

Supporting Information for

**Ni-Catalyzed C(sp²)-H alkylation of *N*-Quinolylbenzamide
using alkylsilyl peroxides as structurally diverse alkyl sources**

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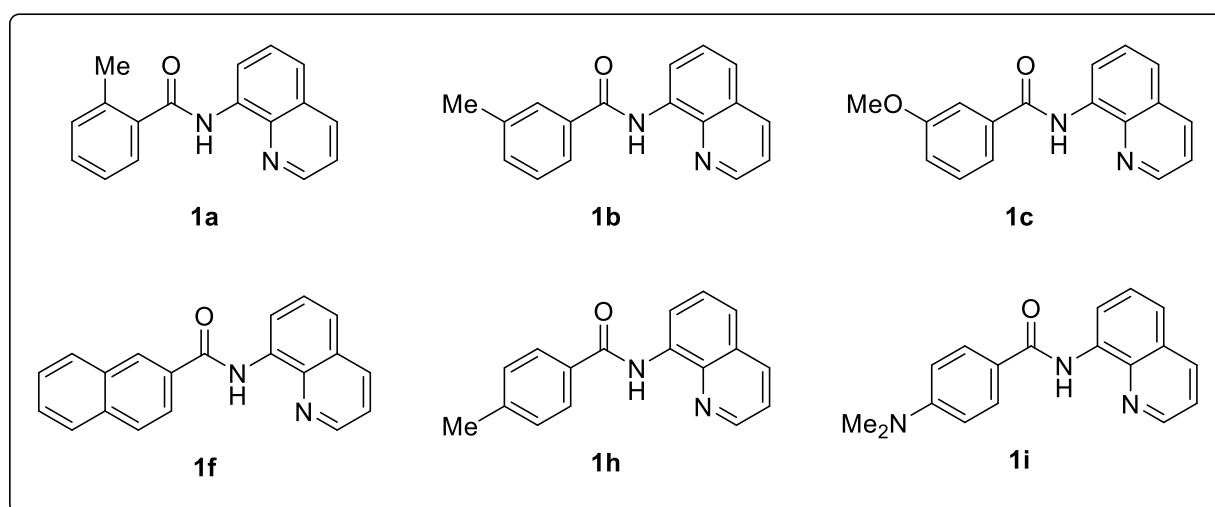
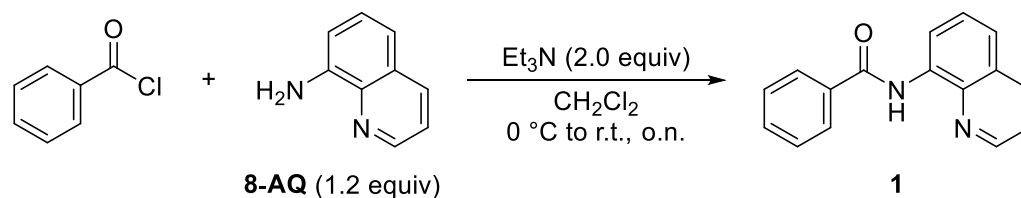
1. General Information

¹H NMR spectra were measured on JEOL JNM-ECA500 (500 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in CDCl₃, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet-doublet, dt = doublet-triplet, ddd = doublet-doublet-doublet), coupling constants (Hz), and assignment. ¹³C NMR spectra were measured on JEOL JNM-ECA500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. High-resolution mass spectra (HRMS) were performed on Bruker micrOTOF. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (Merck, TLC Silica gel 60 F₂₅₄) were used. The products were purified by flash column chromatography on silica gel (Kanto Chemical, Silica gel 60 N, spherical, neutral, 40-50 μm or FUJIFILM Wako, Wakosil[®], 60, spherical, 64-210 μm) or preparative thin layer chromatography silica gel (PLC 60 F₂₅₄. 0.5 mm). Commercially available reagents and solvents were purchased from CHEM-IMPEX INT'L INC., FUJIFILM Wako, Oakwood Chemical, Sigma-Aldrich and TCI, and used as received. DMF was used a Super Dehydrated DMF purchased from FUJIFILM Wako. Alkylsilyl peroxides (ASPs) were prepared according to the literature procedures.^[1] All reactions were performed under N₂ atmosphere, and NMR yields were determined by ¹H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

2. General Procedure for the Preparation of *N*-Quinolylylbenzamide Substrates

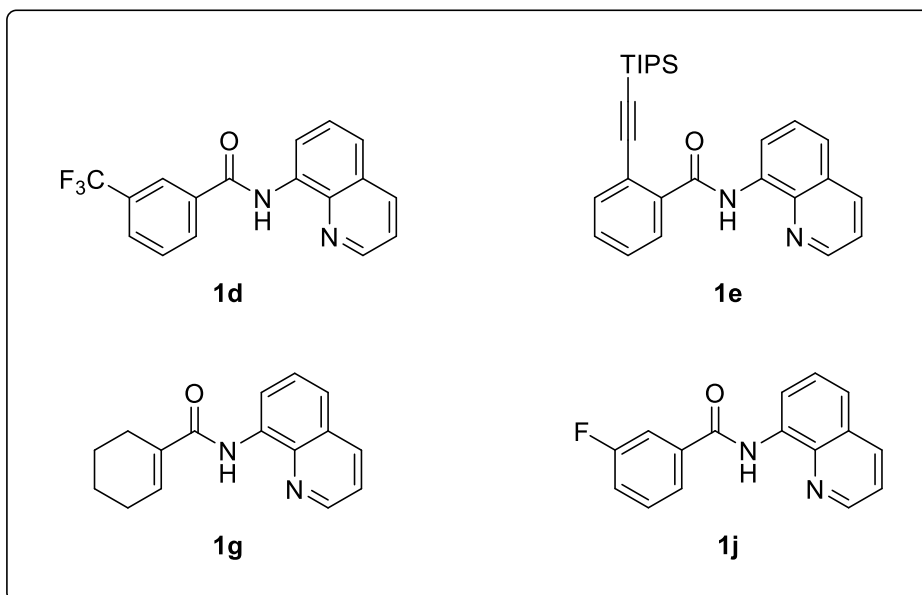
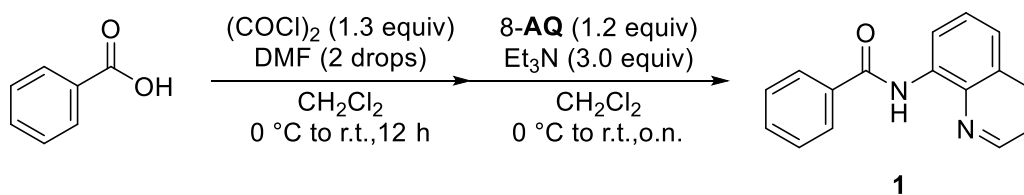
All aromatic amides bearing an 8-aminoquinoline moiety were prepared by general procedures A or B.^[2,3] Spectral data of **1a–1k** matched those previously reported in the literatures.^[2–4]

General Procedure A



To an oven-dried side-arm flask were added 8-aminoquinoline (**8-AQ**, 1.2 equiv), Et_3N (2.0 equiv) and dry CH_2Cl_2 (1.0 M), and the resulting solution was stirred at $0\text{ }^\circ\text{C}$ for 10 minutes. To the reaction mixture was added a solution of acid chloride in CH_2Cl_2 dropwisely at $0\text{ }^\circ\text{C}$, and the solution was then warmed to room temperature. After being stirred overnight, the reaction mixture was quenched with sat. NH_4Cl aq. and the organic layer was extracted with EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane / EtOAc = 5 / 1 – 2 / 1) to afford desired aromatic amides **1**.

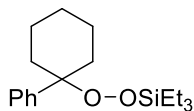
General Procedure B



To an oven-dried side-arm flask were added benzoic acid, DMF (2 drops) and dry CH_2Cl_2 (0.3 M) under N_2 atmosphere. Oxalyl chloride (1.3 equiv) was added dropwise at $0\text{ }^\circ\text{C}$. The reaction mixture was stirred at room temperature for 12 h. The resulting acid chloride was used immediately without further purification. To another oven-dried side-arm flask were added 8-aminoquinoline (**8-AQ**, 1.2 equiv), Et_3N (3.0 equiv) and dry CH_2Cl_2 (1.0 M), and the resulting solution was stirred at $0\text{ }^\circ\text{C}$ for 10 minutes. To the reaction mixture was added a solution of the acid chloride in CH_2Cl_2 dropwisely at $0\text{ }^\circ\text{C}$, and the solution was then warmed to room temperature. After being stirred overnight, the reaction mixture was quenched with sat. NH_4Cl aq. and the organic layer was extracted with EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane / EtOAc = 5 / 1 – 3 / 1) to afford desired aromatic amides **1**.

3. Characterization Data of Unreported Alkylsilyl Peroxides

Triethyl((1-phenylcyclohexyl)peroxy)silane (2b)



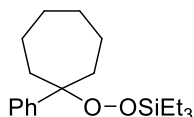
Colorless oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.46 (2H, d, $J = 7.4$ Hz), 7.31 (2H, t, $J = 7.7$ Hz), 7.23 (1H, t, $J = 7.4$ Hz), 2.17-2.14 (2H, m), 1.80-1.67 (5H, m), 1.55-1.51 (2H, m), 1.31-1.26 (1H, m), 0.93 (9H, t, $J = 7.9$ Hz), 0.65 (6H, q, $J = 7.9$ Hz).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 146.0, 127.9, 126.8, 126.2, 83.9, 34.5, 25.8, 22.3, 6.9, 3.9.

HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{SiNa}$: m/z 329.1907 ($[\text{M} + \text{Na}]^+$), found: m/z 329.1908 ($[\text{M} + \text{Na}]^+$).

Triethyl((1-phenylcycloheptyl)peroxy)silane (2e)



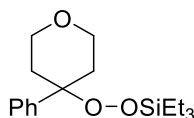
Colorless oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.47-7.44 (2H, m), 7.32-7.29 (2H, m), 7.23-7.20 (1H, m), 2.13 (2H, ddd, $J = 14.9, 9.0, 1.3$ Hz), 2.02 (2H, ddd, $J = 14.9, 9.8, 1.3$ Hz), 1.79-1.72 (2H, m), 1.69-1.62 (2H, m), 1.59-1.49 (4H, m), 0.95 (9H, t, $J = 7.9$ Hz), 0.67 (6H, q, $J = 7.9$ Hz).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 147.2, 127.9, 126.6, 126.1, 88.7, 38.2, 30.6, 23.2, 6.9, 3.9.

HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{32}\text{O}_2\text{SiNa}$: m/z 343.2064 ($[\text{M} + \text{Na}]^+$), found: m/z 343.2068 ($[\text{M} + \text{Na}]^+$).

Triethyl((4-phenyltetrahydro-2H-pyran-4-yl)peroxy)silane (2f)



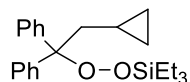
Colorless oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.44 (2H, d, $J = 7.7$ Hz), 7.34 (2H, t, $J = 7.5$ Hz), 7.28-7.26 (3H, m), 3.87-3.79 (4H, m), 2.18 (2H, m), 2.11-2.04 (2H, m), 0.90 (9H, t, $J = 7.9$ Hz), 0.63 (6H, q, $J = 7.9$ Hz).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 144.5, 128.1, 127.4, 126.0, 81.2, 64.1, 34.3, 6.8, 3.9.

HRMS (ESI) calculated for C₁₇H₂₈O₃SiNa: *m/z* 331.1700 ([M + Na]⁺), found: *m/z* 331.1701 ([M + Na]⁺).

((2-Cyclopropyl-1,1-diphenylethyl)peroxy)triethylsilane (2h)



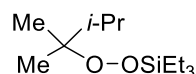
Colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 7.32-7.30 (4H, m), 7.28-7.24 (4H, m), 7.23-7.20 (2H, m), 2.36 (2H, d, *J* = 6.5 Hz), 1.30-1.26 (1H, m), 0.86 (9H, t, *J* = 7.9 Hz), 0.56 (6H, q, *J* = 7.9 Hz), 0.25-0.22 (2H, m), -0.11- -0.14 (2H, m).

¹³C NMR (125 MHz, CDCl₃) δ 144.5, 127.9, 127.5, 126.9, 89.3, 41.4, 6.8, 6.1, 4.7, 3.9.

HRMS (ESI) calculated for C₂₃H₃₂O₂SiNa: *m/z* 391.2064 ([M + Na]⁺), found: *m/z* 391.2064 ([M + Na]⁺).

((2,3-Dimethylbutan-2-yl)peroxy)triethylsilane (2i)



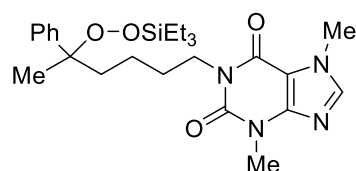
Colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 1.96-1.90 (1H, m), 1.12 (6H, s), 0.98 (9H, t, *J* = 7.9 Hz), 0.87 (6H, d, *J* = 7.1 Hz), 0.66 (6H, q, *J* = 7.9 Hz).

