}H NMR of **1be**


9.99
9.98
9.63
9.61
9.61
9.60
8.94
8.92
8.75
8.73
8.53
8.52
8.51
8.50
8.39
8.37
8.37
8.35
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.39
7.38
7.38
7.37
6.52
NO2
Br
1.00
0.98
0.95
0.98
0.96
1.02
5.13
1.96
f1 (ppm)

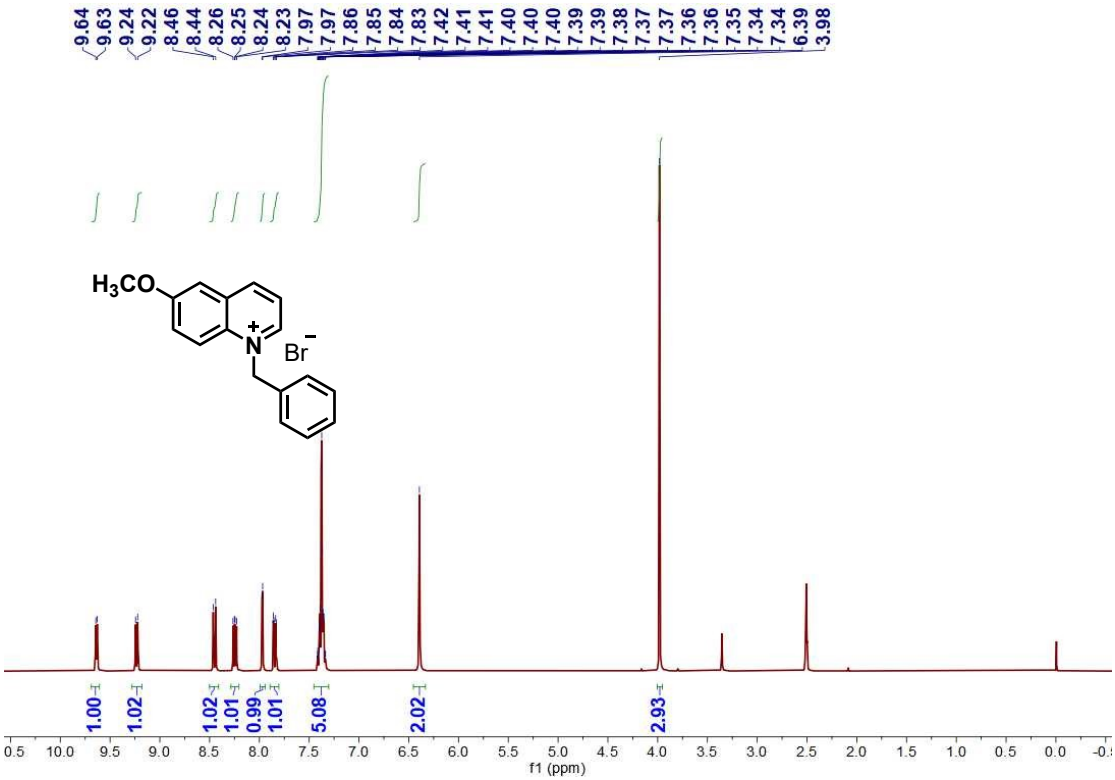
^{1}H NMR and ^{13}C NMR of **1bf**



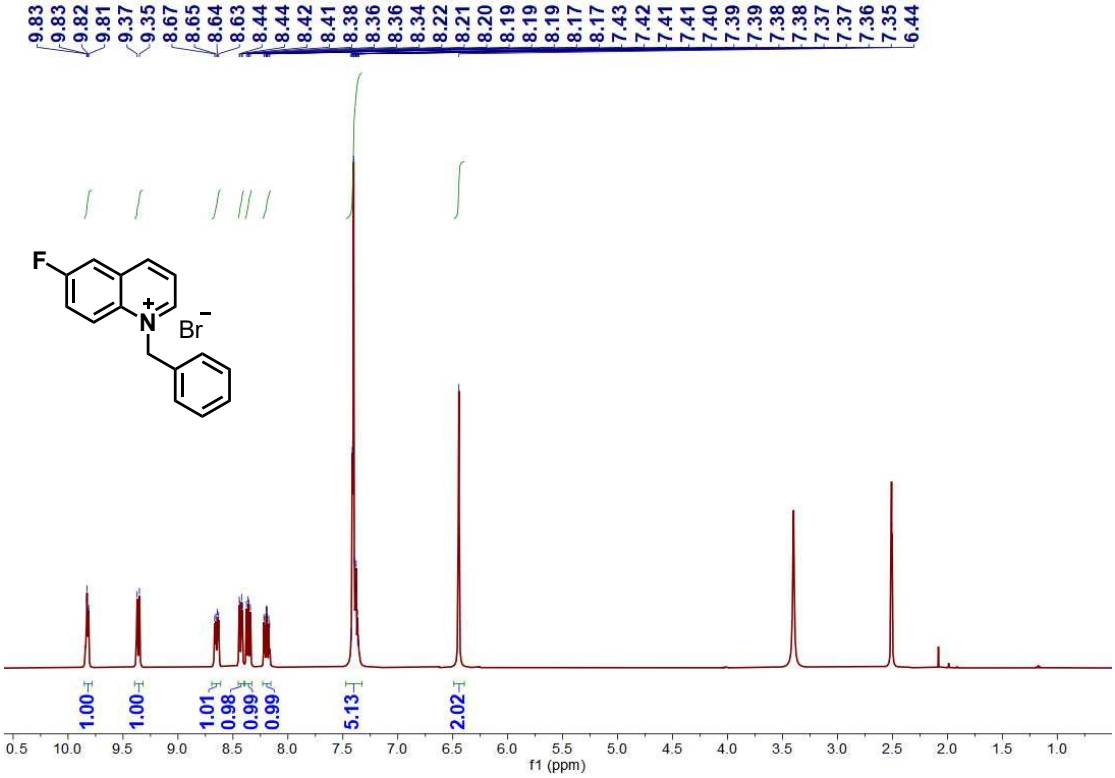
^{1}H NMR of **1bg**



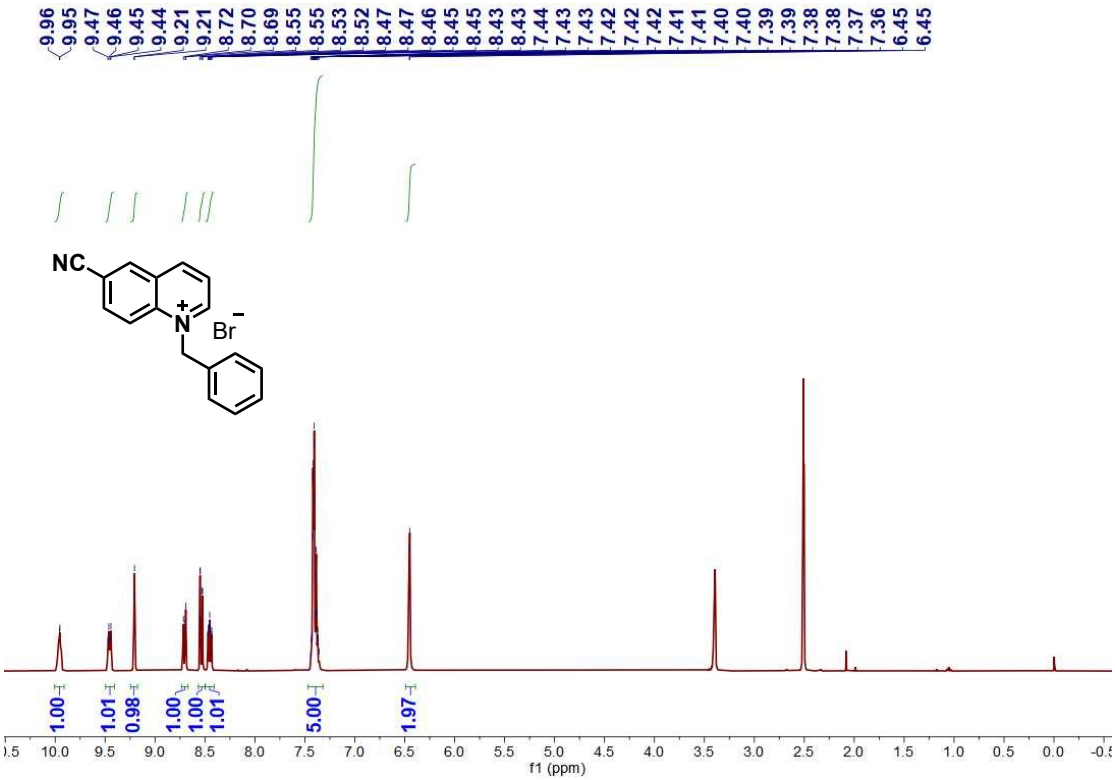
^{1}H NMR of **1bh**



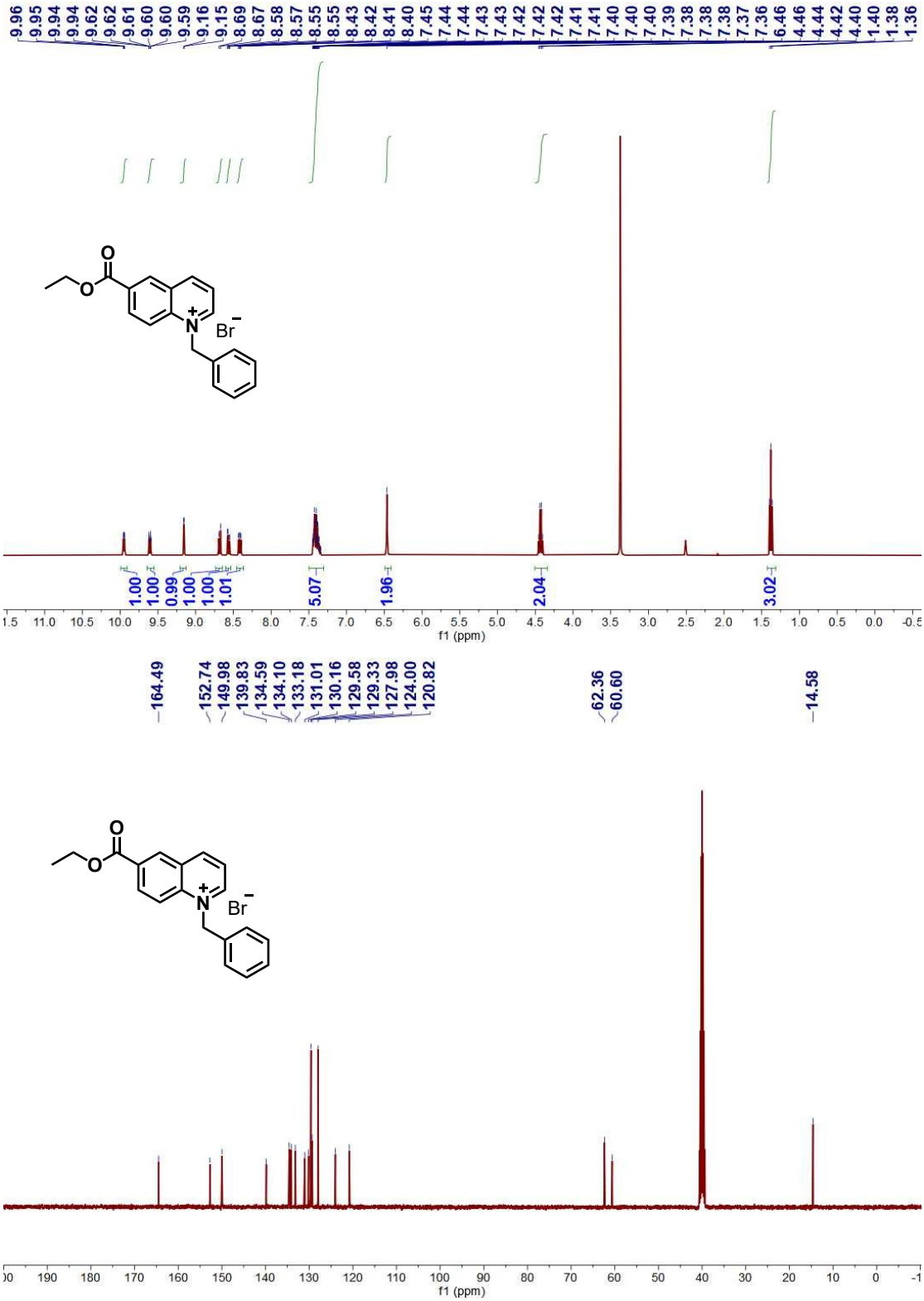
^{1}H NMR of **1bi**



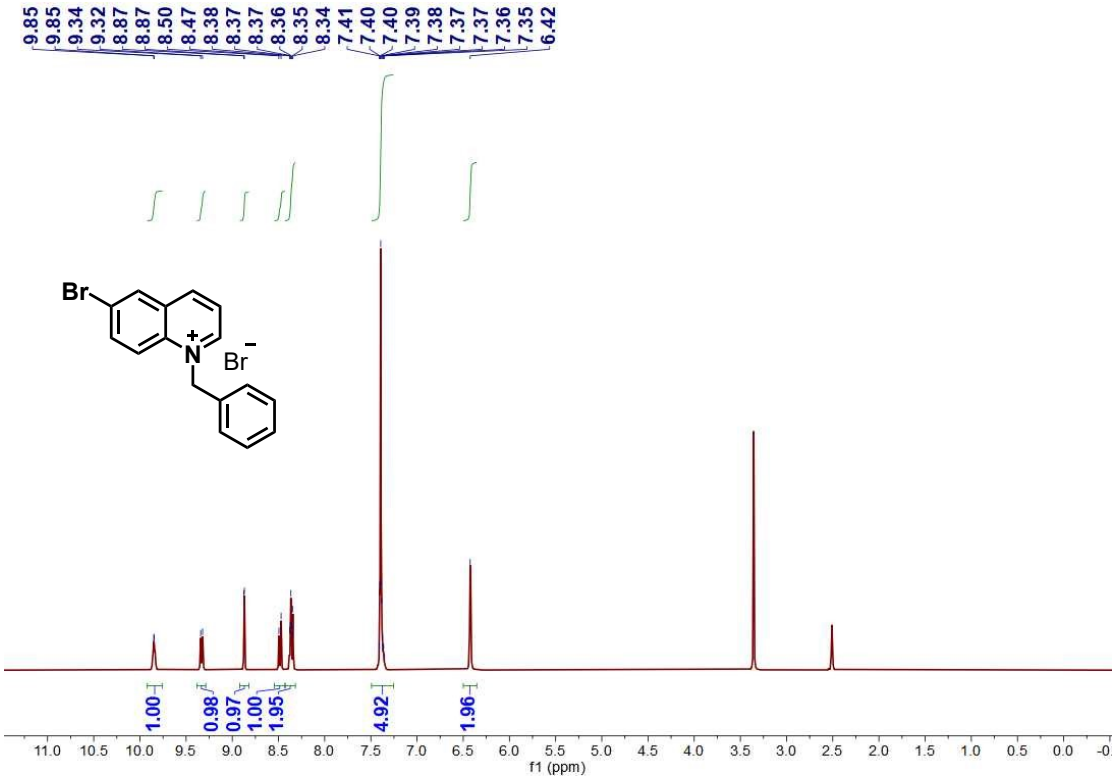
^{1}H NMR of **1bj**



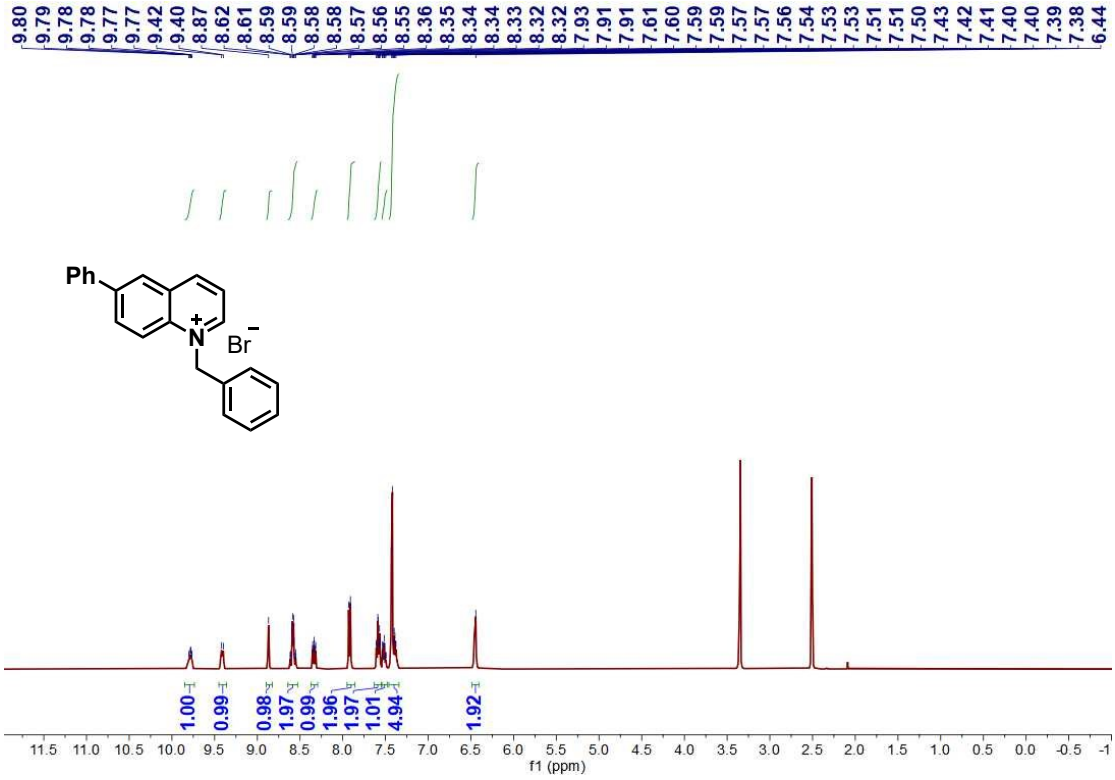
^{1}H NMR and ^{13}C NMR of **1bk**

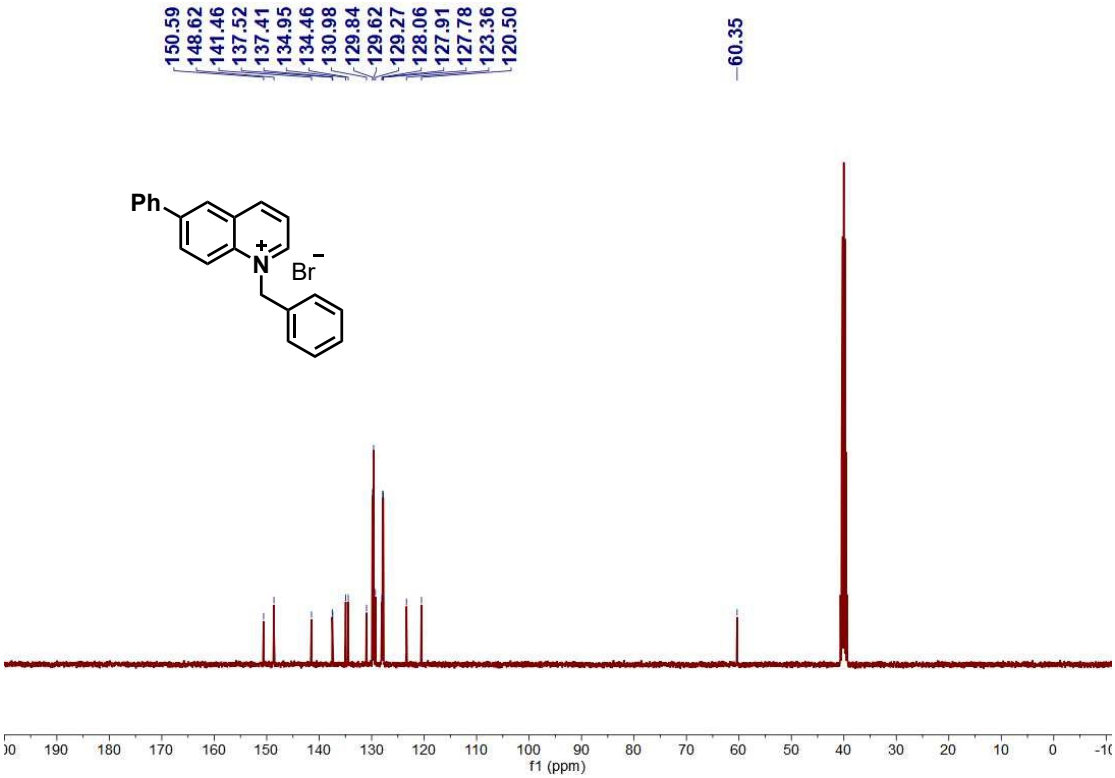


^{1}H NMR of **1bl**

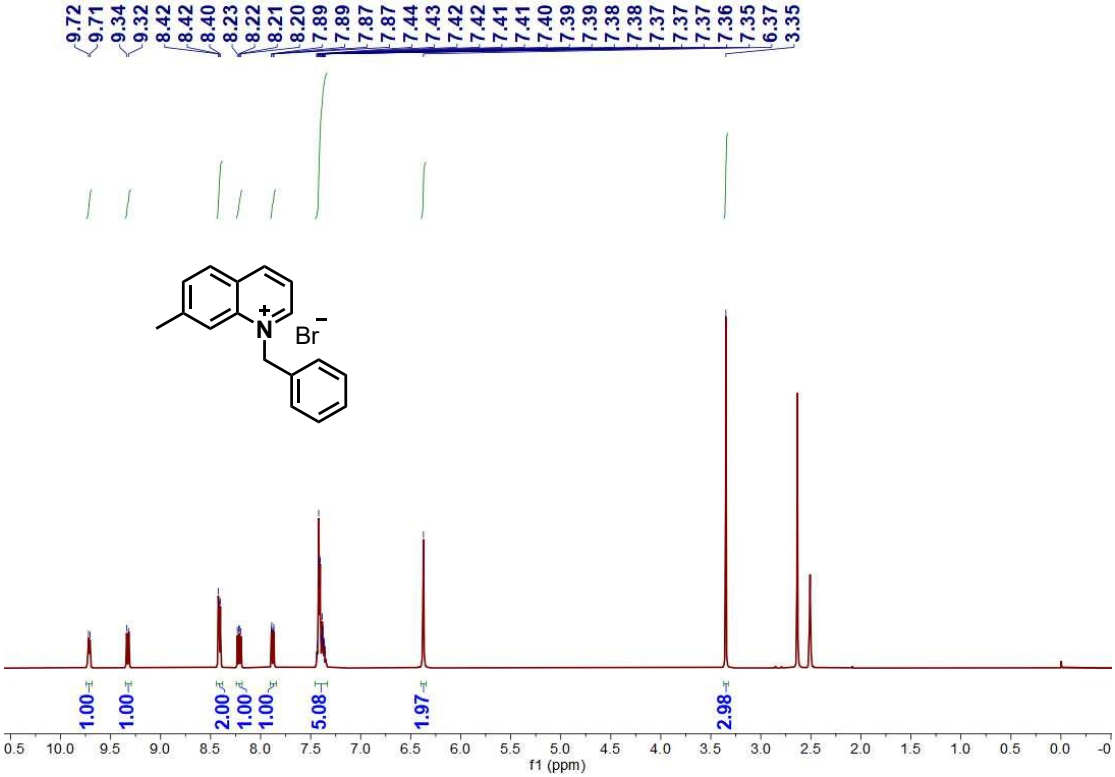


^{1}H NMR and ^{13}C NMR of **1bm**

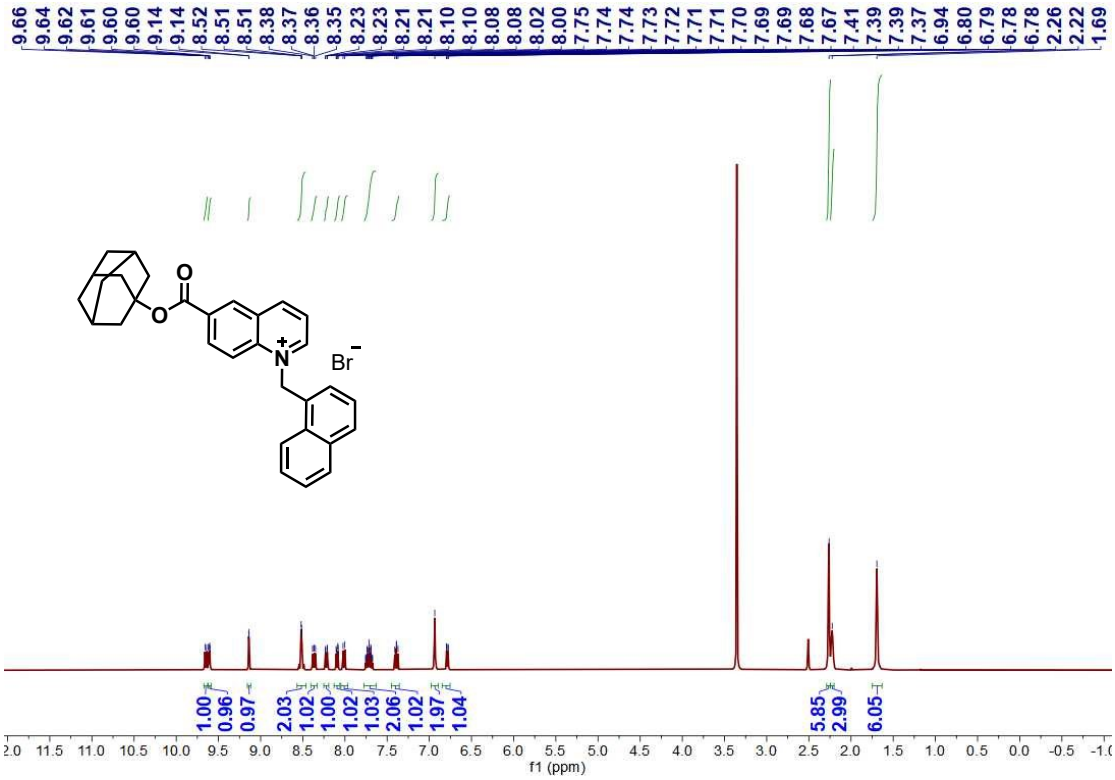


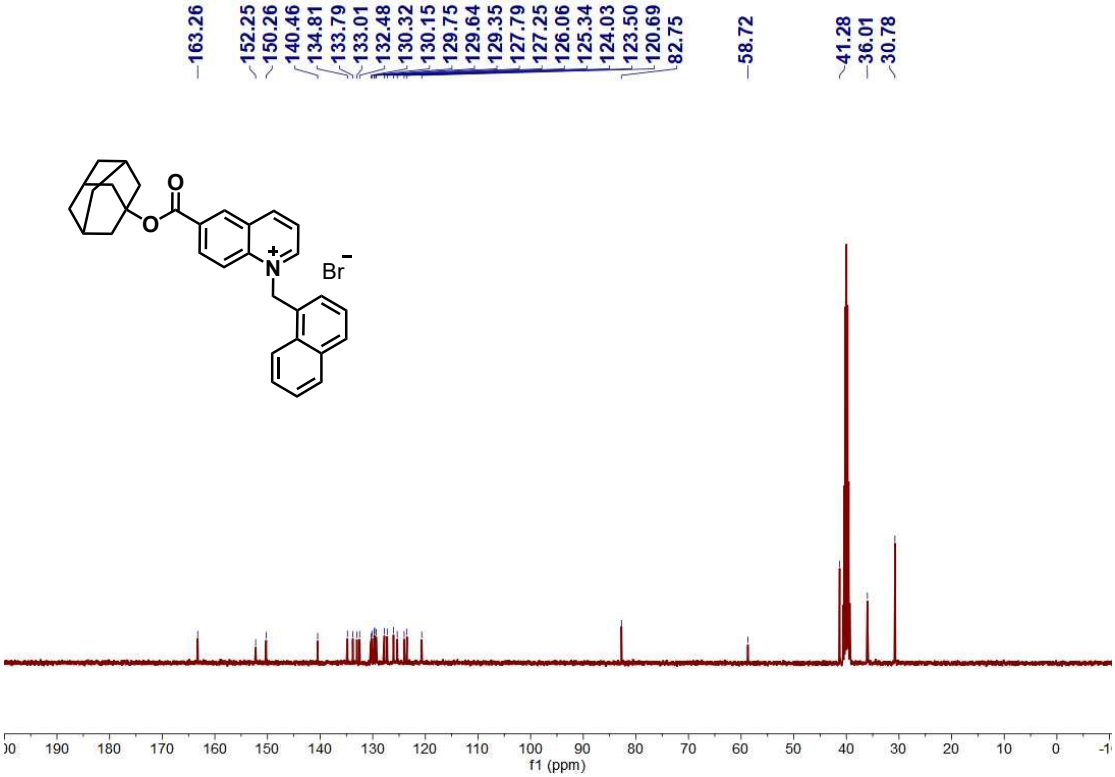

150.59
148.62
141.46
137.52
137.41
134.95
134.46
130.98
129.84
129.62
129.27
128.06
127.91
127.78
123.36
120.50
60.35
Ph
N
Br
f1 (ppm)

^{1}H NMR of **1bn**

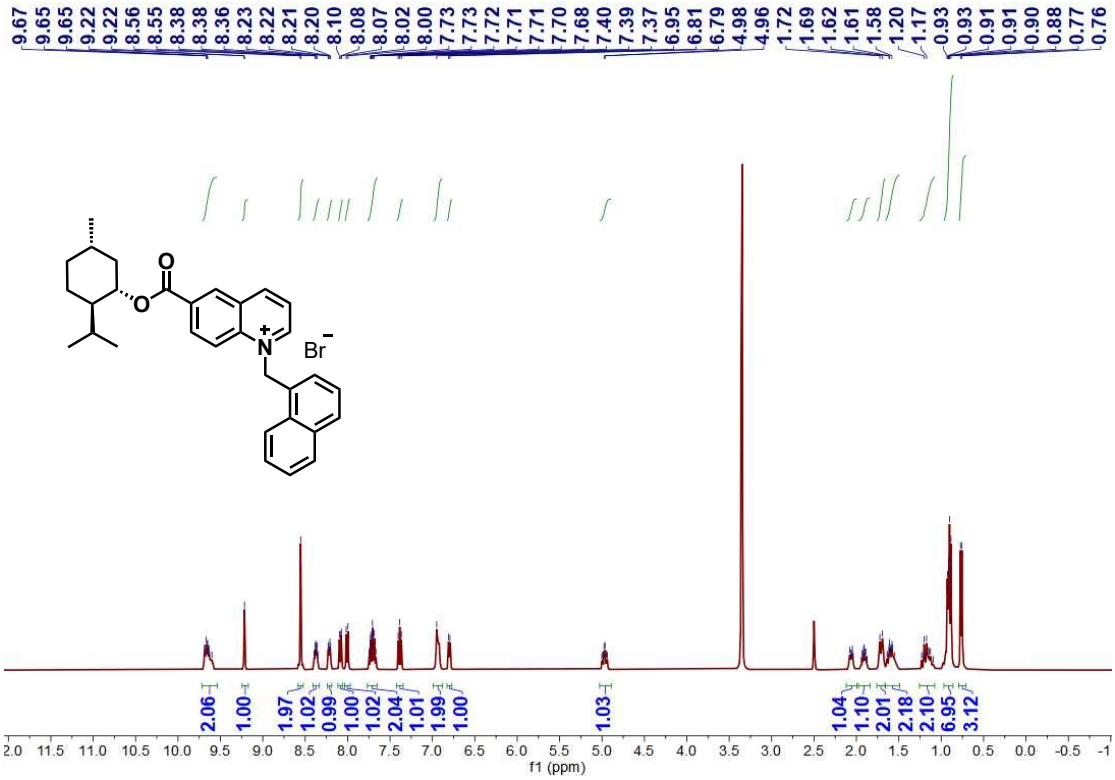

9.72
9.71
9.34
9.32
8.42
8.42
8.40
8.23
8.22
8.21
8.20
7.89
7.89
7.87
7.87
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.35
6.37
3.35
N
Br
1.00
1.00
2.00
1.00
1.00
5.08
1.97
2.98
f1 (ppm)