¹³C NMR (125 MHz, CDCl₃) δ 85.0, 34.6, 21.3, 17.7, 7.0, 4.0.

HRMS (ESI) calculated for C₁₂H₂₈O₂SiNa: *m/z* 255.1751 ([M + Na]⁺), found: *m/z* 255.1751 ([M + Na]⁺).

3,7-Dimethyl-1-(5-phenyl-5-((triethylsilyl)peroxy)hexyl)-3,7-dihydro-1H-purine-2,6-dione (2j)



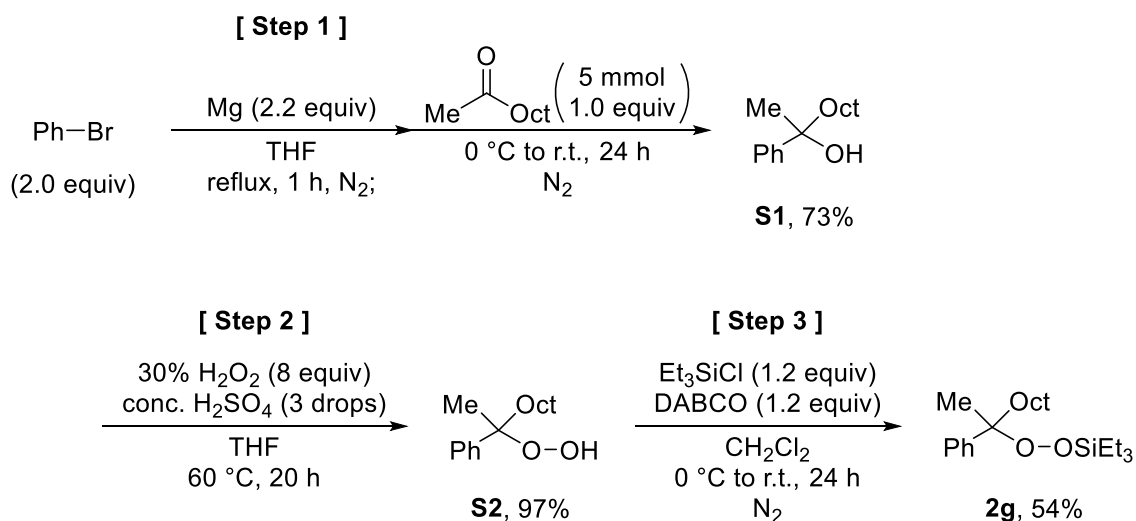
Colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 7.48 (1H, s), 7.36 (2H, d, *J* = 7.5 Hz), 7.30 (2H, t, *J* = 7.7 Hz), 7.21 (1H, t, *J* = 7.5 Hz), 3.97 (3H, s), 3.92 (2H, t, *J* = 7.8 Hz), 3.55 (3H, s), 1.92-1.78 (2H, m), 1.61 (3H, s), 1.56 (2H, m), 1.31-1.22 (2H, m), 0.97 (9H, t, *J* = 7.9 Hz), 0.68 (6H, q, *J* = 7.9 Hz).

¹³C NMR (125 MHz, CDCl₃) δ 155.3, 151.5, 148.8, 144.9, 141.5, 127.9, 126.7, 125.9, 107.7, 85.7, 41.3, 40.2, 33.6, 29.7, 28.3, 23.7, 21.4, 6.9, 3.9.

HRMS (ESI) calculated for C₂₅H₃₈O₄N₄SiNa: m/z 509.2555 ([M + Na]⁺), found: m/z 509.2558 ([M + Na]⁺).

4. Synthesis of Triethyl((2-phenyldecan-2-yl)peroxy)silane (**2g**)



[Step 1]

To a suspension of flame-dried Mg turnings (0.27 g, 11 mmol, 2.2 equiv) in dry THF (13 mL) was added PhBr (1.1 mL, 10 mmol, 2.0 equiv) carefully under N₂ atmosphere. After being refluxed for 1 h, the obtained solution of PhMgBr was cooled down to 0 °C and then decane-2,3-dione (0.95 mL, 5 mmol, 1.0 equiv) was added dropwisely. After being stirred at room temperature for 24 h, the reaction mixture was quenched with sat. NH₄Cl aq. at 0 °C and extracted with EtOAc three times. The combined organic layers were dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane / EtOAc = 8 / 1) to afford **S1** as a colorless oil (0.91 g, 73%). Spectral data of **S1** matched those previously reported in the literature.^[5]

[Step 2]^[6]

To a solution of **S1** (683 mg, 2.8 mmol, 1.0 equiv) in THF (3 mL) was added a mixture of 30% H₂O₂ aq. (2.5 mL) with a few drops of conc. H₂SO₄ slowly. After being stirred at 60 °C for 20 h, the reaction mixture was diluted with H₂O and then extracted with CH₂Cl₂ three times. The combined organic layers were dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (CH₂Cl₂) to afford hydroperoxide **S2** as a colorless oil (686 mg, 94%). Spectral data of **S2** matched those previously reported in the literature.^[6]

[Step 3]

To a solution of **S2** (686 mg, 2.6 mmol, 1.0 equiv) and 1,4-diazabicyclo[2.2.2]octane (DABCO, 349 mg, 3.1 mmol, 1.3 equiv) in dry CH₂Cl₂ (10 mL) was added Et₃SiCl (523 μL, 3.1 mmol, 1.3

equiv) dropwisely at 0 °C under N₂ atmosphere. After being stirred at room temperature for 24 h, the reaction mixture was diluted with H₂O and then extracted with CH₂Cl₂ three times. The combined organic layers were dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane / CH₂Cl₂= 20 / 1) to afford triethyl((2-phenyldecan-2-yl)peroxy)silane (**2g**) as a colorless oil (533 mg, 54%).

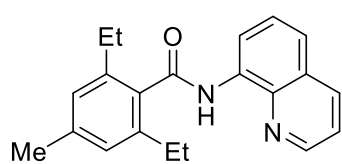
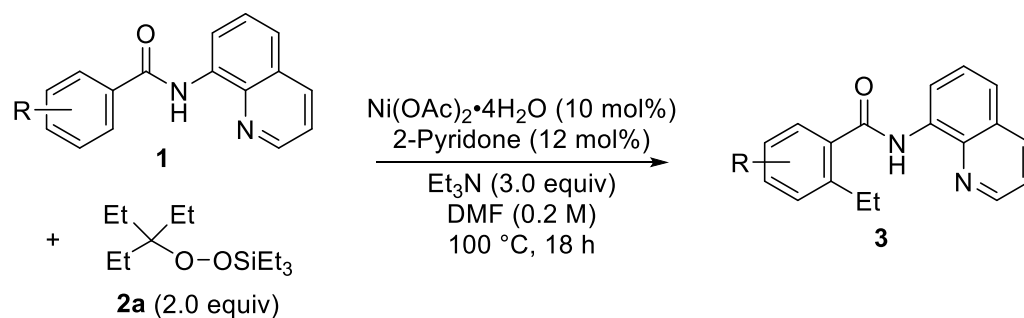
¹H NMR (500 MHz, CDCl₃) δ 7.39-7.37 (2H, m), 7.33-7.29 (2H, m), 7.24-7.22 (1H, m), 1.80-1.73 (2H, m), 1.60 (3H, s), 1.28-1.12 (12H, m), 0.98 (9H, t, *J* = 8.0 Hz), 0.86 (3H, t, *J* = 7.5 Hz), 0.68 (6H, q, *J* = 7.5 Hz).

¹³C NMR (125 MHz, CDCl₃) δ 145.3, 127.9, 126.7, 126.0, 85.9, 40.6, 32.0, 30.1, 29.6, 29.4, 24.0, 23.6, 22.8, 14.2, 6.9, 4.0.

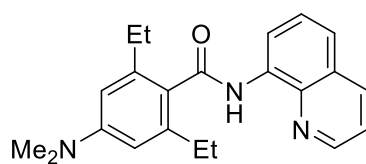
HRMS (ESI) calculated for C₂₂H₄₀O₂SiNa: *m/z* 387.2690 ([M + Na]⁺), found: *m/z* 387.2698 ([M + Na]⁺).

5. Optimization of Reaction Conditions

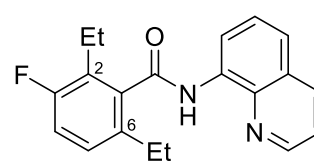
5-1. Ethylation Reactions of Benzamides 1h–1j Using 2.0 equiv of ASP 2a without LiBr



3h + 3h', 78%
di (**3h**) / mono (**3h'**)
= 44 / 34

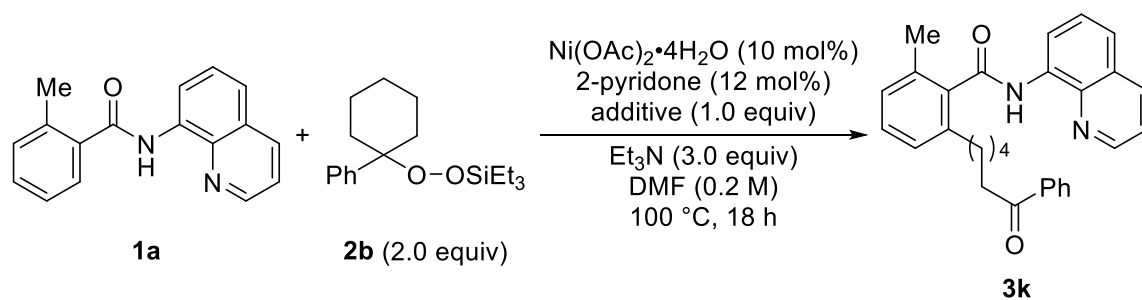


3i + 3i', 89%
di (**3i**) / mono (**3i'**)
= 57 / 32



3j + 3j', 79%
di (**3j**) / mono 6-Et (**3j'**)
= 40 / 39

5-2. Effect of Additives on the Reaction with Cyclic ASP 2b



entry	additive	1a (%) ^b	3k (%) ^b
1	-	67	8
2	LiCl	46	43
3	LiBr	0	94 (85 ^c)
4	LiI	84	22
5	LiBF ₄	75	13
6	NaBr	trace	85
7	KBr	53	22
8	Bu ₄ NBr	52	37

^aThe reactions were performed on a 0.2 mmol scale in DMF (1.0 mL) under a N₂ atmosphere. ^bYields were determined by ¹H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. ^cIsolated yield.

6. General Procedures for Ni-catalyzed AQ-directed C(sp²)-H Alkylation Reactions with ASPs

General Procedure A

To the solution of benzamide **1** (0.2 mmol, 1.0 equiv), Ni(OAc)₂•4H₂O (5.0 mg, 0.02 mmol, 10 mol%), and 2-pyridone (2.3 mg, 0.024 mmol, 12 mol%) in DMF (1.0 mL) were added ASP **2** (0.4 mmol, 2.0 equiv) and Et₃N (84 μL, 0.6 mmol, 3.0 equiv) at room temperature under N₂ atmosphere. The reaction mixture was stirred at 100 °C for 18 h. After being cooled to room temperature, the reaction mixture was passed through a short silica gel / Na₂SO₄ plug eluting with EtOAc. The obtained solution was concentrated and the residue was purified by flash column chromatography on silica gel to afford desired coupling products.

General Procedure B

To the solution of benzamide **1** (0.2 mmol, 1.0 equiv), Ni(OAc)₂•4H₂O (5.0 mg, 0.02 mmol, 10 mol%), 2-pyridone (2.3 mg, 0.024 mmol, 12 mol%), and LiBr (17.4 mg, 0.2 mmol, 1.0 equiv) in DMF (1.0 mL) were added ASP **2** (0.4 mmol, 2.0 equiv) and Et₃N (84 μL, 0.6 mmol, 3.0 equiv) at room temperature under N₂ atmosphere. The reaction mixture was stirred at 100 °C for 18 h. After being cooled to room temperature, the reaction mixture was passed through a short silica gel / Na₂SO₄ plug eluting with EtOAc. The obtained solution was concentrated and the residue was purified by flash column chromatography on silica gel to afford desired coupling products.

General Procedure C

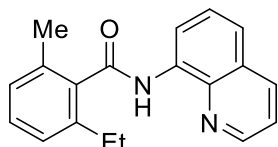
To the solution of benzamide **1** (0.2 mmol, 1.0 equiv), Ni(OAc)₂•4H₂O (5.0 mg, 0.02 mmol, 10 mol%), 2-pyridone (2.3 mg, 0.024 mmol, 12 mol%), and LiBr (17.4 mg, 0.2 mmol, 1.0 equiv) in DMF (1.0 mL) were added ASP **2** (0.8 mmol, 4.0 equiv) and Et₃N (84 μL, 0.6 mmol, 3.0 equiv) at room temperature under N₂ atmosphere. The reaction mixture was stirred at 100 °C for 18 h. After being cooled to room temperature, the reaction mixture was passed through a short silica gel / Na₂SO₄ plug eluting with EtOAc. The obtained solution was concentrated and the residue was purified by flash column chromatography on silica gel to afford desired coupling products.

General Procedure D

To the solution of benzamide **1** (0.2 mmol, 1.0 equiv), Ni(OAc)₂•4H₂O (5.0 mg, 0.02 mmol, 10 mol%), 2-pyridone (2.3 mg, 0.024 mmol, 12 mol%), and LiBr (17.4 mg, 0.2 mmol, 1.0 equiv) in DMF (1.0 mL) were added ASP **2** (0.4 mmol, 2.0 equiv) and Et₃N (84 μL, 0.6 mmol, 3.0 equiv) at room temperature under N₂ atmosphere. After the reaction mixture was stirred at 100 °C for 9 h, an

additional ASP 2 (0.4 mmol, 2.0 equiv) was added and the mixture was further stirred at 100 °C for 9 h. After being cooled to room temperature, the reaction mixture was passed through a short silica gel / Na₂SO₄ plug eluting with EtOAc. The obtained solution was concentrated and the residue was purified by flash column chromatography on silica gel to afford desired coupling products.

2-Ethyl-6-methyl-N-(quinolin-8-yl)benzamide (3a)

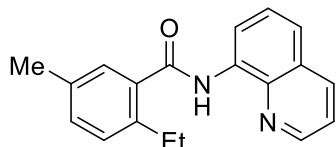


White solid, 46.7 mg, 80% yield (procedure A).

¹H NMR (500 MHz, CDCl₃) δ 9.93 (1H, s), 9.00 (1H, d, *J* = 7.4 Hz), 8.74 (1H, dd, *J* = 4.2, 1.5 Hz), 8.18 (1H, dd, *J* = 8.2, 1.7 Hz), 7.63-7.56 (2H, m), 7.45 (1H, dd, *J* = 8.3, 4.3 Hz), 7.30 (1H, t, *J* = 7.7 Hz), 7.15 (2H, dd, *J* = 21.7, 7.5 Hz), 2.76 (2H, q, *J* = 7.6 Hz), 2.43 (3H, s), 1.27 (3H, t, *J* = 7.5 Hz).

The spectral data of this compound are consistent with those previously reported in the literature.^[2]

2-Ethyl-5-methyl-N-(quinolin-8-yl)benzamide (3b)

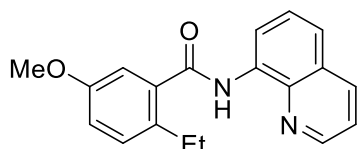


Colorless oil, 42.0 mg, 72% yield (procedure A).

¹H NMR (500 MHz, CDCl₃) δ 10.14 (1H, s), 8.95 (1H, d, *J* = 7.7 Hz), 8.78 (1H, dd, *J* = 4.1, 1.6 Hz), 8.18 (1H, dd, *J* = 8.4, 1.6 Hz), 7.62-7.54 (2H, m), 7.47-7.44 (2H, m), 7.25 (2H, s), 2.90 (2H, q, *J* = 7.6 Hz), 2.40 (3H, s), 1.28 (3H, t, *J* = 7.5 Hz).

The spectral data of this compound are consistent with those previously reported in the literature.^[7]

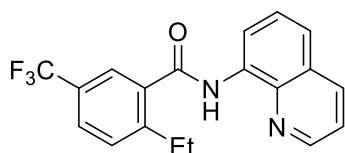
2-Ethyl-5-methoxy-N-(quinolin-8-yl)benzamide (3c)



White solid, 44.4 mg, 72% yield (procedure A).

¹H NMR (500 MHz, CDCl₃) δ 10.17 (1H, s), 8.95 (1H, d, *J* = 6.8 Hz), 8.77 (1H, dd, *J* = 4.3, 2.0 Hz), 8.18 (1H, dd, *J* = 8.2, 1.4 Hz), 7.60-7.54 (2H, m), 7.45 (1H, m), 7.27-7.26 (1H, m), 7.18 (1H, d, *J* = 2.6 Hz), 6.99 (1H, dd, *J* = 8.5, 2.6 Hz), 3.85 (3H, s), 2.87 (2H, q, *J* = 7.8 Hz), 1.28 (3H, t, *J* = 7.7 Hz). The spectral data of this compound are consistent with those previously reported in the literature.^[7]

2-Ethyl-*N*-(quinolin-8-yl)-5-(trifluoromethyl)benzamide (3d)

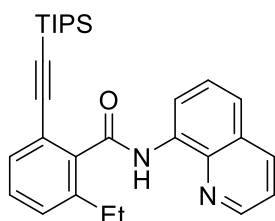


White solid, 50.4 mg, 73% yield (procedure A).

¹H NMR (500 MHz, CDCl₃) δ 10.18 (1H, s), 8.92 (1H, dd, *J* = 6.8, 1.7 Hz), 8.79 (1H, dd, *J* = 4.5, 1.5 Hz), 8.20 (1H, dd, *J* = 8.4, 1.6 Hz), 7.87 (1H, s), 7.69 (1H, d, *J* = 6.8 Hz), 7.64-7.58 (2H, m), 7.48 (2H, q, *J* = 4.2 Hz), 2.99 (2H, q, *J* = 7.6 Hz), 1.33 (3H, t, *J* = 7.5 Hz).

The spectral data of this compound are consistent with those previously reported in the literature.^[8]

2-Ethyl-*N*-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (3e)

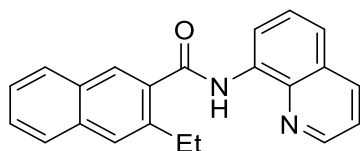


Colorless oil, 72.2 mg, 79% yield (procedure A).

¹H NMR (500 MHz, CDCl₃) δ 10.07 (1H, s), 9.00 (1H, dd, *J* = 7.4, 1.4 Hz), 8.73 (1H, dd, *J* = 4.1, 1.6 Hz), 8.16 (1H, dd, *J* = 8.2, 1.7 Hz), 7.60-7.53 (2H, m), 7.44-7.41 (2H, m), 7.35-7.28 (2H, m), 2.79 (2H, q, *J* = 7.6 Hz), 1.27 (3H, t, *J* = 7.5 Hz), 0.78-0.76 (21H, m).

The spectral data of this compound are consistent with those previously reported in the literature.^[2]

3-Ethyl-*N*-(quinolin-8-yl)-2-naphthamide (3f)

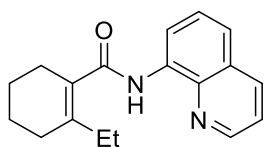


White solid, 46.4 mg, 71% yield (procedure A).

¹H NMR (500 MHz, CDCl₃) δ 10.32 (1H, s), 8.99 (1H, d, *J* = 7.7 Hz), 8.77 (1H, m), 8.20 (1H, m), 8.16 (1H, s), 7.91 (1H, d, *J* = 7.9 Hz), 7.85 (1H, d, *J* = 7.9 Hz), 7.78 (1H, s), 7.63 (1H, t, *J* = 7.9 Hz), 7.59-7.45 (4H, m), 3.12 (2H, q, *J* = 7.6 Hz), 1.37 (3H, t, *J* = 7.5 Hz).

The spectral data of this compound are consistent with those previously reported in the literature.^[9]

2-Ethyl-*N*-(quinolin-8-yl)cyclohex-1-ene-1-carboxamide (3g)

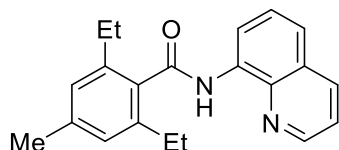


White foam, 36.7 mg, 75% yield (procedure B).

¹H NMR (500 MHz, CDCl₃) δ 9.84 (1H, s), 8.86 (1H, d, *J* = 7.7 Hz), 8.81 (1H, dd, *J* = 4.1, 1.6 Hz), 8.17 (1H, dd, *J* = 8.4, 1.6 Hz), 7.57-7.50 (2H, m), 7.45 (1H, dd, *J* = 8.3, 4.2 Hz), 2.43 (2H, s), 2.28 (2H, q, *J* = 7.5 Hz), 2.17-2.14 (2H, m), 1.74-1.67 (4H, m), 1.12 (3H, t, *J* = 7.5 Hz).

The spectral data of this compound are consistent with those previously reported in the literature.^[9]

2,6-Diethyl-4-methyl-*N*-(quinolin-8-yl)benzamide (3h)



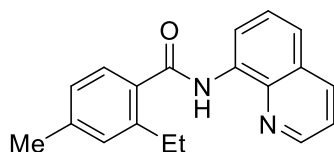
Colorless oil, 45.5 mg, 71% yield (procedure C).

¹H NMR (500 MHz, CDCl₃) δ 9.94 (1H, s), 8.99 (1H, d, *J* = 7.4 Hz), 8.72 (1H, dd, *J* = 3.8, 1.3 Hz), 8.17 (1H, dd, *J* = 8.2, 1.4 Hz), 7.62-7.55 (2H, m), 7.44 (1H, dd, *J* = 6.3, 4.2 Hz), 6.99 (2H, s), 2.86-2.25 (4H, q, *J* = 7.5 Hz), 2.38 (3H, s), 1.27 (6H, t, *J* = 7.5 Hz).

¹³C NMR (125 MHz, CDCl₃) δ 169.3, 148.4, 140.9, 139.2, 138.6, 136.4, 134.7, 134.6, 128.1, 127.6, 127.0, 121.9, 121.8, 116.8, 26.6, 21.5, 16.1.

HRMS (ESI) calculated for C₂₁H₂₃ON₂: *m/z* 319.1805 ([M + H]⁺), found: *m/z* 319.1806 ([M + H]⁺).

2-Ethyl-4-methyl-*N*-(quinolin-8-yl)benzamide (3h')

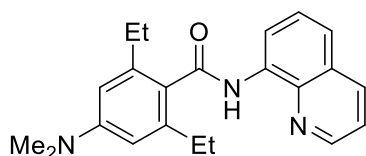


Colorless oil, 20.0 mg, 34% yield (procedure A).

¹H NMR (500 MHz, CDCl₃) δ 10.18 (1H, s), 8.94 (1H, d, *J* = 7.1 Hz), 8.77 (1H, dd, *J* = 4.1, 0.8 Hz), 8.18 (1H, dt, *J* = 8.2, 1.3 Hz), 7.61-7.53 (3H, m), 7.45 (1H, m), 7.16-7.12 (2H, m), 2.93 (2H, q, *J* = 7.6 Hz), 2.41 (3H, s), 1.30 (3H, t, *J* = 7.7 Hz).

The spectral data of this compound are consistent with those previously reported in the literature.^[8]

4-(Dimethylamino)-2,6-diethyl-*N*-(quinolin-8-yl)benzamide (3i)



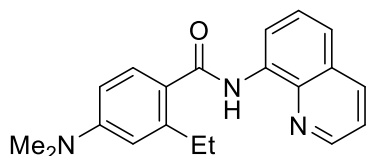
Yellow oil, 50.9 mg, 73% yield (procedure C).

¹H NMR (500 MHz, CDCl₃) δ 9.94 (1H, s), 9.00 (1H, d, *J* = 7.4 Hz), 8.71 (1H, dd, *J* = 4.3, 2.0 Hz), 8.16 (1H, dd, *J* = 8.2, 1.7 Hz), 7.60 (1H, t, *J* = 7.9 Hz), 7.55-7.53 (1H, m), 7.43 (1H, dd, *J* = 8.5, 4.2 Hz), 6.51 (2H, s), 3.01 (6H, s), 2.73 (4H, q, *J* = 7.5 Hz), 1.27 (6H, t, *J* = 7.5 Hz).

¹³C NMR (125 MHz, CDCl₃) δ 169.8, 151.2, 148.3, 142.3, 138.6, 136.4, 135.0, 128.1, 127.6, 126.3, 121.7, 121.6, 116.6, 110.2, 40.6, 27.3, 16.3.

HRMS (ESI) calculated for C₂₂H₂₆ON₃: *m/z* 348.2070 ([*M* + H]⁺), found: *m/z* 348.2075 ([*M* + H]⁺).

4-(Dimethylamino)-2-ethyl-*N*-(quinolin-8-yl)benzamide (3i')

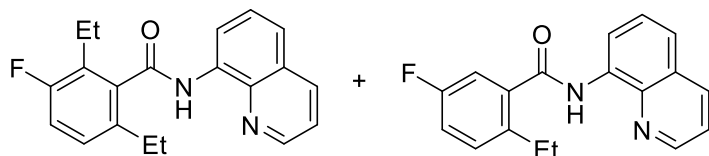


Yellow oil, 20.3 mg, 32% yield (procedure A).