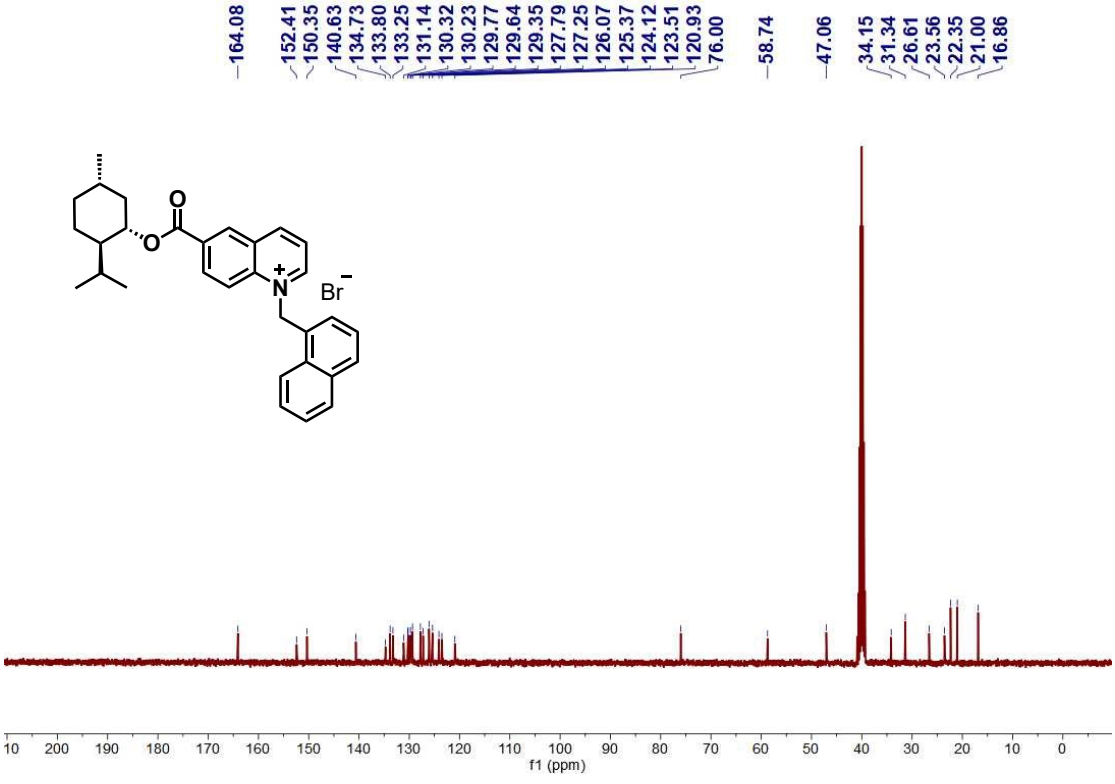
^{1}H NMR and ^{13}C NMR of **1bo**



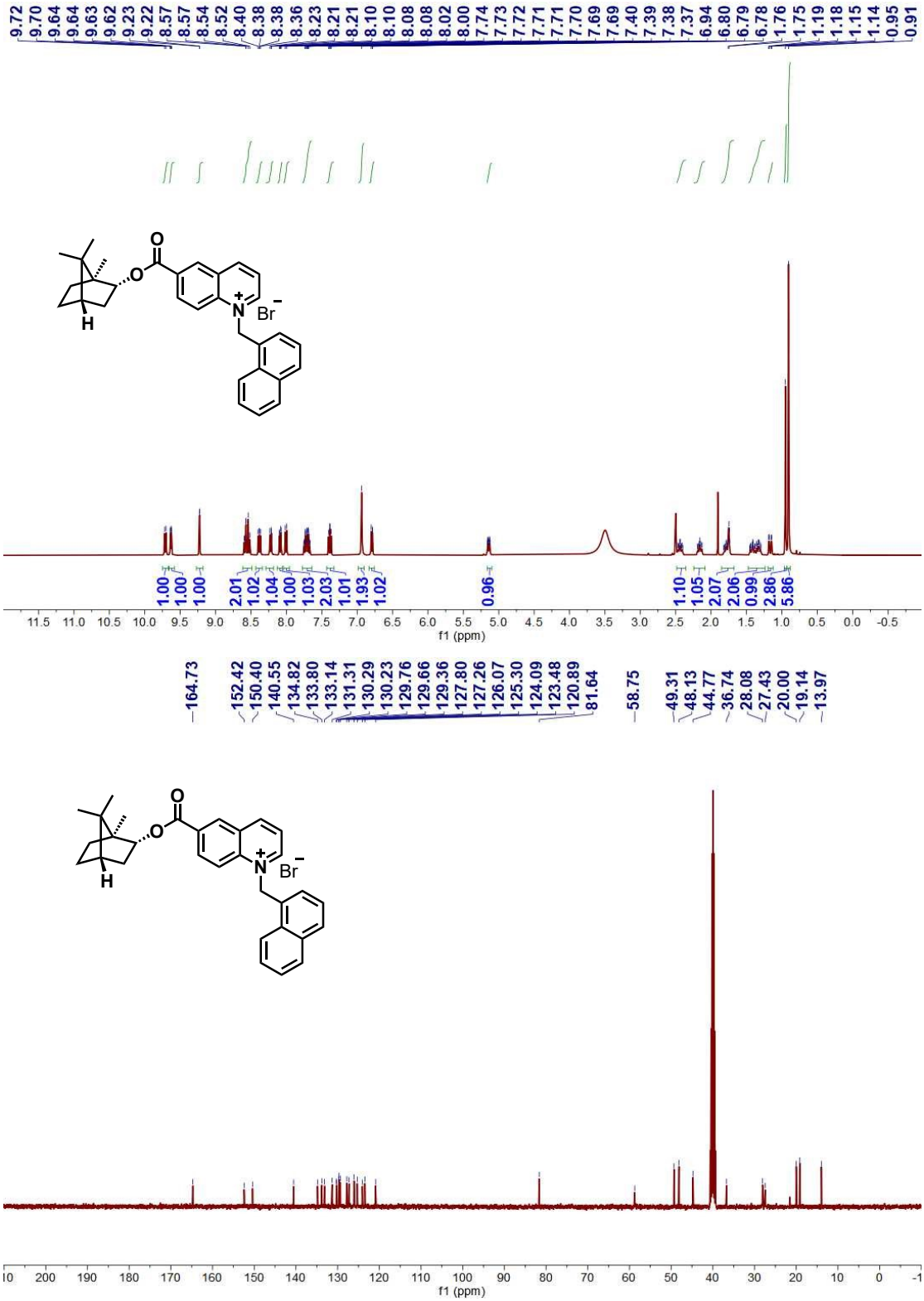


^{1}H NMR and ^{13}C NMR of **1bp**

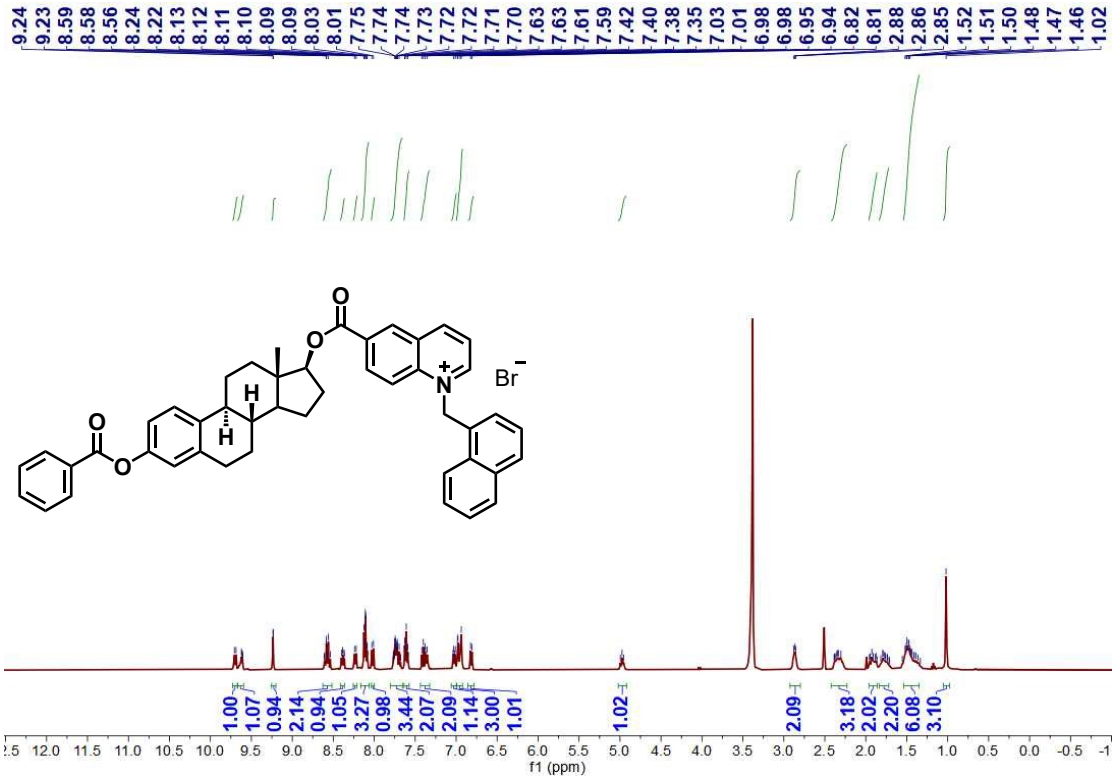


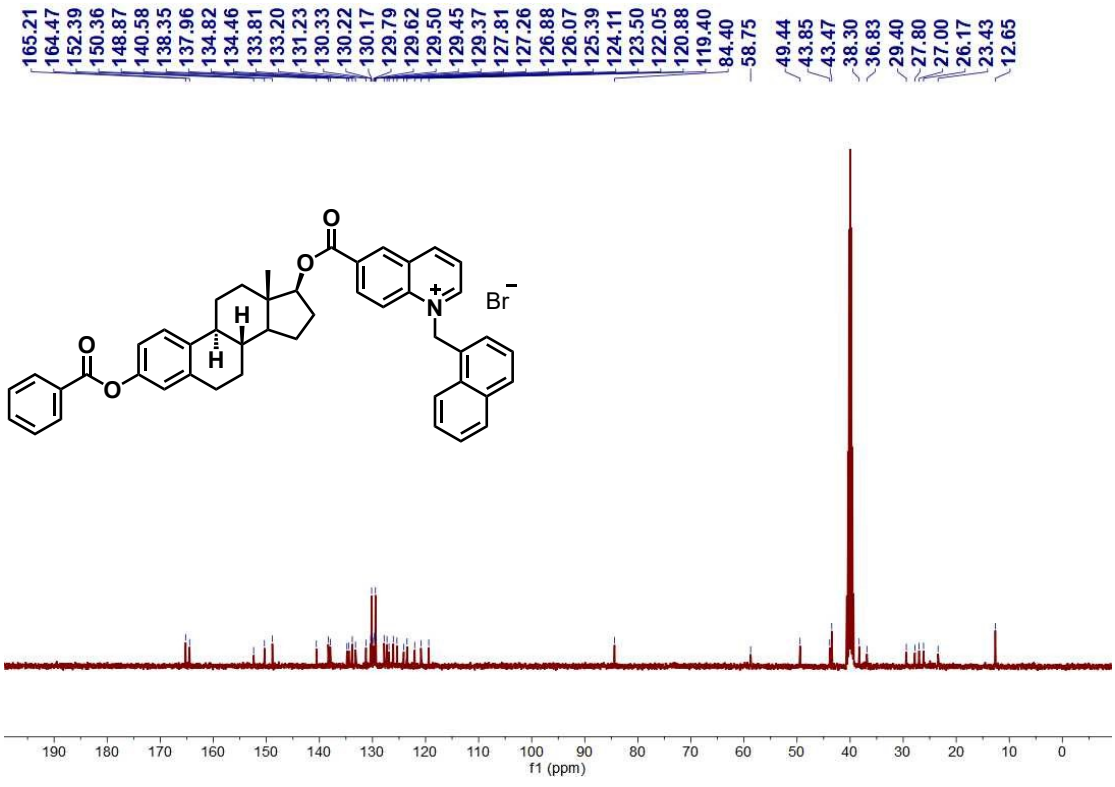


^{1}H NMR and ^{13}C NMR of **1bq**

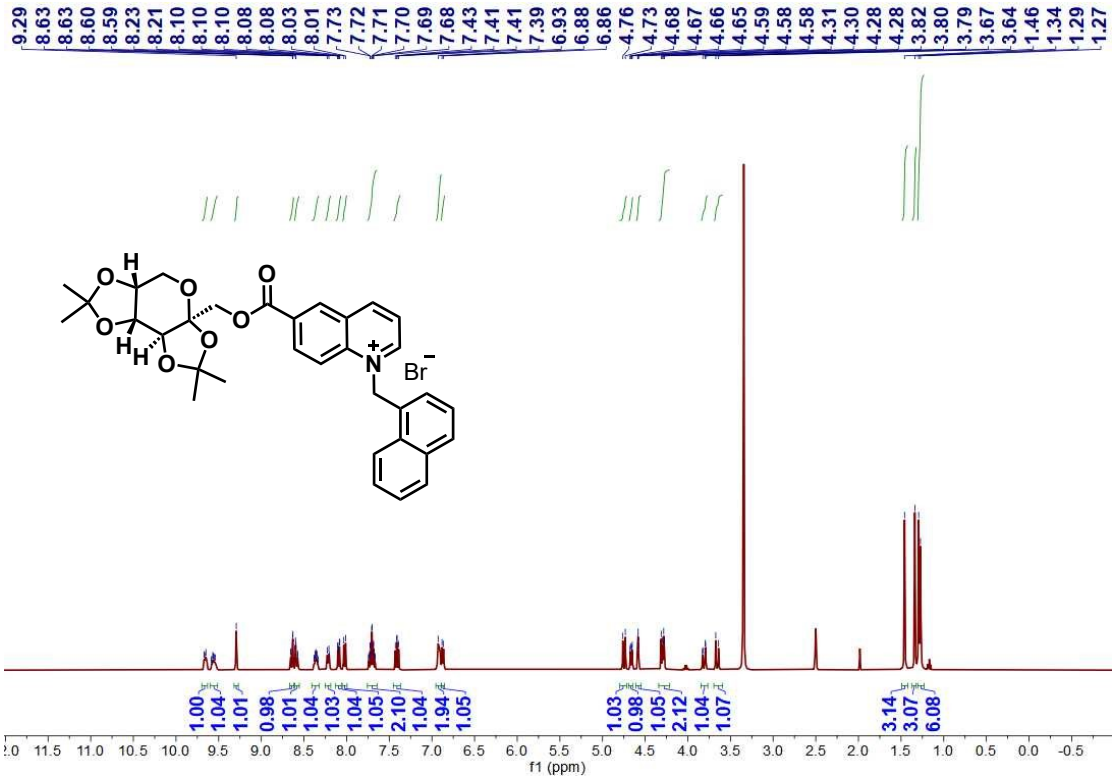


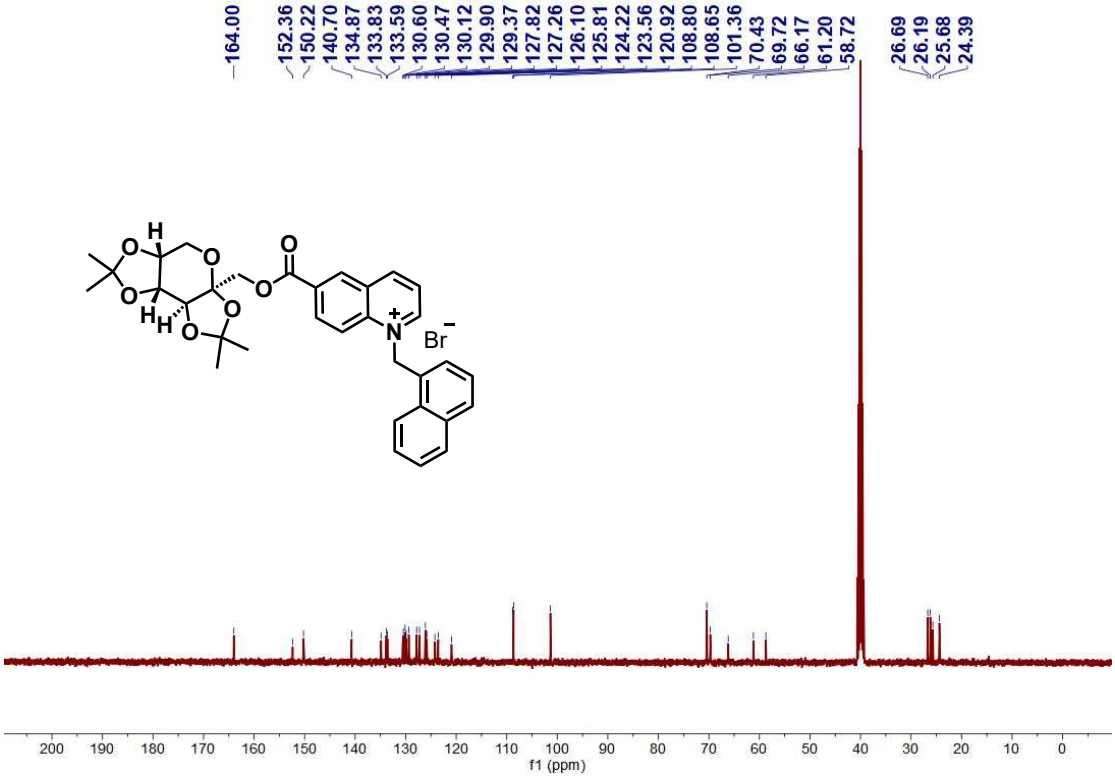
^{1}H NMR and ^{13}C NMR of **1br**



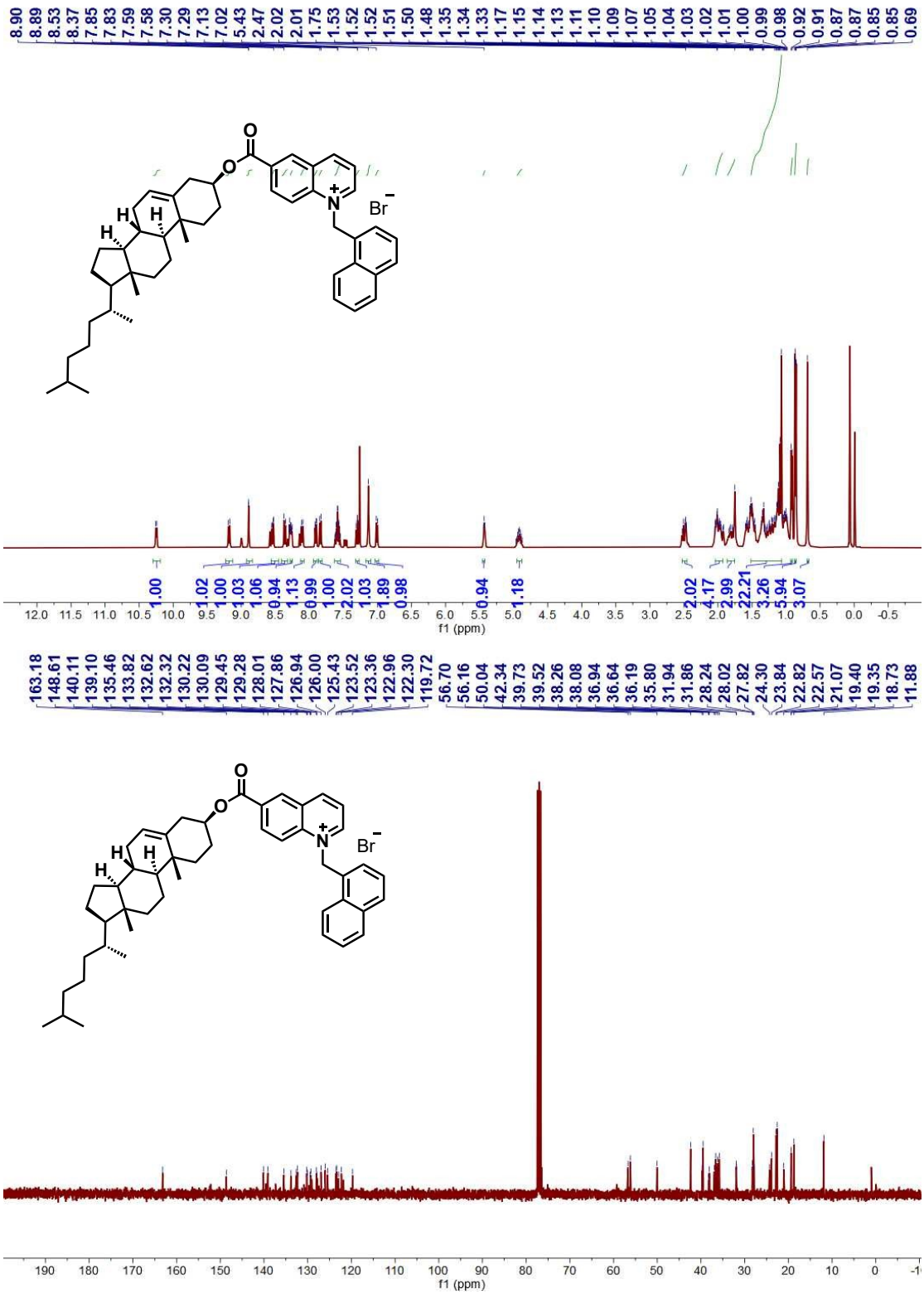


^{1}H NMR and ^{13}C NMR of **1bs**

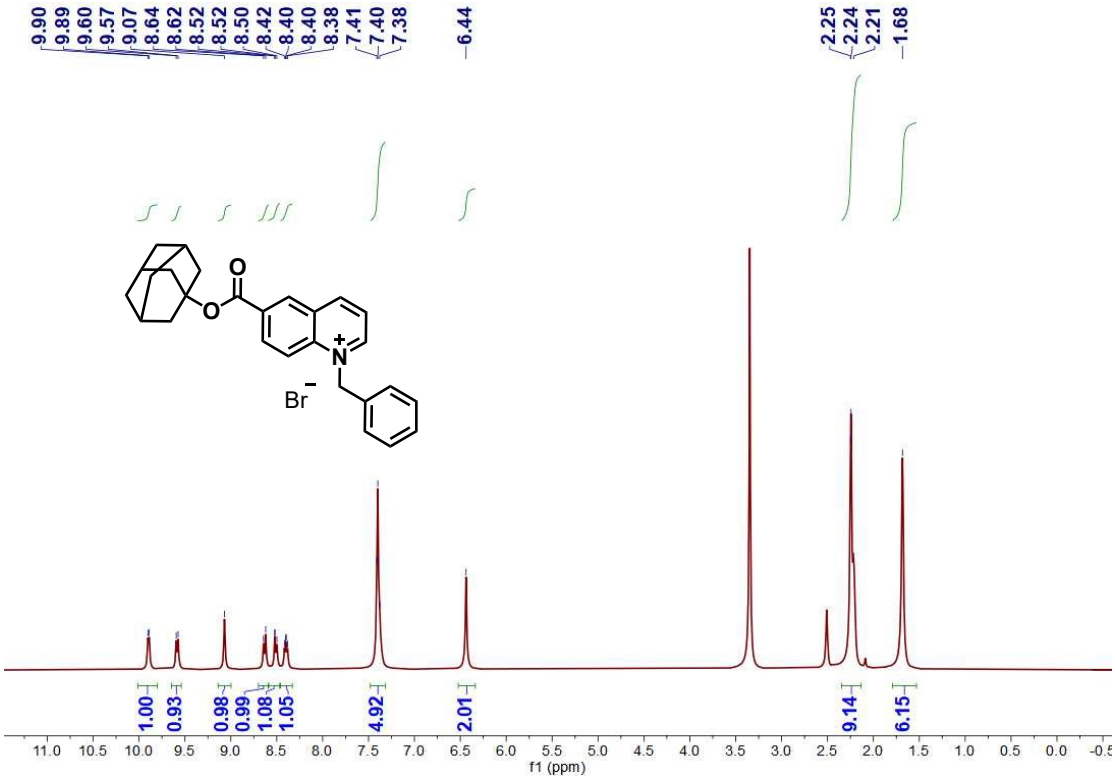


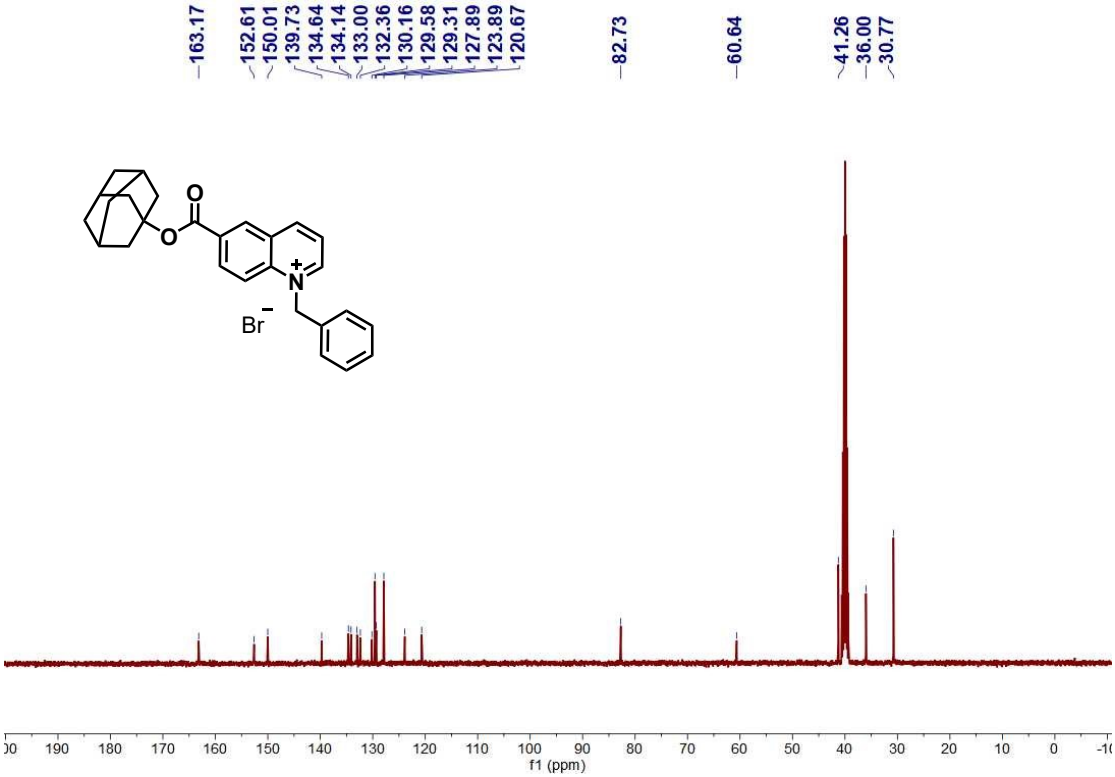


^{1}H NMR and ^{13}C NMR of **1bt**

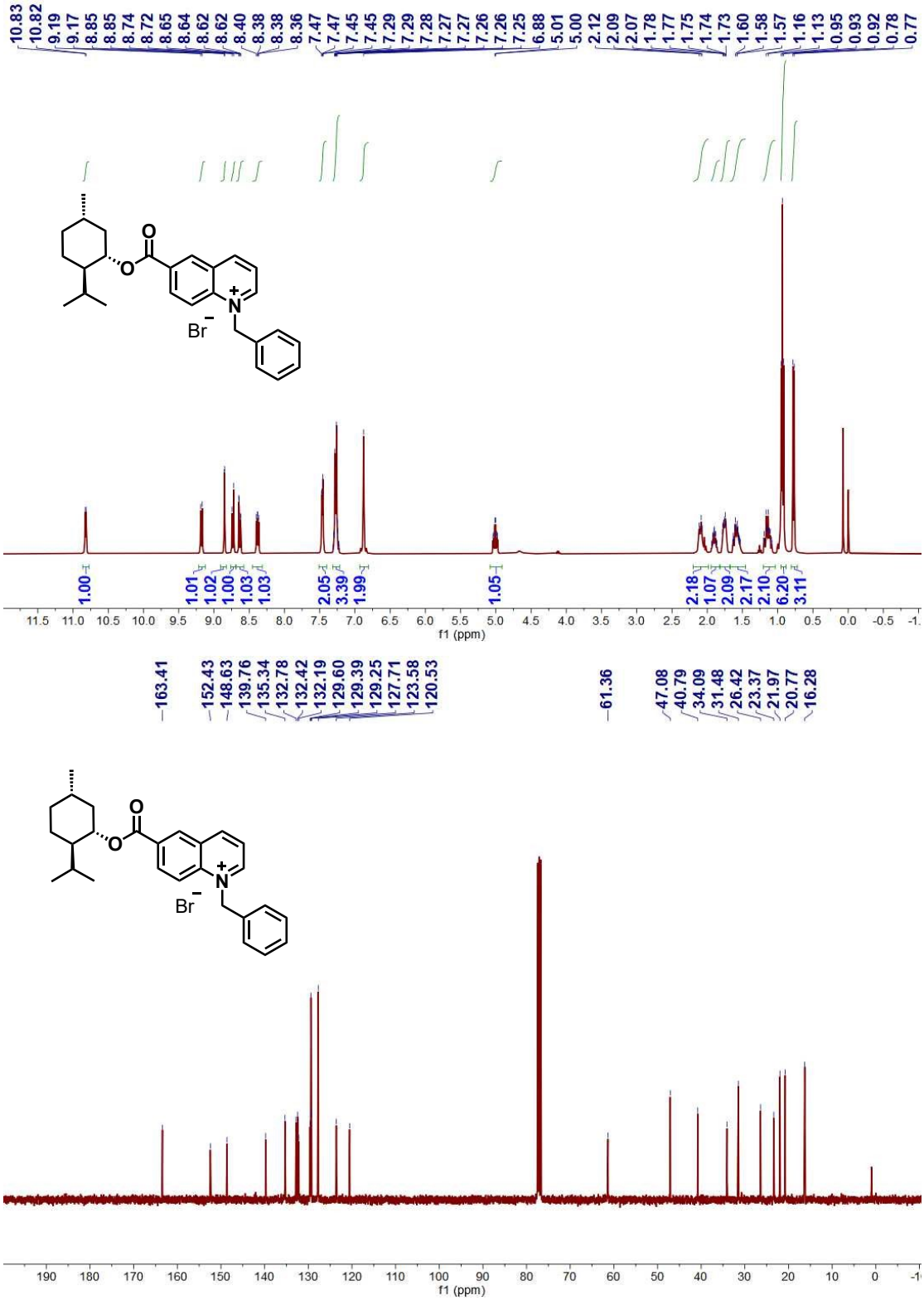


^{1}H NMR and ^{13}C NMR of **1bu**

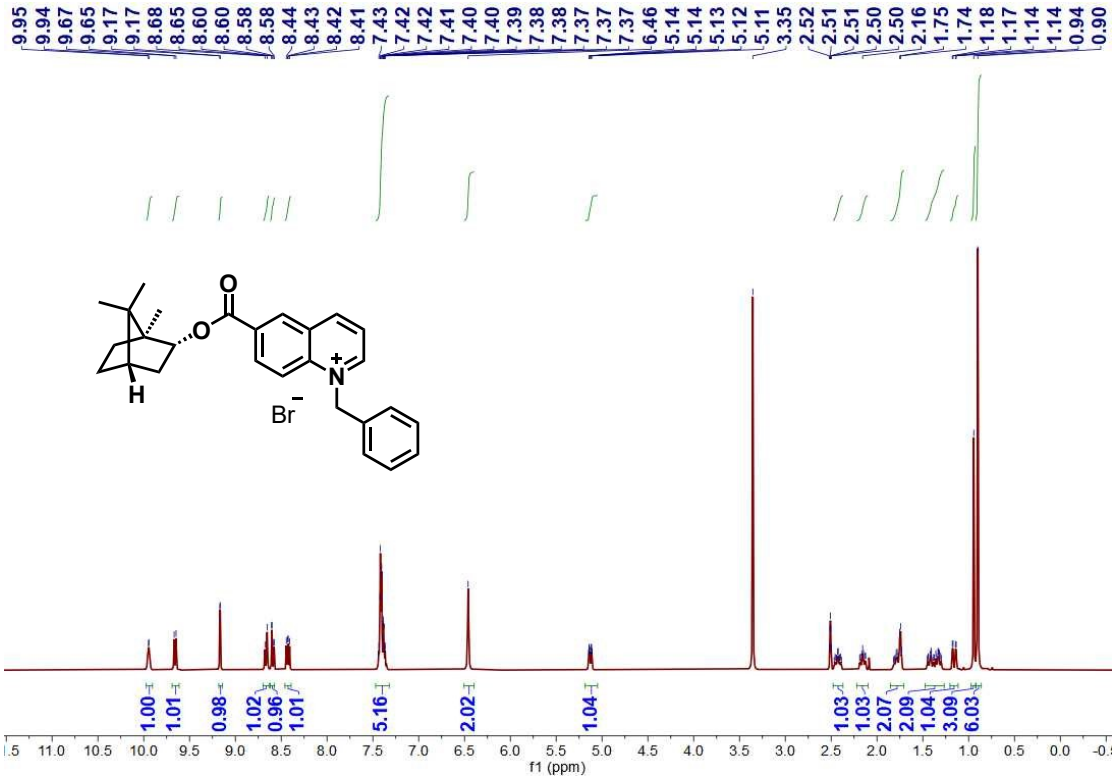


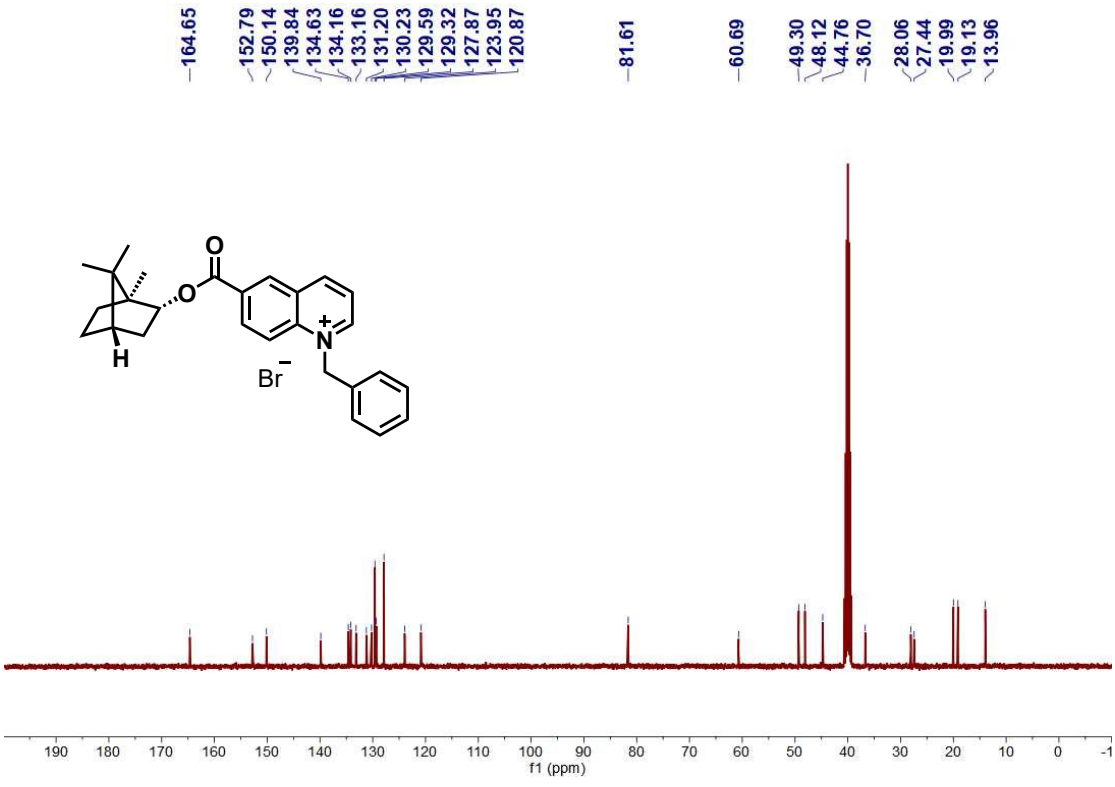


^{1}H NMR and ^{13}C NMR of **1bv**

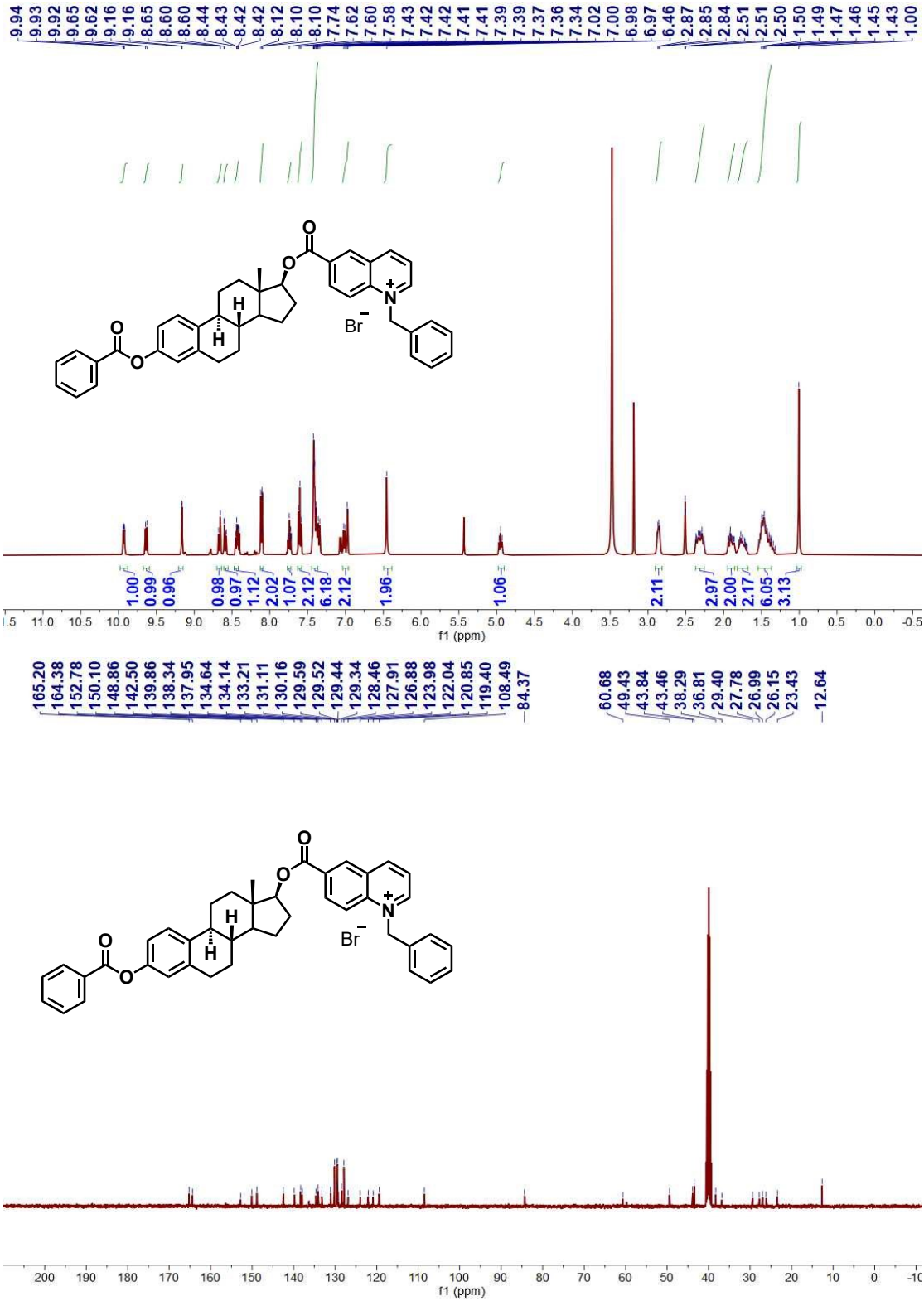


^{1}H NMR and ^{13}C NMR of **1bw**

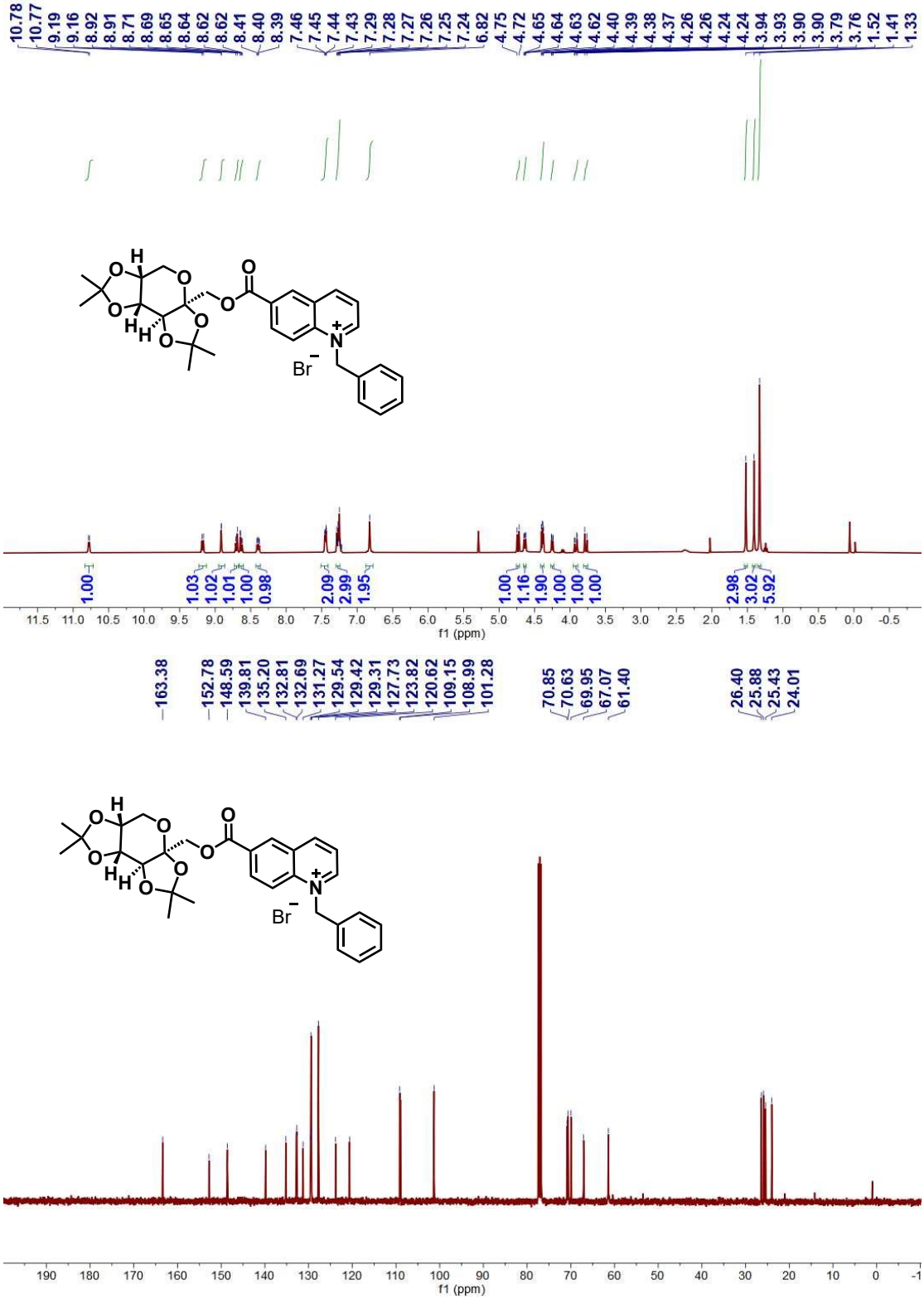




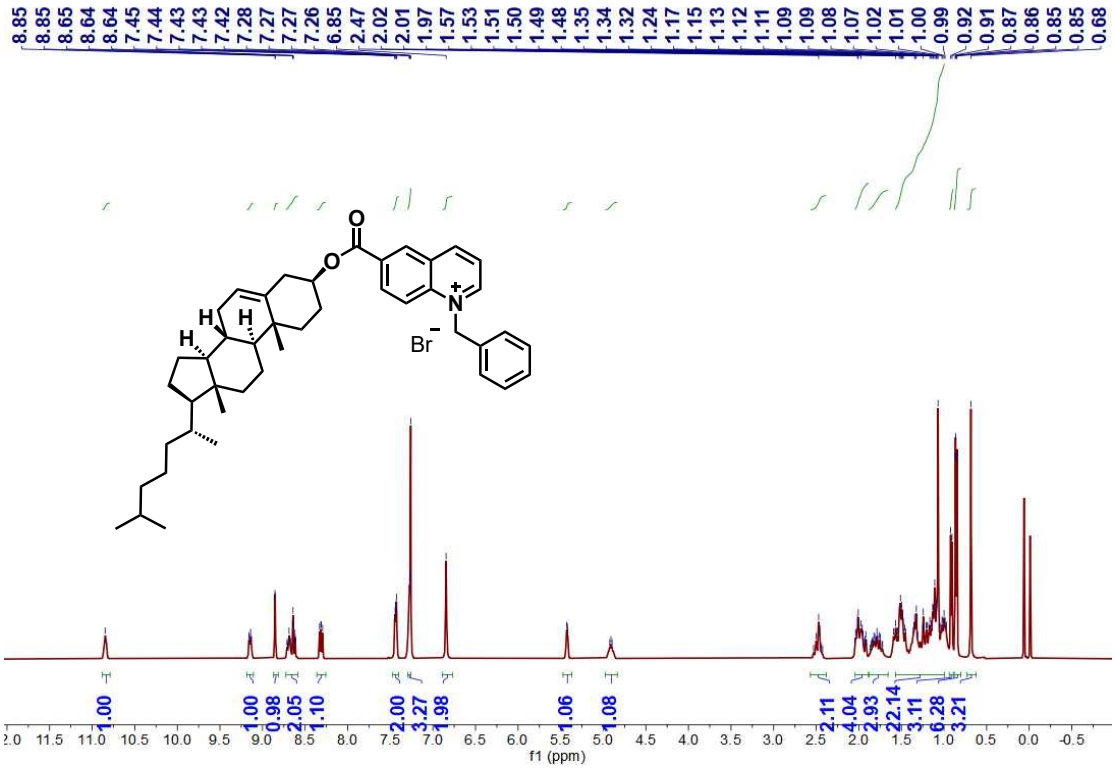
^{1}H NMR and ^{13}C NMR of **1bx**

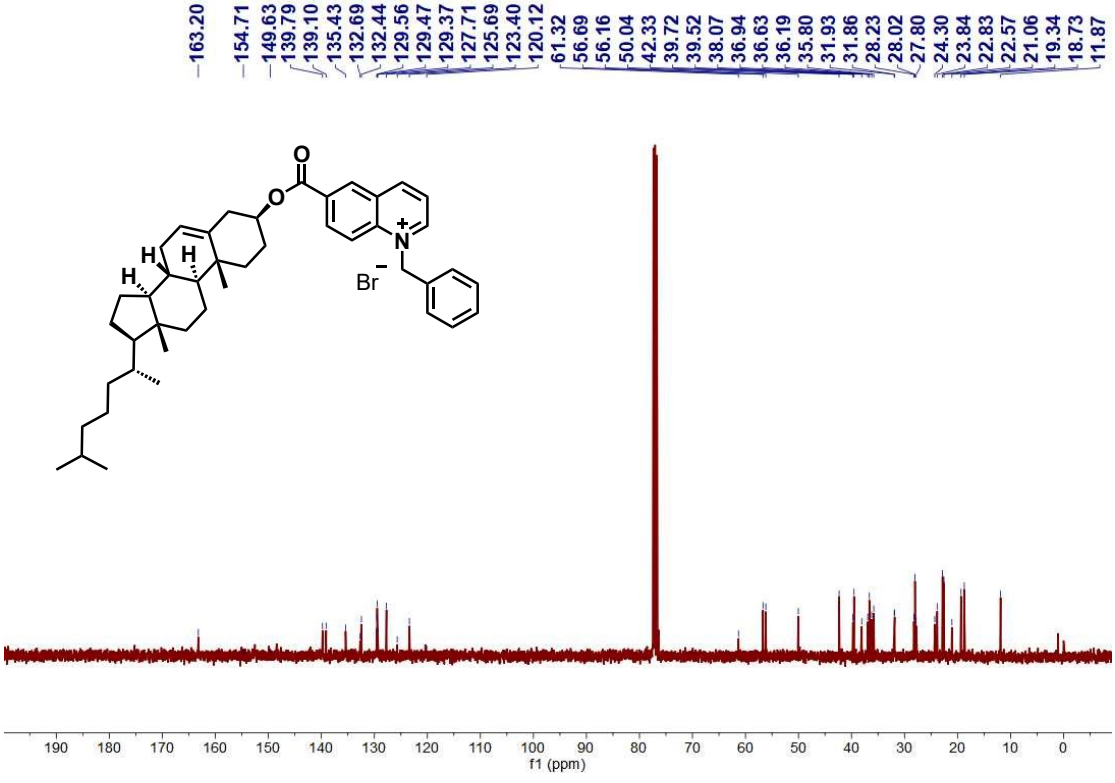


^{1}H NMR and ^{13}C NMR of **1by**

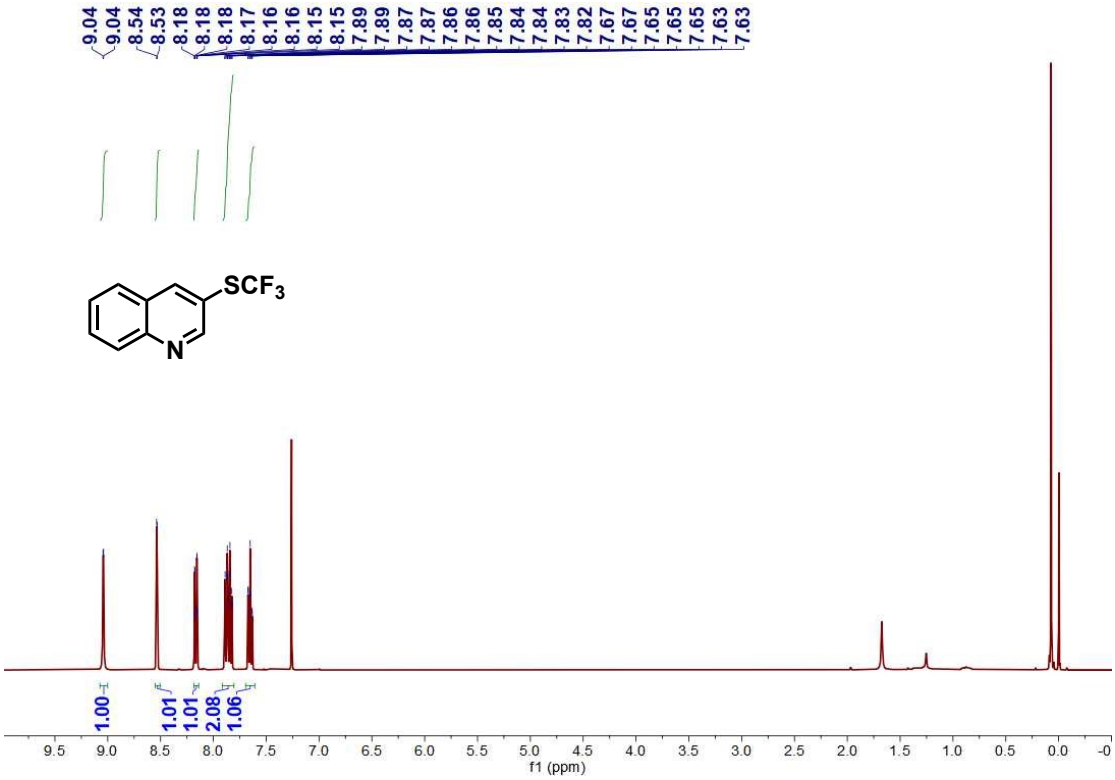


^{1}H NMR and ^{13}C NMR of **1bz**

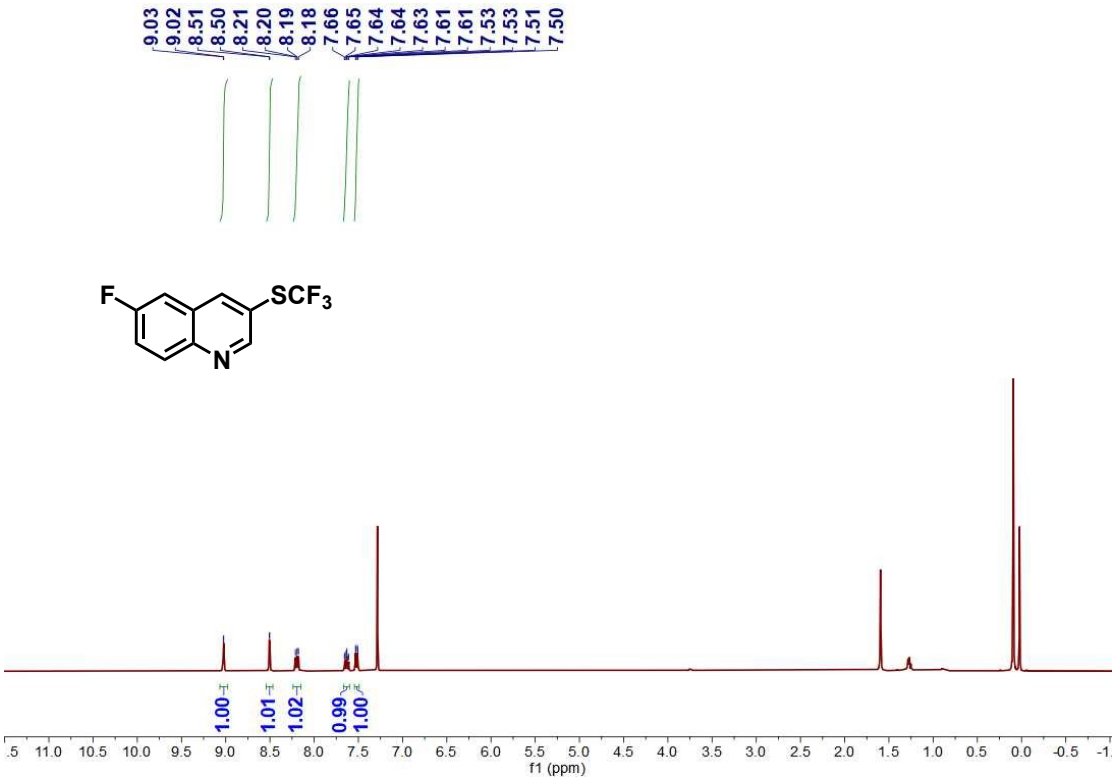


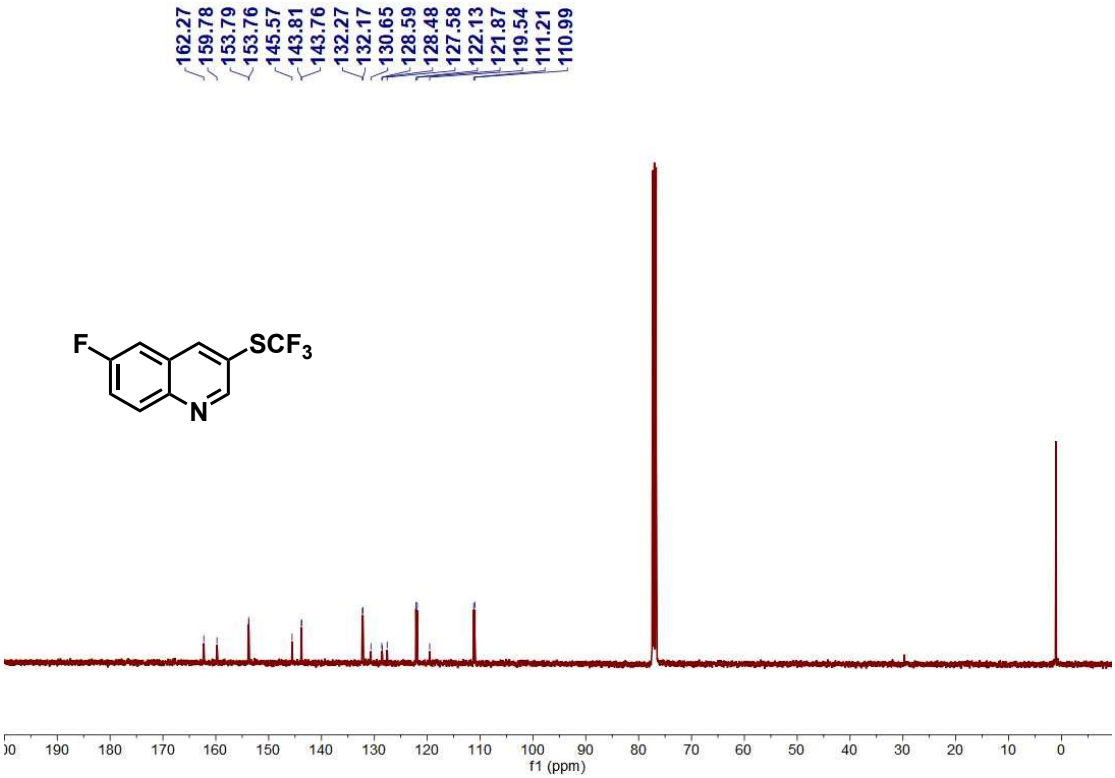


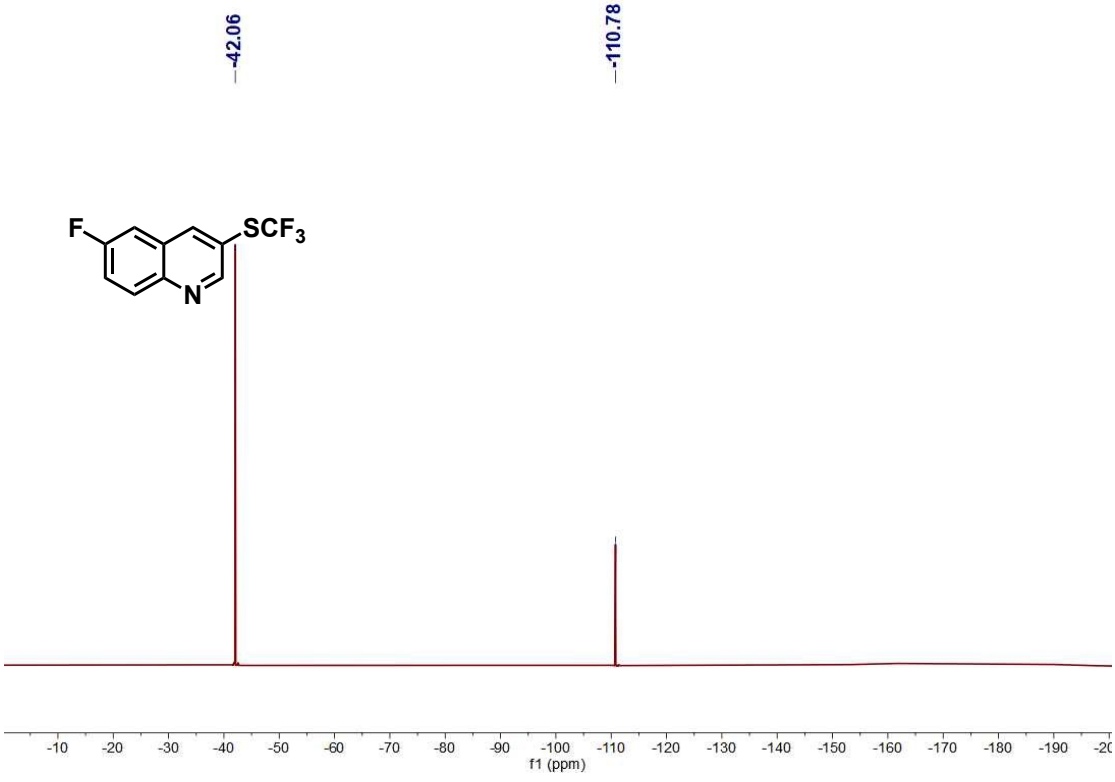
^{1}H NMR of **3a**



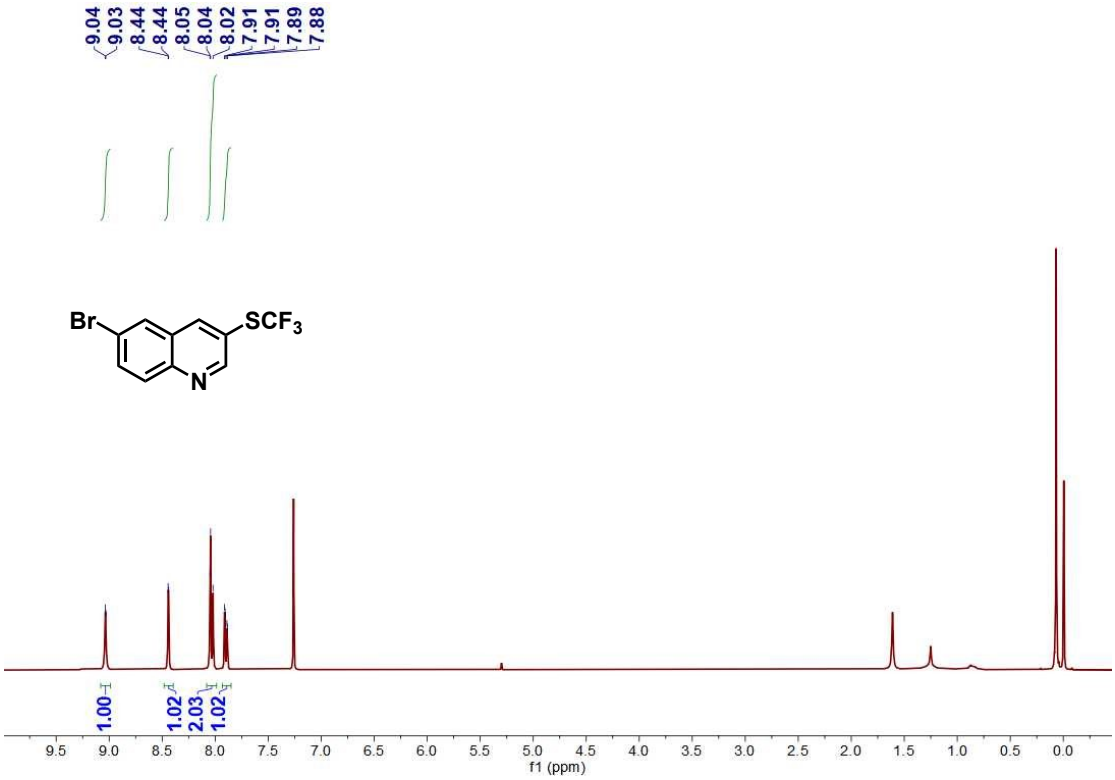
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3b**