¹H NMR (500 MHz, CDCl₃) δ 10.21 (1H, s), 8.92 (1H, d, *J* = 7.7 Hz), 8.77 (1H, dd, *J* = 4.0, 1.4 Hz), 8.17 (1H, dd, *J* = 8.2, 1.4 Hz), 7.65 (1H, d, *J* = 9.1 Hz), 7.58 (1H, t, *J* = 7.9 Hz), 7.51 (1H, d, *J* = 7.4 Hz), 7.44 (1H, dd, *J* = 4.2 Hz), 6.64-6.62 (2H, m), 3.18-2.89 (8H, m), 1.33 (3H, t, *J* = 7.5 Hz).

The spectral data of this compound are consistent with those previously reported in the literature.^[9]

2,6-Diethyl-3-fluoro-*N*-(quinolin-8-yl)benzamide (3j) and 2-Ethyl-5-fluoro-*N*-(quinolin-8-yl)benzamide (3j')



Colorless oil, 48.7 mg, 79% yield (**3j**: 40%, **3j'**: 39%, procedure A).

33.0 mg, 52% yield (**3j**: 44%, **3j'**: 8%, procedure C).

Each product was characterized by analyzing the ^1H NMR of a mixture of products, **3j** / **3j'** = 1.0 / 0.96.

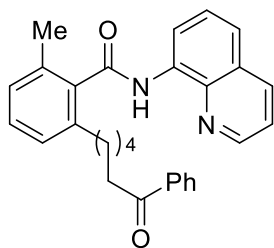
^1H NMR (500 MHz, CDCl_3) δ 10.16 (0.96H, s), 9.95 (1H, s), 8.97 (1H, dd, $J = 7.2, 1.6$ Hz), 8.92 (0.96H, $J = 7.2, 1.6$ Hz), 8.79 (0.96H, dd, $J = 4.5, 2.0$ Hz), 8.74 (1H, dd, $J = 4.5, 2.0$ Hz), 8.20 (1.96H, m), 7.64-7.57 (3.92H, m), 7.49-7.45 (1.92H, m), 7.36-7.28 (1.96H, m), 7.16-7.12 (1.96H, m), 7.07 (1H, t, $J = 9.5$ Hz), 2.90 (1.92H, q, $J = 7.6$ Hz), 2.71 (4H, q, $J = 7.6$ Hz), 1.31-1.23 (8.76H, m).

^{13}C NMR (125 MHz, CDCl_3) δ 167.5, 167.1, 160.8 (d, $J = 247$ Hz), 159.6 (d, $J = 245$ Hz), 148.5 (Two peaks were overlapped.), 138.7 (d, $J = 3.6$ Hz), 138.6, 138.5, 137.8 (d, $J = 6.0$ Hz), 136.54 (Two peaks were overlapped.), 136.51, 136.4 (d, $J = 3.6$ Hz), 134.6, 134.3, 131.5 (d, $J = 7.2$ Hz), 128.1 (Two peaks were overlapped.), 128.0, 127.8, 127.7, 127.5 (Two peaks were overlapped.), 122.3, 122.2, 121.9 (Two peaks were overlapped.), 117.3 (d, $J = 20$ Hz), 116.9, 116.8, 116.2 (d, $J = 23$ Hz), 114.3 (d, $J = 23$ Hz), 26.1, 26.0, 20.9 (d, $J = 2.4$ Hz), 16.3, 16.1, 15.5.

HRMS (ESI) (**3j**) calculated for $\text{C}_{20}\text{H}_{20}\text{ON}_2\text{F}$: m/z 323.1554 ($[\text{M} + \text{H}]^+$), found: m/z 323.1554 ($[\text{M} + \text{H}]^+$).

HRMS (ESI) (**3j'**) calculated for $\text{C}_{18}\text{H}_{16}\text{ON}_2\text{F}$: m/z 295.1241 ($[\text{M} + \text{H}]^+$), found: m/z 295.1249 ($[\text{M} + \text{H}]^+$).

2-Methyl-6-(6-oxo-6-phenylhexyl)-*N*-(quinolin-8-yl)benzamide (**3k**)



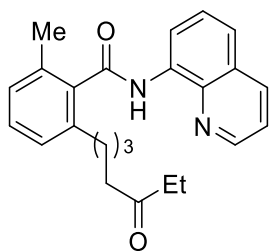
Yellow oil, 74.6 mg, 85% yield (procedure B).

^1H NMR (500 MHz, CDCl_3) δ 9.92 (1H, s), 8.97 (1H, dd, $J = 7.1, 1.7$ Hz), 8.71 (1H, dd, $J = 4.1, 1.6$ Hz), 8.16 (1H, dd, $J = 8.2, 1.7$ Hz), 7.86 (2H, dd, $J = 8.3, 1.3$ Hz), 7.60-7.51 (3H, m), 7.43-7.40 (3H, m), 7.30-7.26 (2H, m), 7.13 (2H, dd, $J = 10.1, 7.8$ Hz), 2.83 (2H, t, $J = 7.4$ Hz), 2.74 (2H, t, $J = 7.8$ Hz), 2.43 (3H, s), 1.77-1.71 (2H, m), 1.69-1.63 (2H, m), 1.41-1.35 (2H, m).

^{13}C NMR (125 MHz, CDCl_3) δ 200.5, 169.0, 148.4, 139.4, 138.6, 137.9, 137.1, 136.5, 134.7, 134.5, 133.0, 129.2, 128.6, 128.4, 128.2, 128.0, 127.6, 127.0, 122.1, 121.8, 116.9, 38.5, 33.5, 31.5, 29.3, 24.2, 19.7.

HRMS (ESI) calculated for $C_{29}H_{29}O_2N_2$: m/z 437.2224 ($[M + H]^+$), found: m/z 437.2219 ($[M + H]^+$).

2-Methyl-6-(5-oxoheptyl)-*N*-(quinolin-8-yl)benzamide (3l)



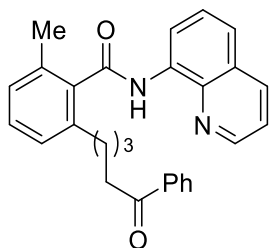
Yellow oil, 63.1 mg, 84% yield (procedure B).

1H NMR (500 MHz, $CDCl_3$) δ 9.91 (1H, s), 8.98 (1H, dd, $J = 7.5, 1.6$ Hz), 8.74 (1H, dd, $J = 4.3, 2.0$ Hz), 8.19 (1H, dd, $J = 8.2, 1.7$ Hz), 7.63-7.56 (2H, m), 7.45 (1H, dd, $J = 8.3, 4.2$ Hz), 7.29-7.26 (1H, m), 7.13 (2H, t, $J = 6.7$ Hz), 2.71 (2H, t, $J = 7.8$ Hz), 2.42 (3H, s), 2.29 (2H, t, $J = 7.5$ Hz), 2.25 (2H, q, $J = 7.4$ Hz), 1.70-1.64 (2H, m), 1.57-1.53 (2H, m), 0.92 (3H, t, $J = 7.4$ Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 211.6, 168.9, 148.4, 138.9, 138.6, 137.8, 136.4, 134.6, 134.4, 129.2, 128.1, 128.0, 127.5, 126.9, 122.1, 121.8, 116.8, 42.1, 35.8, 33.3, 31.3, 23.7, 19.6, 7.8.

HRMS (ESI) calculated for $C_{24}H_{26}O_2N_2Na$: m/z 397.1886 ($[M + Na]^+$), found: m/z 397.1885 ($[M + Na]^+$).

2-Methyl-6-(5-oxo-5-phenylpentyl)-*N*-(quinolin-8-yl)benzamide (3m)



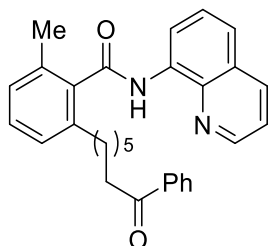
Yellow oil, 68.6 mg, 81% yield (procedure B).

1H NMR (500 MHz, $CDCl_3$) δ 9.93 (1H, s), 8.99 (1H, dd, $J = 7.4, 1.4$ Hz), 8.71 (1H, dd, $J = 4.3, 1.4$ Hz), 8.17 (1H, dd, $J = 8.2, 1.7$ Hz), 7.76-7.75 (2H, m), 7.63-7.56 (2H, m), 7.51-7.48 (1H, m), 7.42 (1H, dd, $J = 8.3, 4.2$ Hz), 7.36 (2H, t, $J = 7.8$ Hz), 7.30-7.27 (1H, m), 7.14 (2H, dd, $J = 16.9, 7.8$ Hz), 2.85 (2H, t, $J = 7.2$ Hz), 2.77 (2H, t, $J = 7.7$ Hz), 2.43 (3H, s), 1.83-1.70 (4H, m).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.2, 169.0, 148.4, 139.0, 138.6, 137.9, 137.0, 136.4, 134.7, 134.5, 132.9, 129.2, 128.5, 128.1, 128.04, 128.01, 127.5, 126.9, 122.1, 121.8, 116.9, 38.3, 33.3, 31.3, 24.0, 19.6.

HRMS (ESI) calculated for $C_{28}H_{26}O_2N_2Na$: m/z 445.1886 ($[M + Na]^+$), found: m/z 445.1887 ($[M + Na]^+$).

2-Methyl-6-(7-oxo-7-phenylheptyl)-N-(quinolin-8-yl)benzamide (3n)



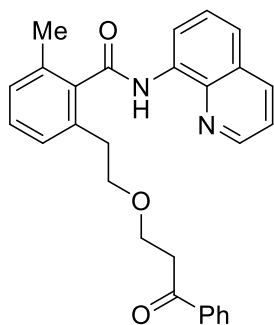
Yellow oil, 79.0 mg, 88% yield (procedure B).

1H NMR (500 MHz, $CDCl_3$) δ 9.93 (1H, s), 8.99 (1H, dd, $J = 7.5, 1.3$ Hz), 8.72 (1H, dd, $J = 4.1, 1.6$ Hz), 8.14 (1H, dd, $J = 8.5, 1.4$ Hz), 7.87 (2H, dd, $J = 8.4, 1.3$ Hz), 7.60 (1H, t, $J = 7.9$ Hz), 7.56-7.53 (2H, m), 7.45-7.40 (3H, m), 7.29-7.26 (1H, m), 7.13 (2H, dd, $J = 10.6, 7.8$ Hz), 2.76 (2H, t, $J = 7.4$ Hz), 2.71 (2H, t, $J = 7.8$ Hz), 2.43 (3H, s), 1.73-1.67 (2H, m), 1.59 (2H, m), 1.35-1.27 (4H, m).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.5, 169.1, 148.5, 139.5, 138.6, 137.9, 137.1, 136.4, 134.7, 134.6, 133.0, 129.2, 128.6, 128.16, 128.13, 127.9, 127.6, 126.9, 122.1, 121.8, 116.9, 38.6, 33.5, 31.7, 29.4, 29.2, 24.2, 19.7.

HRMS (ESI) calculated for $C_{30}H_{30}O_2N_2Na$: m/z 473.2199 ($[M + Na]^+$), found: m/z 473.2193 ($[M + Na]^+$).

2-Methyl-6-(2-(3-oxo-3-phenylpropoxy)ethyl)-N-(quinolin-8-yl)benzamide (3o)



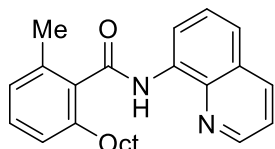
Yellow oil, 20.7 mg, 24% yield (procedure D).

1H NMR (500 MHz, $CDCl_3$) δ 9.96 (1H, s), 8.98 (1H, dd, $J = 7.4, 1.0$ Hz), 8.72 (1H, dd, $J = 4.1, 1.3$ Hz), 8.16 (1H, dd, $J = 8.2, 1.4$ Hz), 7.83 (2H, d, $J = 7.4$ Hz), 7.62-7.51 (3H, m), 7.43-7.39 (3H, m), 7.28-7.25 (1H, m), 7.15 (2H, dd, $J = 16, 7.5$ Hz), 3.80 (2H, t, $J = 6.5$ Hz), 3.75 (2H, t, $J = 7.0$ Hz), 3.11 (2H, t, $J = 6.5$ Hz), 3.00 (2H, t, $J = 7.0$ Hz), 2.42 (3H, s).

^{13}C NMR (125 MHz, CDCl_3) δ 198.6, 168.8, 148.4, 138.7, 138.4, 137.0, 136.5, 135.7, 134.7, 134.5, 133.2, 129.2, 128.6, 128.5, 128.20, 128.16, 127.63, 127.56, 122.2, 121.8, 117.0, 72.0, 66.3, 38.8, 33.9, 19.7.

HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{26}\text{O}_3\text{N}_2\text{Na}$: m/z 461.1836 ($[\text{M} + \text{Na}]^+$), found: m/z 461.1831 ($[\text{M} + \text{Na}]^+$).

2-Methyl-6-octyl-*N*-(quinolin-8-yl)benzamide (3p)

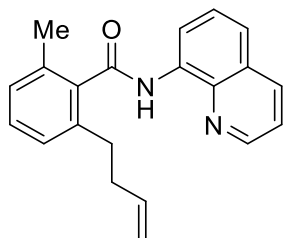


Colorless oil, 45.4 mg, 58% yield (procedure B).

^1H NMR (500 MHz, CDCl_3) δ 9.92 (1H, s), 8.99 (1H, d, $J = 7.7$ Hz), 8.73 (1H, d, $J = 6.0$ Hz), 8.18 (1H, d, $J = 8.2$ Hz), 7.63-7.56 (2H, m), 7.46-7.42 (1H, m), 7.34 (1H, t, $J = 7.5$ Hz), 7.15-7.11 (2H, m), 2.70 (2H, t, $J = 7.9$ Hz), 2.43 (3H, s), 1.68-1.65 (2H, m), 1.25-1.21 (2H, m), 1.16-1.07 (8H, m), 0.78 (3H, t, $J = 7.2$ Hz).

The spectral data of this compound are consistent with those previously reported in the literature.^[3]

2-(But-3-en-1-yl)-6-methyl-*N*-(quinolin-8-yl)benzamide (3q)

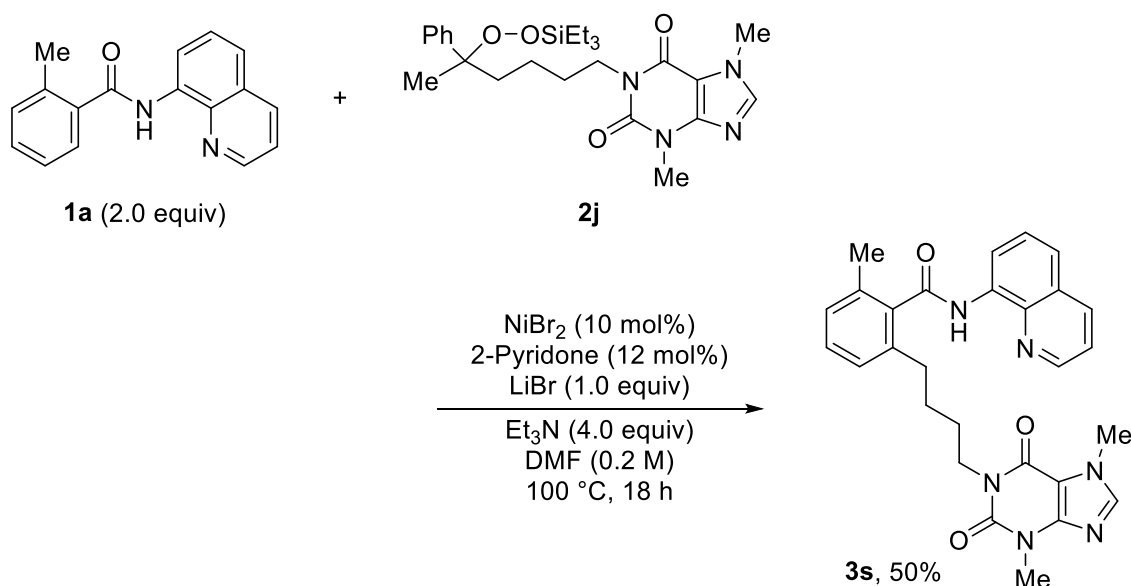


Colorless oil, 34.1 mg, 54% yield (procedure B).

^1H NMR (500 MHz, CDCl_3) δ 9.93 (1H, s), 8.99 (1H, d, $J = 7.7$ Hz), 8.74-8.73 (1H, dd, $J = 4.0, 1.4$ Hz), 8.19 (1H, dd, $J = 8.2, 1.1$ Hz), 7.63-7.57 (2H, m), 7.45 (1H, dd, $J = 8.2, 4.2$ Hz), 7.29 (1H, t, $J = 7.7$ Hz), 7.16-7.13 (2H, m), 5.83-5.74 (1H, m), 4.94-4.86 (2H, m), 2.82 (2H, m), 2.44 (5H, m).

The spectral data of this compound are consistent with those previously reported in the literature.^[3]

7. Synthesis of 2-(4-(3,7-Dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-1-yl)butyl)-6-methyl-N-(quinolin-8-yl)benzamide (3s)



To the solution of ASP **2j** (97.3 mg, 0.2 mmol, 1.0 equiv), benzamide **1a** (104 mg, 0.4 mmol, 2.0 equiv), NiBr₂ (4.4 mg, 0.02 mmol, 10 mol%), 2-pyridone (2.3 mg, 0.024 mmol, 12 mol%), and LiBr (17.4 mg, 0.2 mmol, 1.0 equiv) in DMF (1.0 mL) was added Et₃N (84 μ L, 0.6 mmol, 3.0 equiv) at room temperature under N₂ atmosphere. The reaction mixture was stirred at 100 °C for 18 h. After being cooled to room temperature, the reaction mixture was passed through a short silica gel / Na₂SO₄ plug eluting with EtOAc. The obtained solution was concentrated and the residue was purified by flash column chromatography on silica gel to afford desired coupling products **3s** as a colorless oil (49.5 mg, 50%).

¹H NMR (500 MHz, CDCl₃) δ 9.90 (1H, s), 8.95 (1H, d, J = 7.4 Hz), 8.71 (1H, dd, J = 4.3, 1.4 Hz), 8.17 (1H, d, J = 8.2 Hz), 7.62-7.55 (2H, m), 7.45 (1H, s), 7.43 (1H, dd, J = 8.3, 4.2 Hz), 7.29-7.26 (1H, m), 7.14 (2H, dd, J = 27.5, 7.7 Hz), 3.97-3.94 (2H, m), 3.93 (3H, s), 3.50 (3H, s), 2.77 (2H, t, J = 7.7 Hz), 2.41 (3H, s), 1.80-1.61 (4H, m).

¹³C NMR (125 MHz, CDCl₃) δ 168.9, 155.3, 151.5, 148.8, 148.4, 141.4, 139.1, 138.7, 137.9, 136.4, 134.6, 134.5, 129.2, 128.1, 128.0, 127.6, 127.0, 122.0, 121.8, 117.0, 107.8, 41.3, 33.7, 33.2, 29.8, 29.0, 28.1, 19.7.

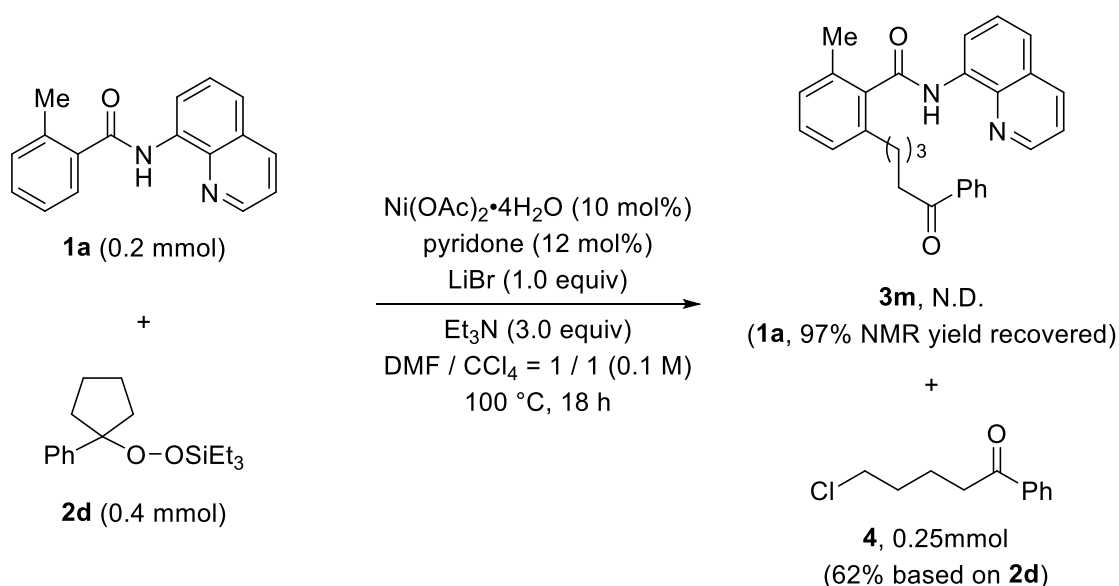
HRMS (ESI) calculated for C₂₈H₂₈O₃N₆Na: m/z 519.2115 ([M + Na]⁺), found: m/z 519.2117 ([M + Na]⁺).

8. Control Experiments

8-1. Competition Experiment (Scheme 3-a)

To a solution of benzamide **1c** (55.6 mg, 0.2 mmol, 1.0 equiv), **1d** (63.3 mg, 0.2 mmol, 1.0 equiv), Ni(OAc)₂•4H₂O (5.0 mg, 0.02 mmol, 10 mol%), and 2-pyridone (2.3 mg, 0.024 mmol, 12 mol%) in DMF (1.0 mL) were added ASP **2a** (49.3 mg, 0.2 mmol, 1.0 equiv) and Et₃N (84 μL, 0.6 mmol, 3.0 equiv) at room temperature under N₂ atmosphere. The reaction mixture was stirred at 100 °C for 18 h. After being cooled to room temperature, the reaction mixture was passed through a short silica gel / Na₂SO₄ plug eluting with EtOAc. The obtained solution was concentrated and the residue was purified by flash column chromatography on silica gel (hexane / EtOAc / MeOH = 200 / 15 / 1) to afford **3c** (2.5 mg, 4% isolated yield) and **3d** (44.2 mg, 64% isolated yield).

8-2. A Control Experiment using Tetrachloromethane (CCl₄) (Scheme 3-b)



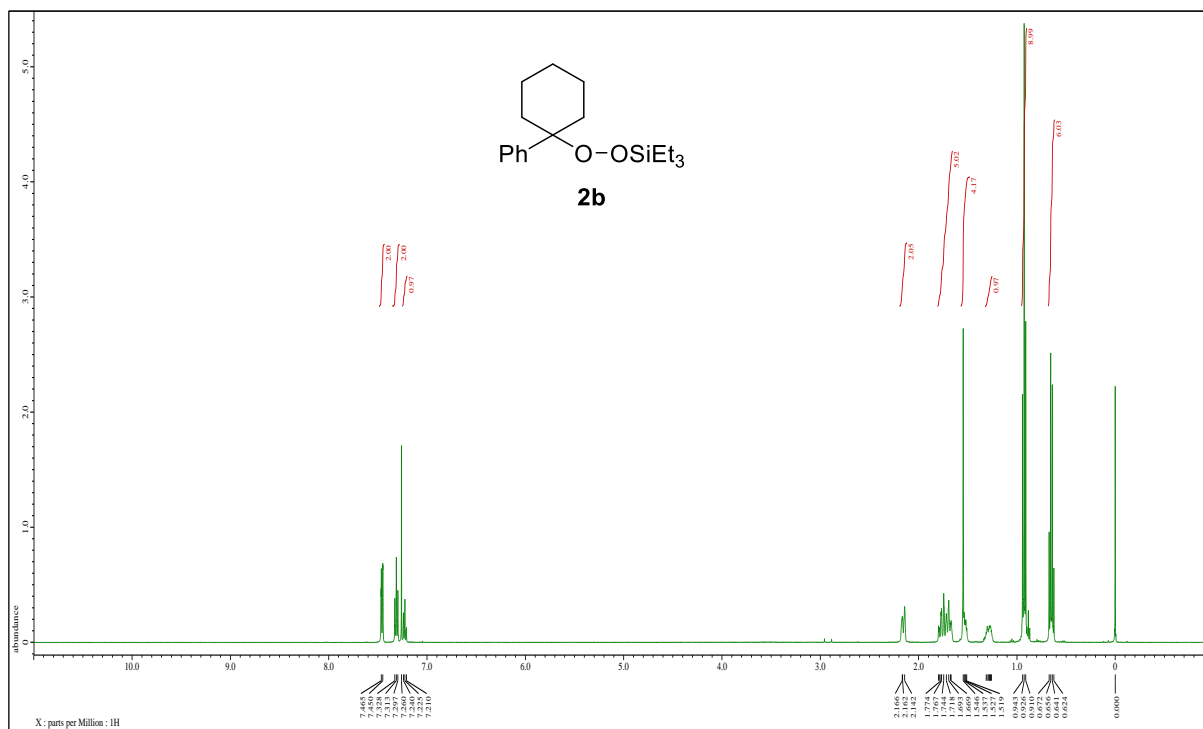
When tetrachloromethane (CCl₄, 1.0 mL) was added to the reaction (0.2 mmol scale) using benzamide **1a** and ASP **2d**, the desired alkylated product (**3m**) was not detected and **1a** was recovered (97% NMR yield). Instead, 5-chloro-1-phenylpentan-1-one (**4**) was obtained in 62% isolated yield (based on **2d**) as a white solid (29.5 mg), which was purified by flash column chromatography on silica gel (hexane / EtOAc = 10 / 1). ¹H NMR spectrum data of **4** matched the one previously reported in the literature.^[10]