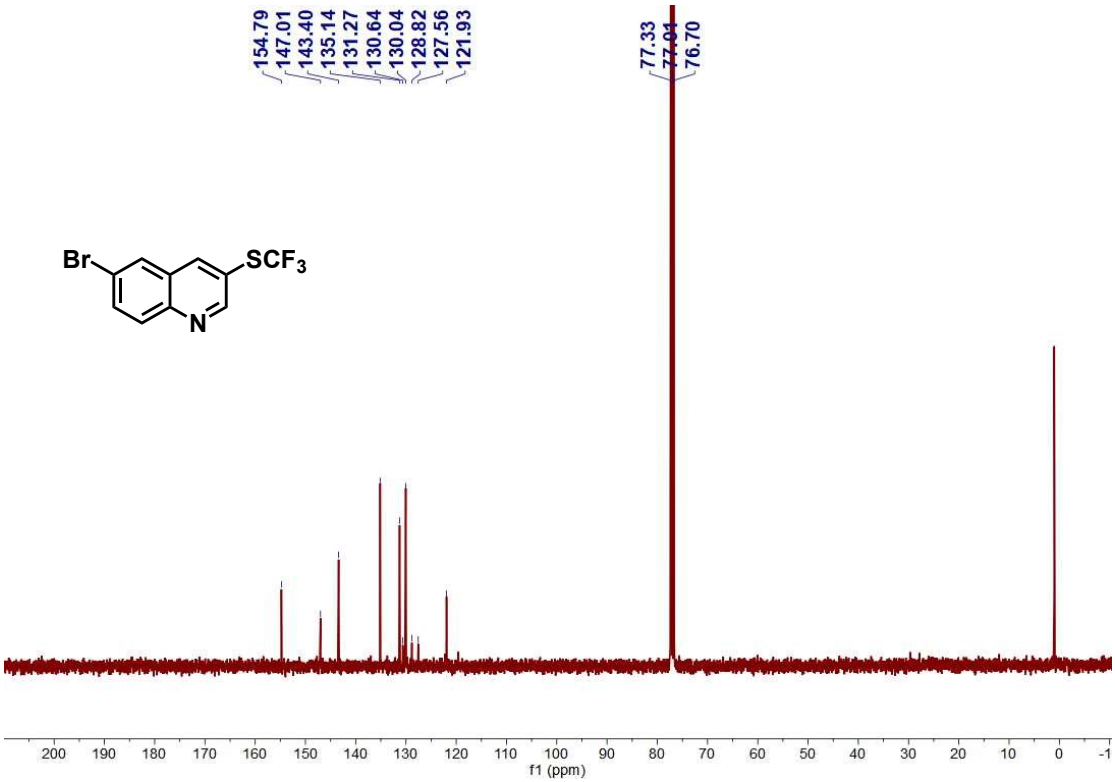


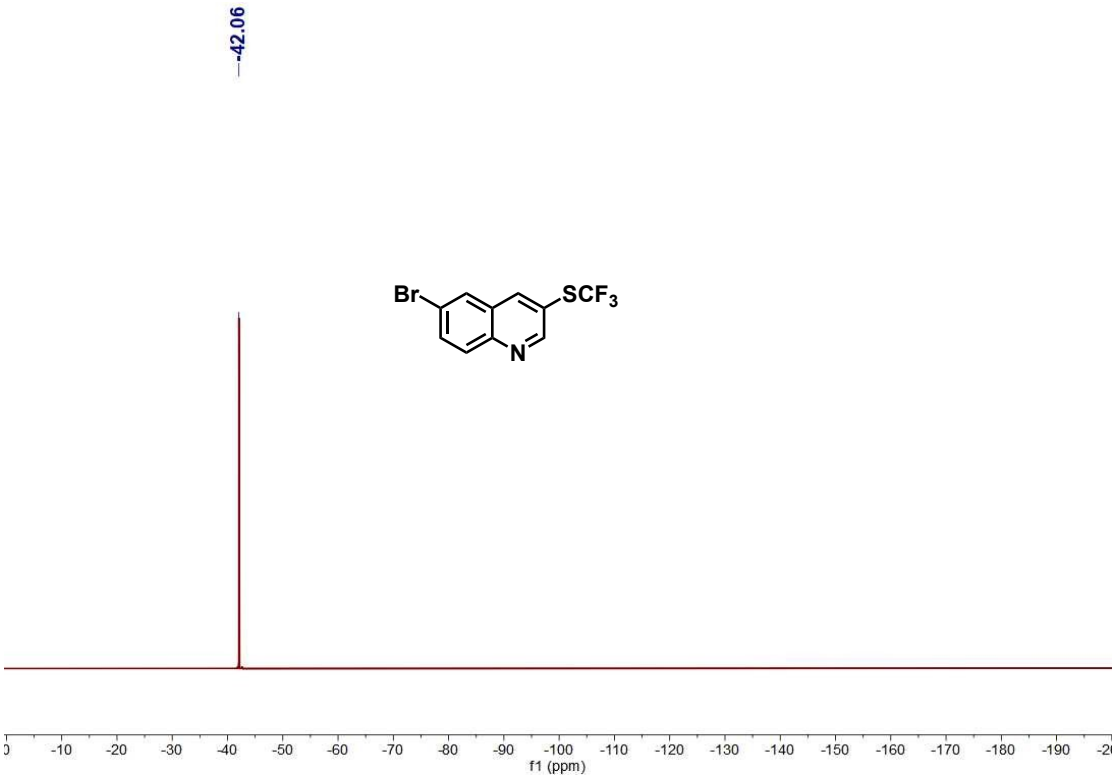

162.27
159.78
153.79
153.76
145.57
143.81
143.76
132.27
132.17
130.65
128.59
128.48
127.58
122.13
121.87
119.54
111.21
110.99
F
SCF3
N
f1 (ppm)


-42.06
-110.78
F
SCF3
N
f1 (ppm)

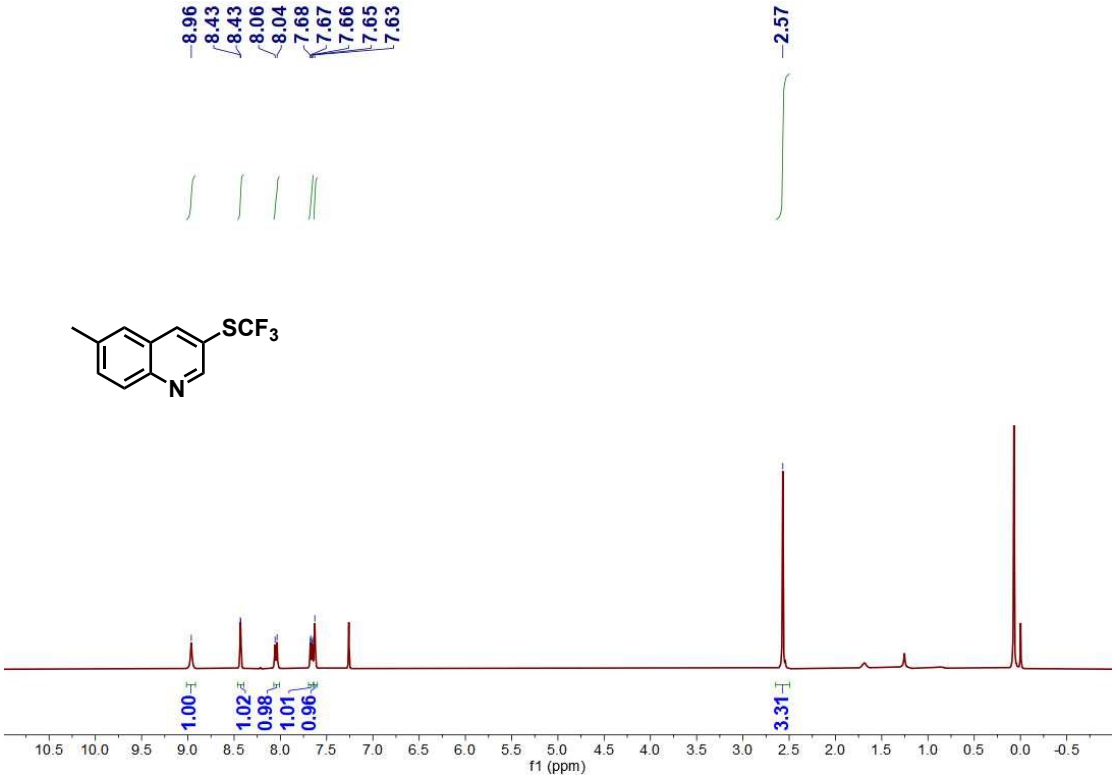
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3c**

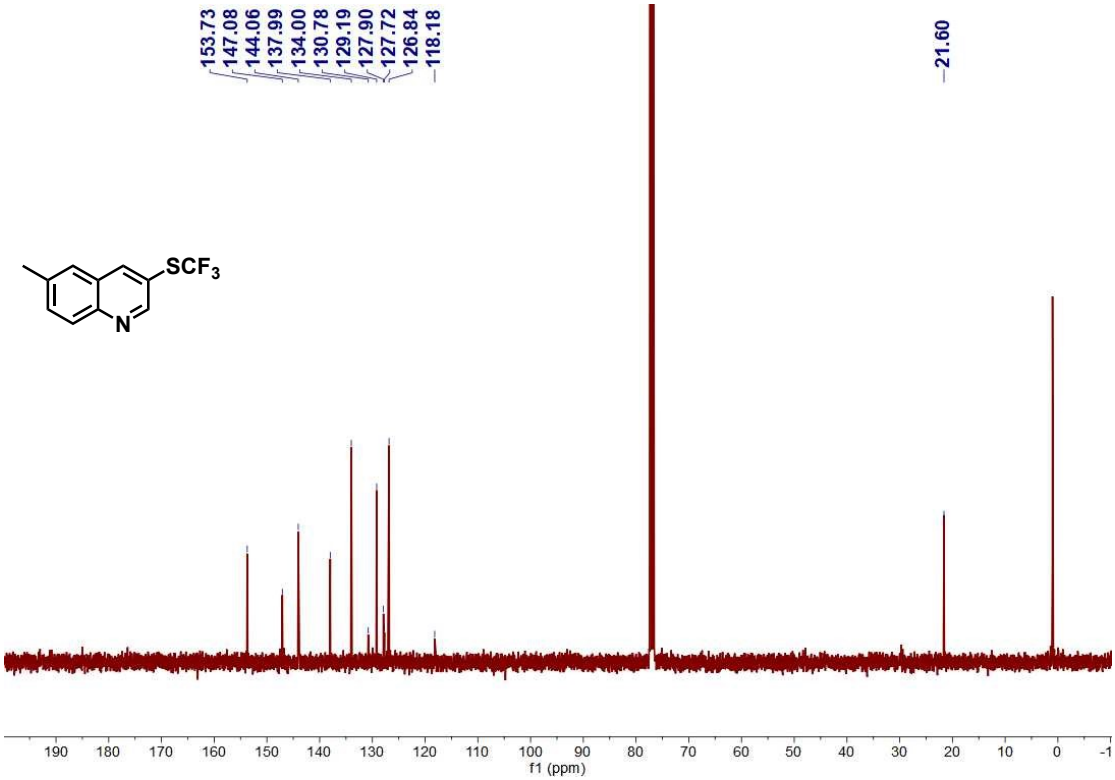


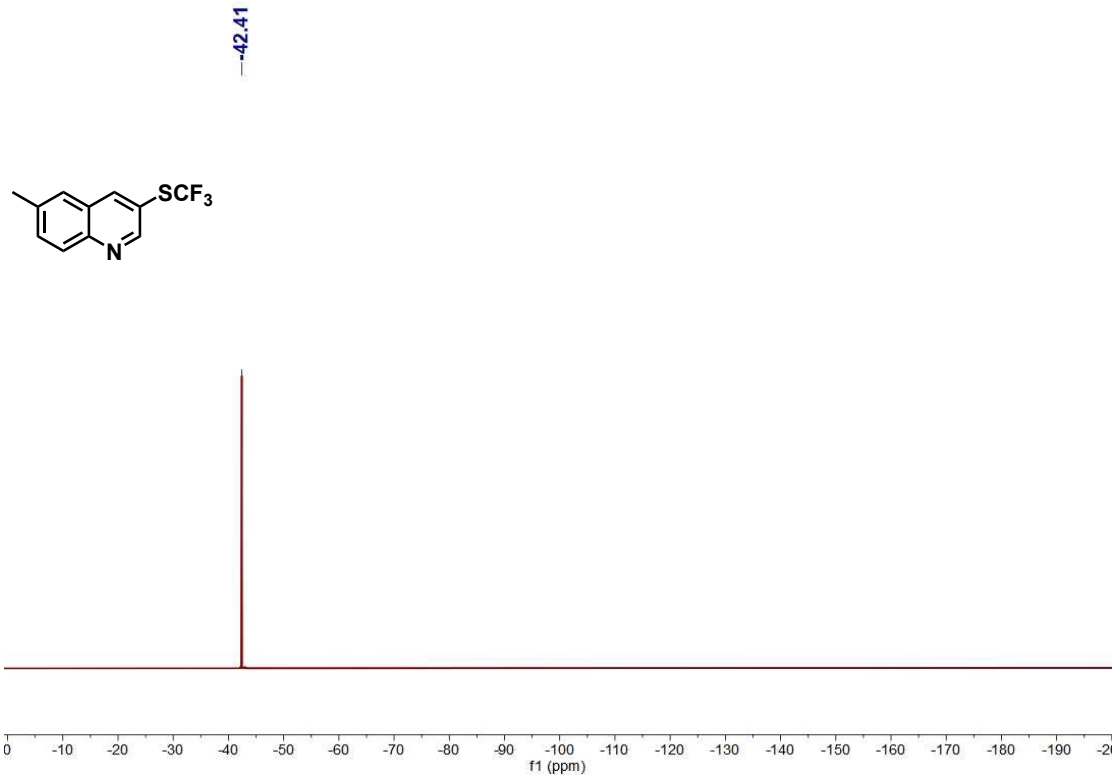




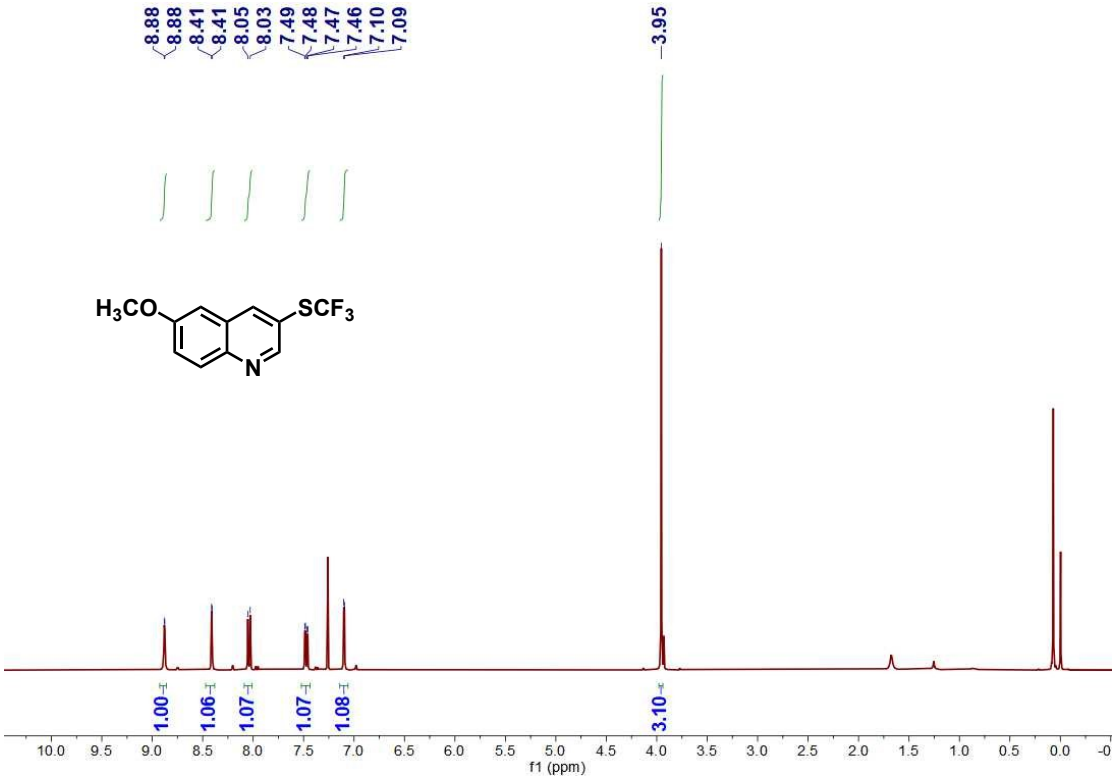
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3d**

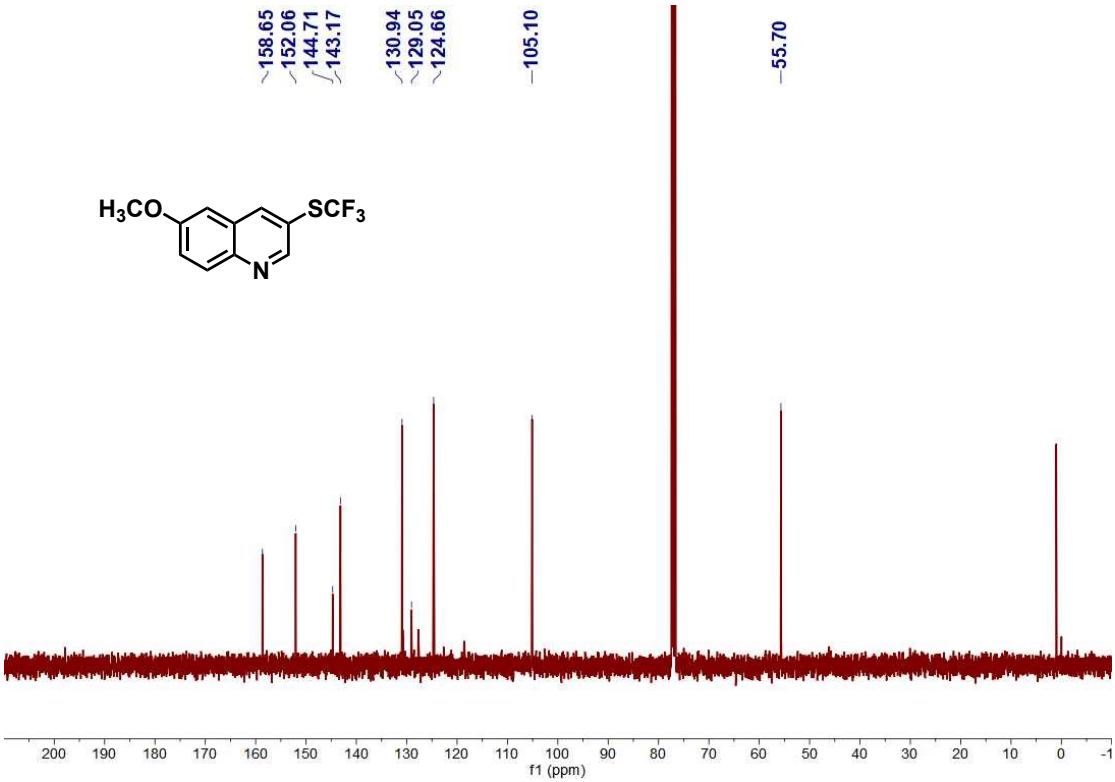


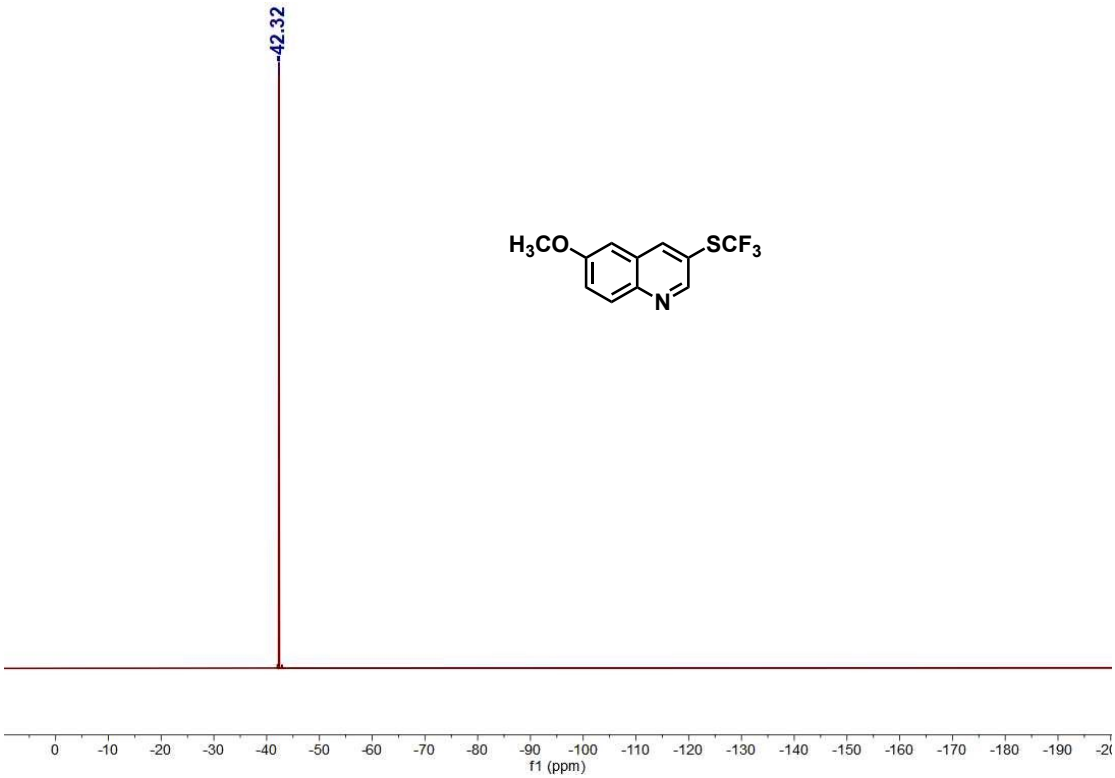

153.73
147.08
144.06
137.99
134.00
130.78
129.19
127.90
127.72
126.84
118.18
21.60
SCF3
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


-42.41
SCF3
N
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

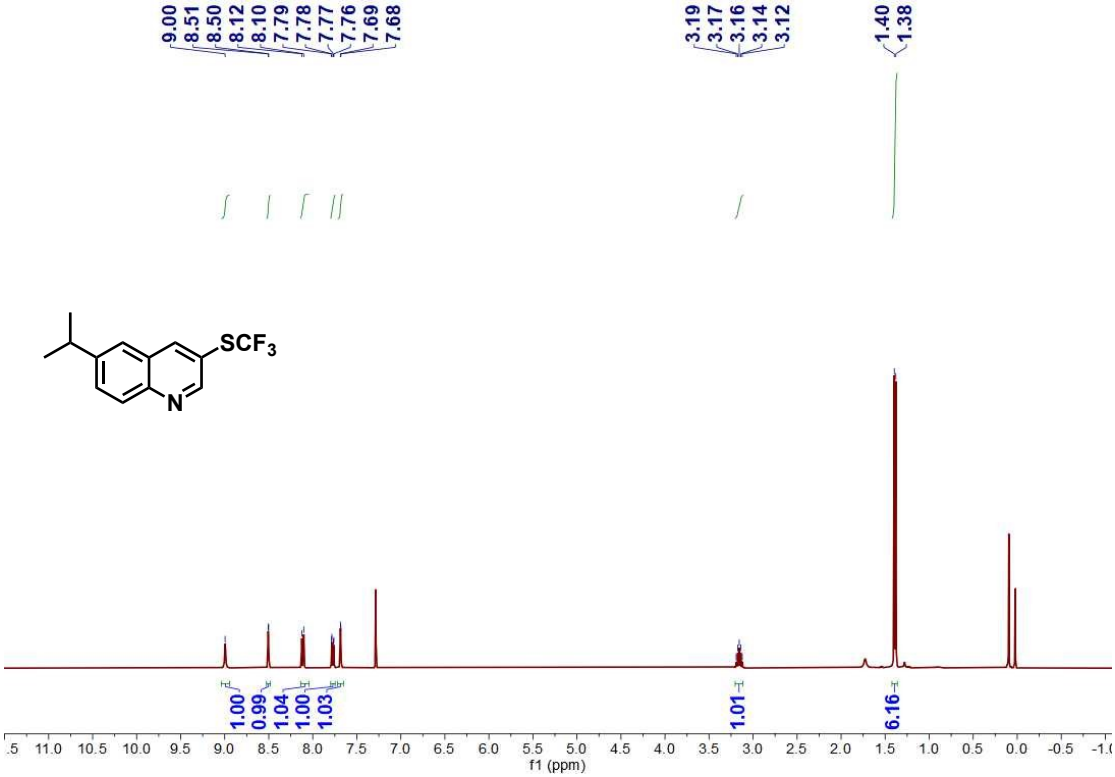
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3e**

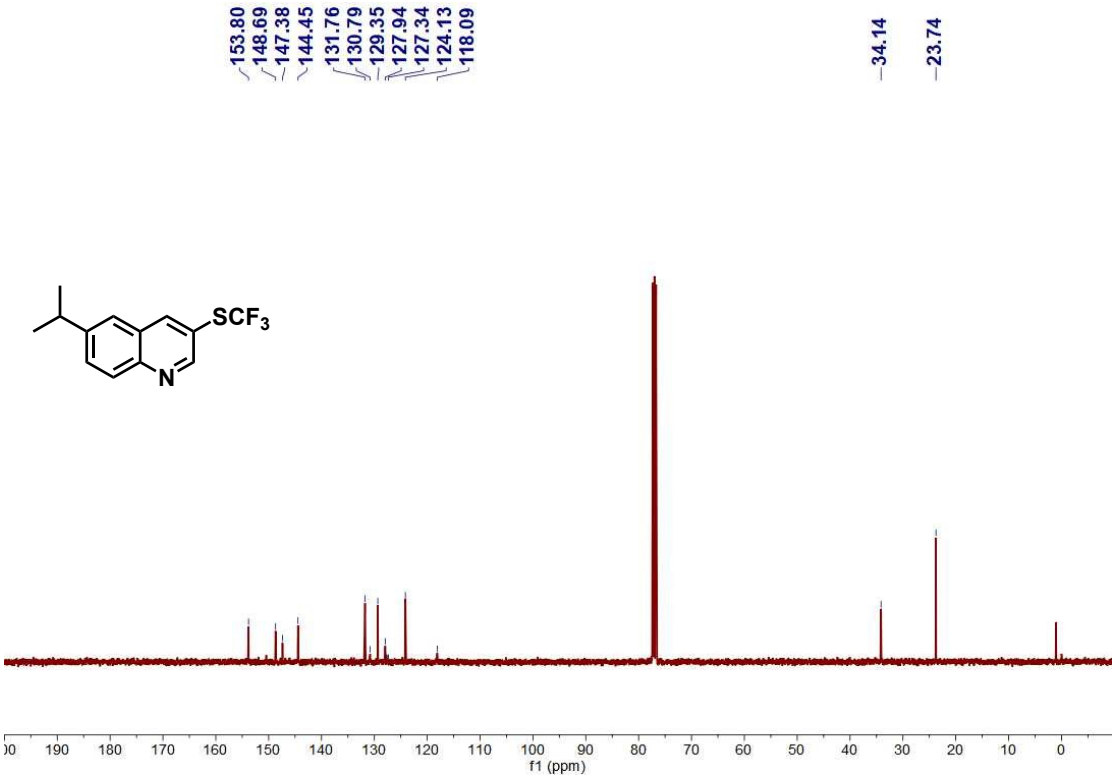


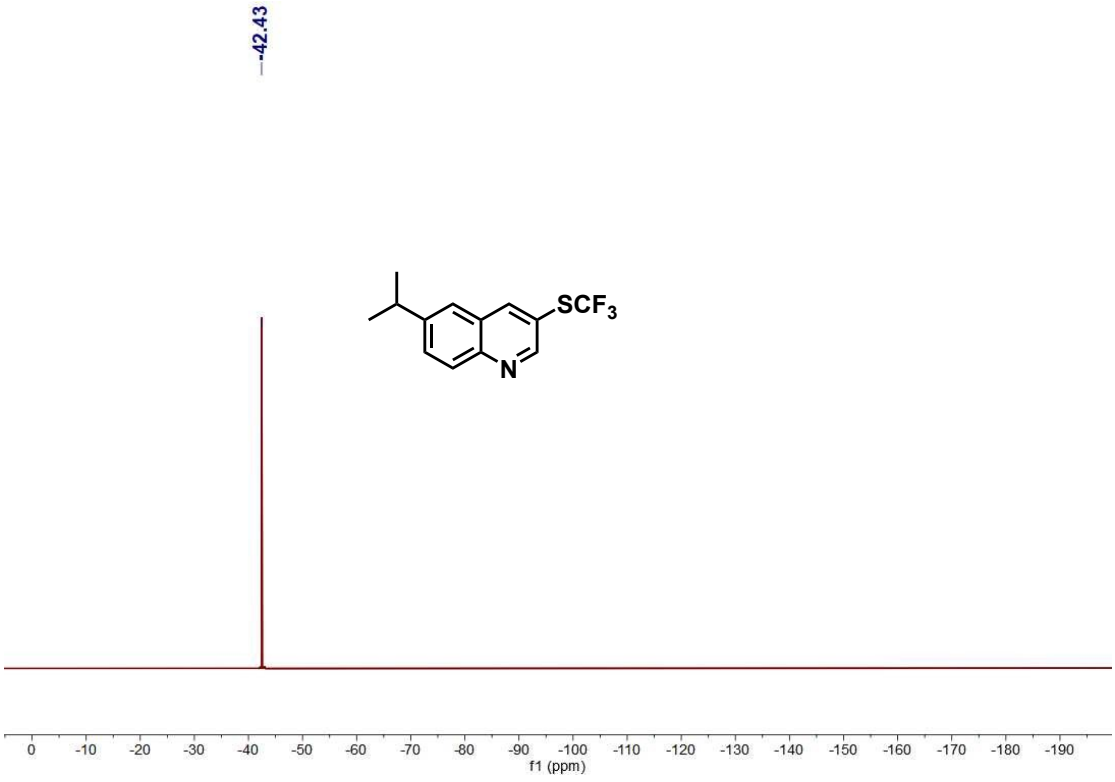




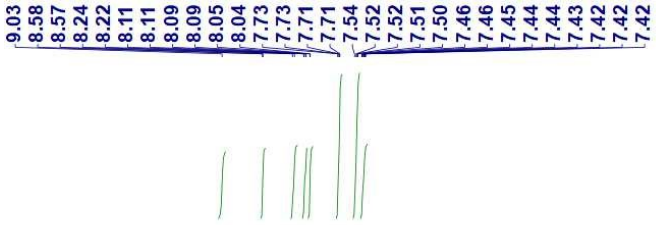
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3f**

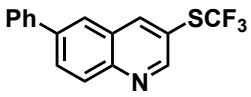


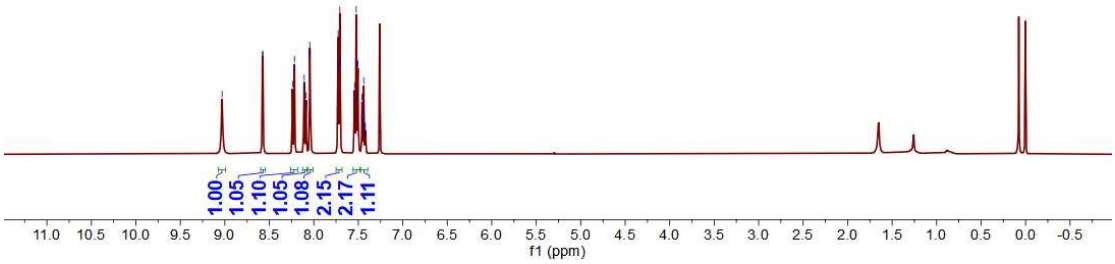

153.80
148.69
147.38
144.45
131.76
130.79
129.35
127.94
127.34
124.13
118.09
34.14
23.74
SCF3
N
f1 (ppm)

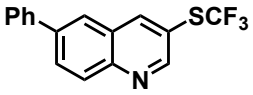

-42.43
SCF3
N
f1 (ppm)

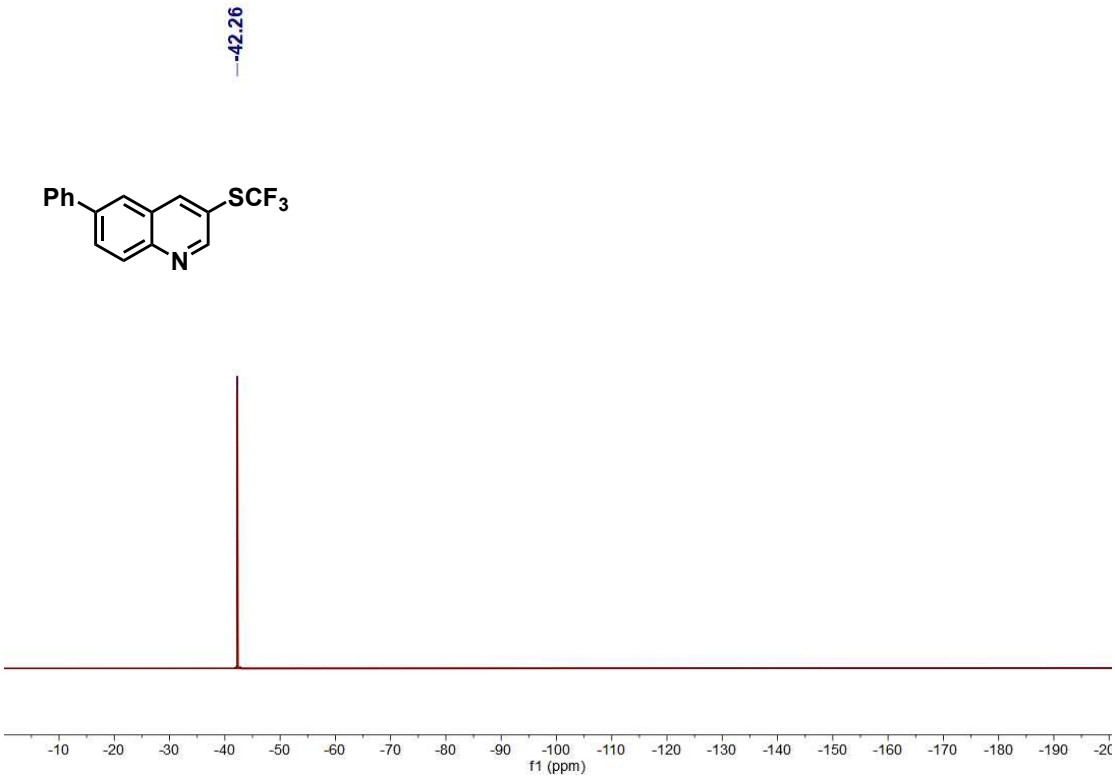
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3g**