9. References

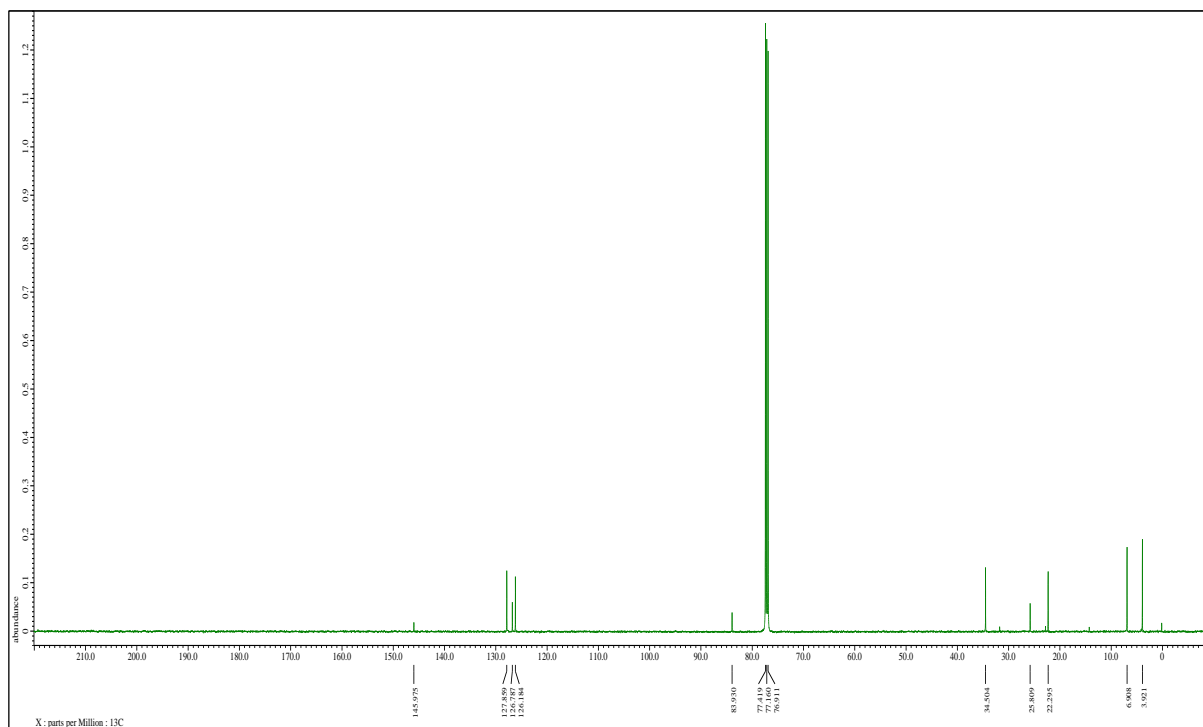
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10. ¹H NMR and ¹³C NMR Spectra

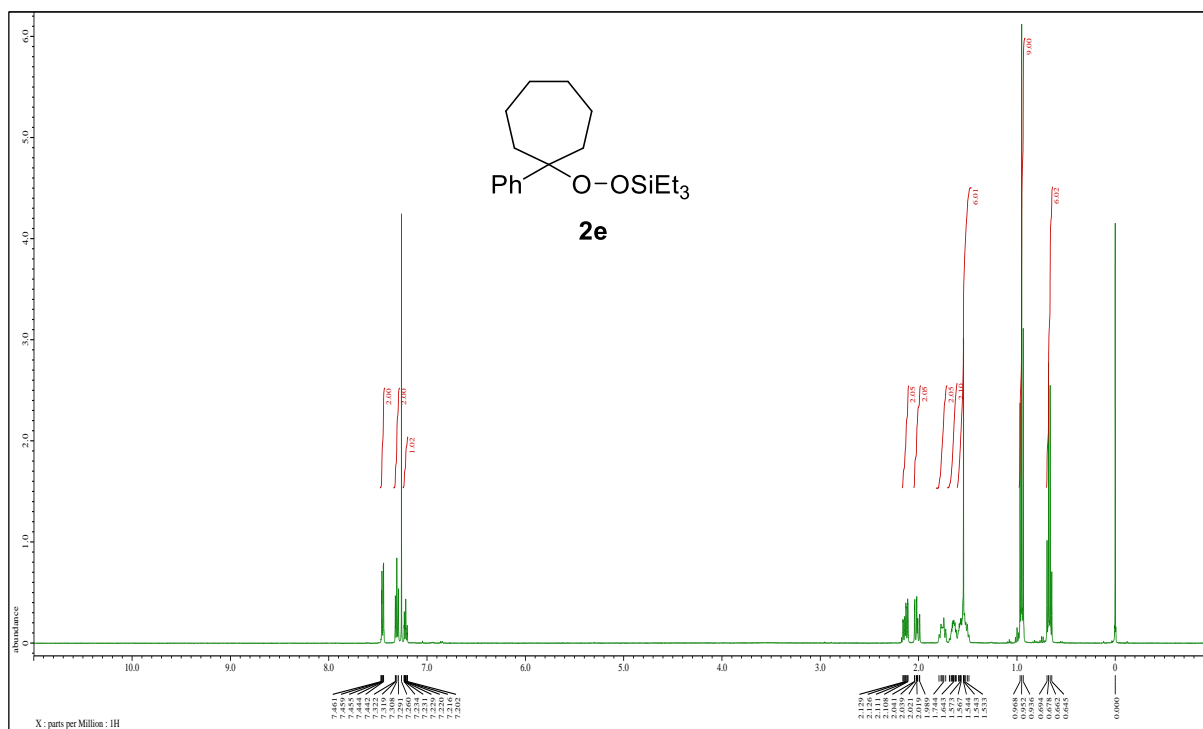
¹H NMR spectrum of **2b** (500 MHz, CDCl₃)



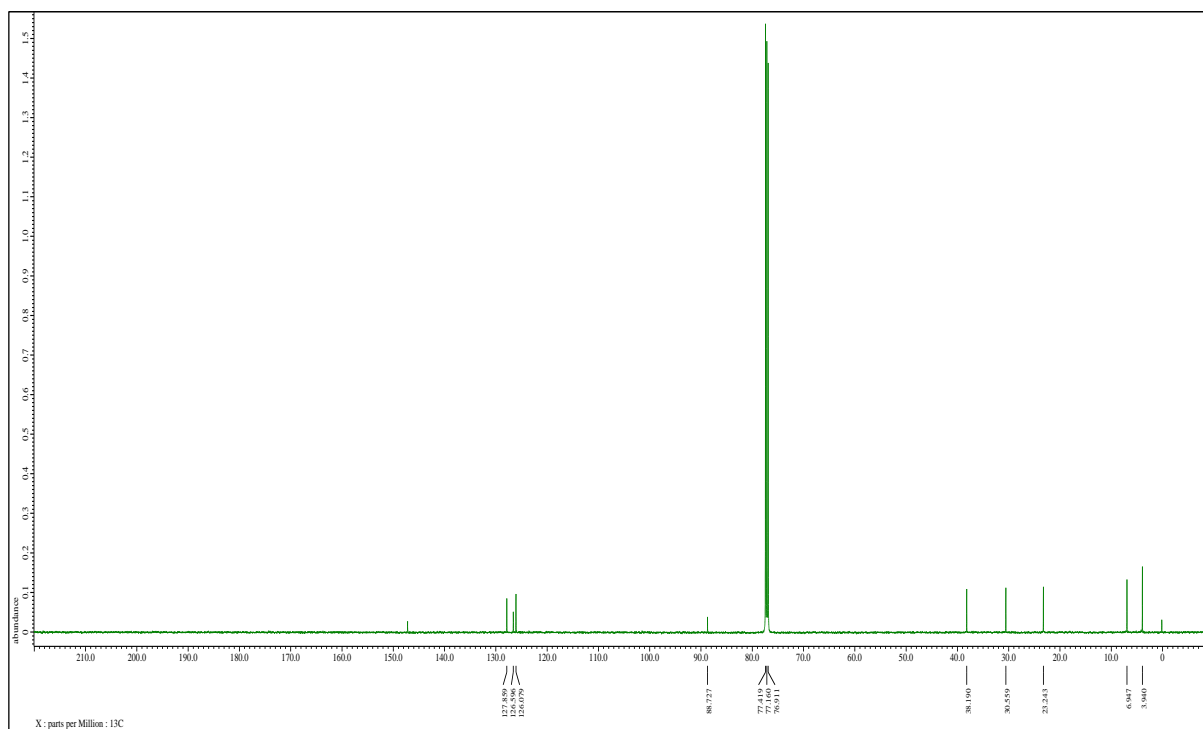
¹³C NMR spectrum of **2b** (125 MHz, CDCl₃)



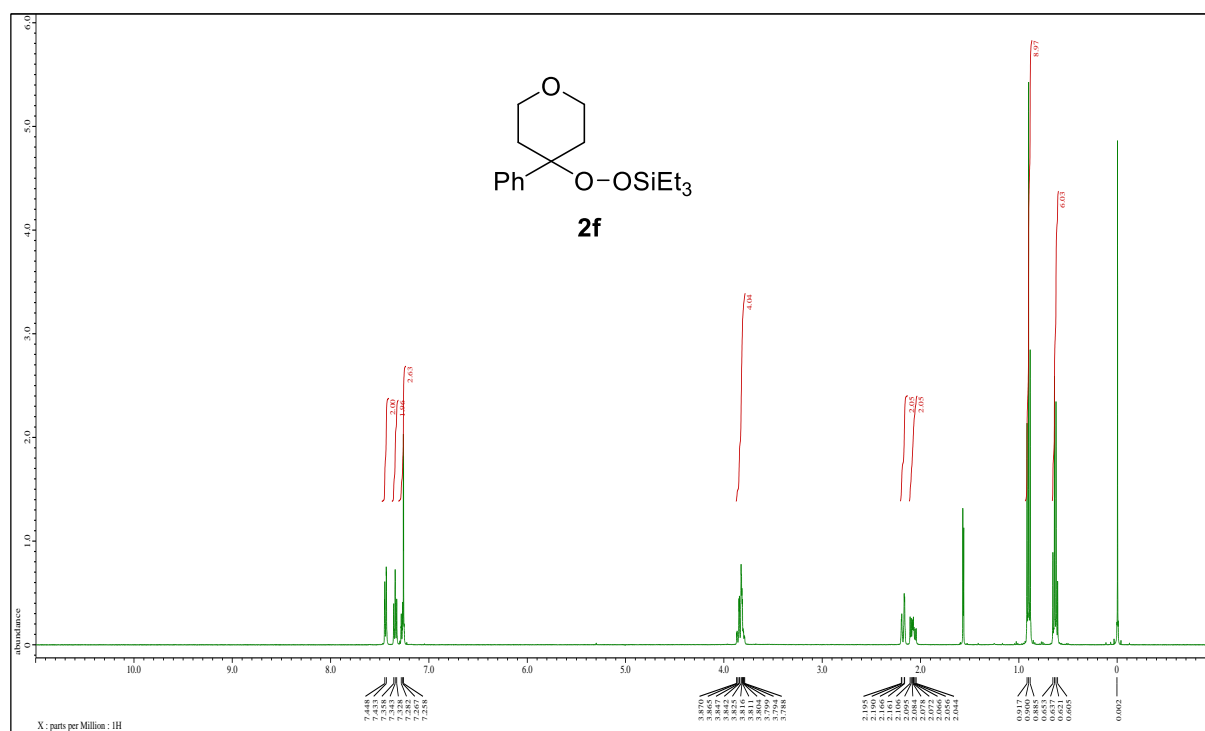
¹H NMR spectrum of **2e** (500 MHz, CDCl₃)



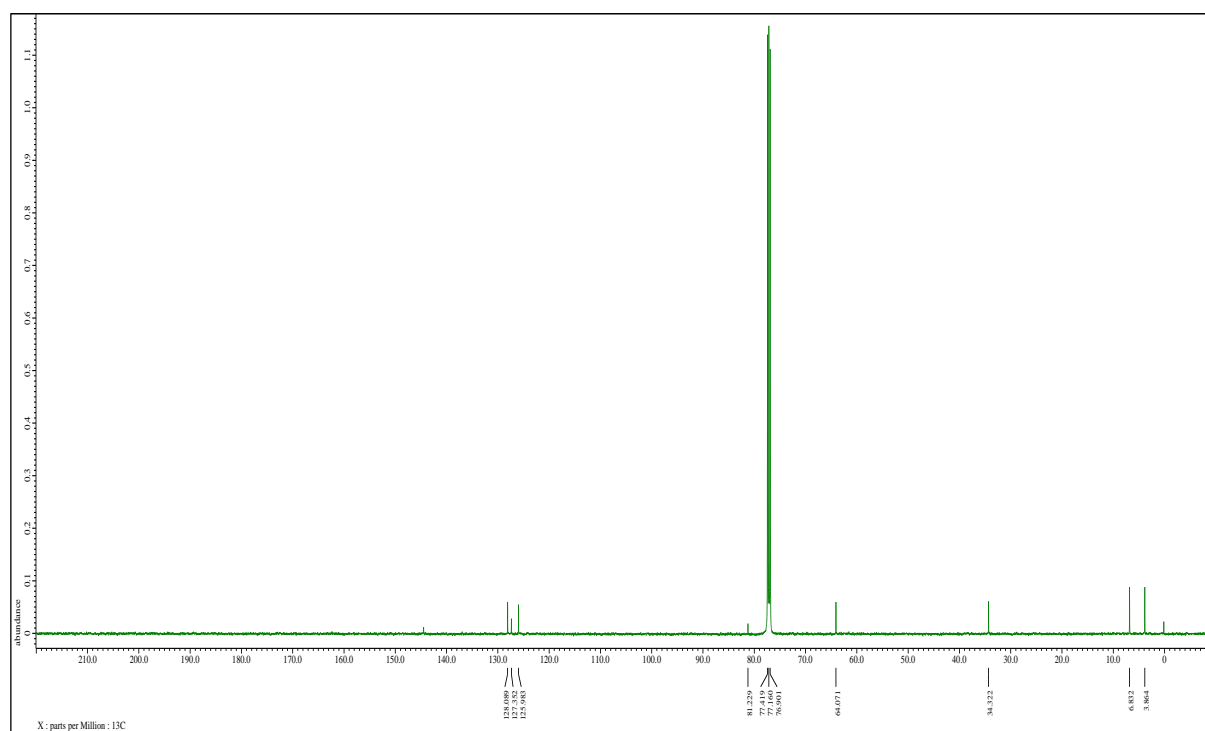
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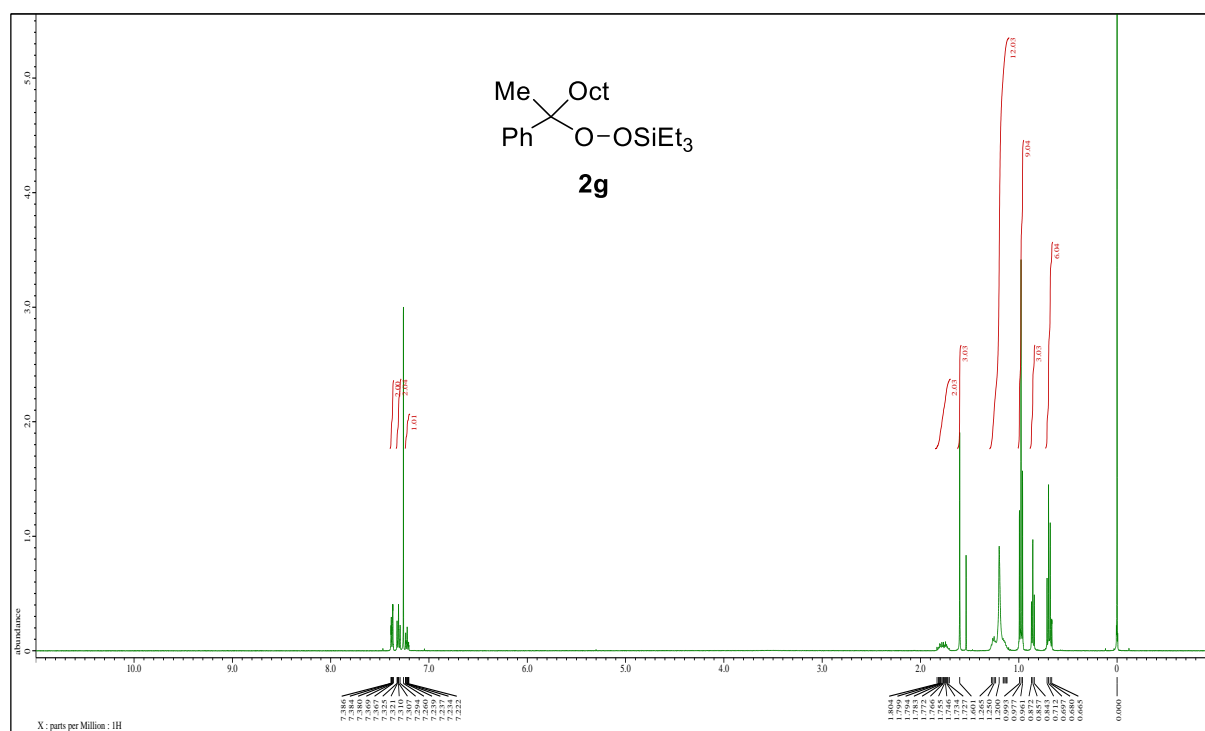
^1H NMR spectrum of **2f** (500 MHz, CDCl_3)



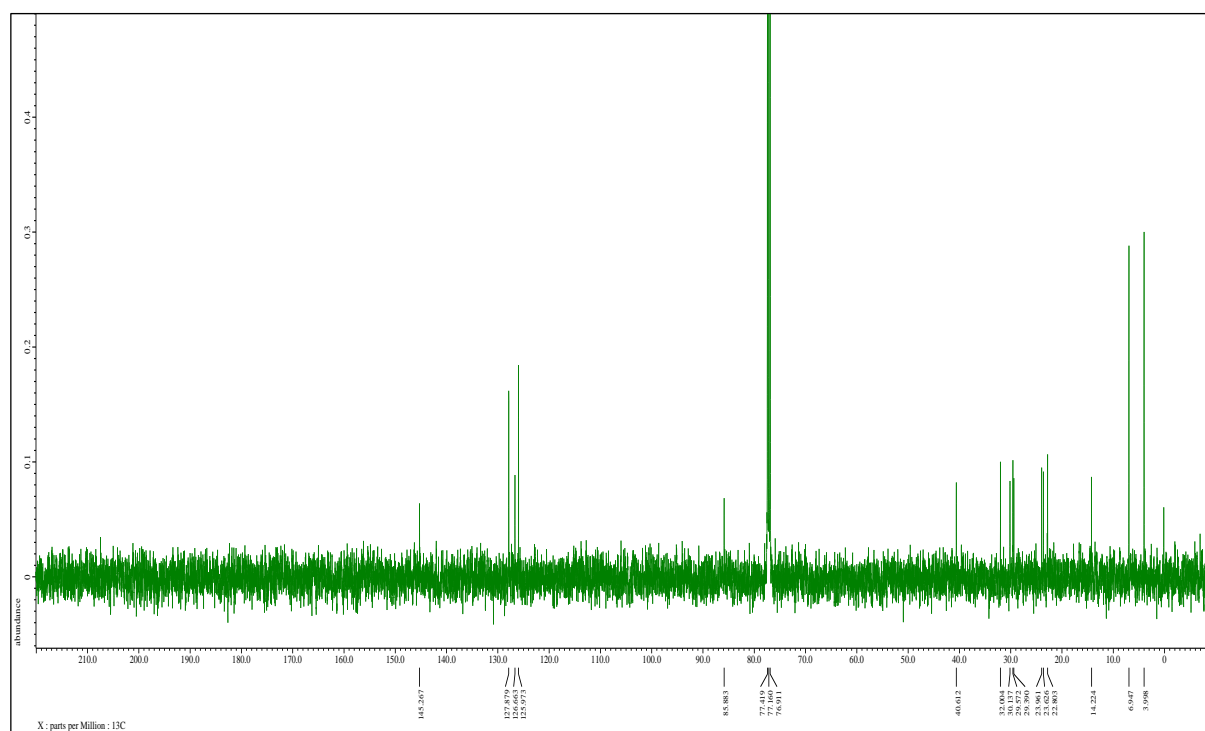
^{13}C NMR spectrum of **2f** (125 MHz, CDCl_3)



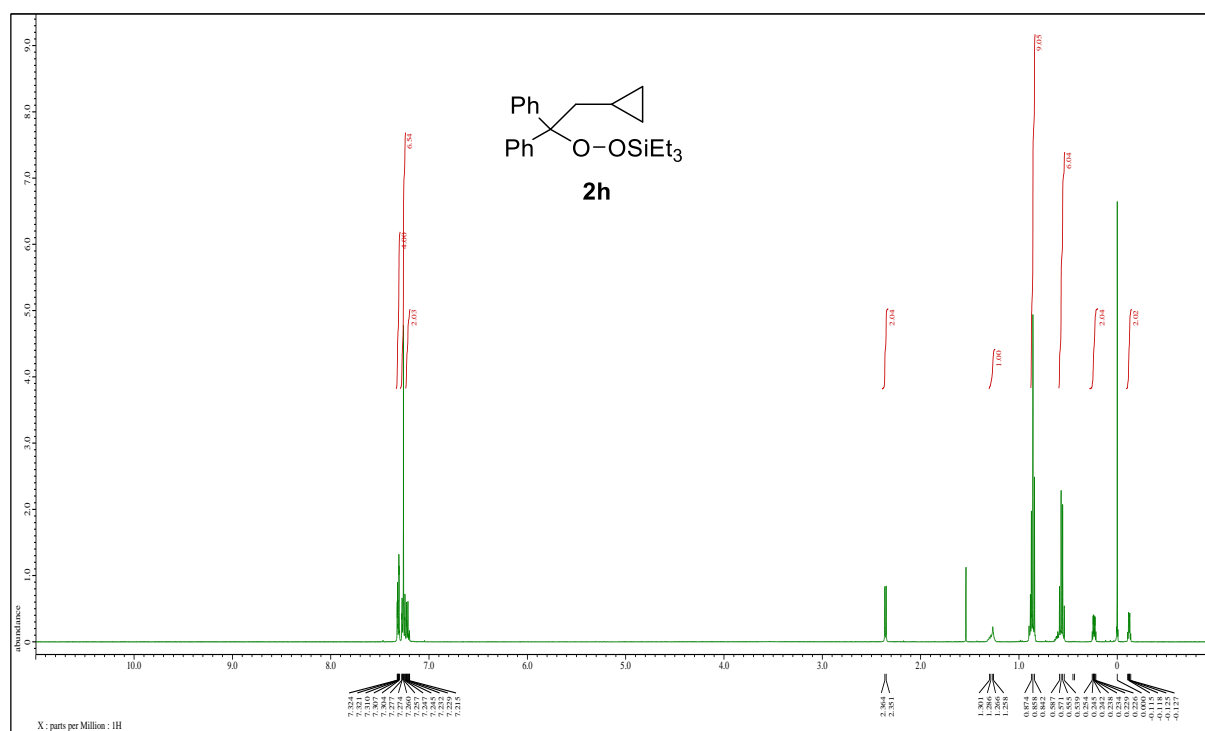
^1H NMR spectrum of **2g** (500 MHz, CDCl_3)



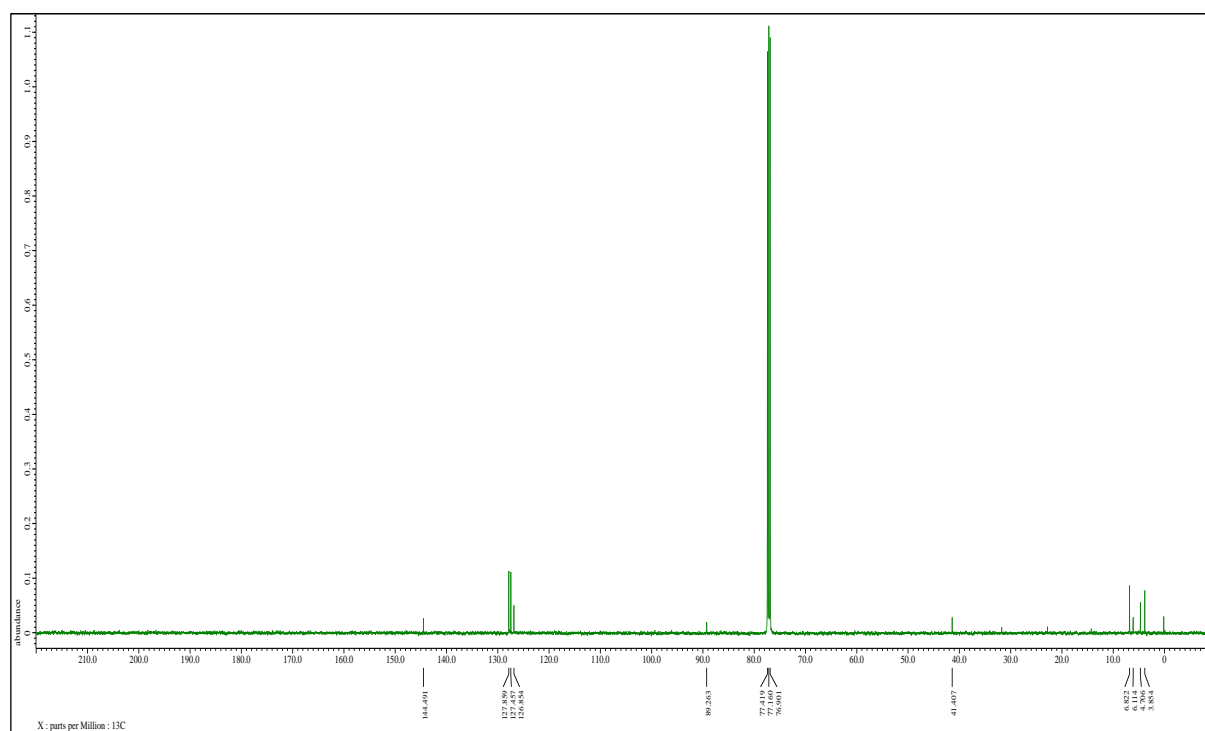
^{13}C NMR spectrum of **2g** (125 MHz, CDCl_3)