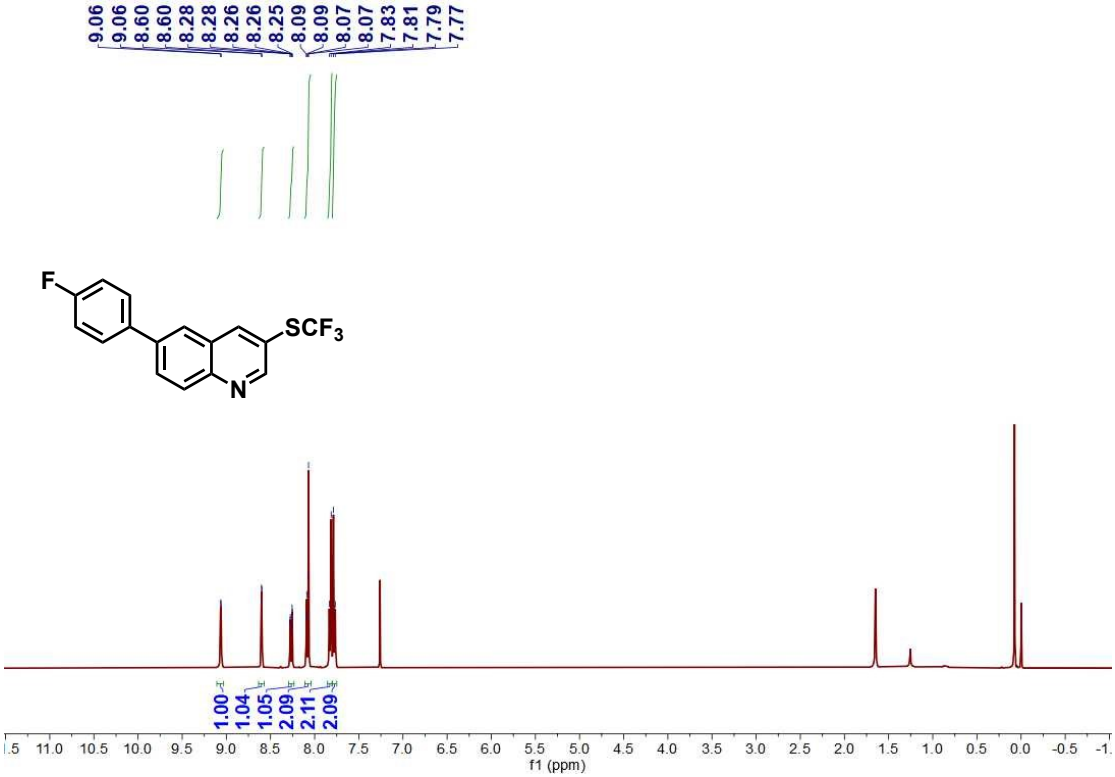


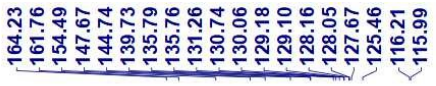


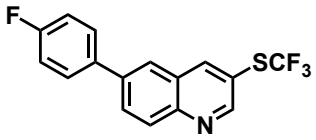


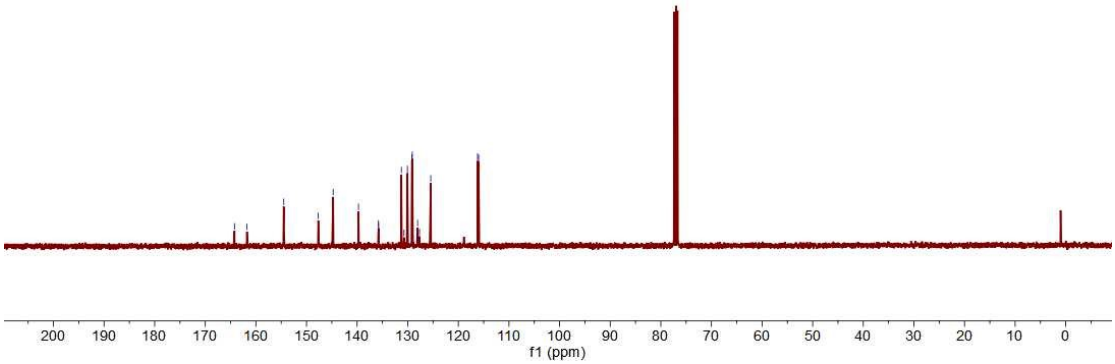


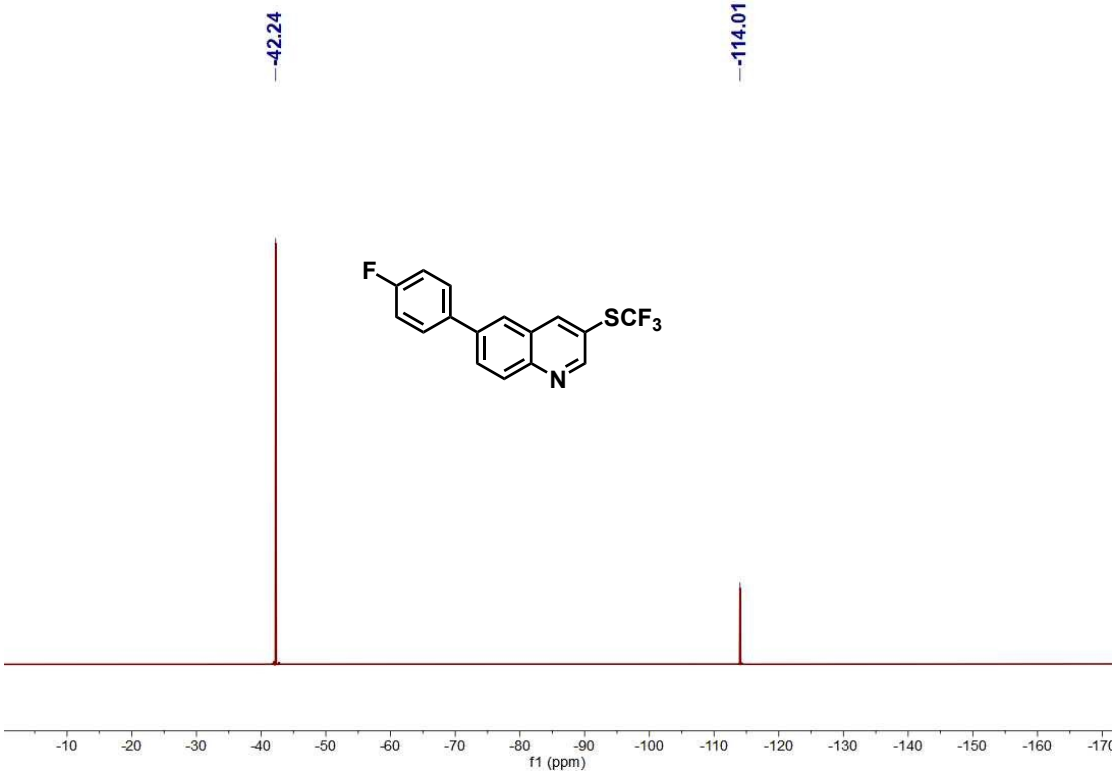
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3h**



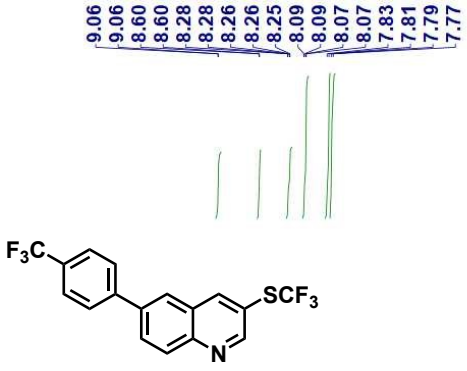

164.23
161.76
154.49
147.67
144.74
139.73
135.79
135.76
131.26
130.74
130.06
129.18
129.10
128.16
128.05
127.67
125.46
116.21
115.99

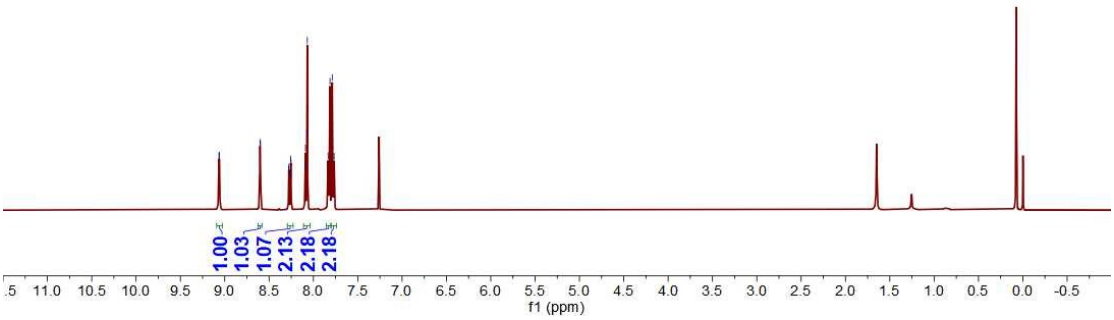

F
SCF3
N

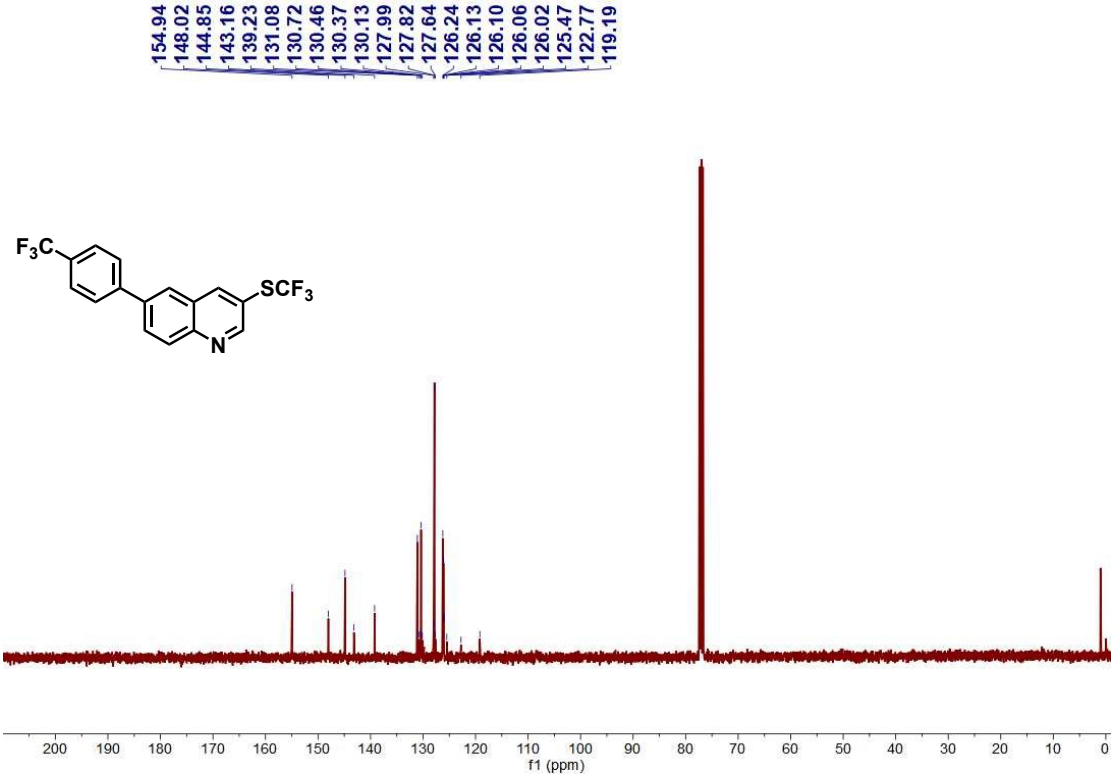

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

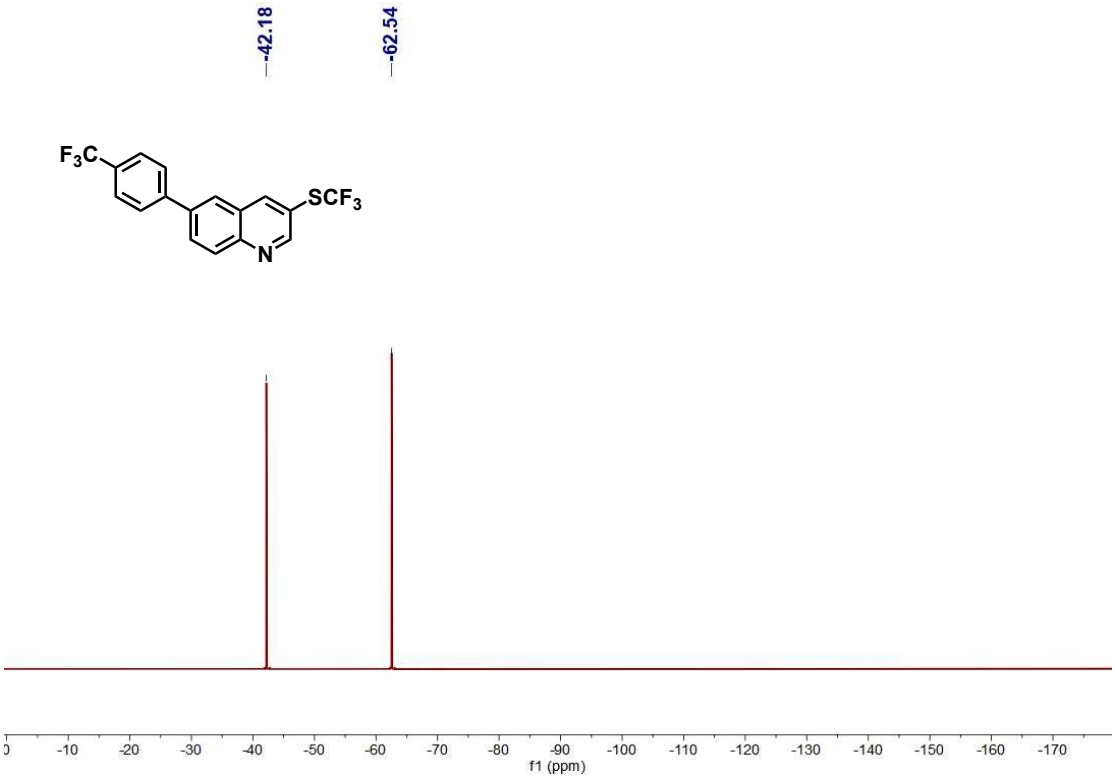

-42.24
-114.01
F
SCF3
N
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3i**

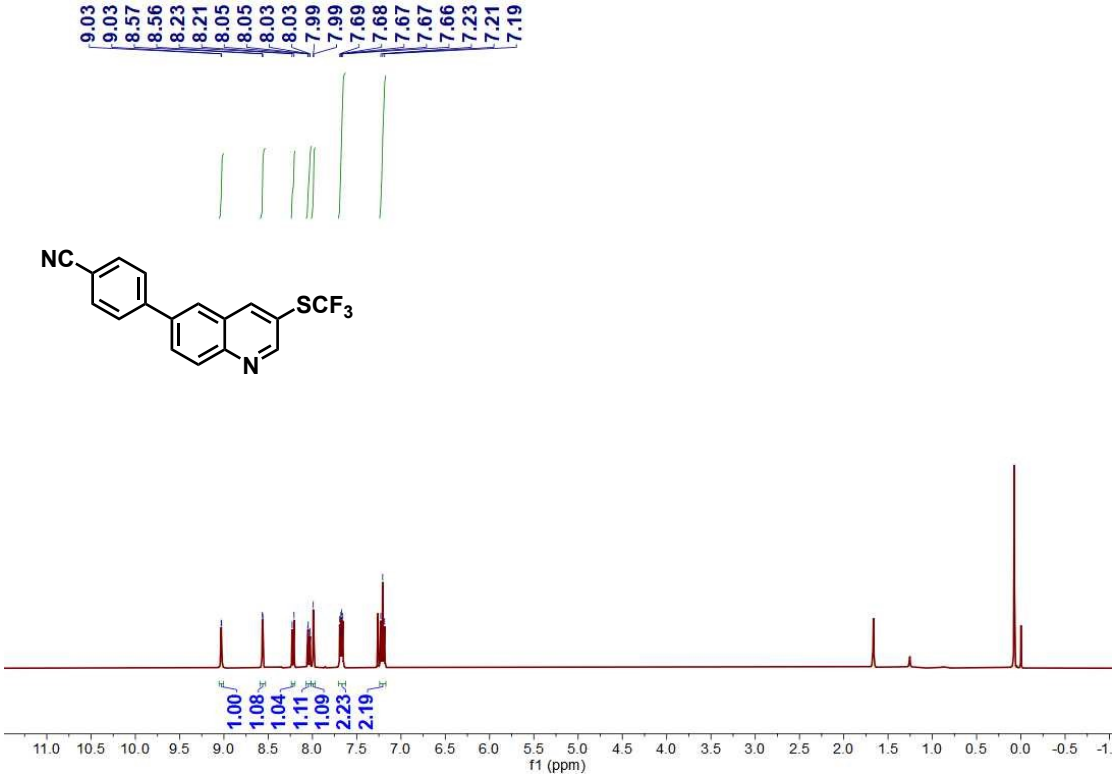




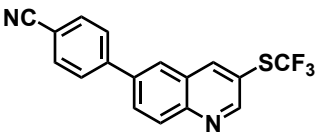


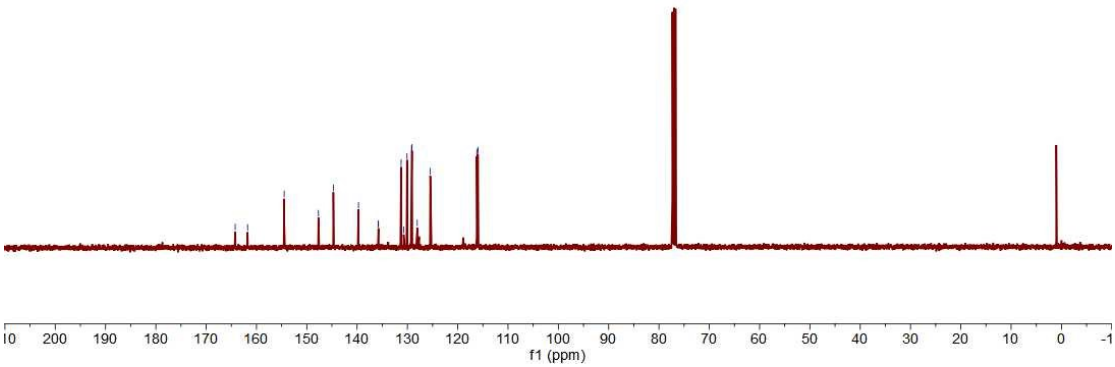


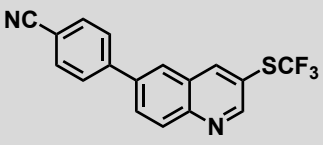
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3j**



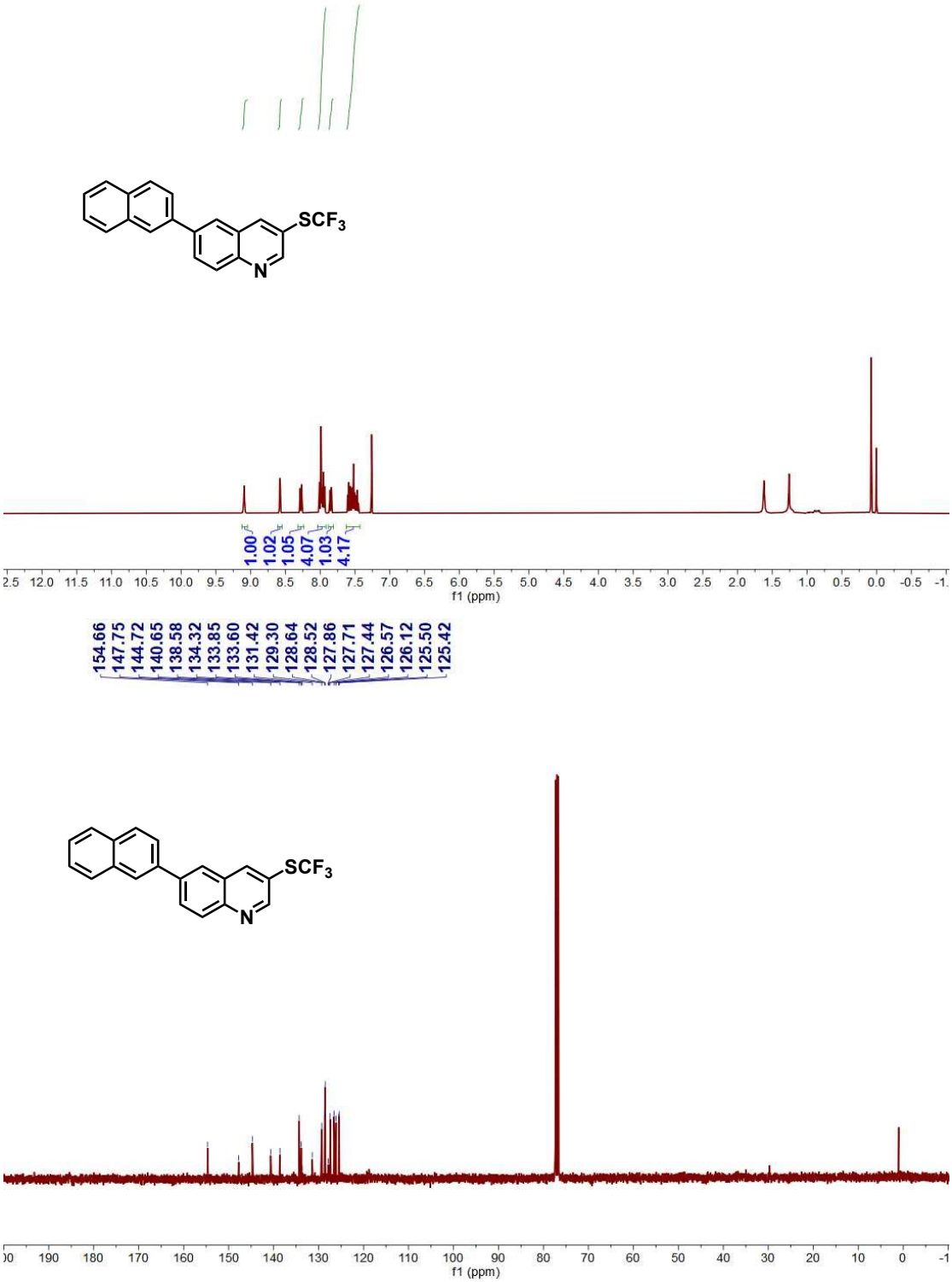

164.23
161.76
154.50
147.68
144.72
139.72
135.79
135.76
131.25
130.75
130.08
129.18
129.10
128.05
125.45
116.21
115.99

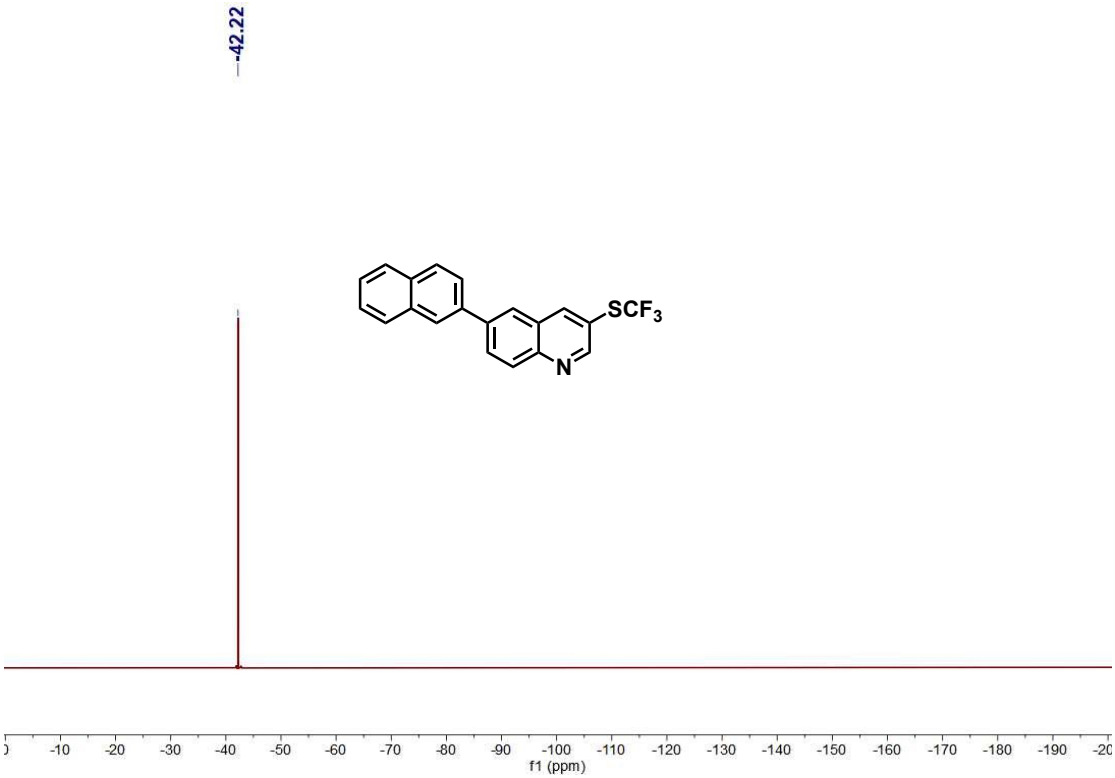

NC
SCF3
N


10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

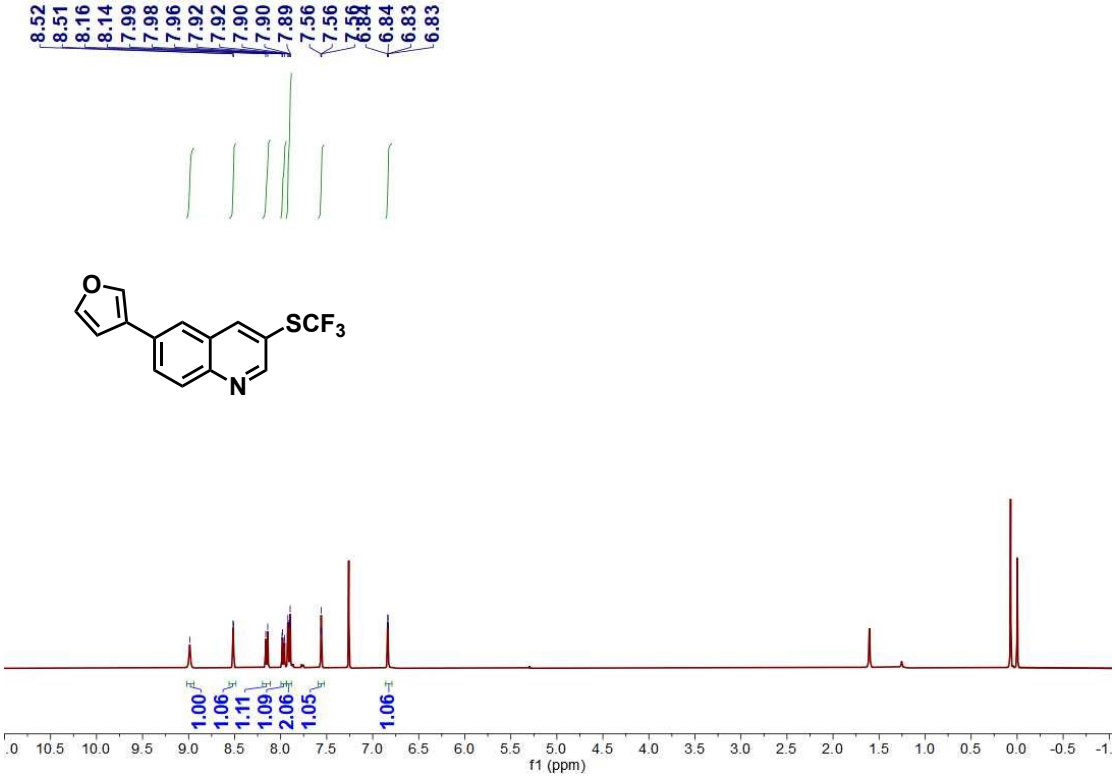

NC
SCF3
N

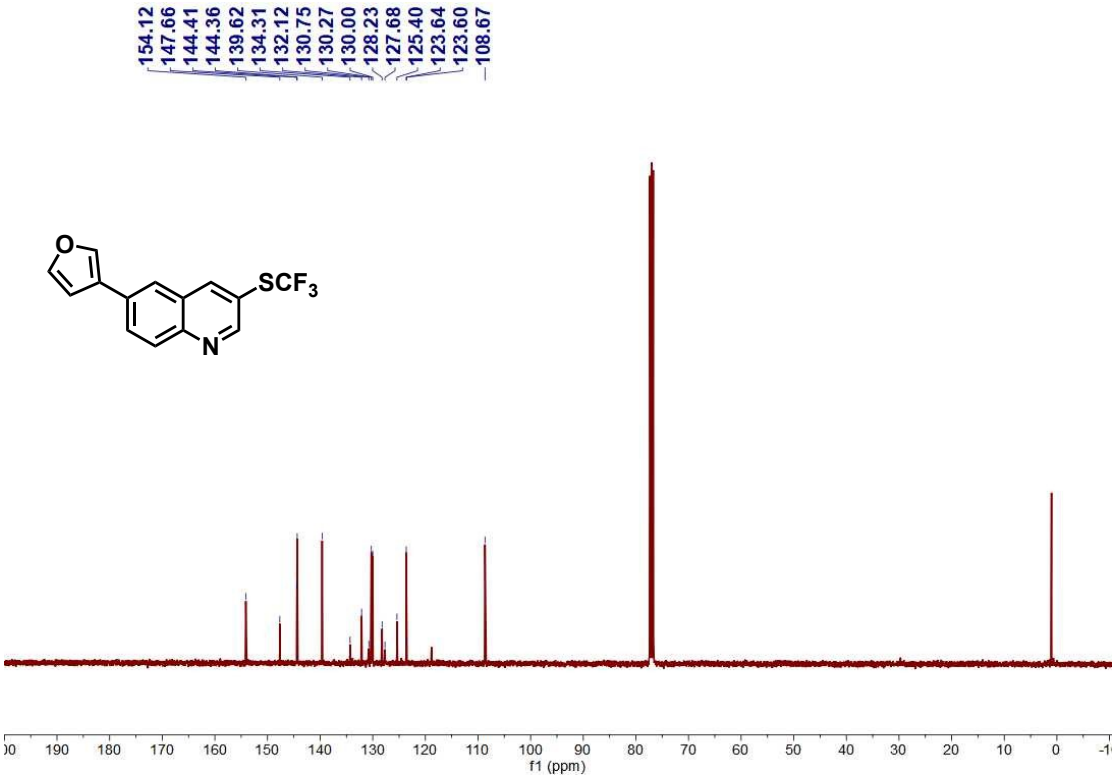
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3k**

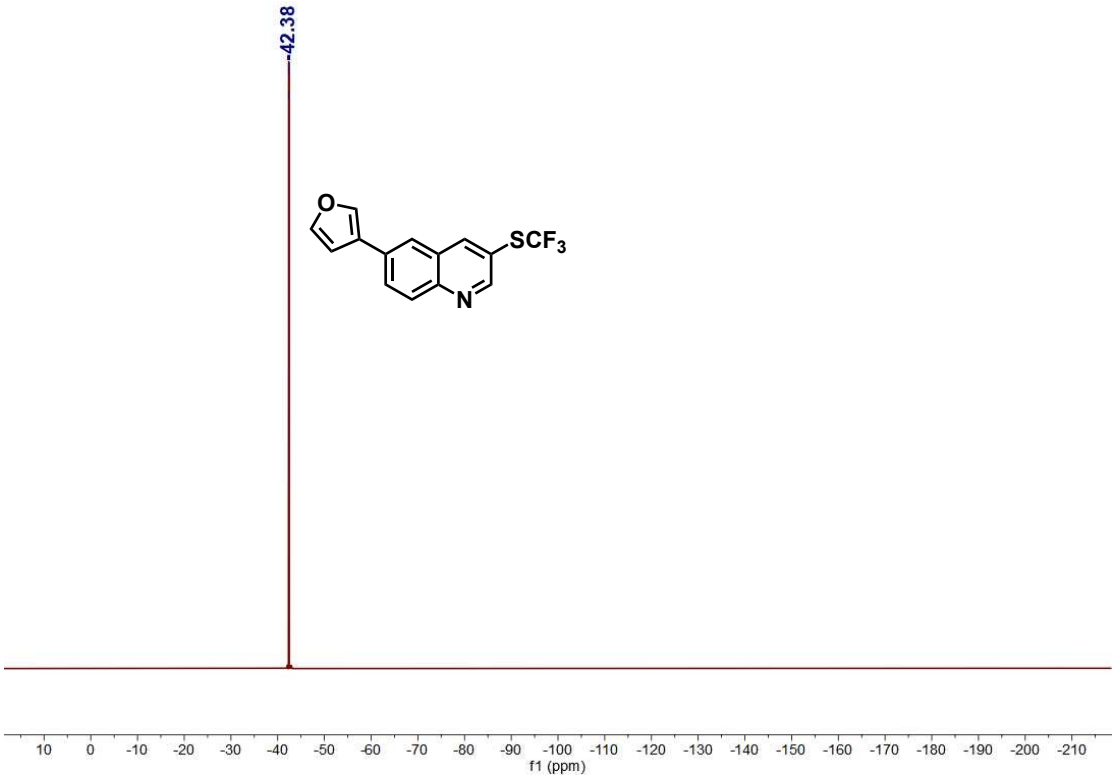




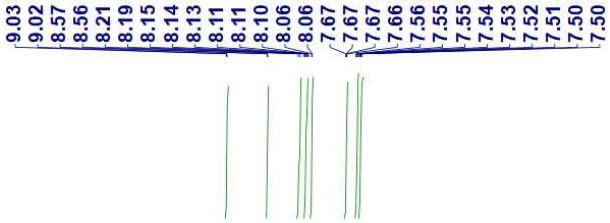
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3l**

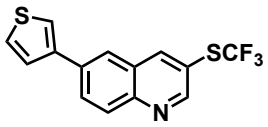


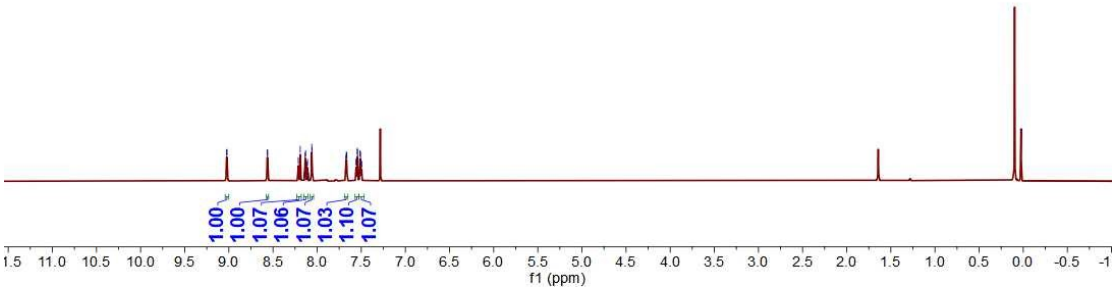

154.12
147.66
144.41
144.36
139.62
134.31
132.12
130.75
130.27
130.00
128.23
127.68
125.40
123.64
123.60
108.67
O
SCF3
N
f1 (ppm)

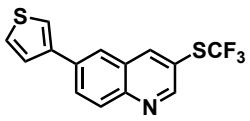

-42.38
O
SCF3
N
f1 (ppm)

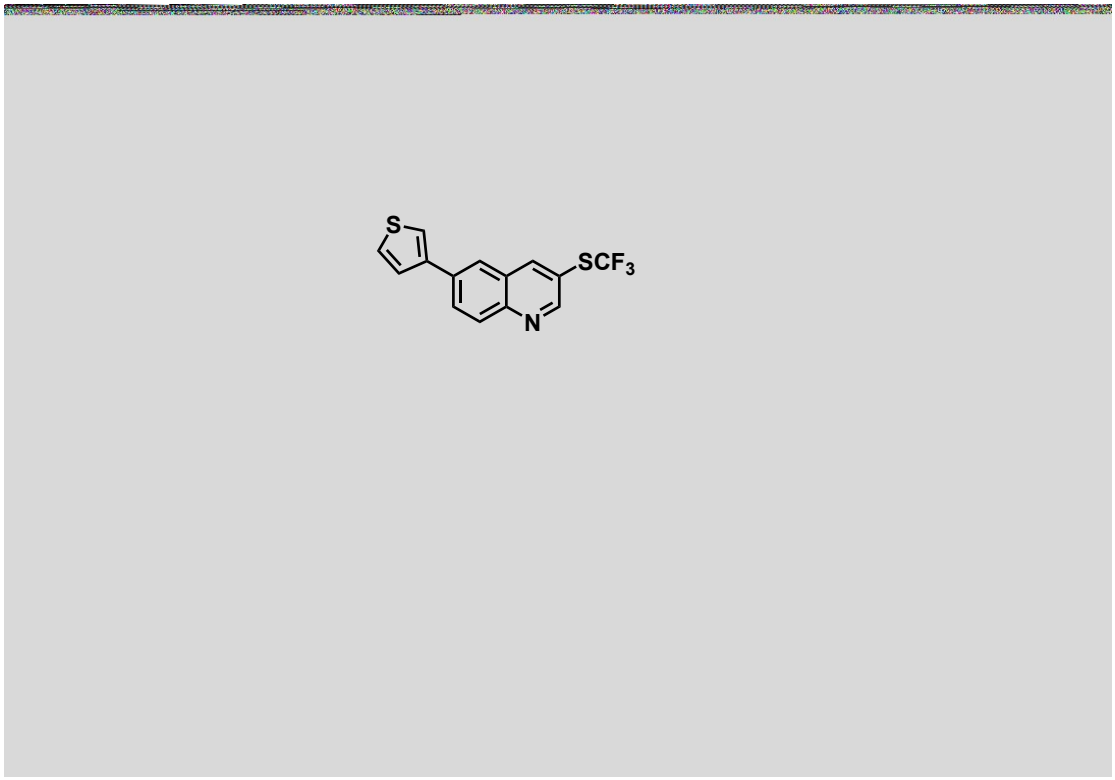
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3m**



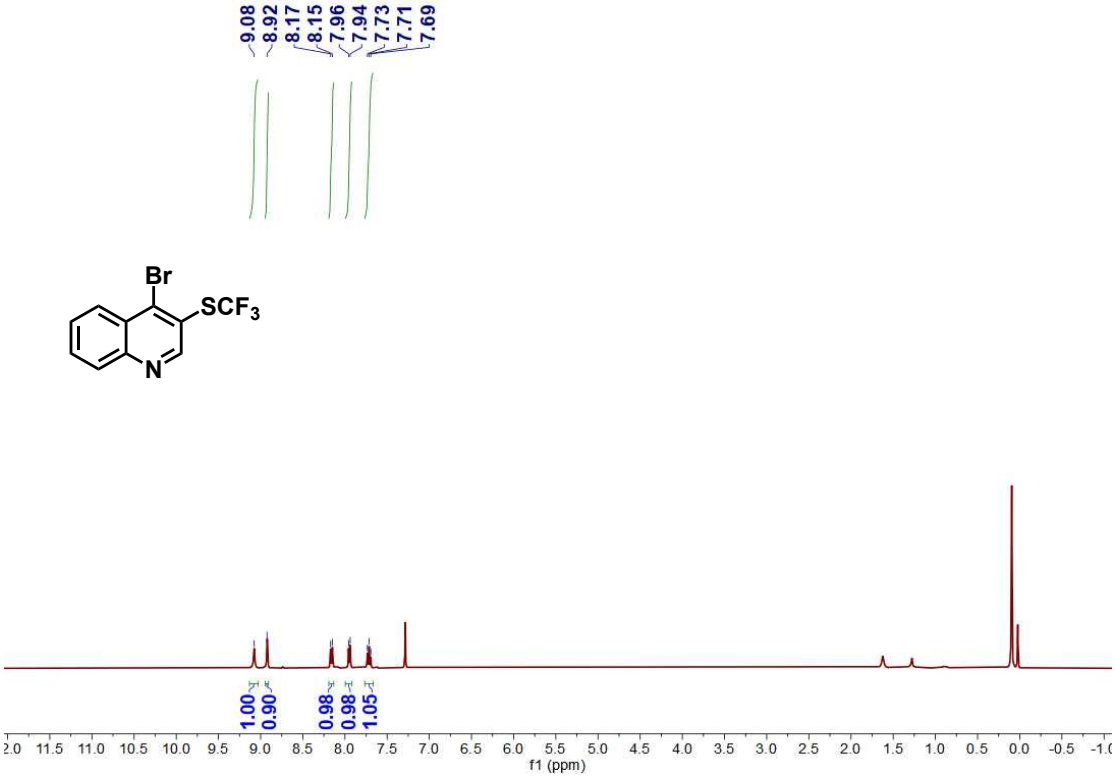


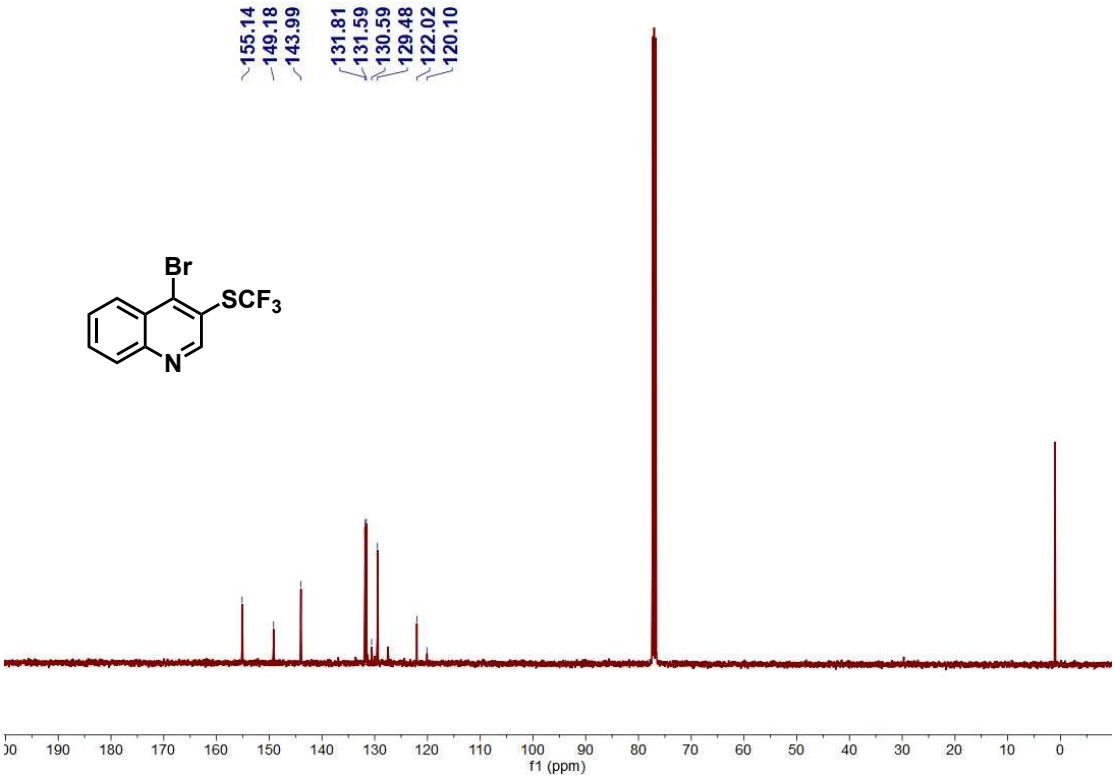


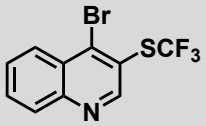




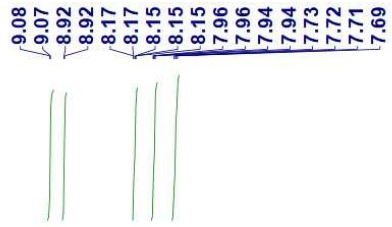
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3n**

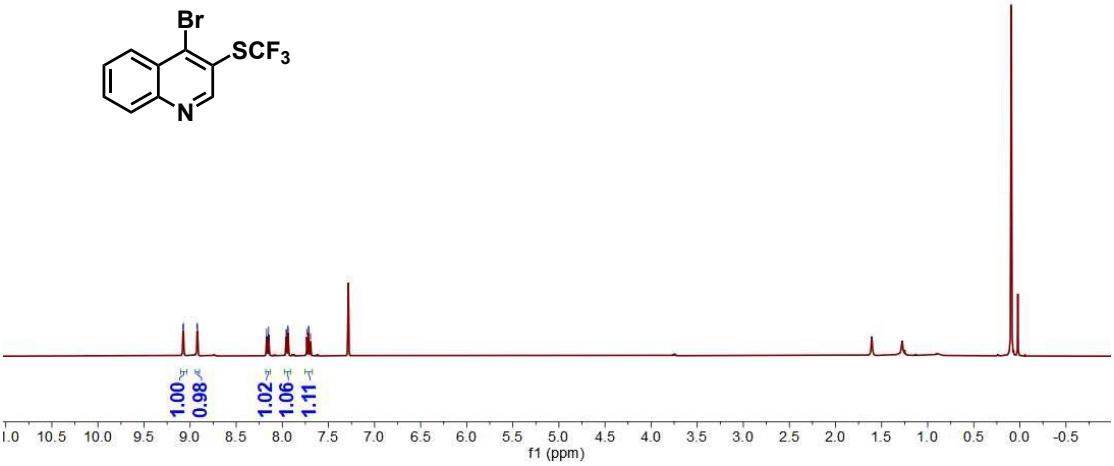


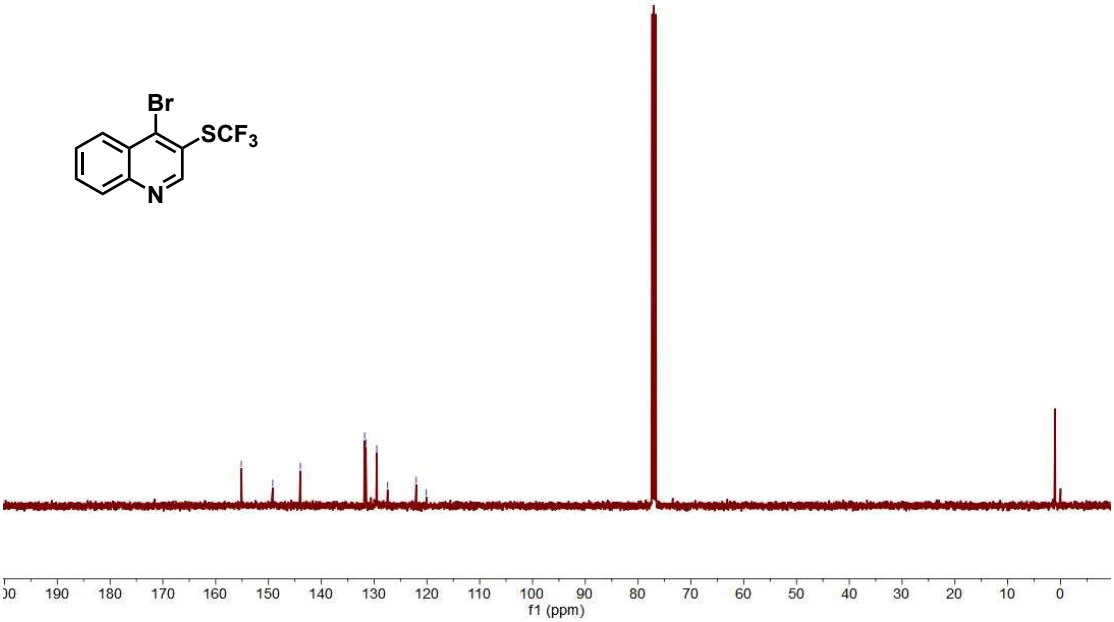

155.14
149.18
143.99
131.81
131.59
130.59
129.48
122.02
120.10
Br
SCF3
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

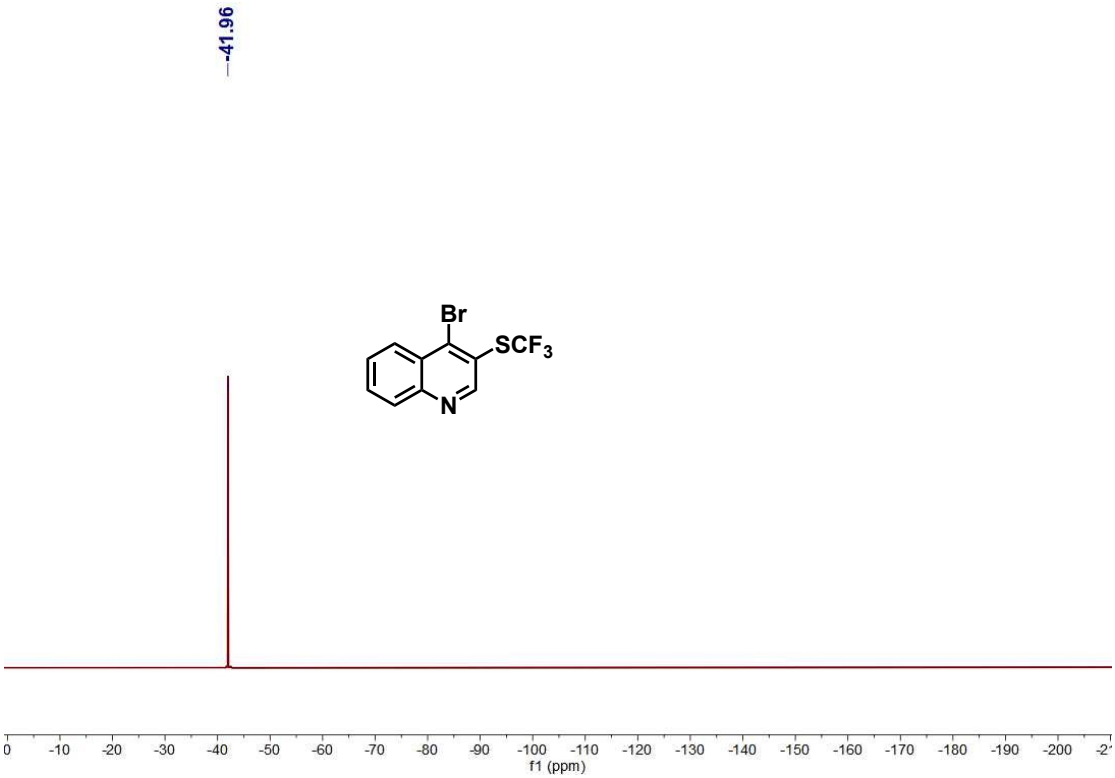

Br
SCF3
N

^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3o**

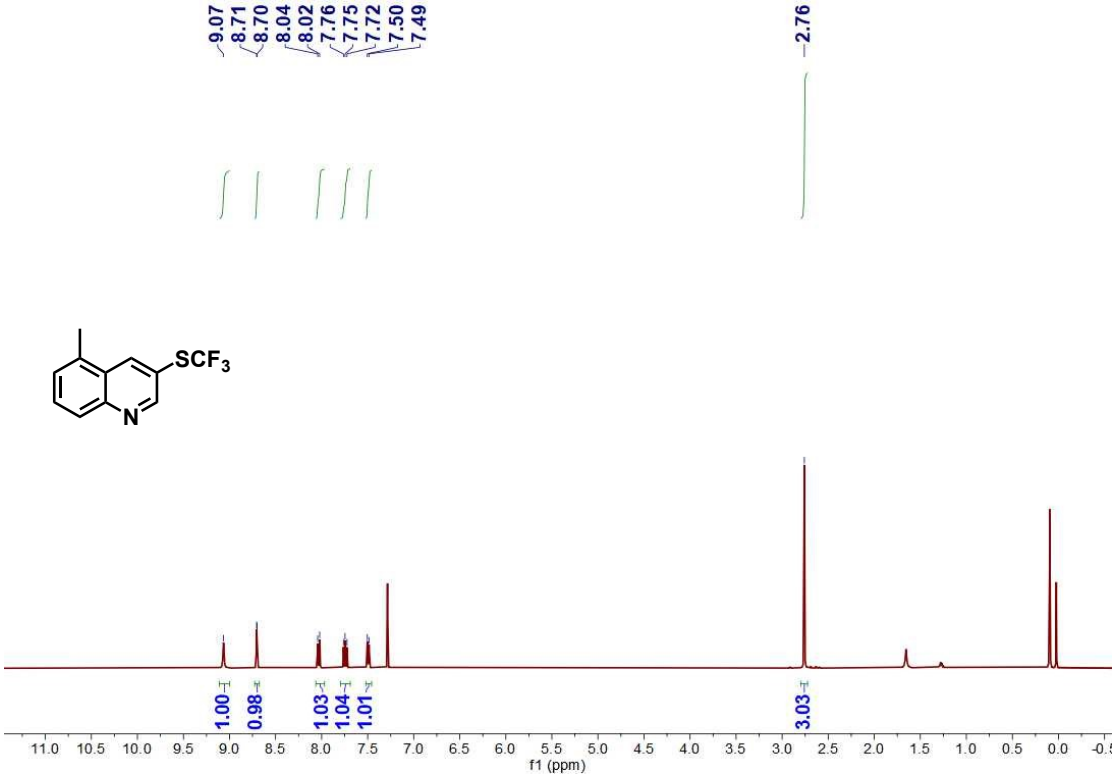


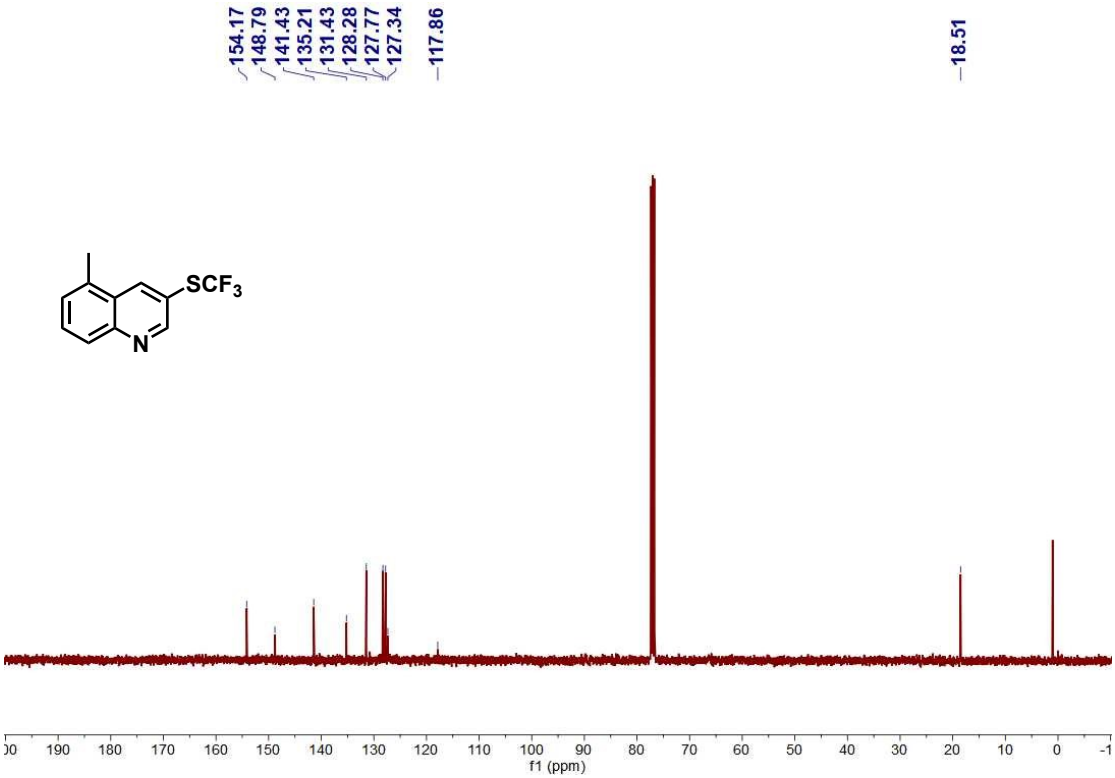


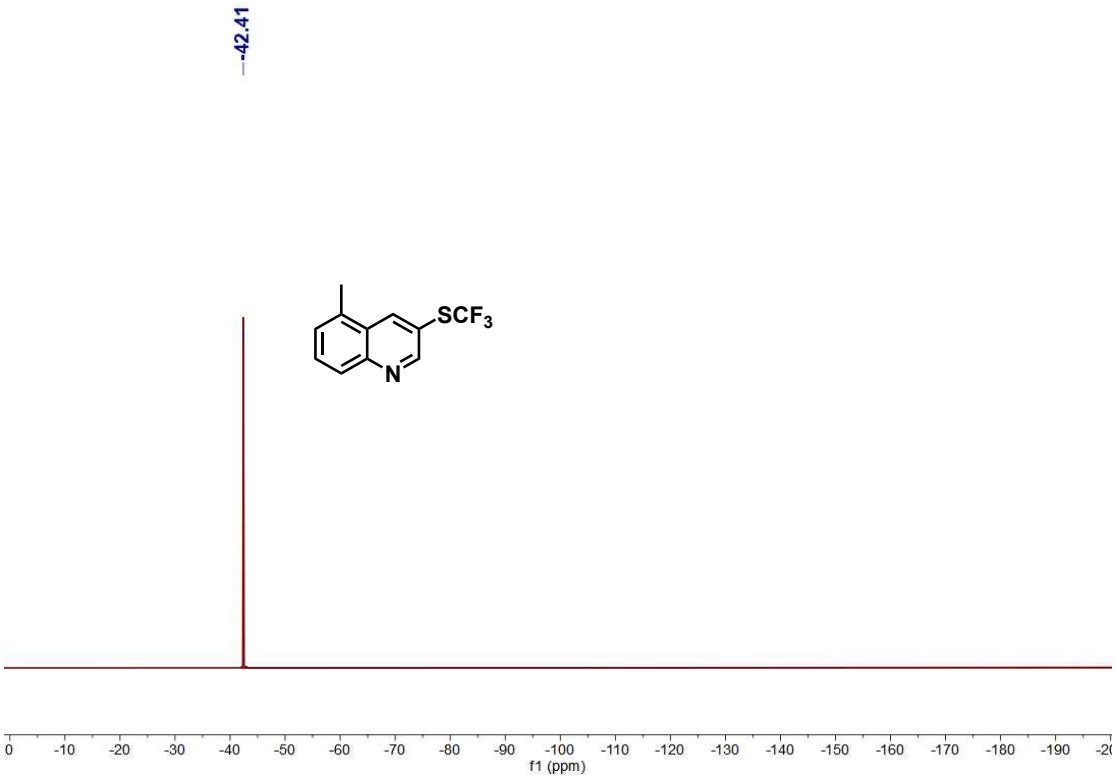




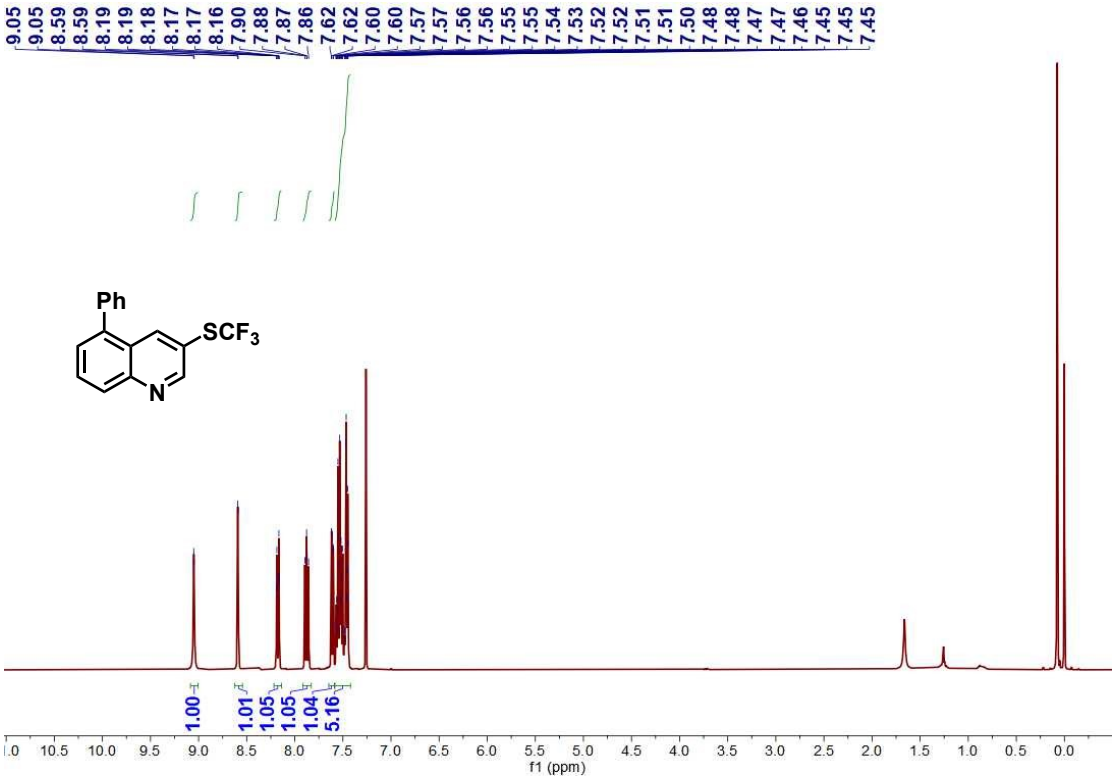
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3p**

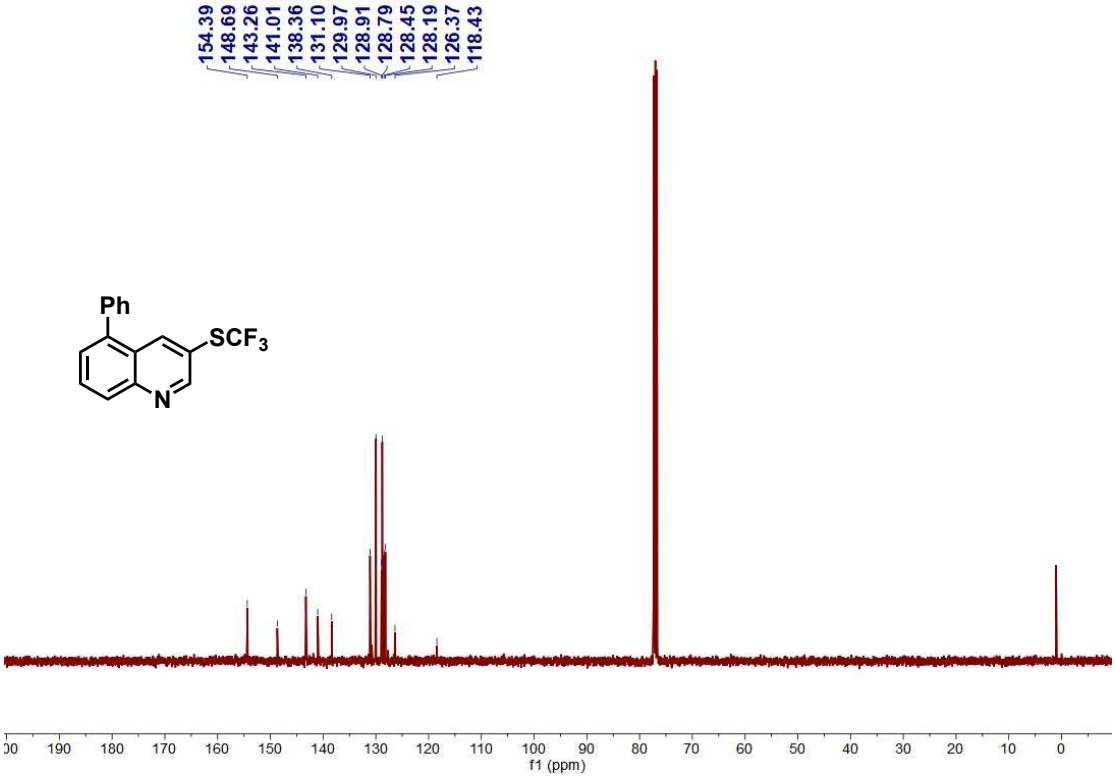


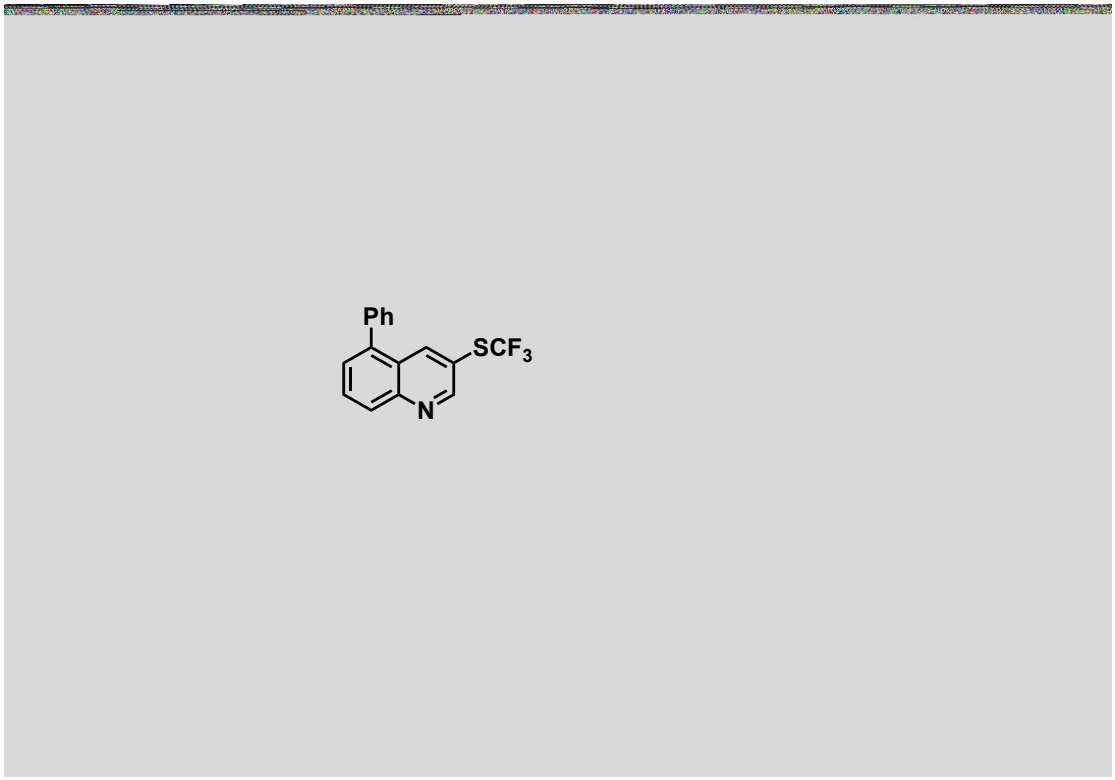

154.17
148.79
141.43
135.21
131.43
128.28
127.77
127.34
117.86
18.51
SCF3
N
f1 (ppm)


-42.41
SCF3
N
f1 (ppm)

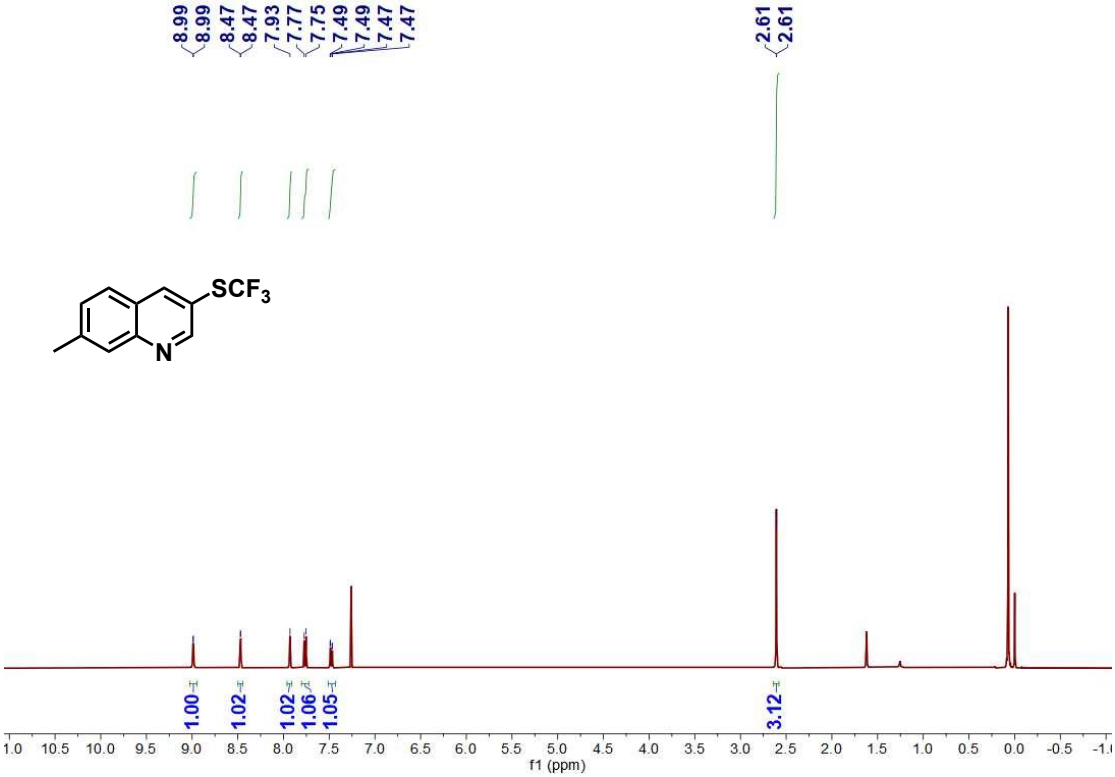
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3q**

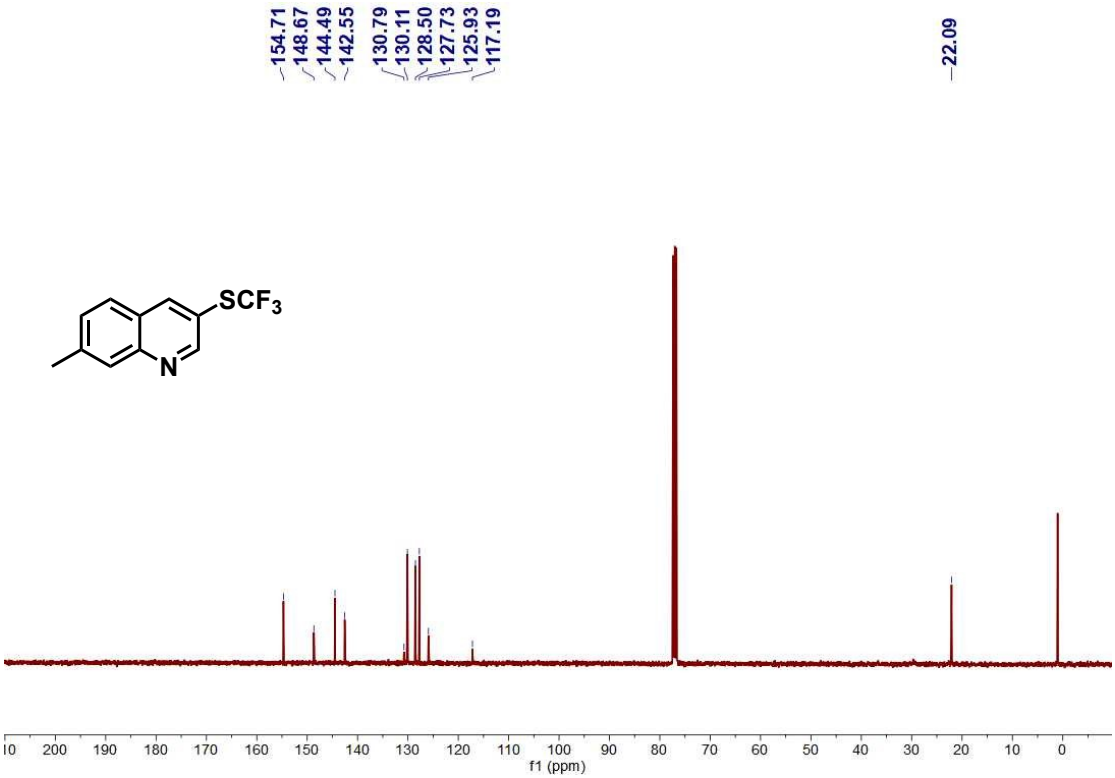


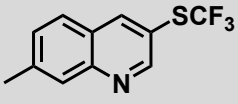




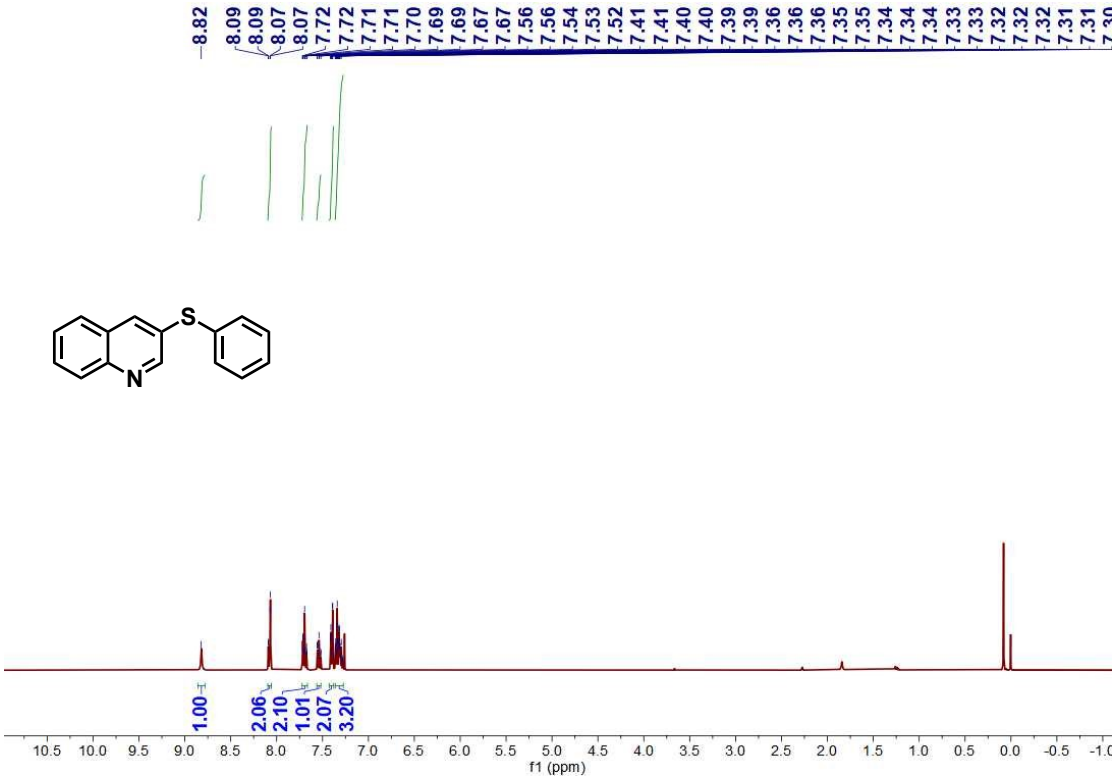
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **3r**



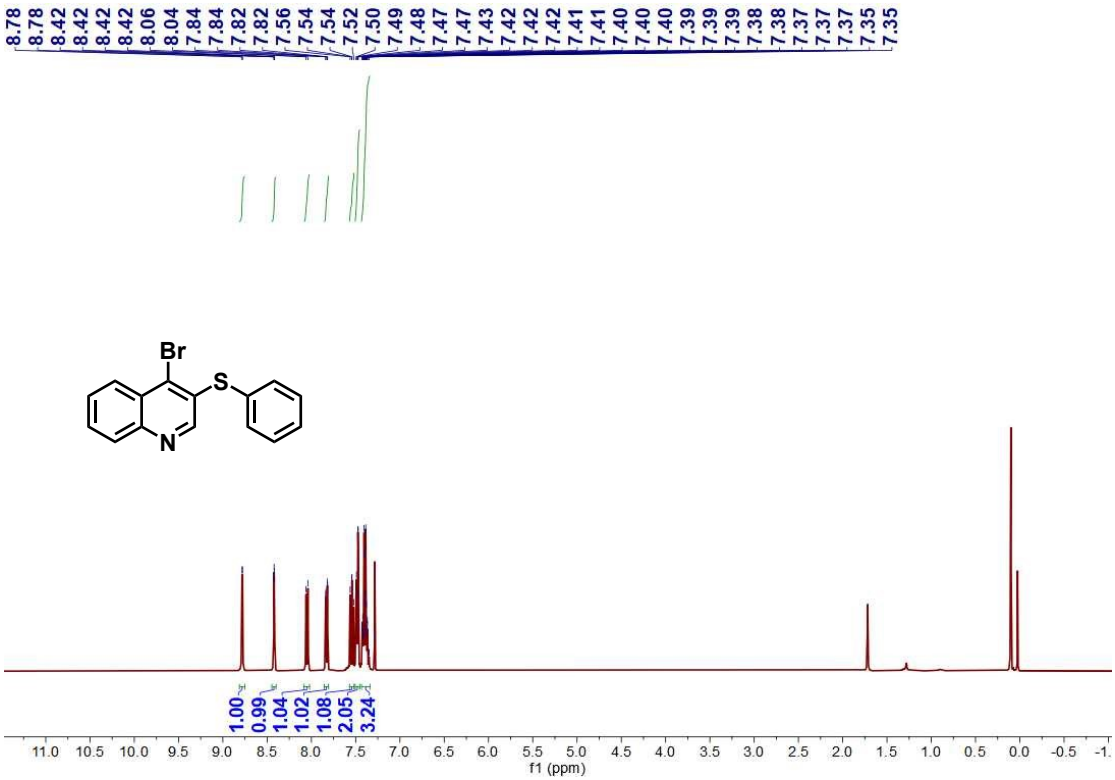

154.71
148.67
144.49
142.55
130.79
130.11
128.50
127.73
125.93
117.19
22.09
SCF3
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

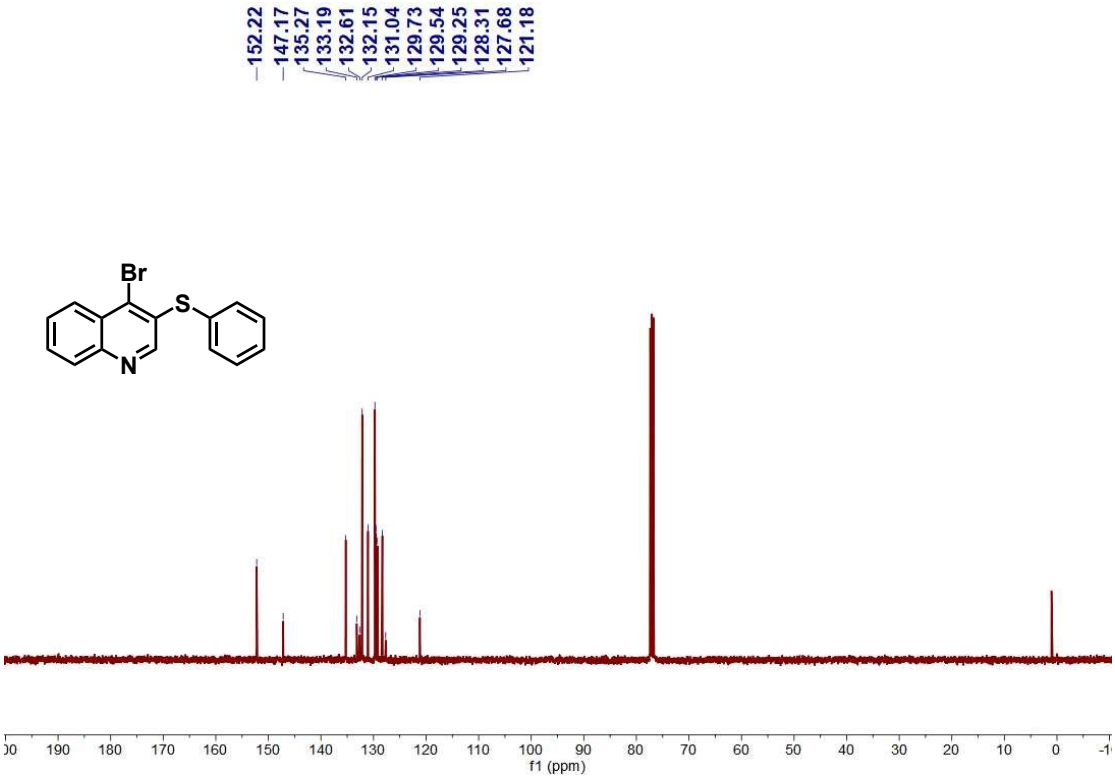

SCF3
N

^{1}H NMR and ^{13}C NMR of **4a**

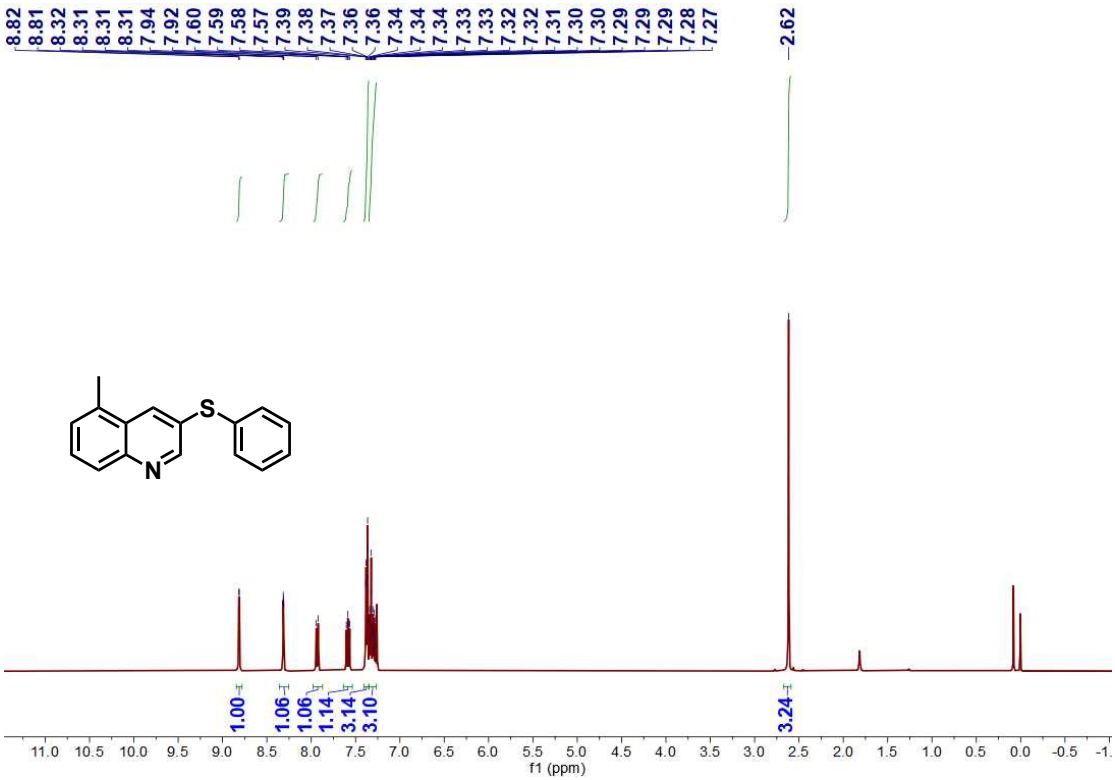


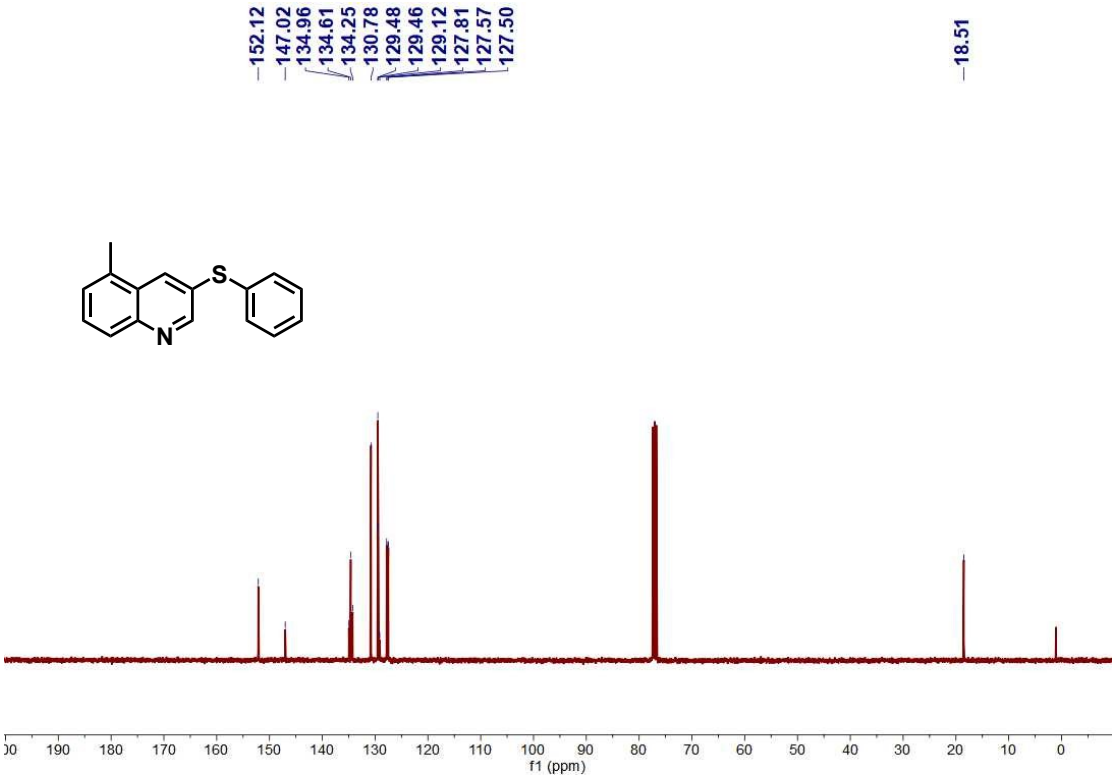
^{1}H NMR and ^{13}C NMR of **4b**



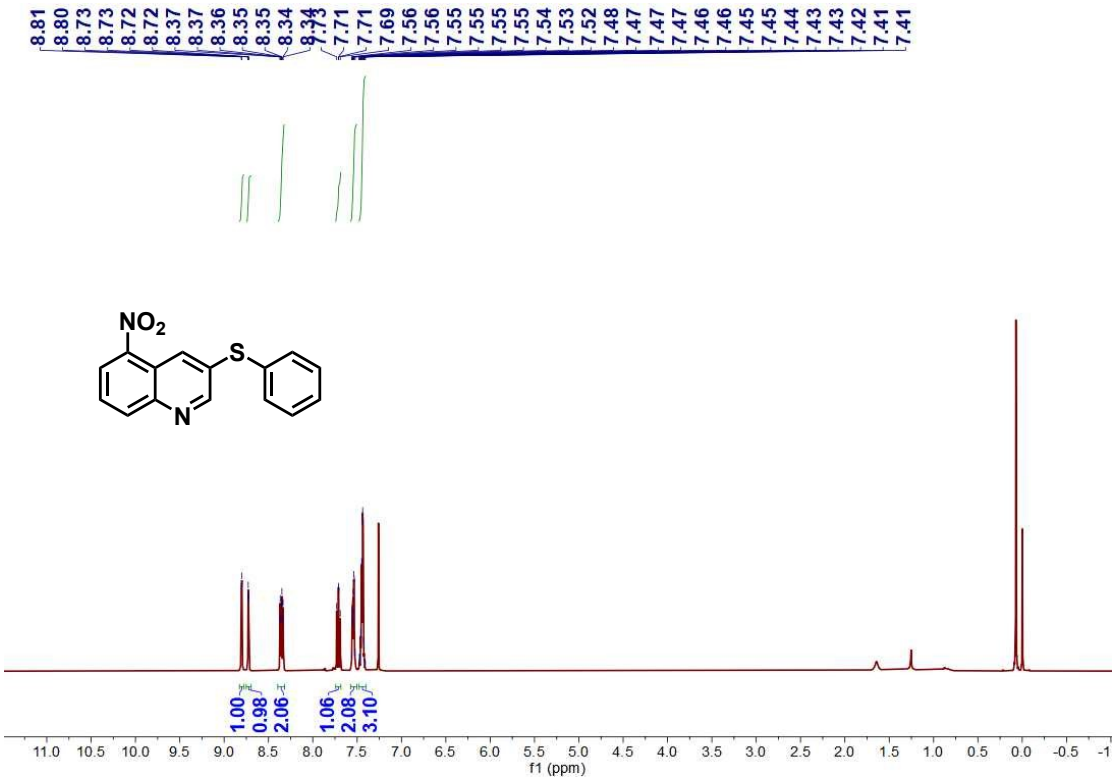


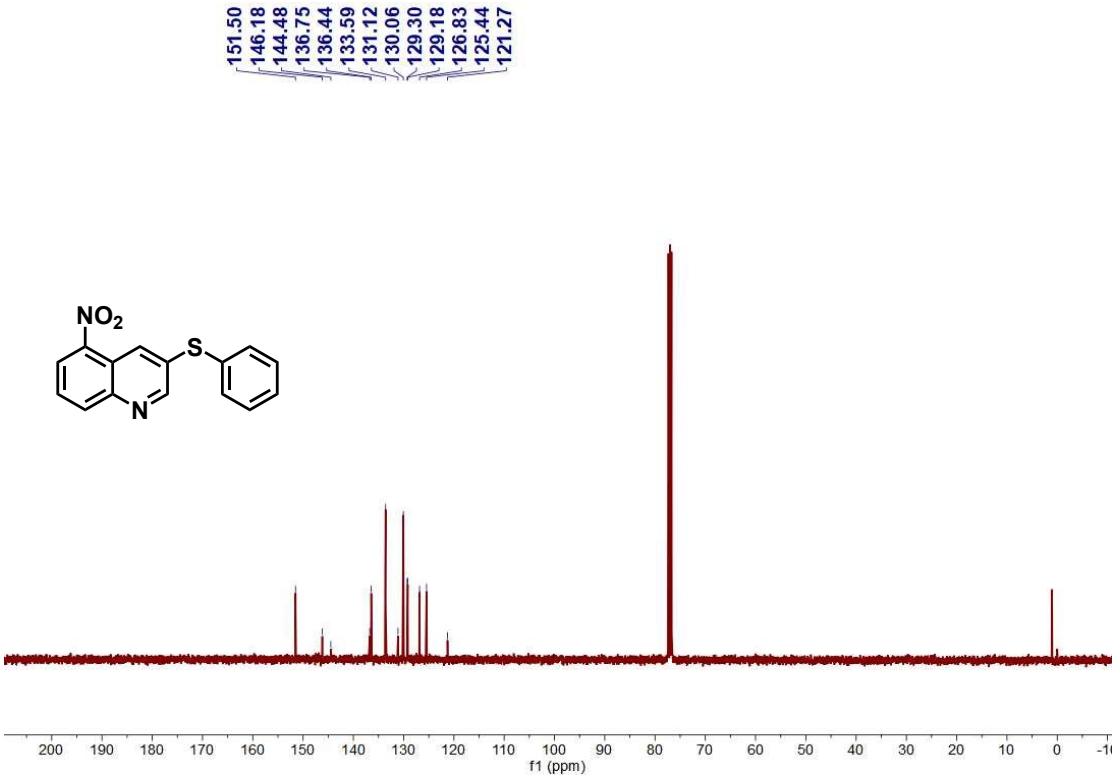
^{1}H NMR and ^{13}C NMR of **4c**



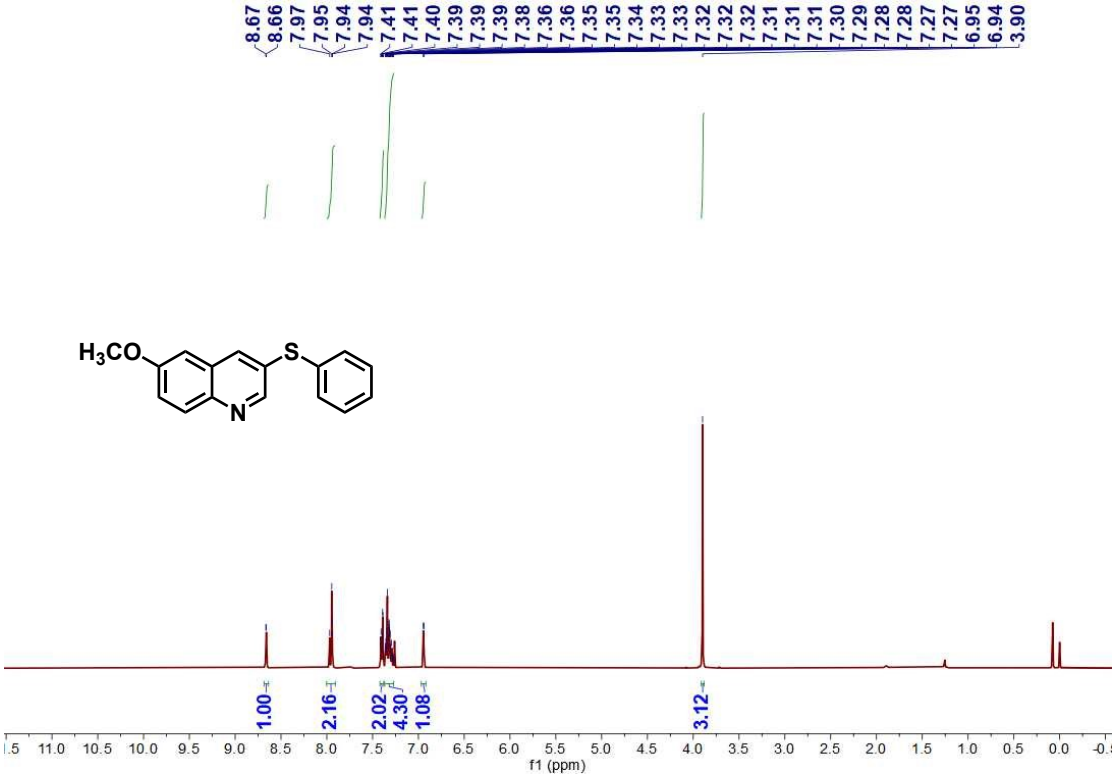


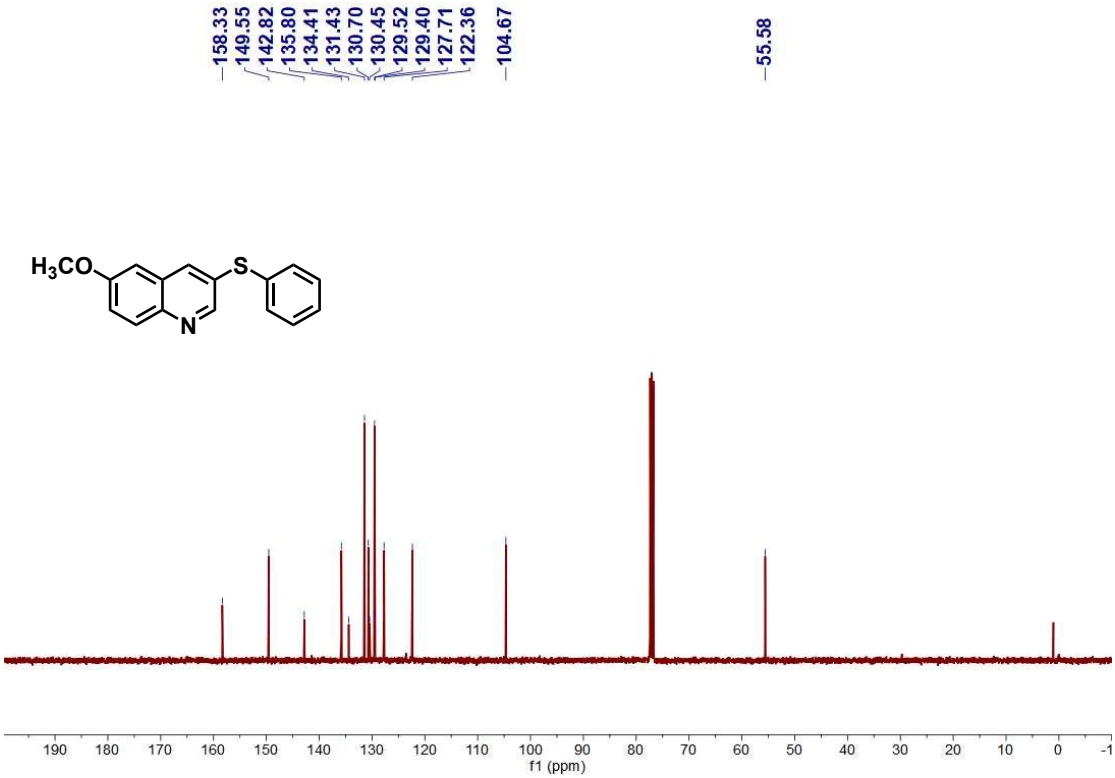
^{1}H NMR and ^{13}C NMR of **4d**



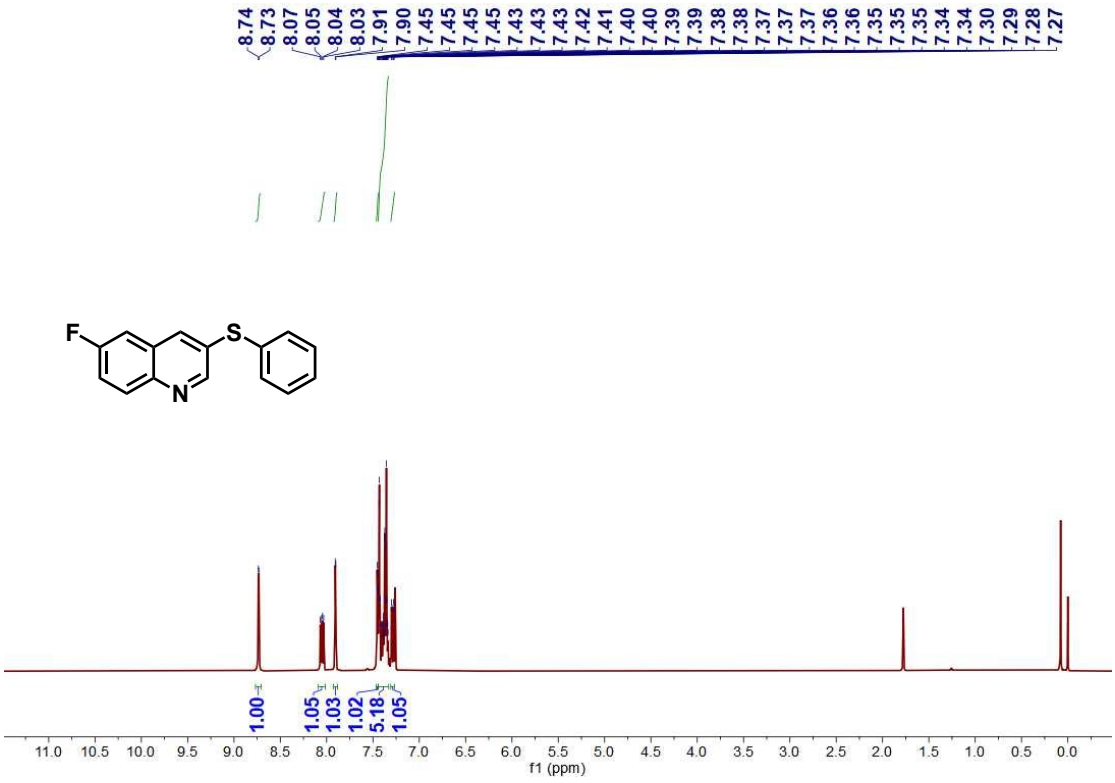


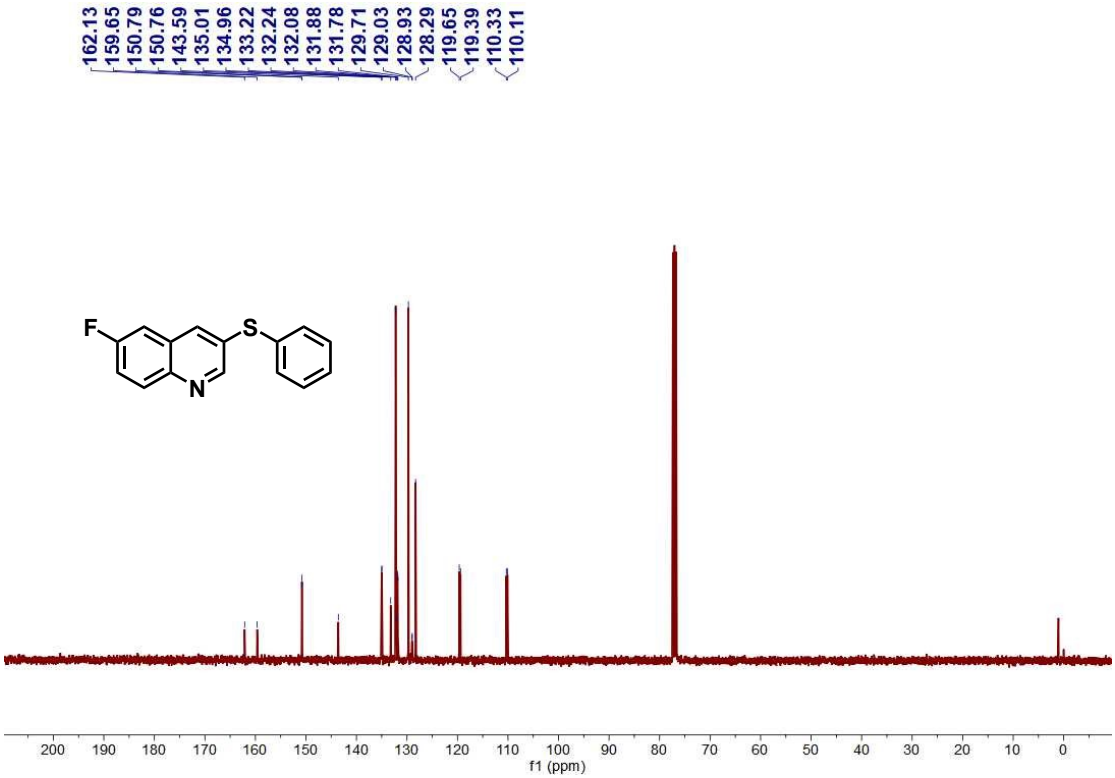
^{1}H NMR and ^{13}C NMR of **4e**



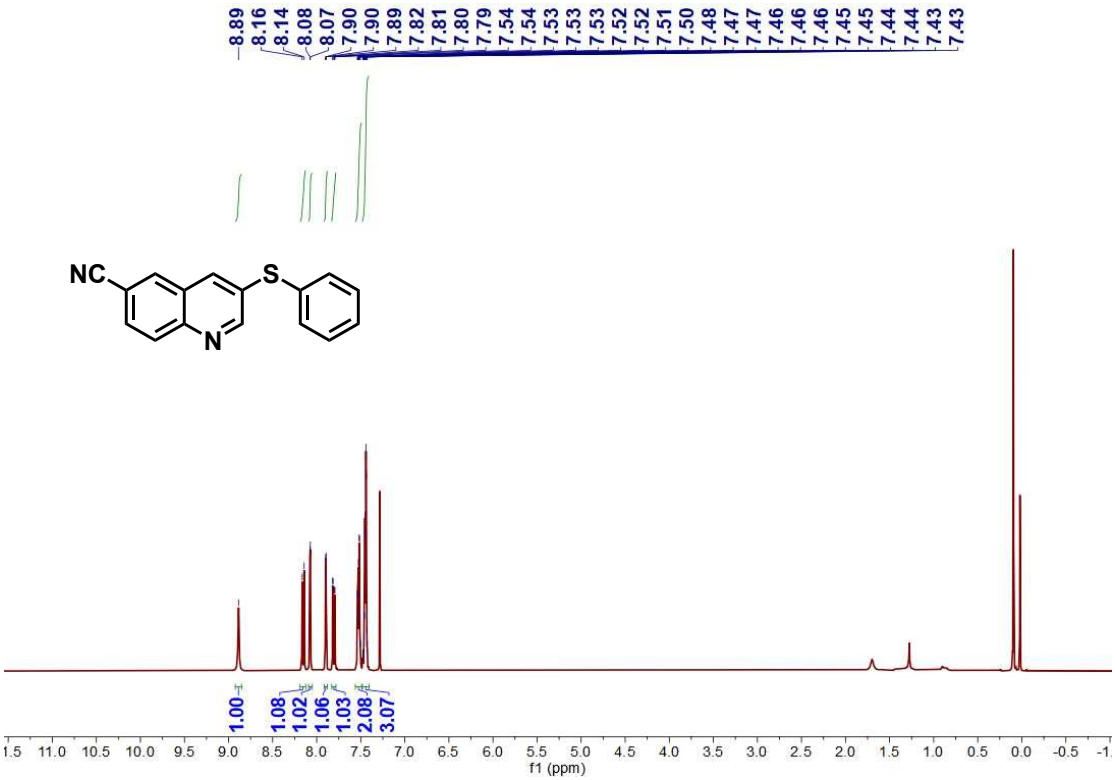


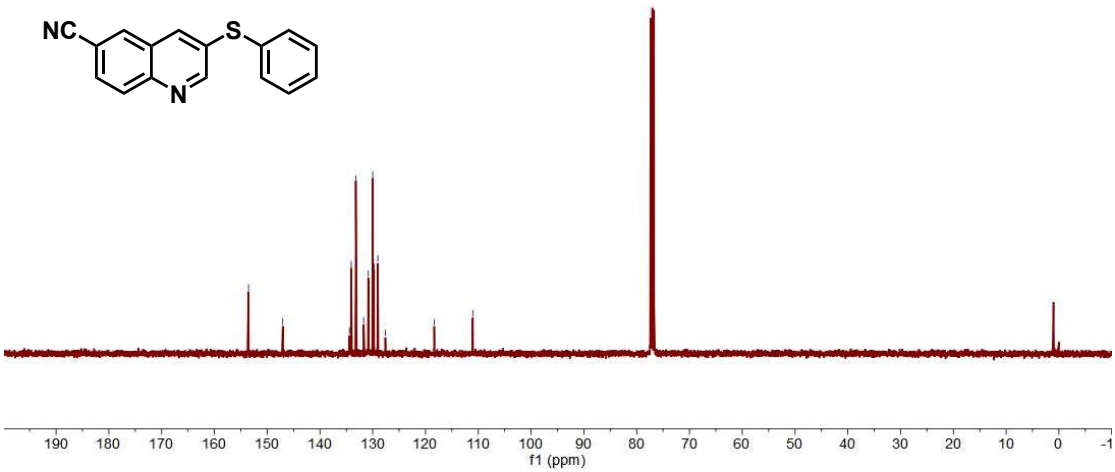
^{1}H NMR and ^{13}C NMR of **4f**



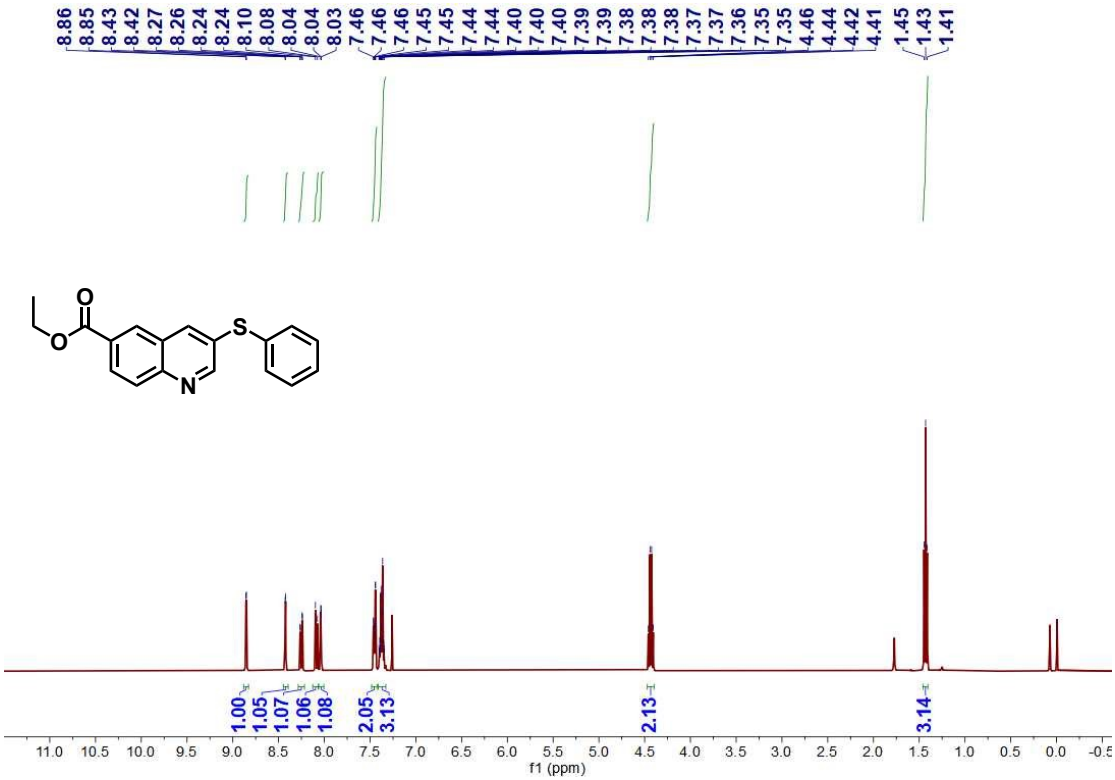


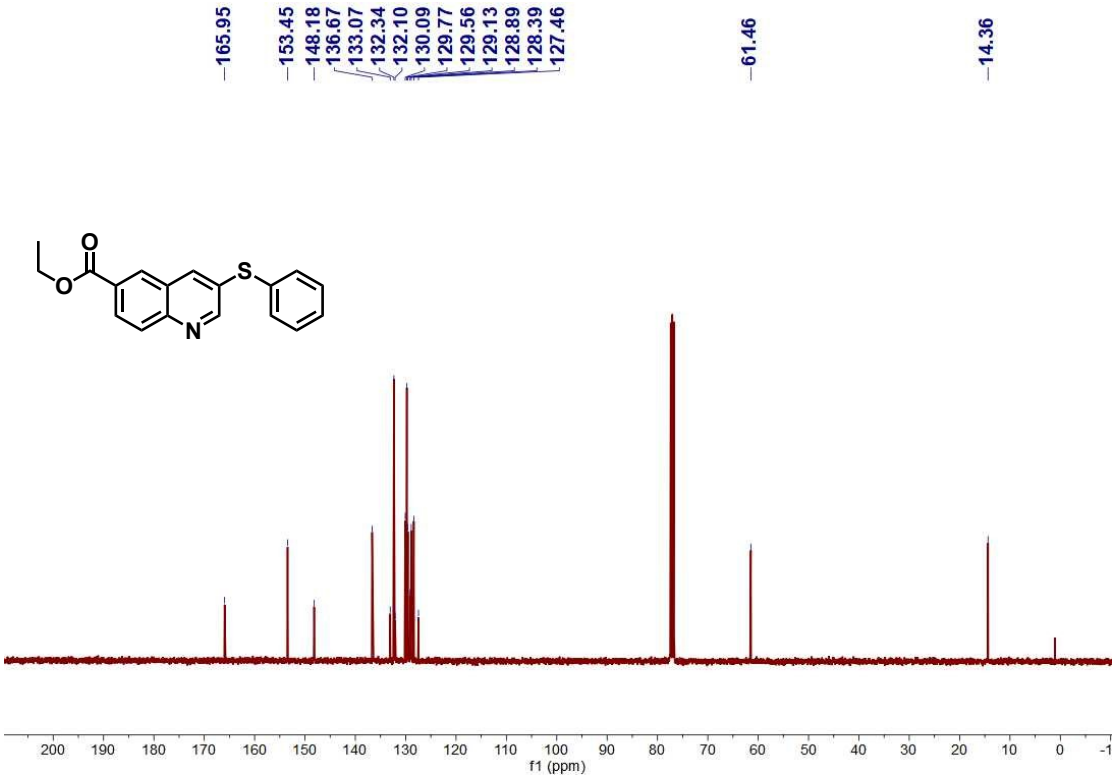
^{1}H NMR and ^{13}C NMR of **4g**



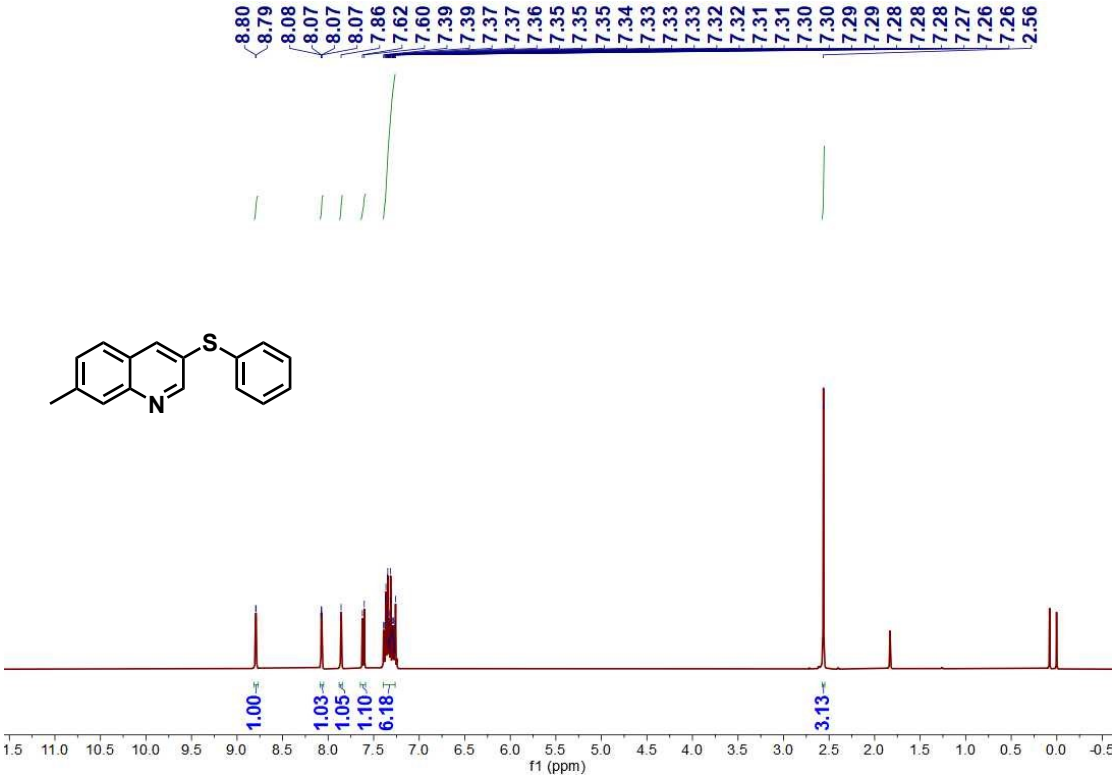


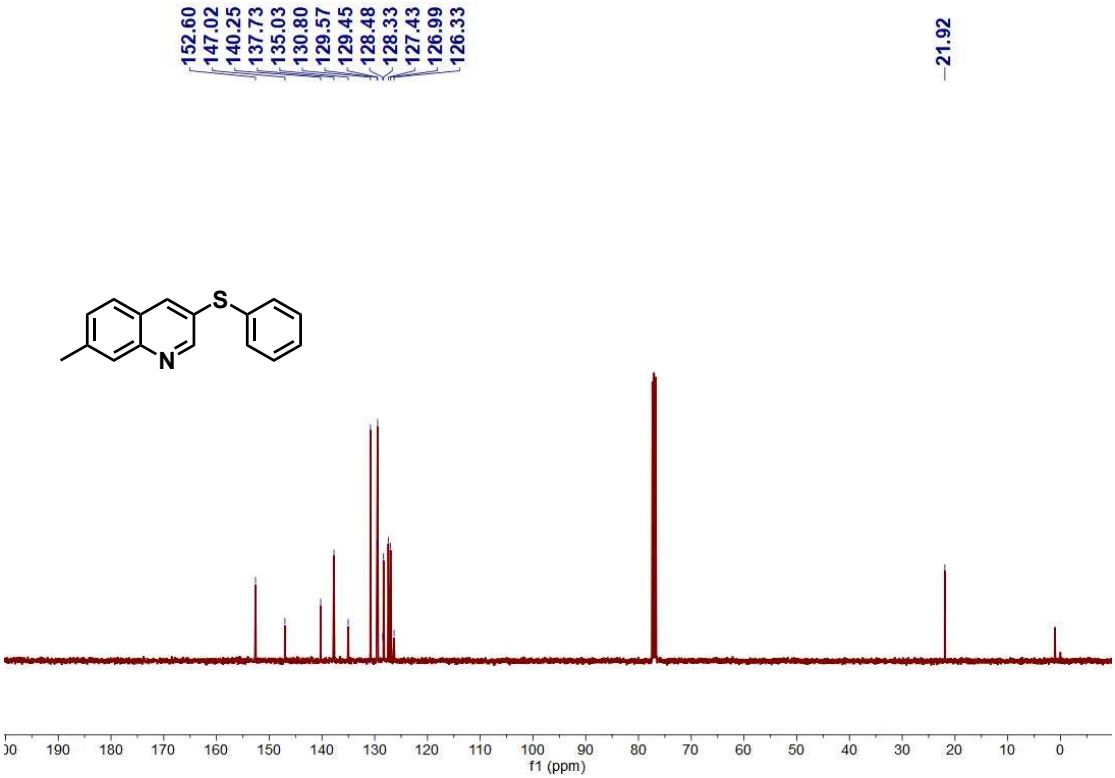
^{1}H NMR and ^{13}C NMR of **4h**



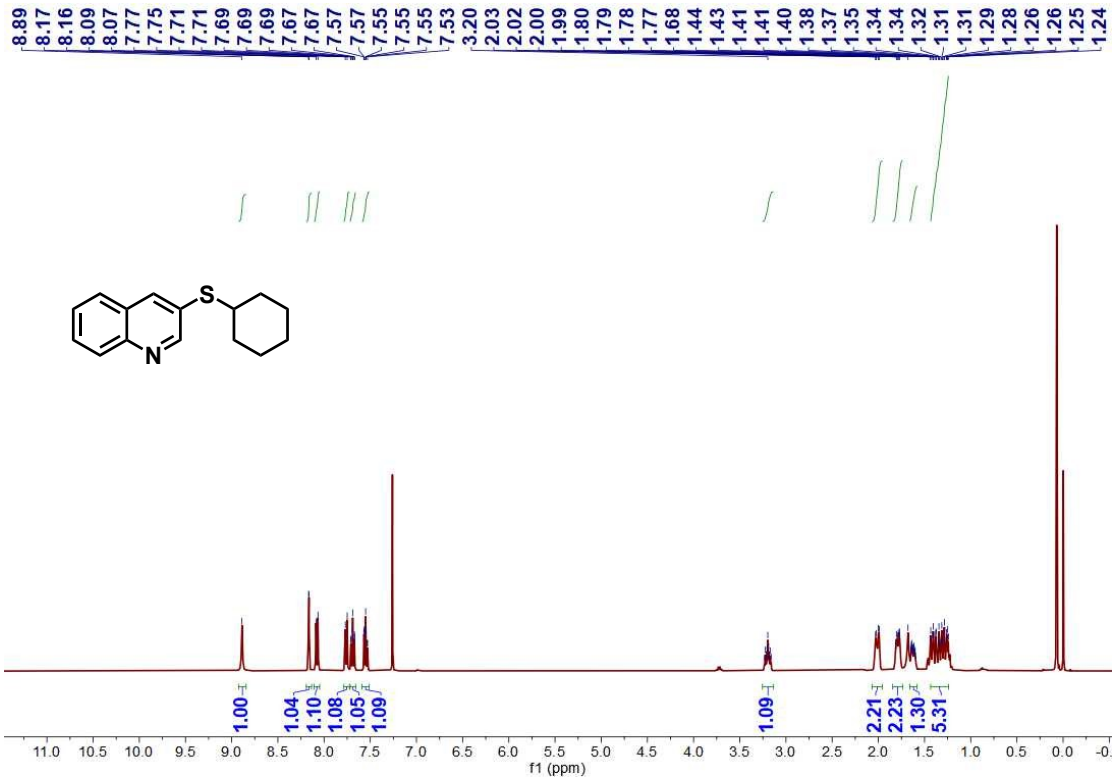


^{1}H NMR and ^{13}C NMR of **4i**

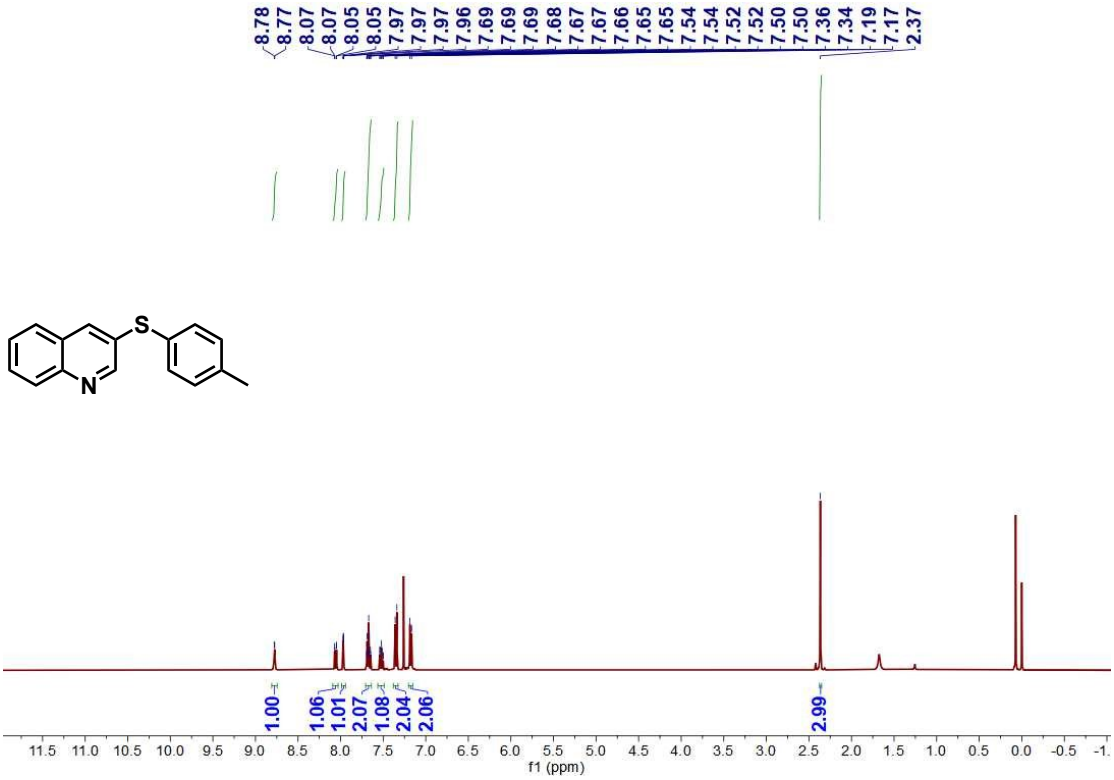




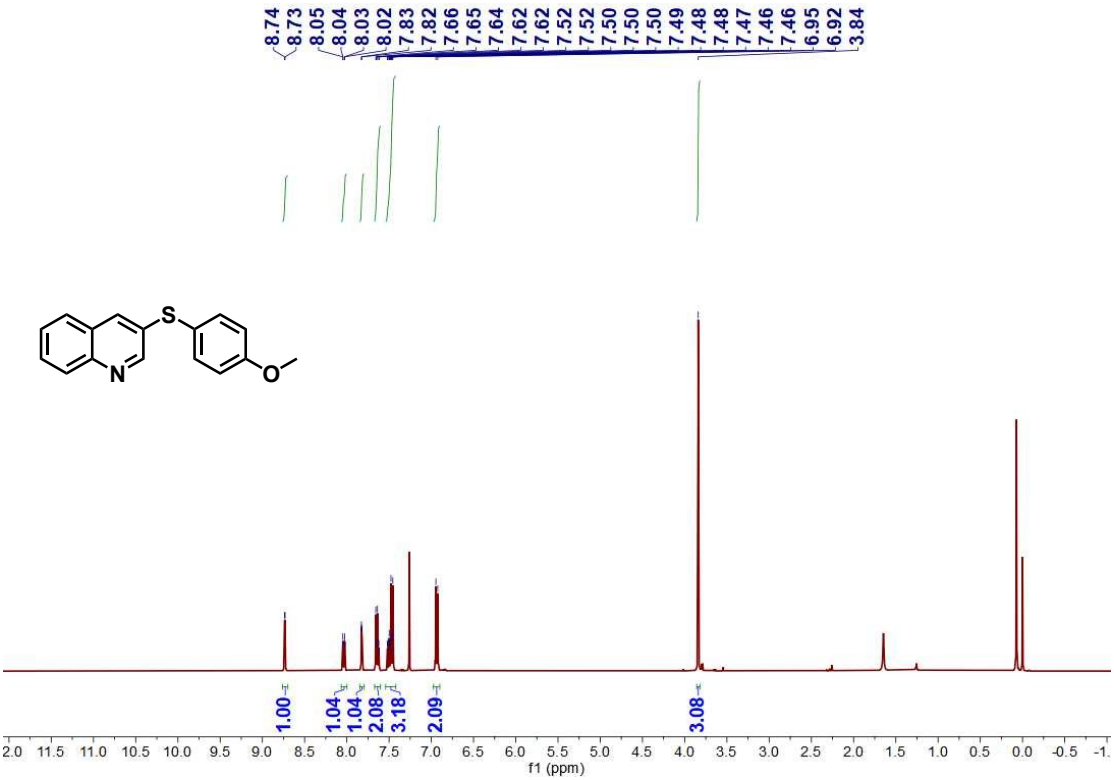
^{1}H NMR and ^{13}C NMR of **4j**



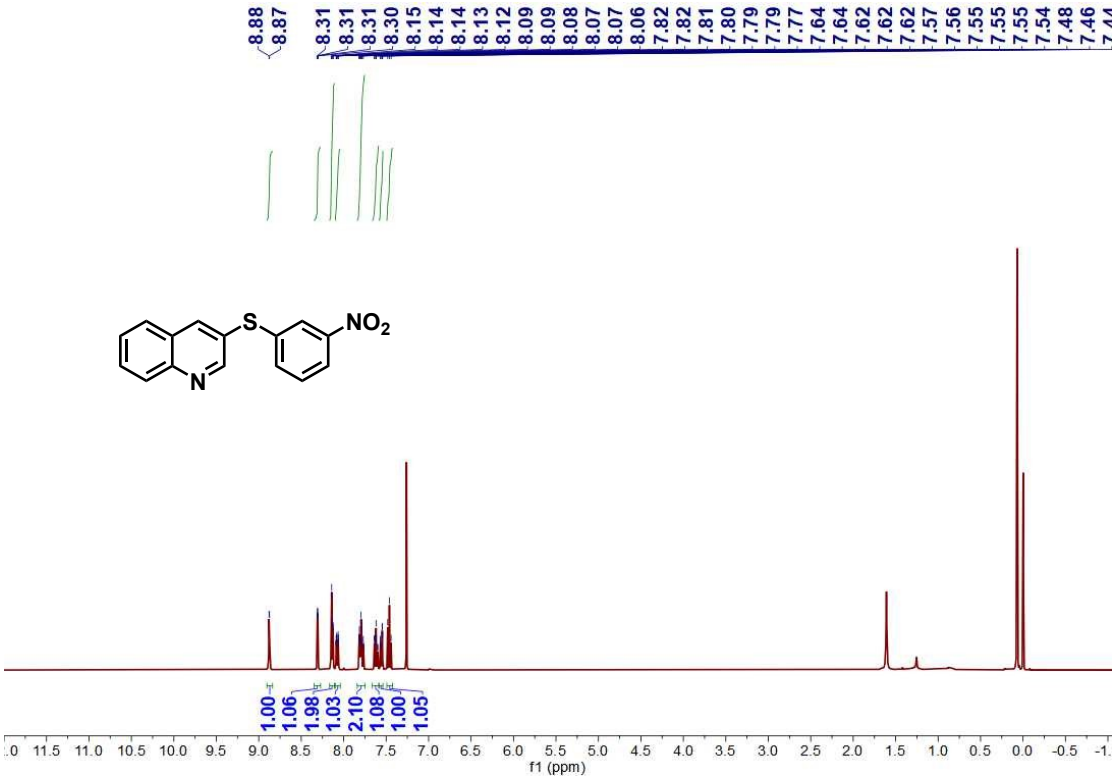
^{1}H NMR and ^{13}C NMR of **4k**

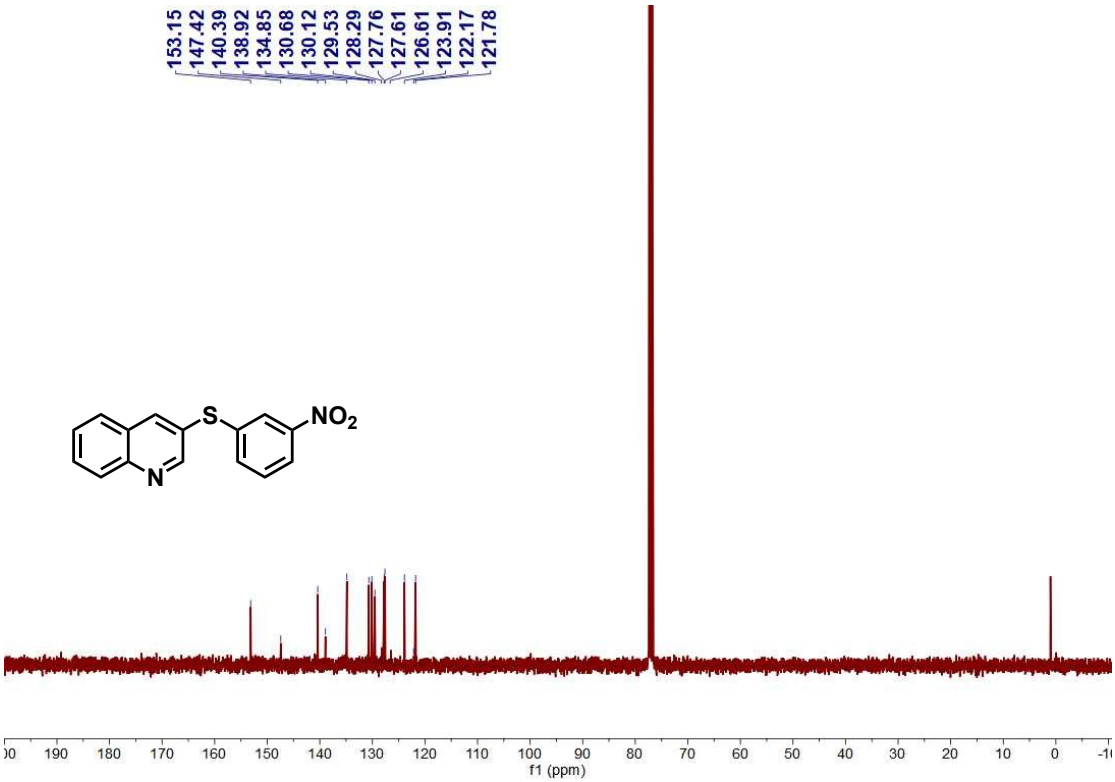


^{1}H NMR and ^{13}C NMR of **4l**

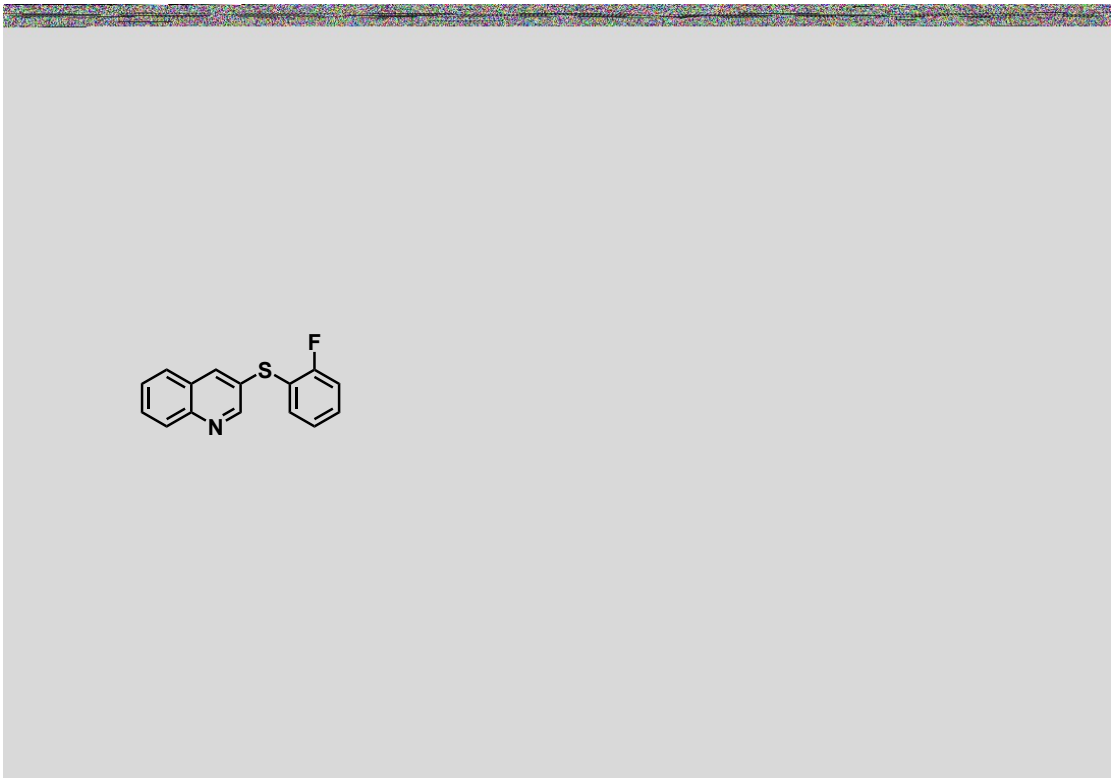


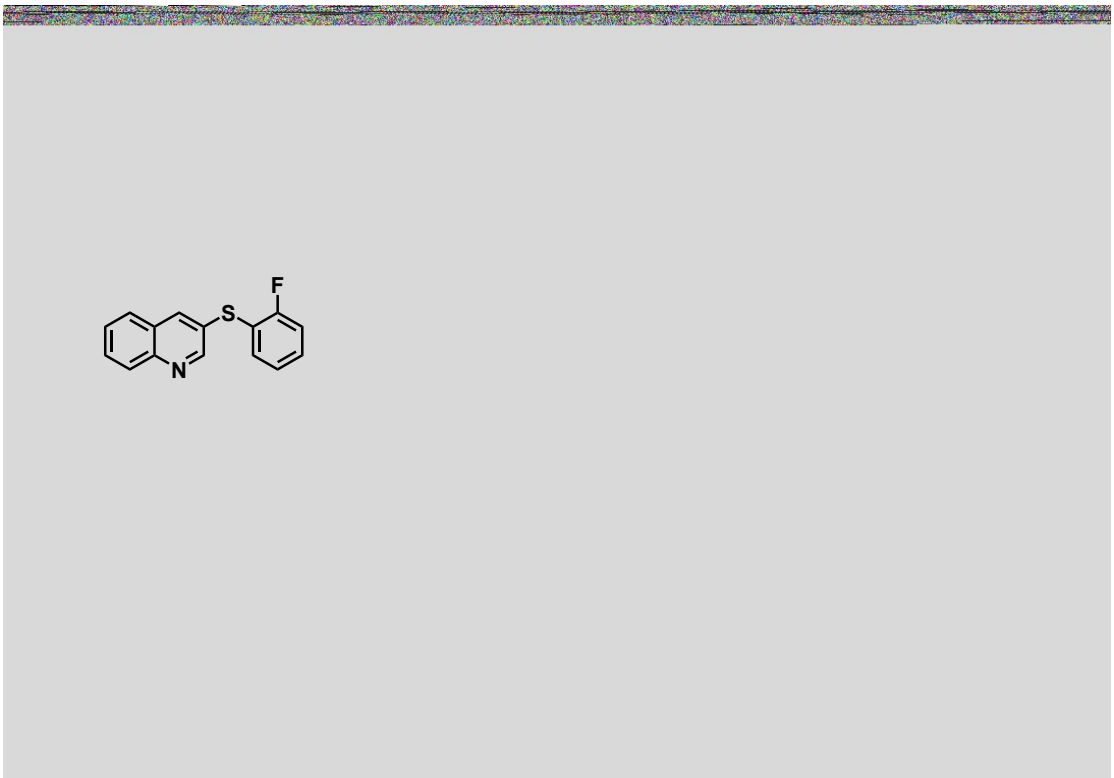
^{1}H NMR and ^{13}C NMR of **4m**



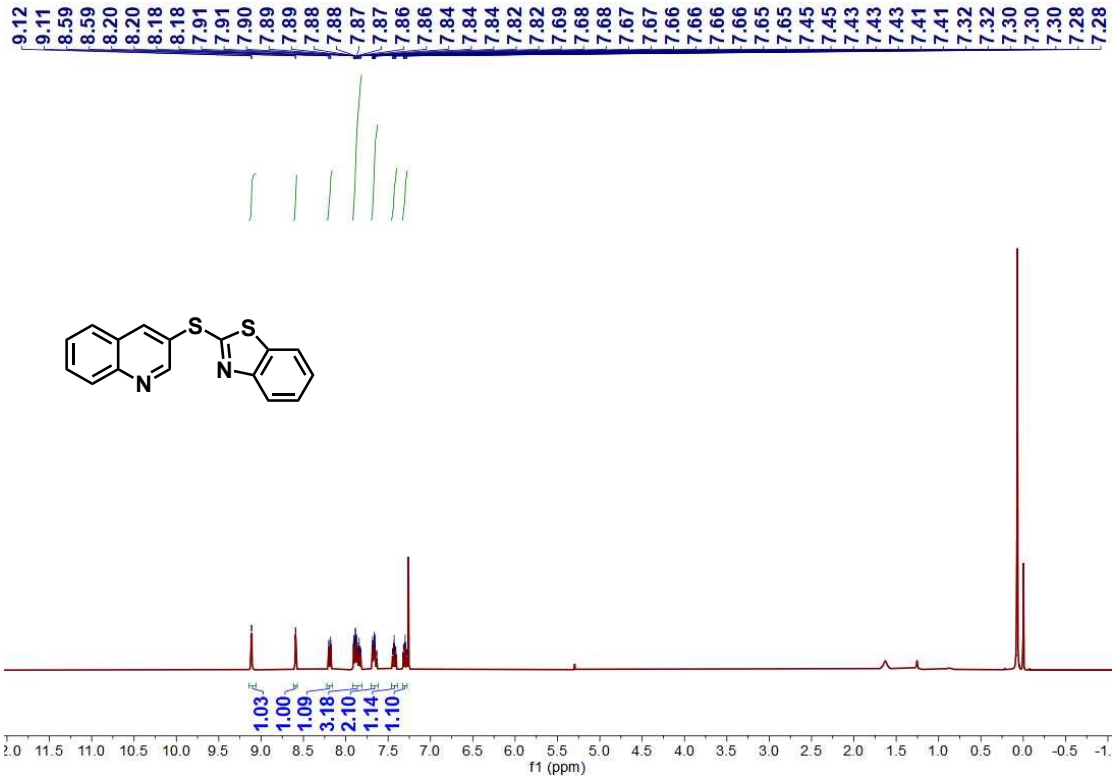


^{1}H NMR and ^{13}C NMR of **4n**

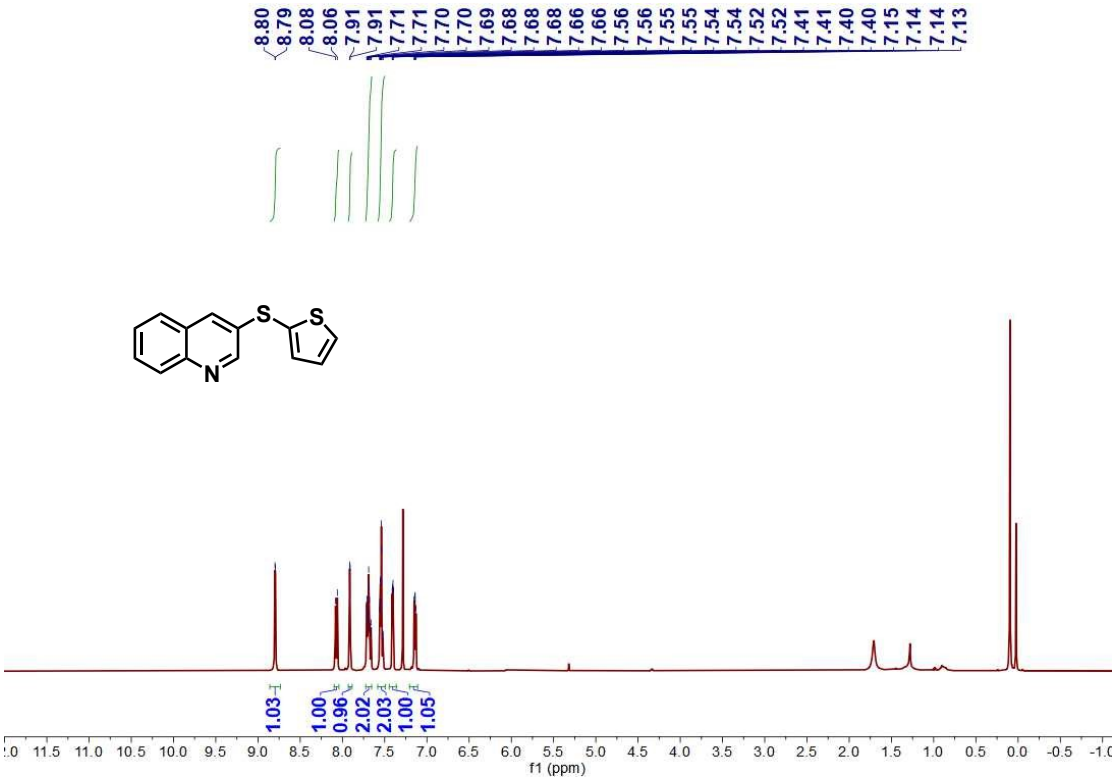


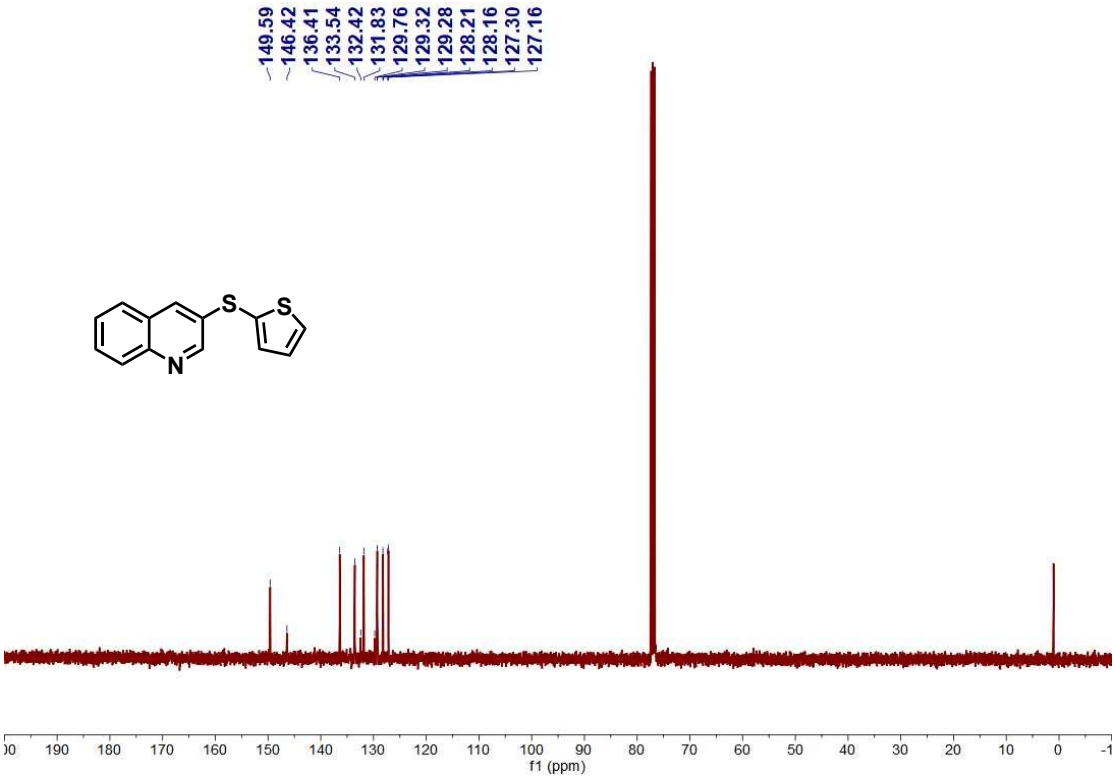


^{1}H NMR of **4o**

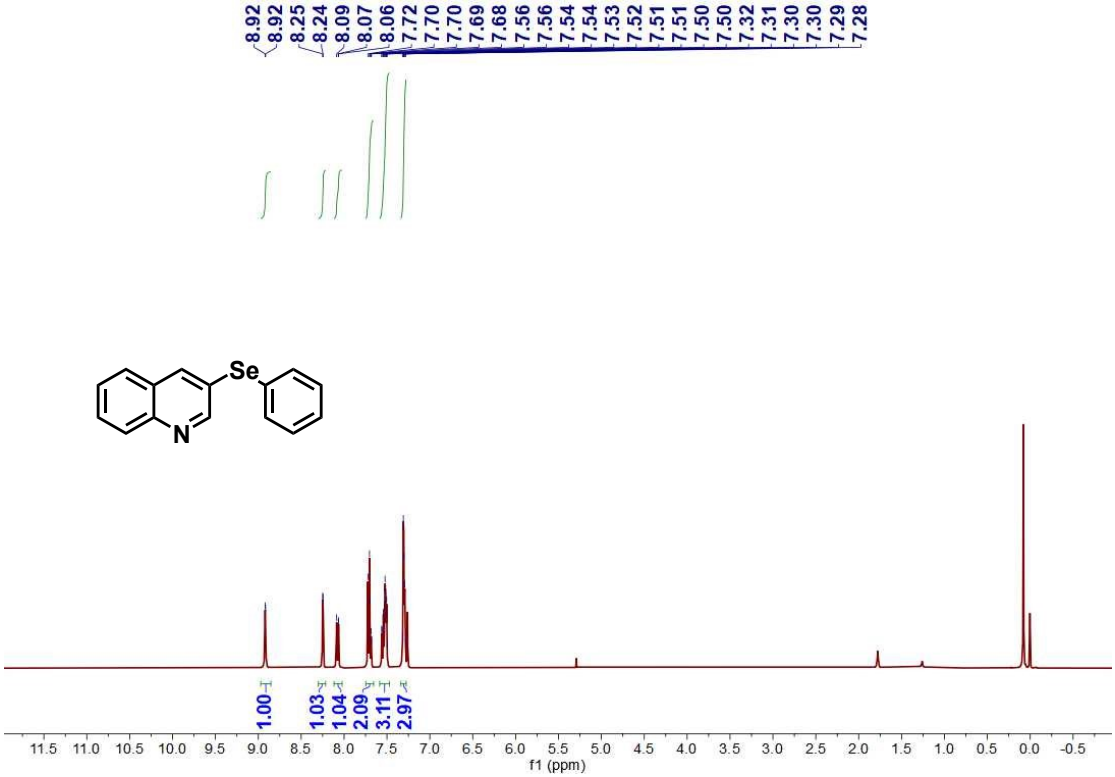


^{1}H NMR and ^{13}C NMR of **4p**

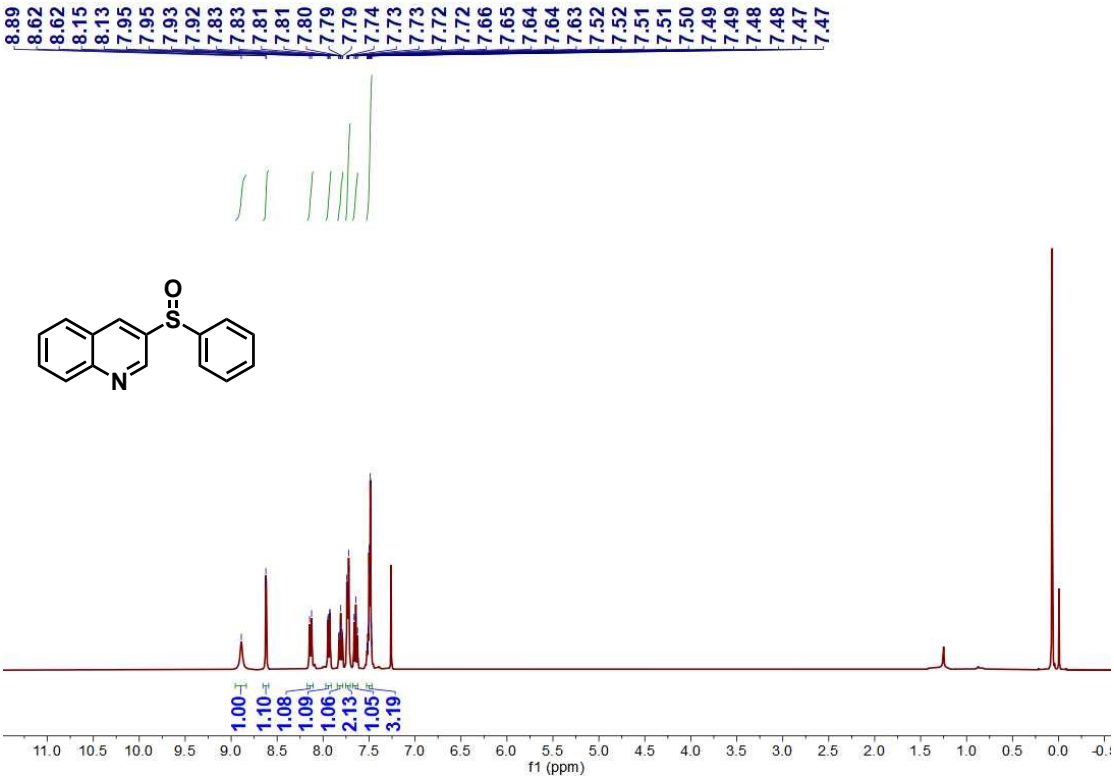



149.59
146.42
136.41
133.54
132.42
131.83
129.76
129.32
129.28
128.21
128.16
127.30
127.16
S
S
N
f1 (ppm)

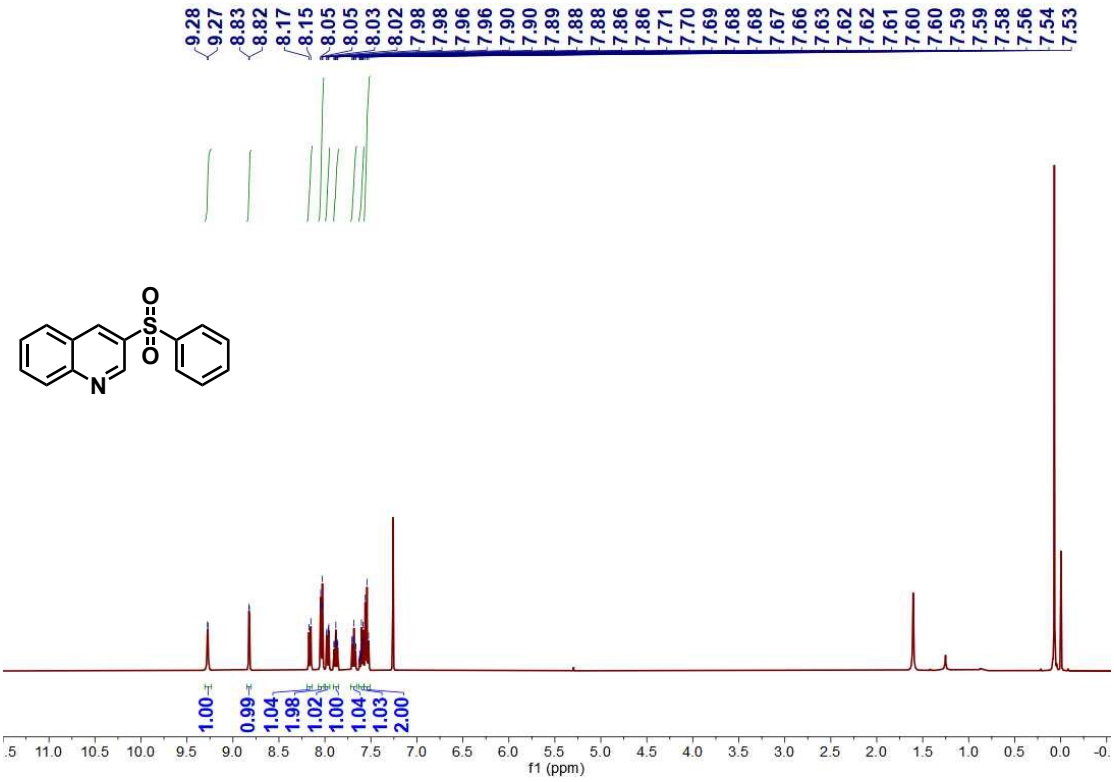
^{1}H NMR of **4q**


8.92
8.92
8.25
8.24
8.09
8.07
8.06
7.72
7.70
7.70
7.69
7.68
7.56
7.56
7.54
7.54
7.53
7.52
7.51
7.51
7.50
7.50
7.32
7.31
7.30
7.30
7.29
7.28
Se
N
1.00
1.03
1.04
2.09
3.11
2.97
f1 (ppm)

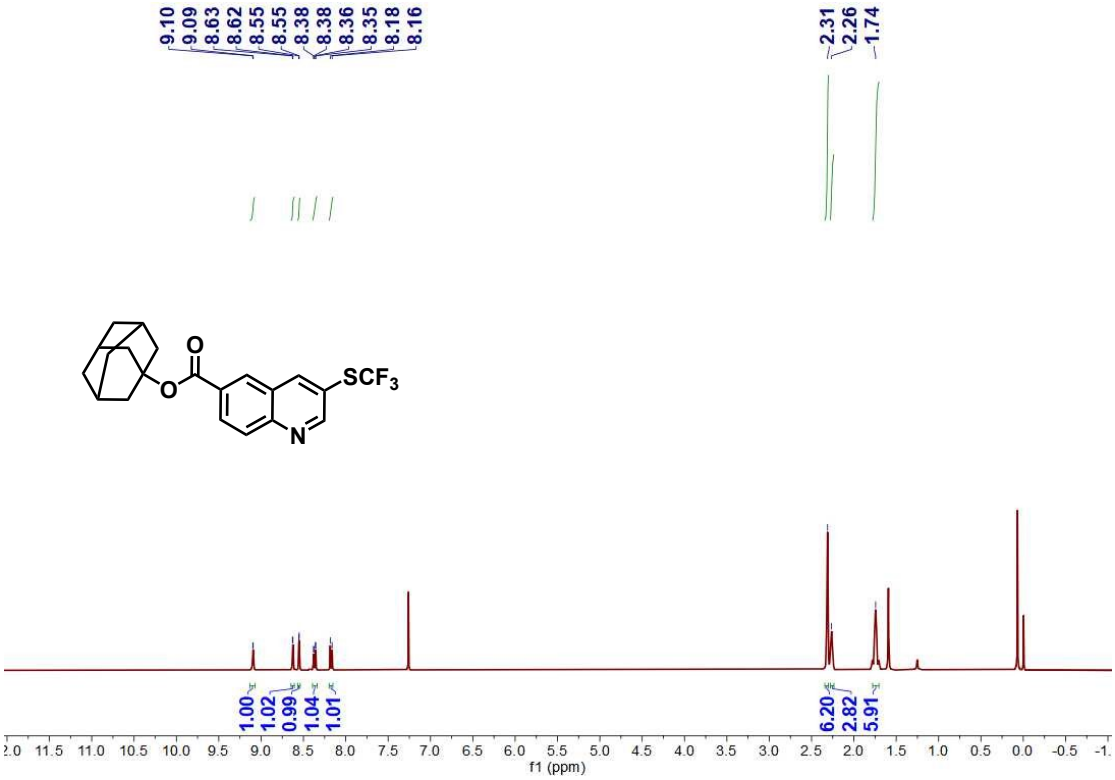
^{1}H NMR of **4aa**

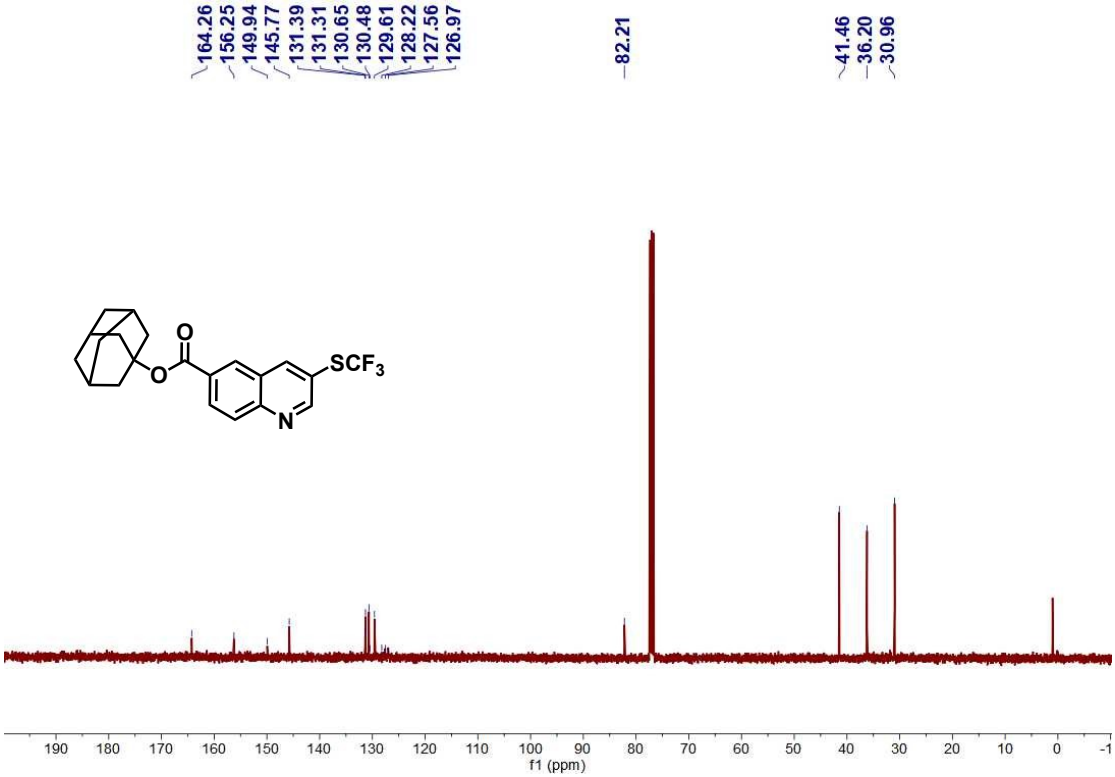


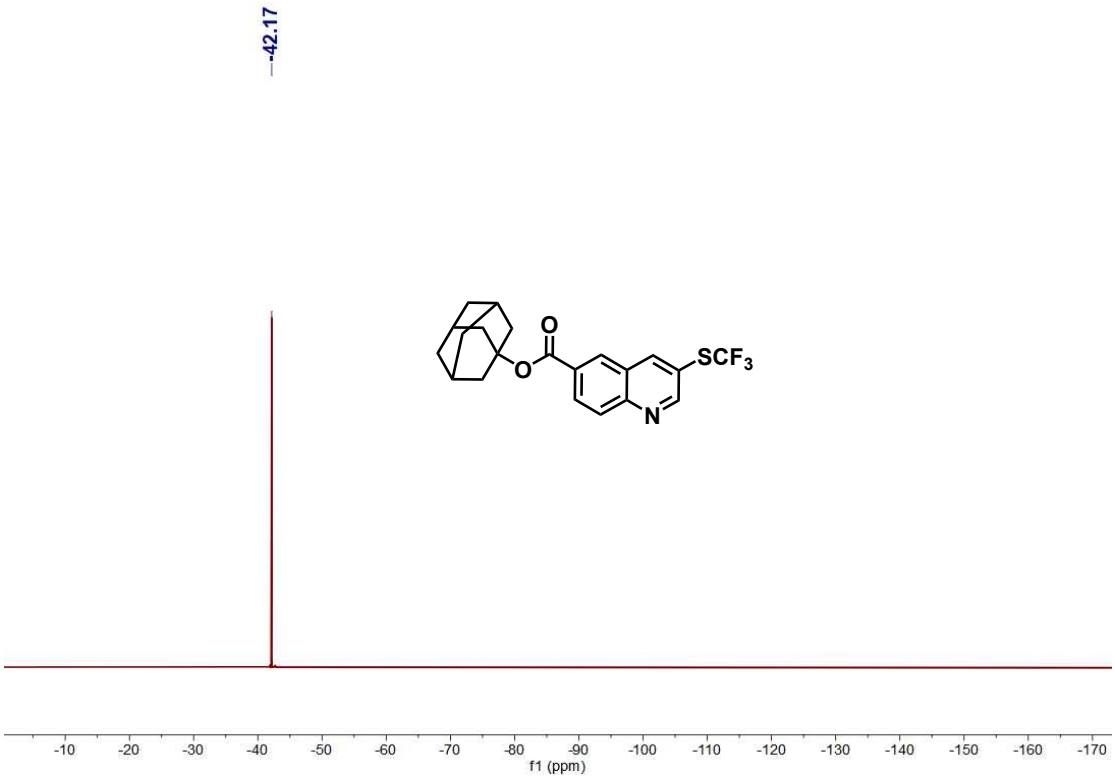
^{1}H NMR of **4ab**



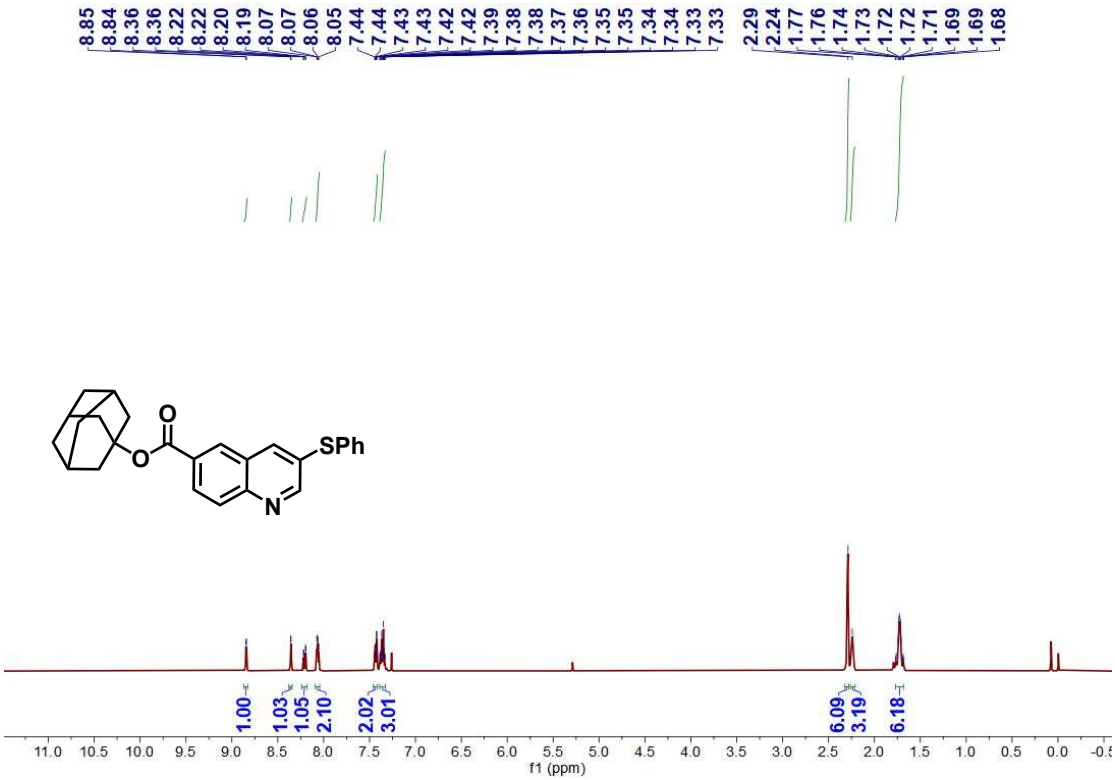
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **5a**

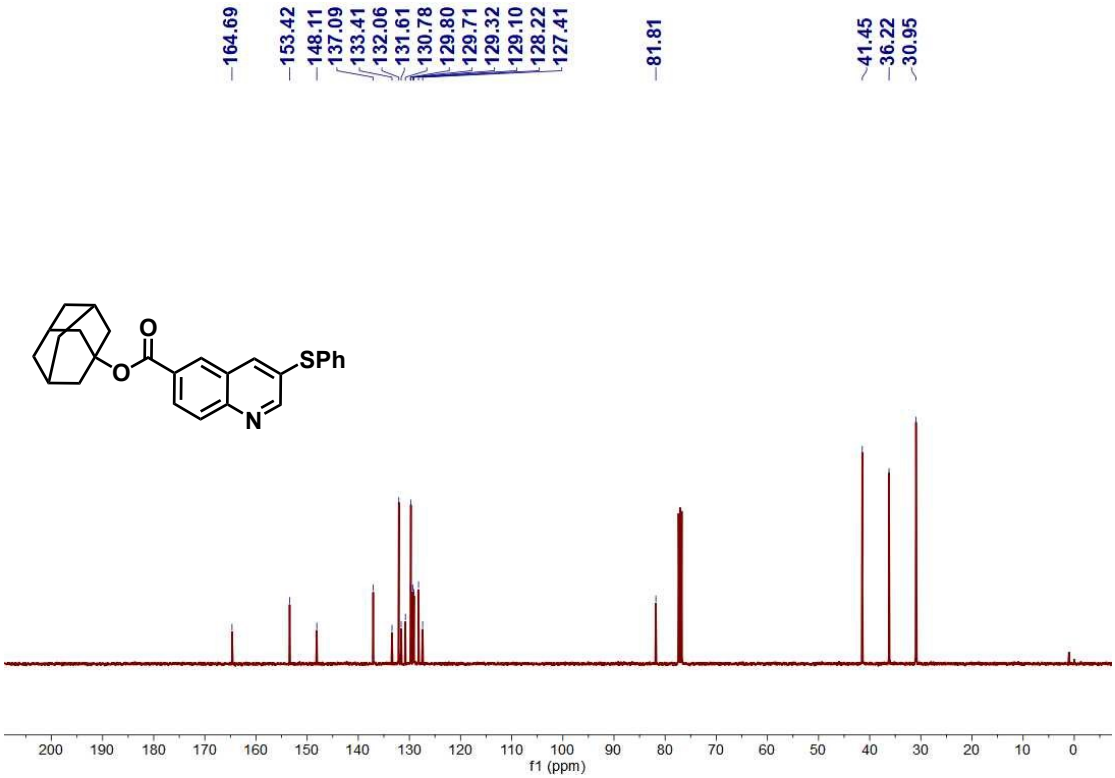




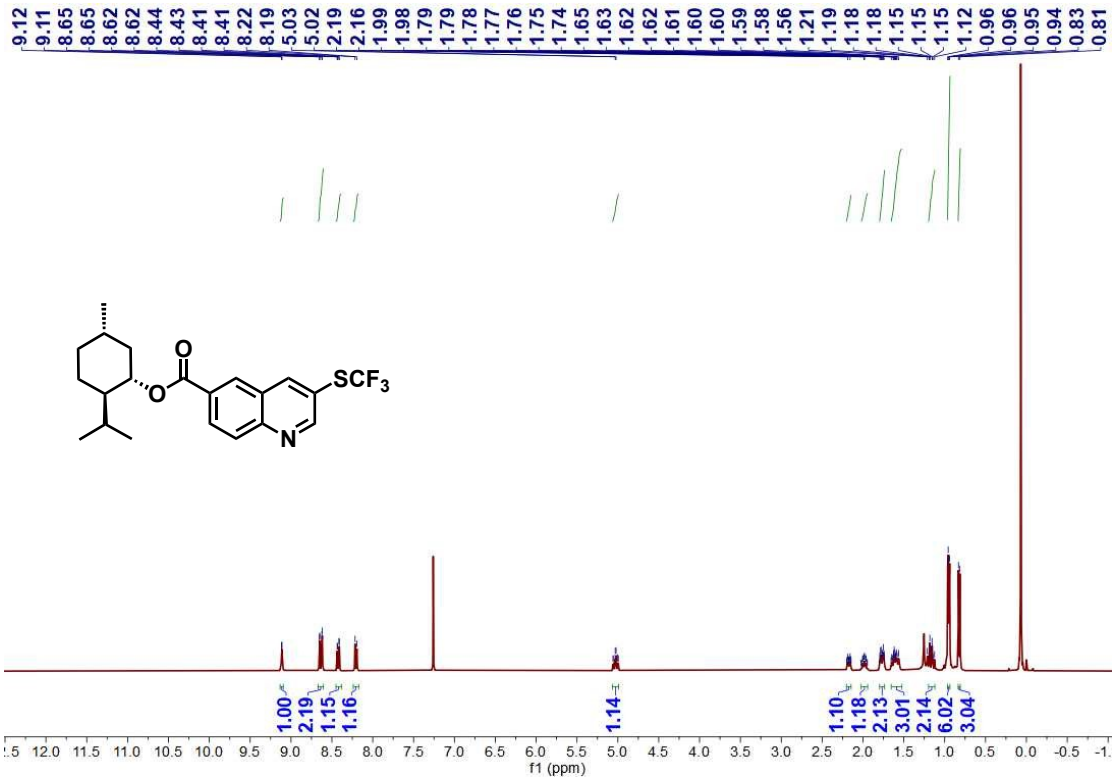


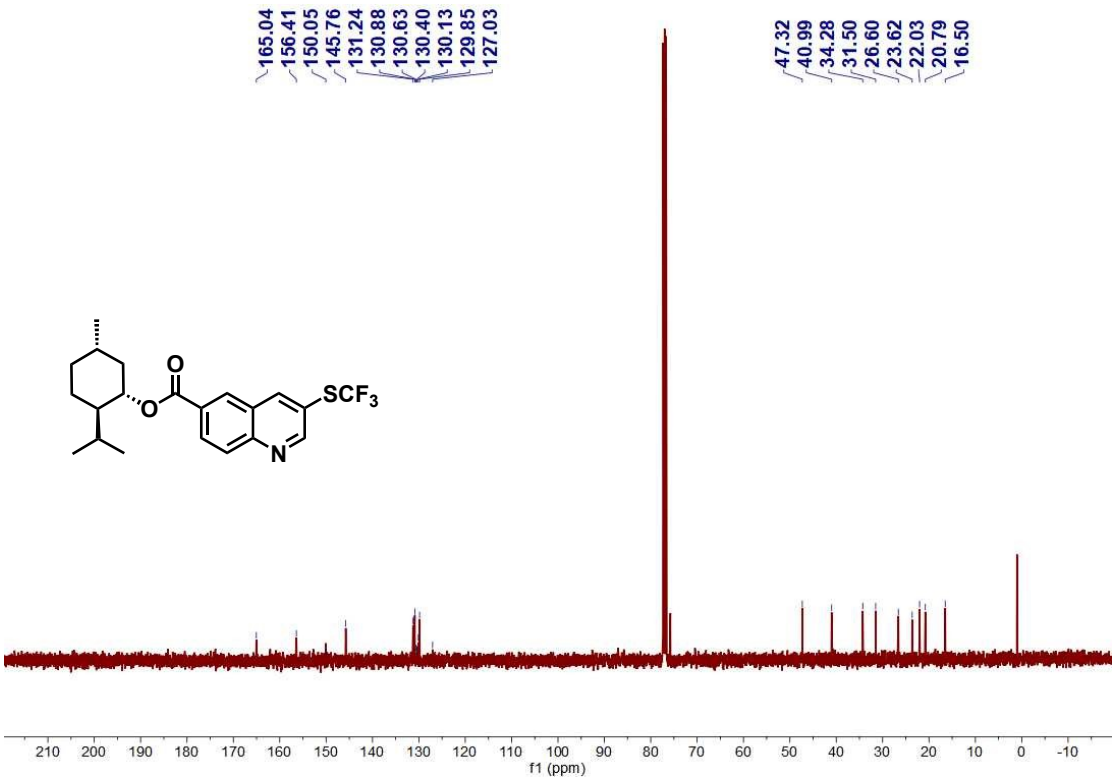
^{1}H NMR and ^{13}C NMR of **5b**

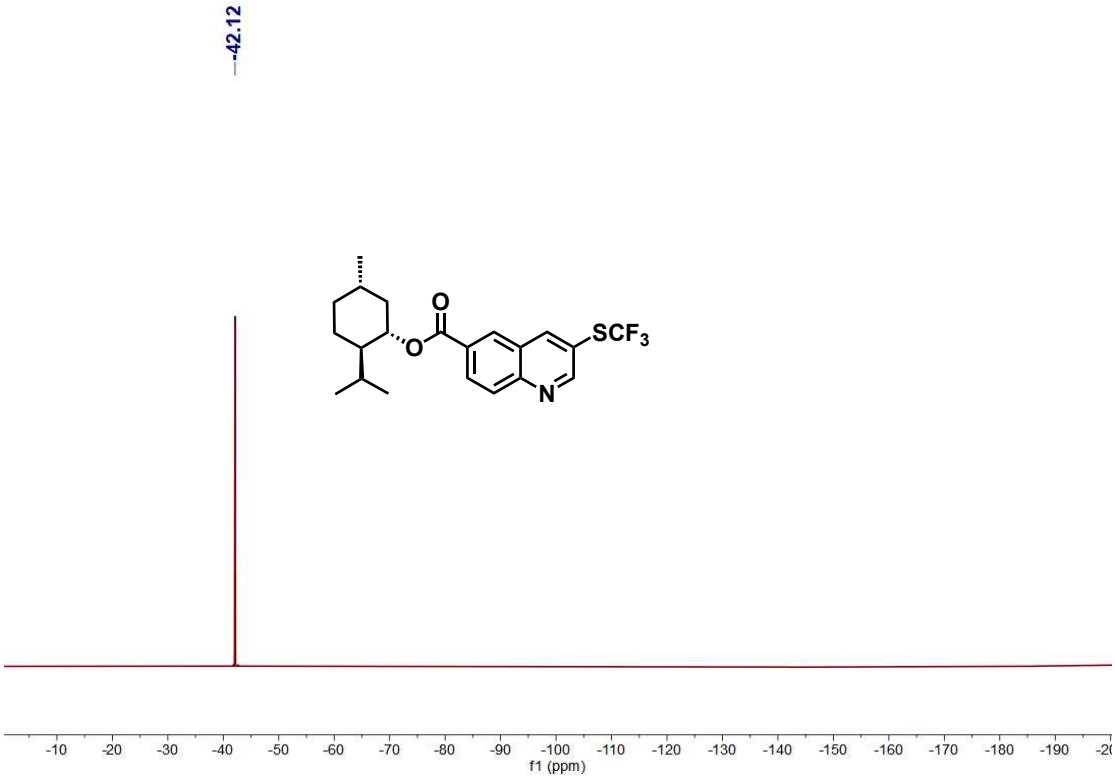




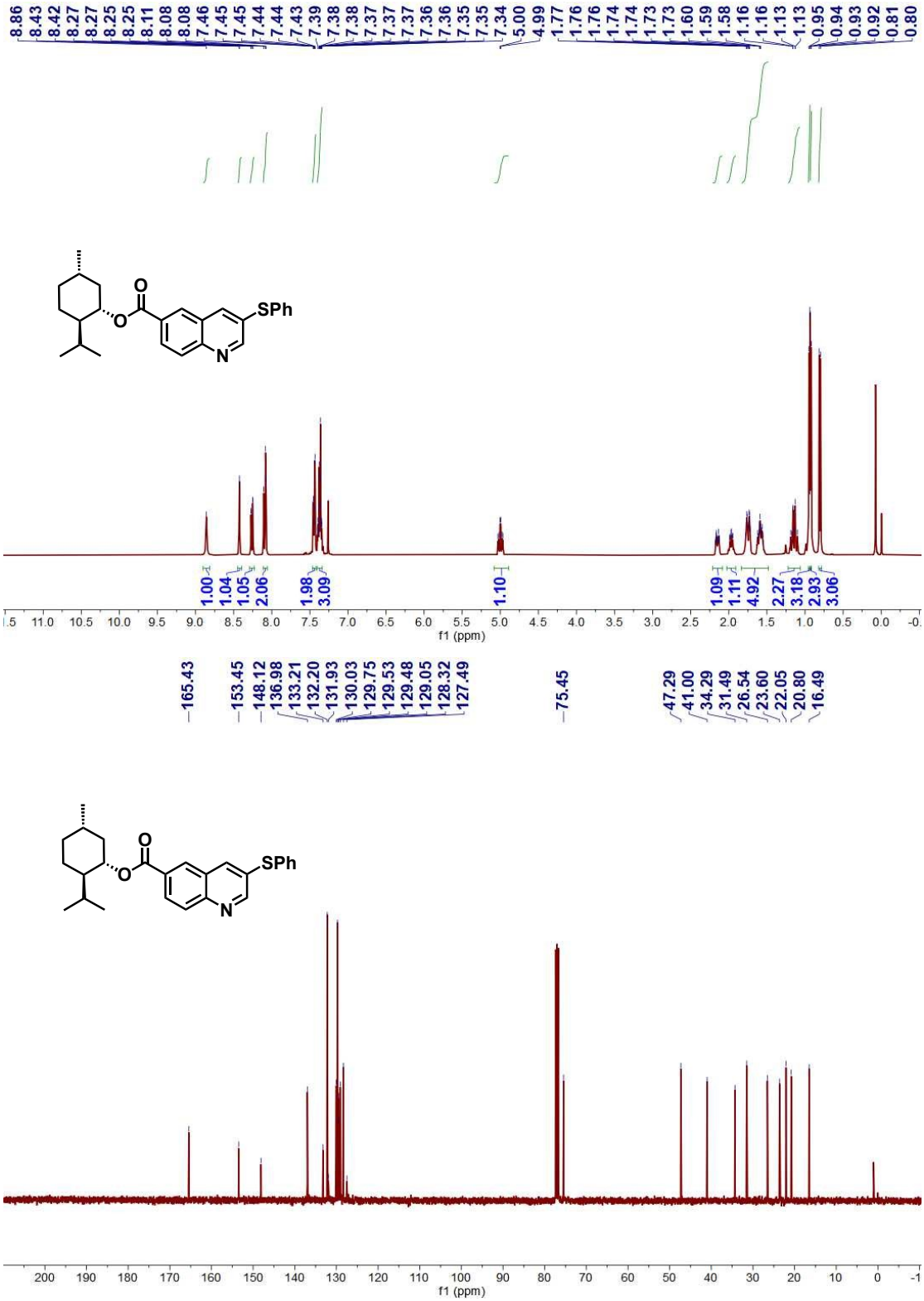
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **6a**



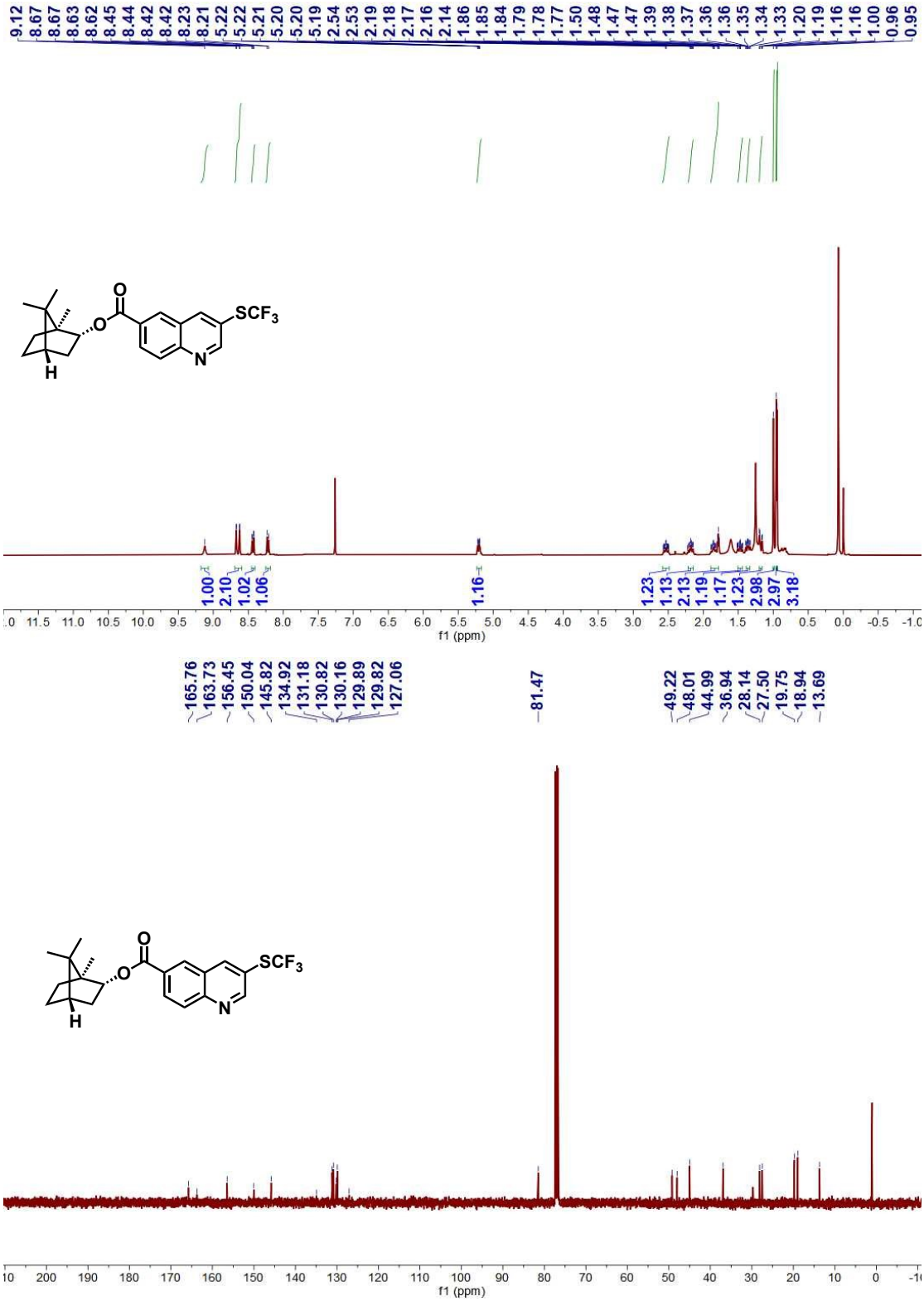

165.04
156.41
150.05
145.76
131.24
130.88
130.63
130.40
130.13
129.85
127.03
47.32
40.99
34.28
31.50
26.60
23.62
22.03
20.79
16.50
O
O
SCF3
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

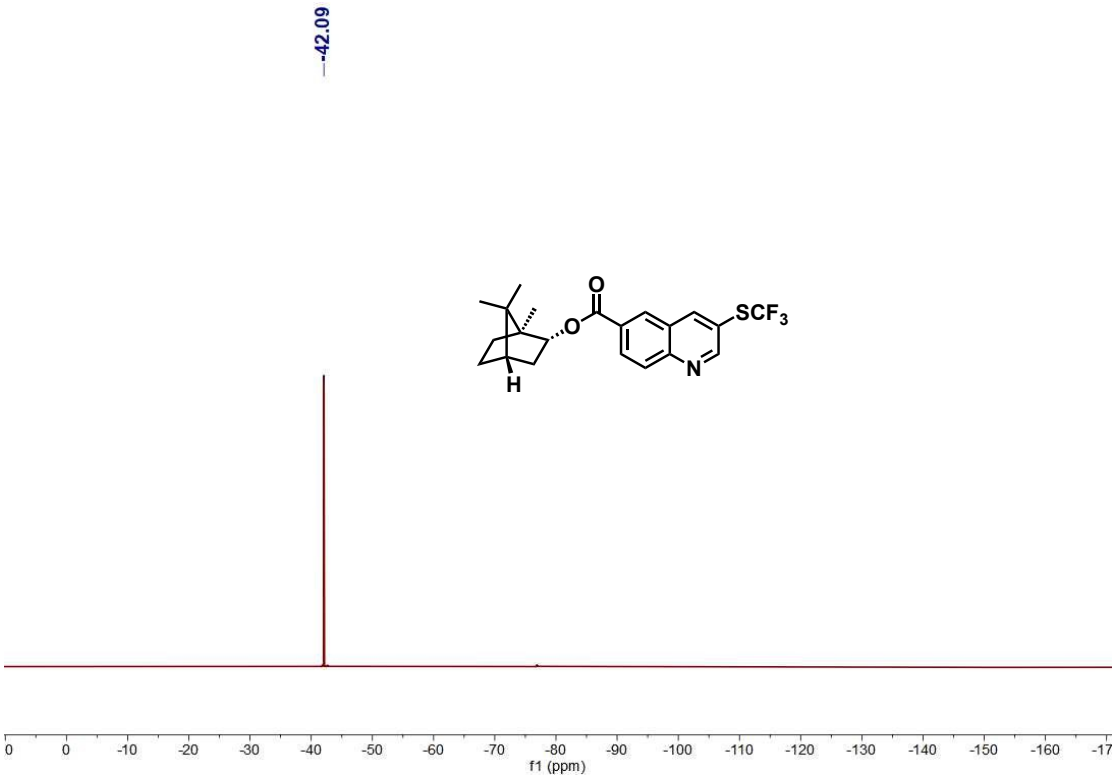

-42.12
O
O
SCF3
N
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

^{1}H NMR and ^{13}C NMR of **6b**

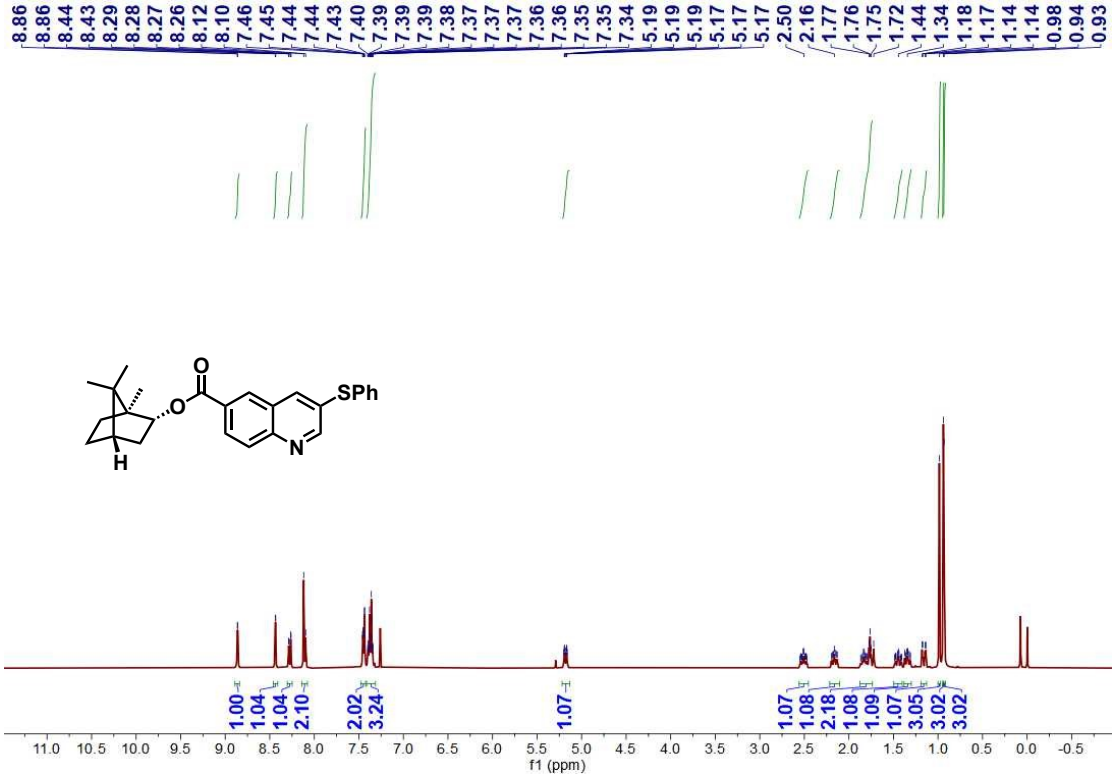


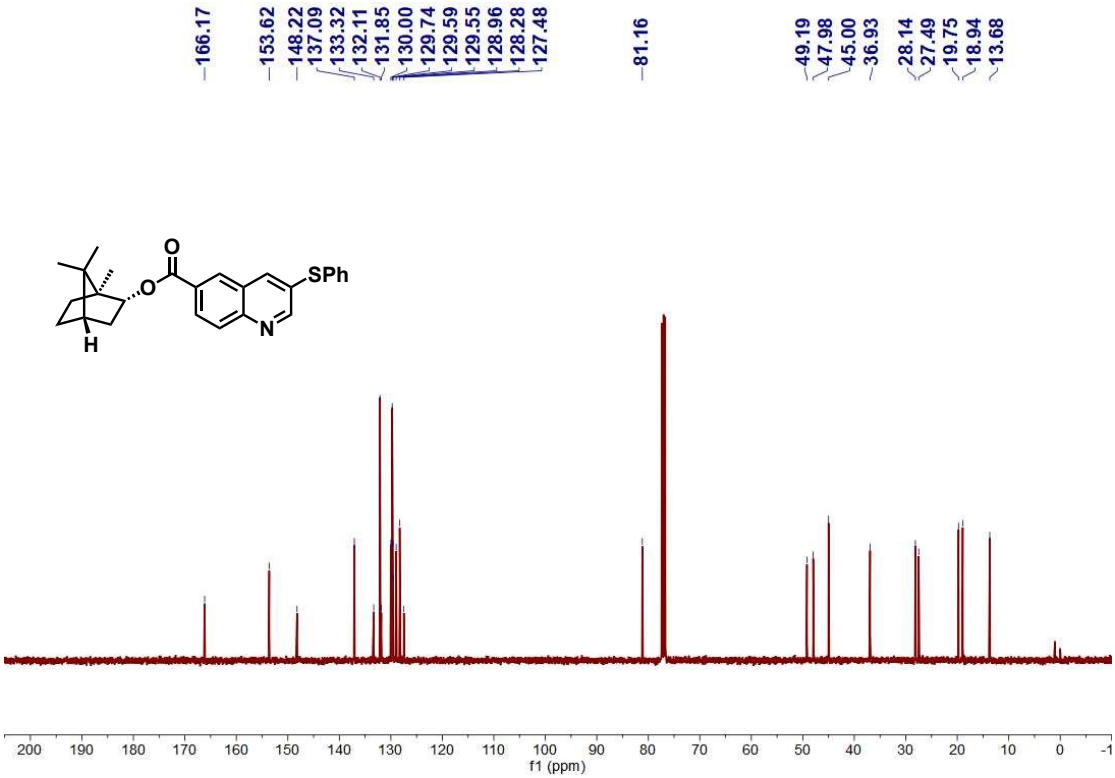
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **7a**



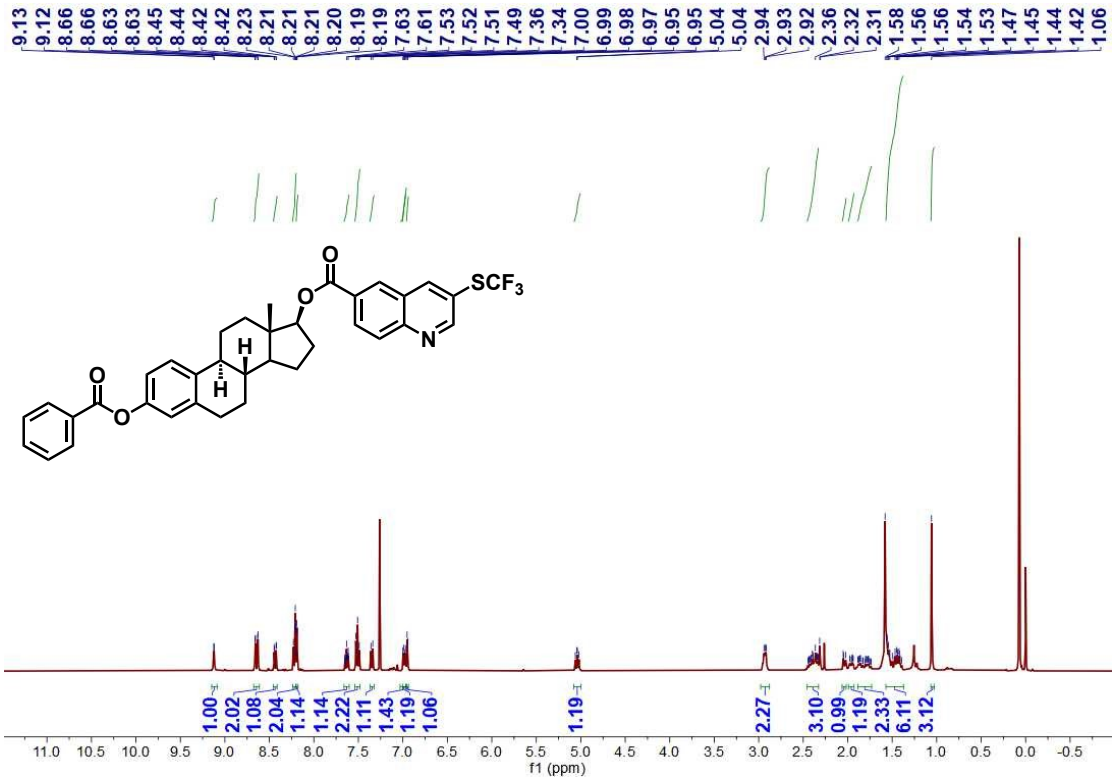


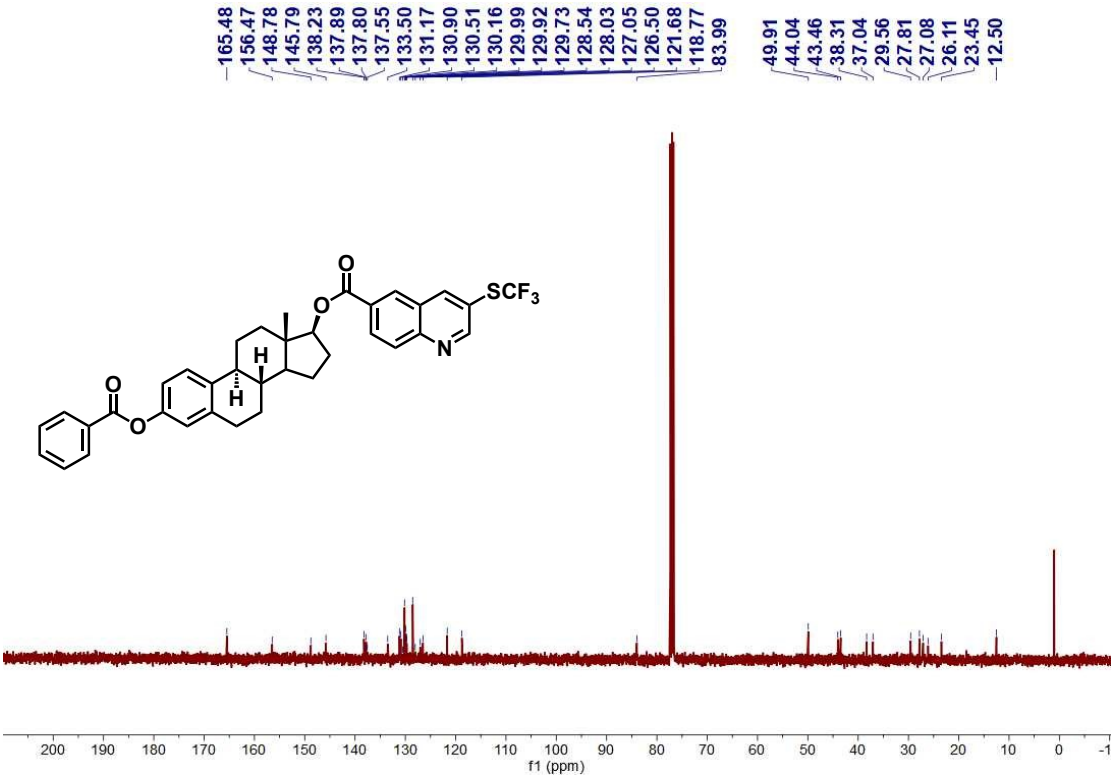
^{1}H NMR and ^{13}C NMR of **7b**





^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **8a**

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145.79
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137.89
137.80
137.55
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131.17
130.90
130.51
130.16
129.99
129.92
129.73
128.54
128.03
127.05
126.50
121.68
118.77
83.99
49.91
44.04
43.46
38.31
37.04
29.56
27.81
27.08
26.11
23.45
12.50
SCF3
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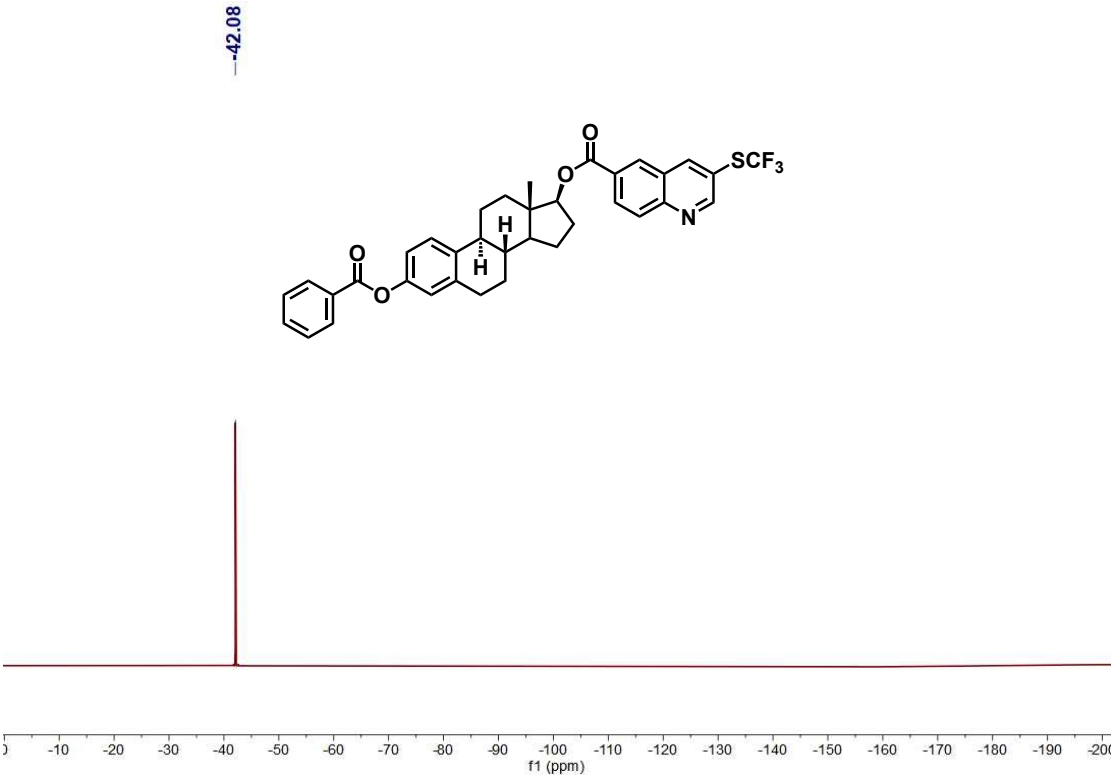
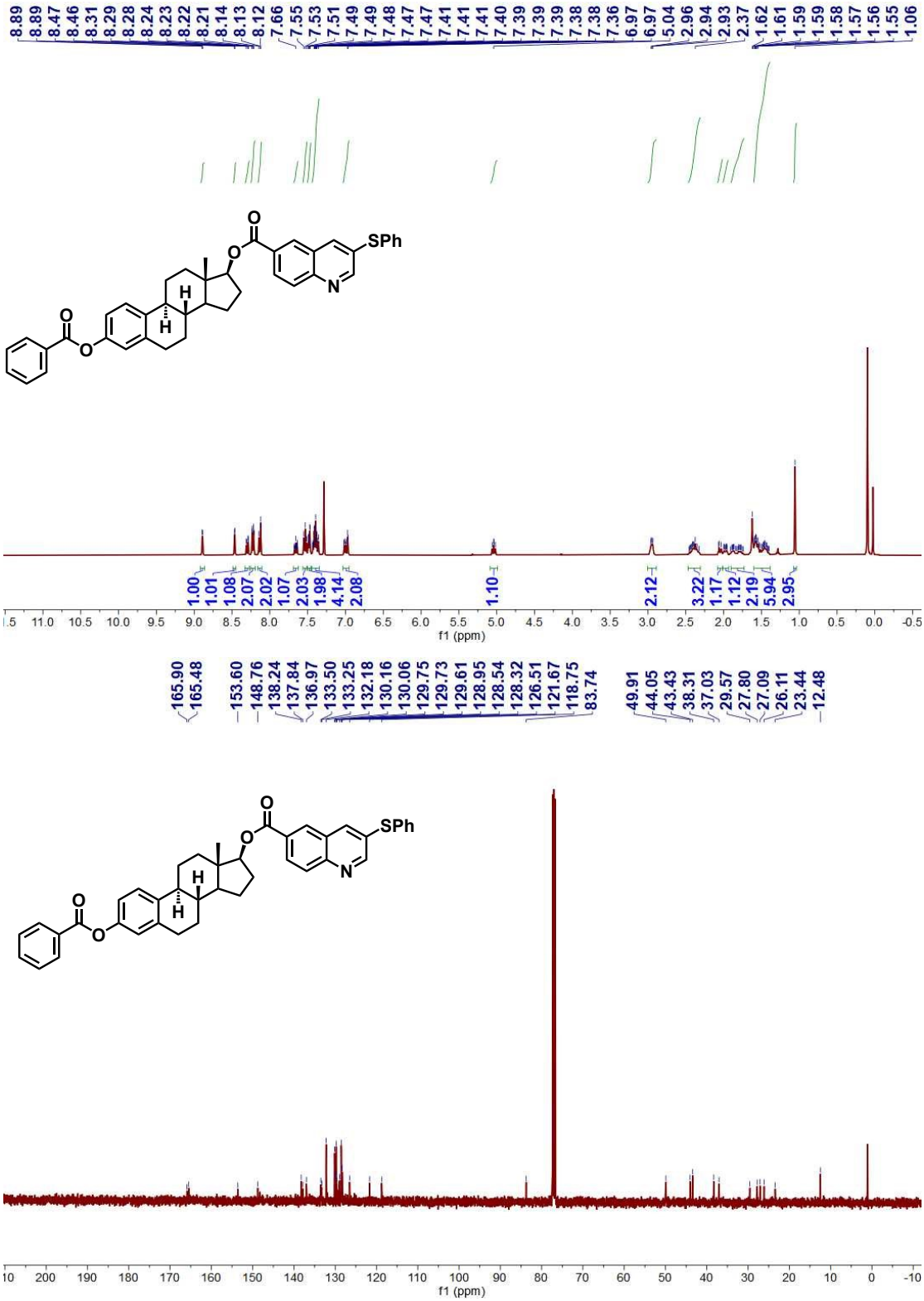
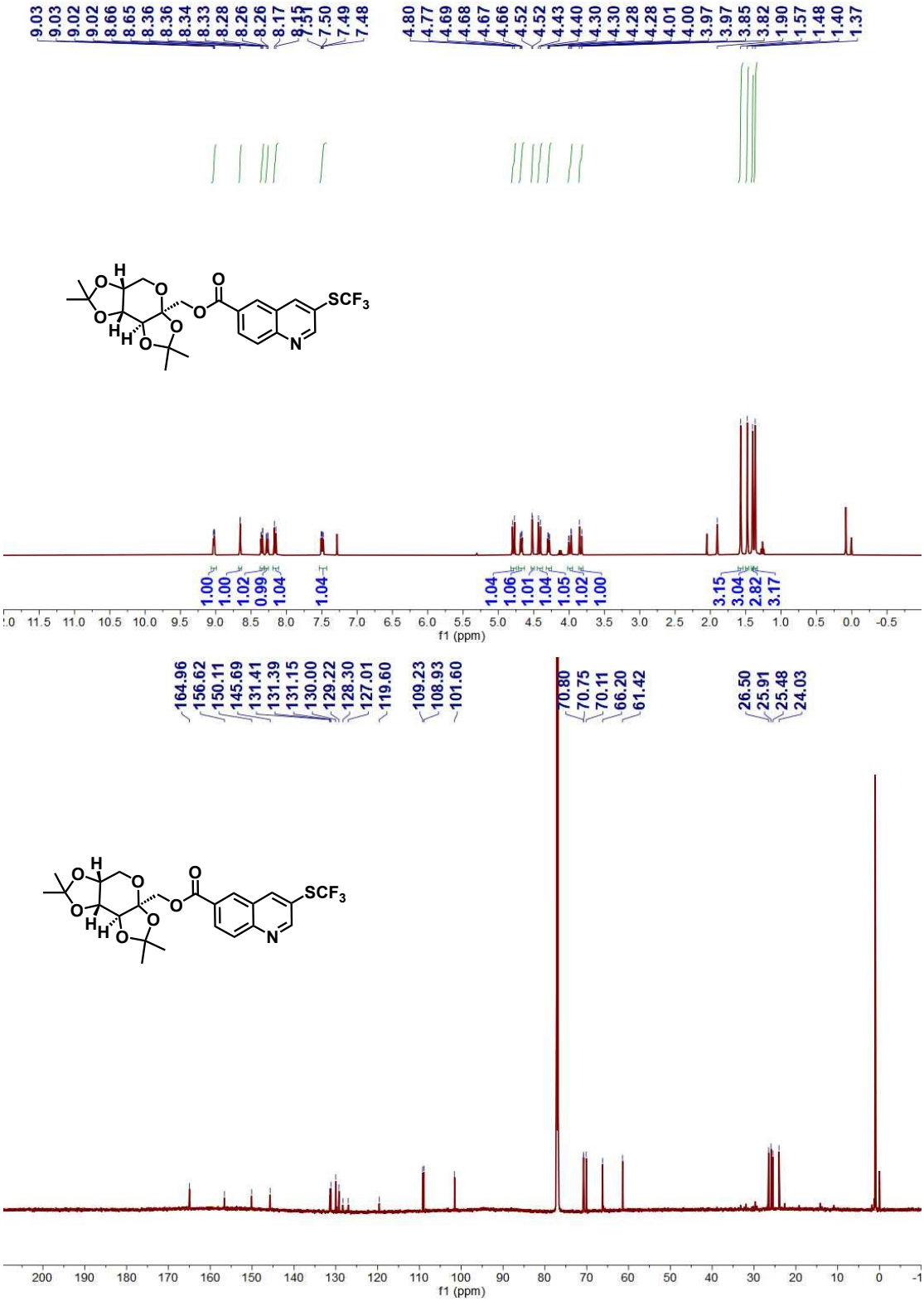
O
O
O
H
H
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

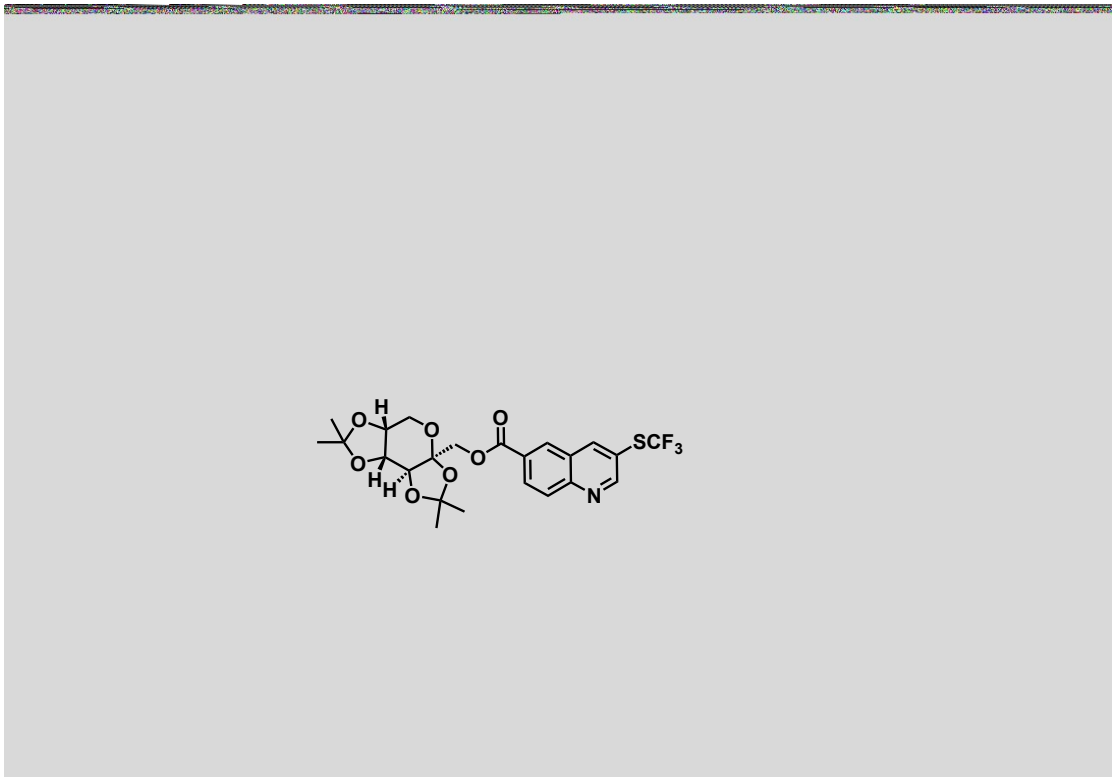

-42.08
SCF3
O
O
O
O
H
H
N
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

^{1}H NMR and ^{13}C NMR of **8b**

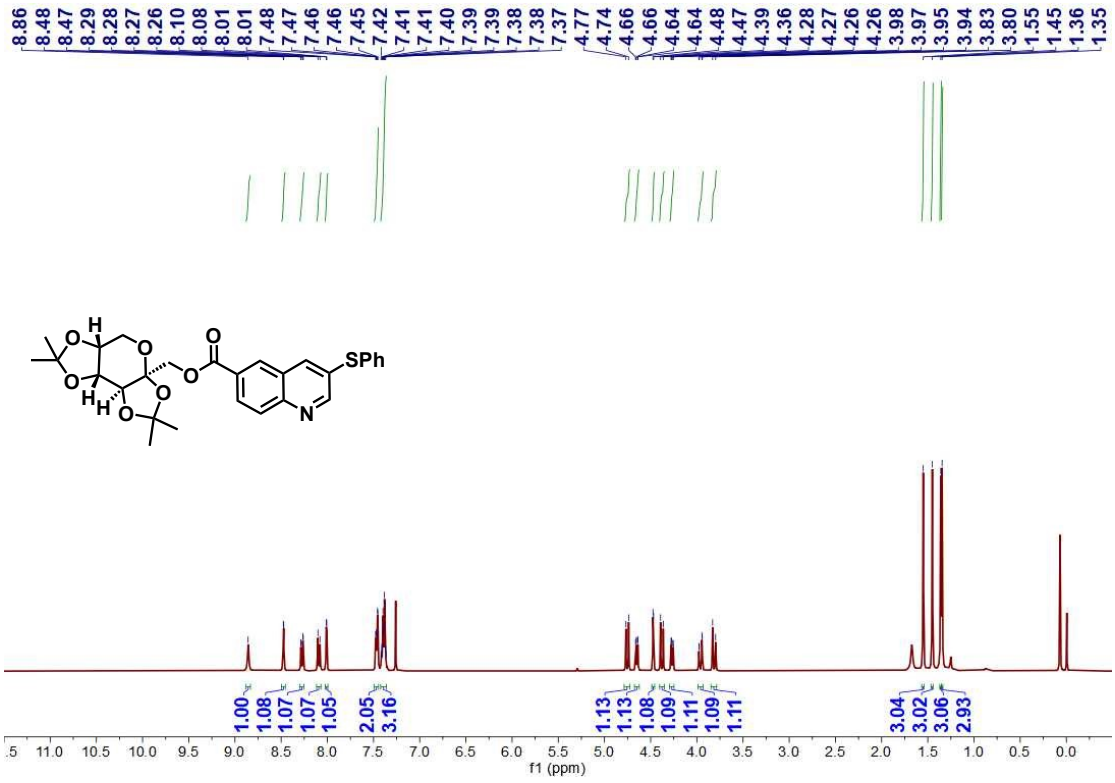


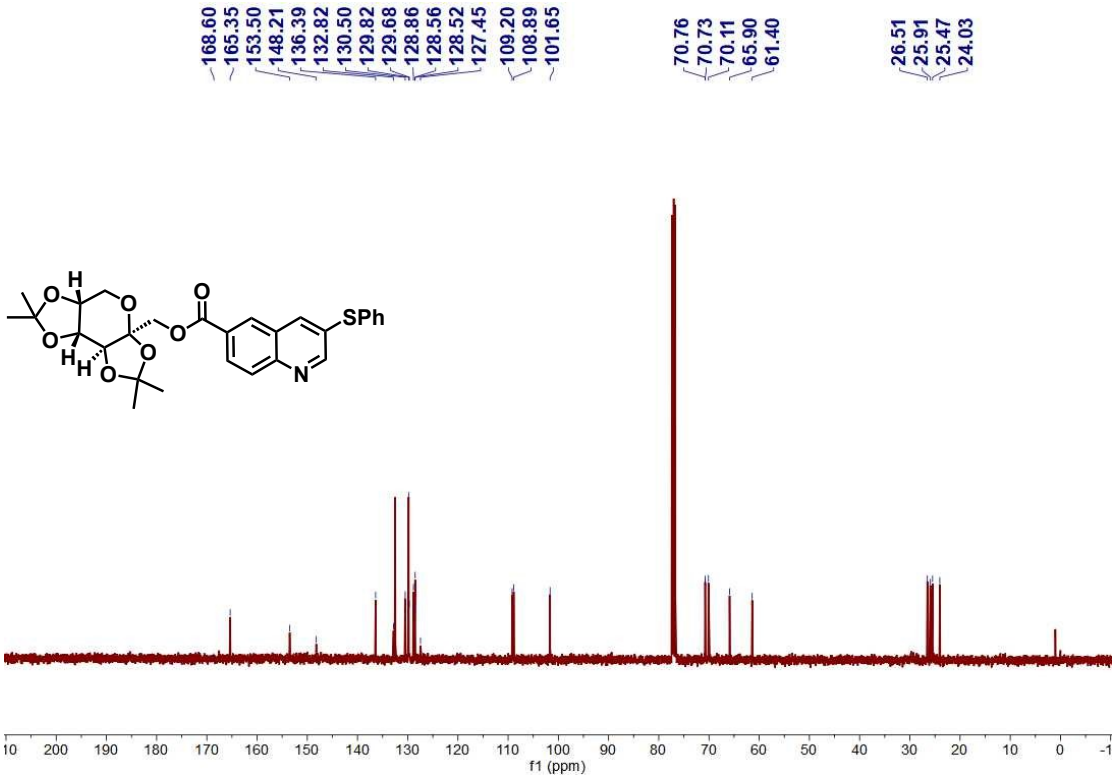
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **9a**



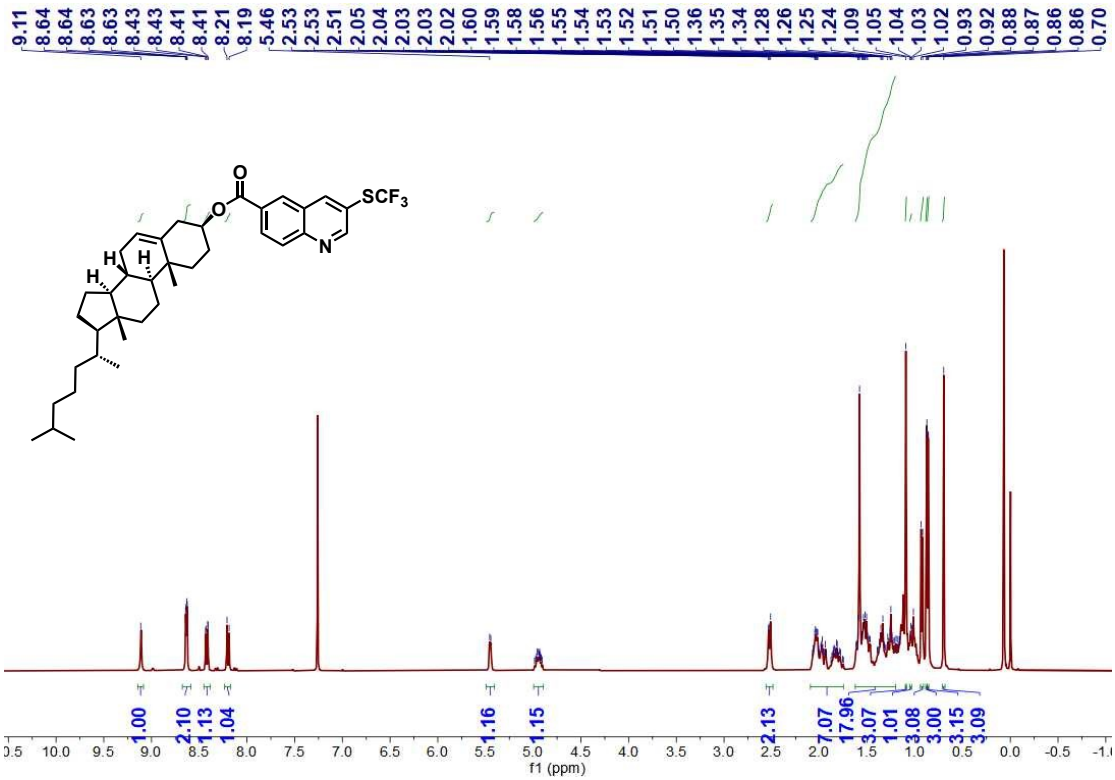


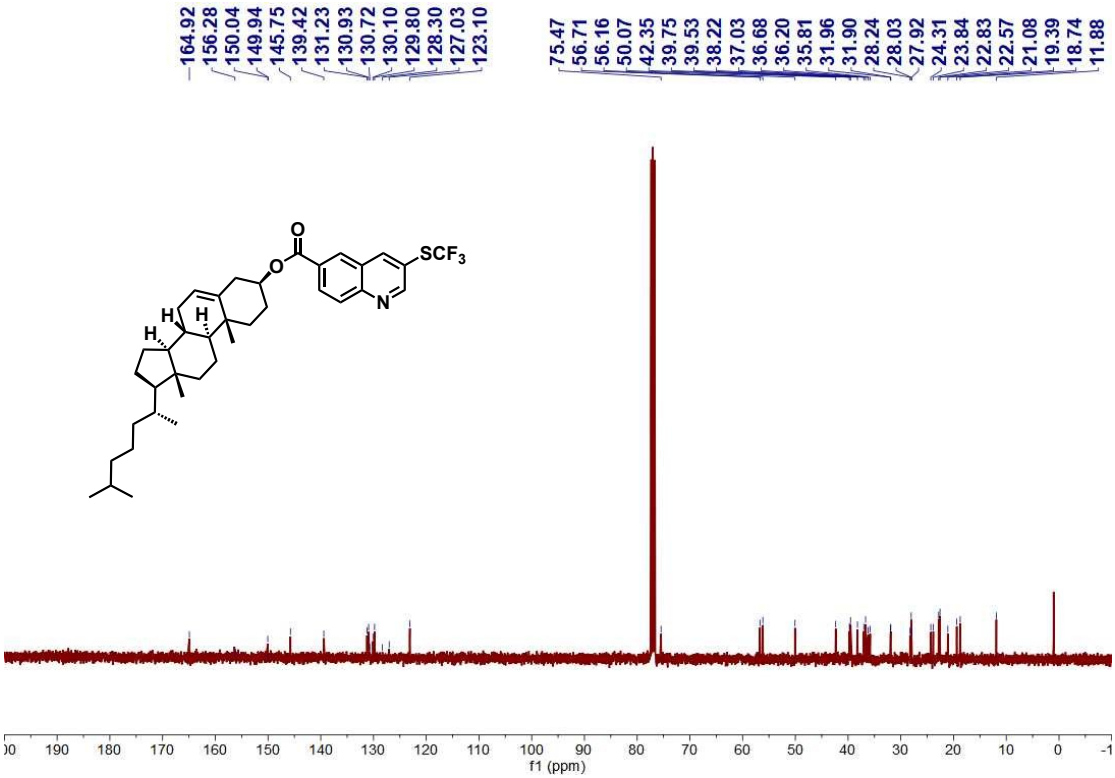
^{1}H NMR and ^{13}C NMR of **9b**





^{1}H NMR, ^{13}C NMR and ^{19}F NMR of **10a**




164.92
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150.04
149.94
145.75
139.42
131.23
130.93
130.72
130.10
129.80
128.30
127.03
123.10
75.47
56.71
56.16
50.07
42.35
39.75
39.53
38.22
37.03
36.68
36.20
35.81
31.96
31.90
28.24
28.03
27.92
24.31
23.84
22.83
22.57
21.08
19.39
18.74
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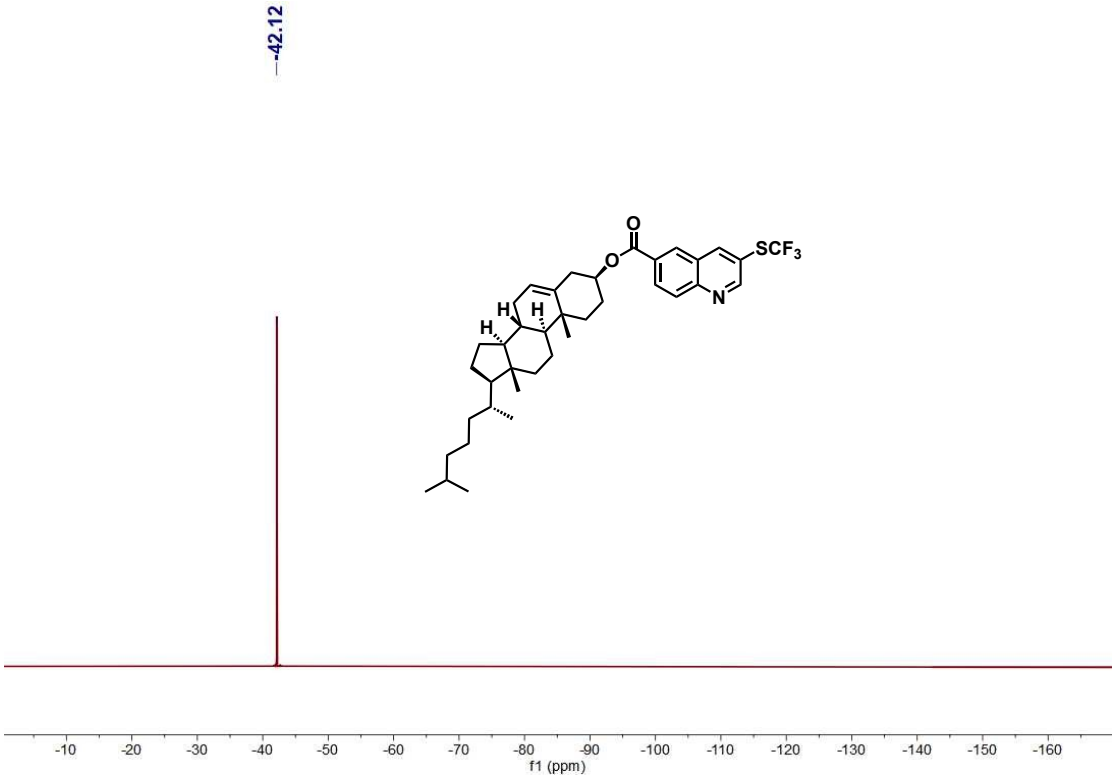
O
O
SCF3
N
H
H
f1 (ppm)


-42.12
O
O
SCF3
N
H
H
f1 (ppm)

^{1}H NMR and ^{13}C NMR of **10b**