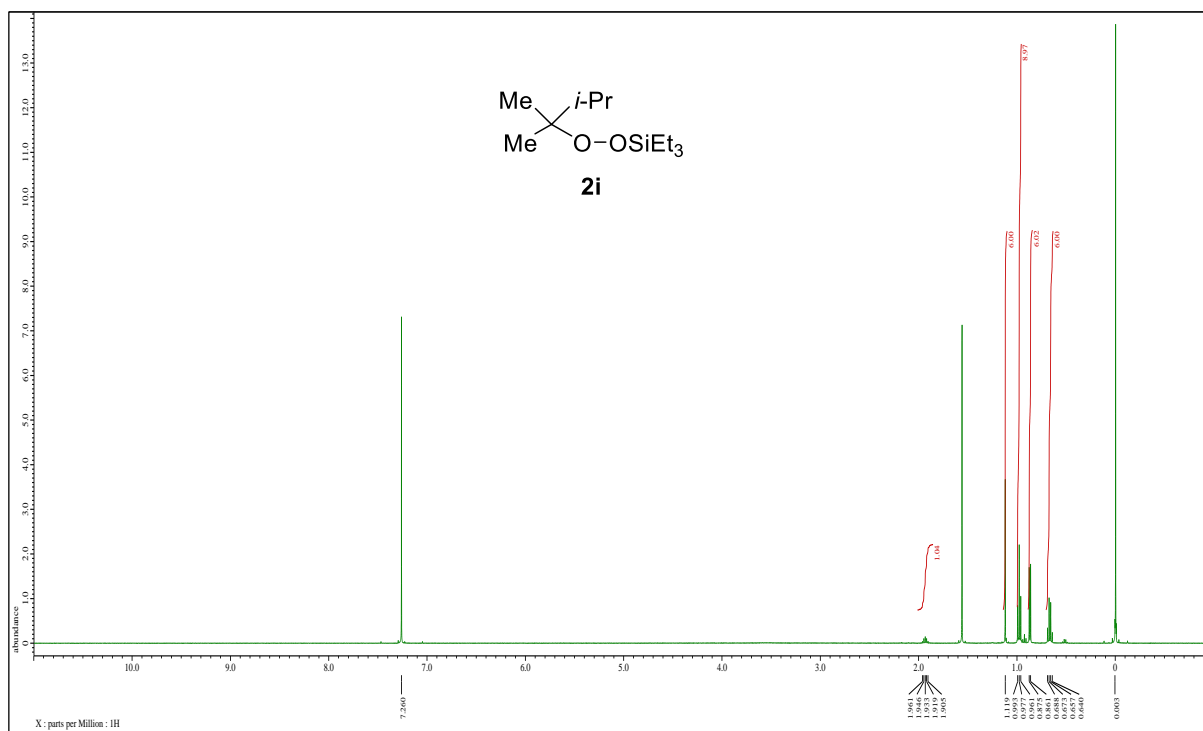
^1H NMR spectrum of **2h** (500 MHz, CDCl_3)



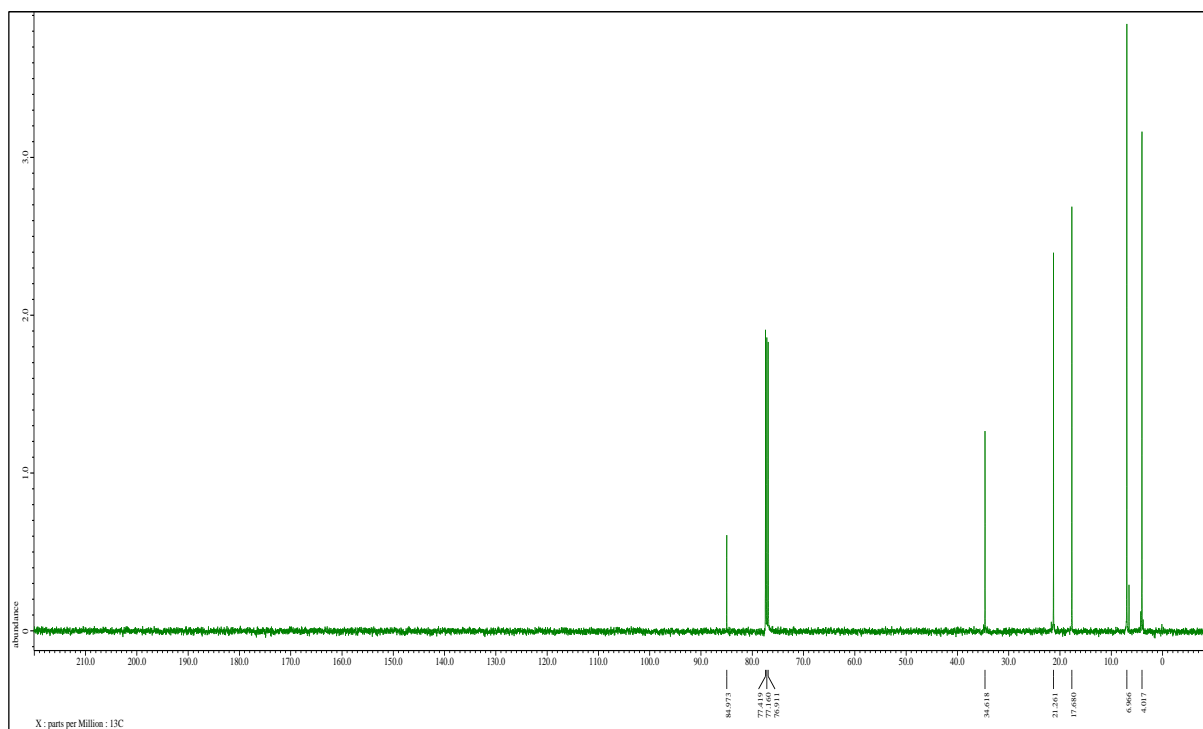
^{13}C NMR spectrum of **2h** (125 MHz, CDCl_3)



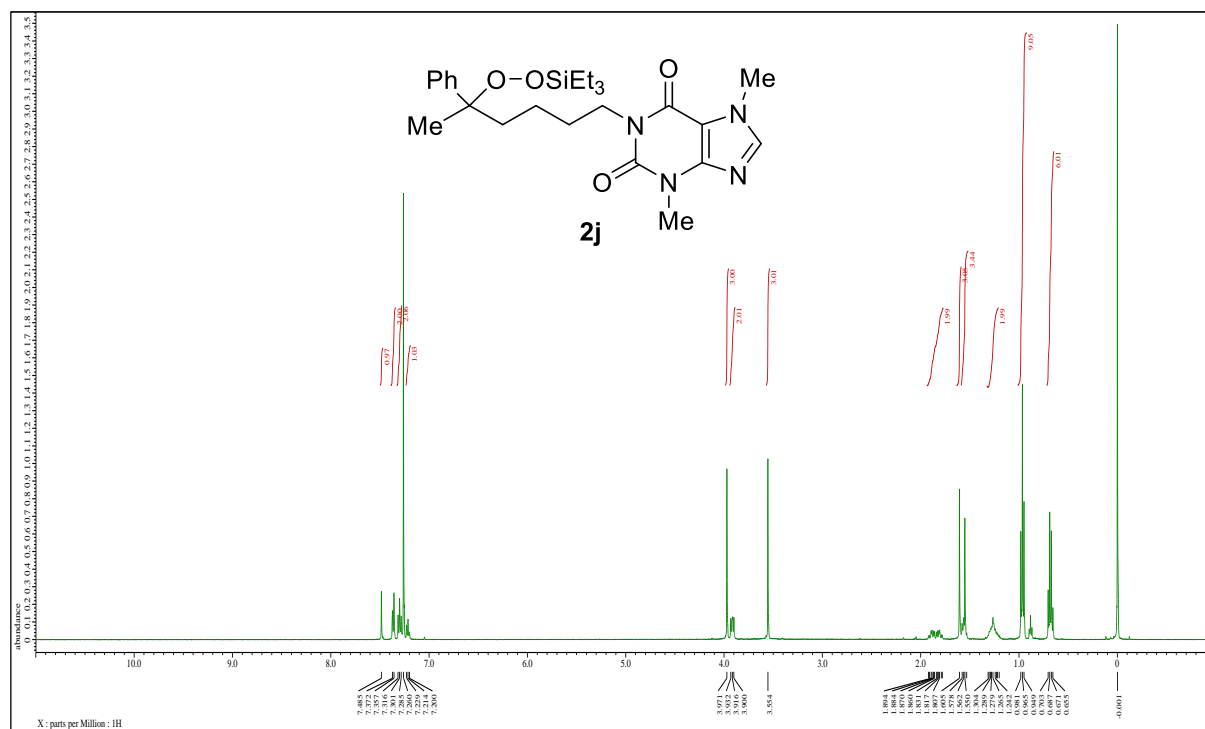
^1H NMR spectrum of **2i** (500 MHz, CDCl_3)



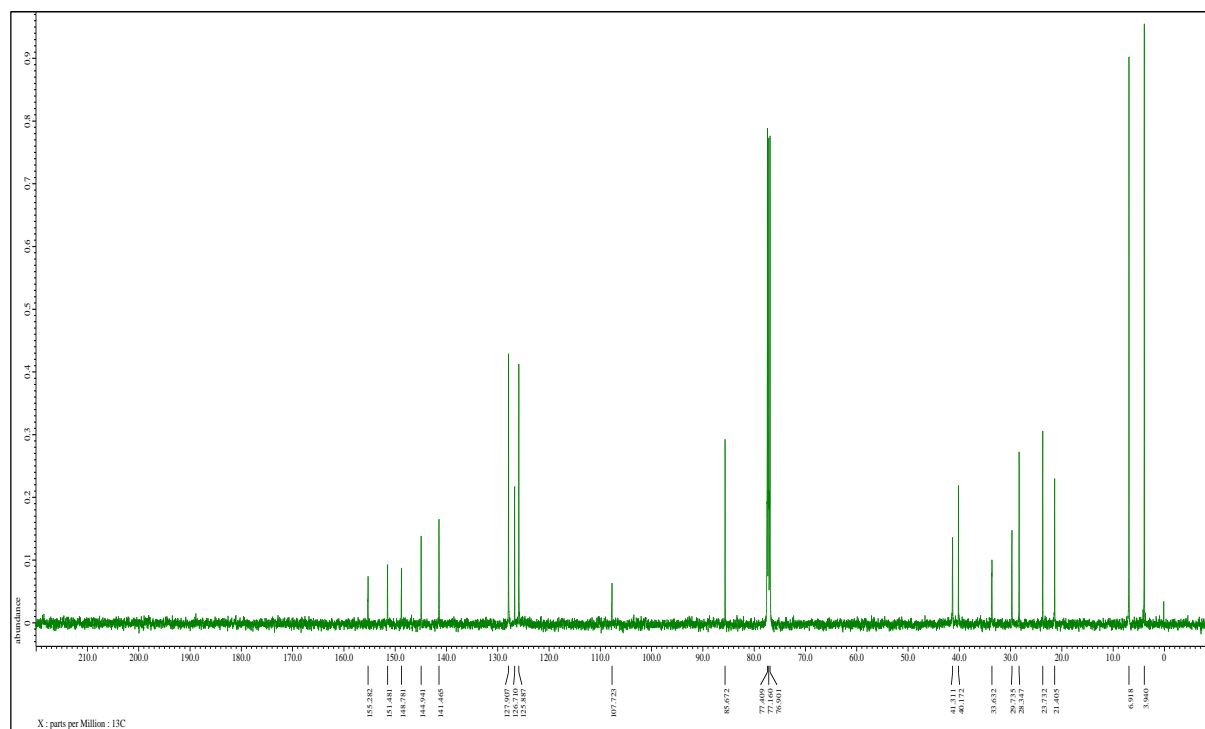
^{13}C NMR spectrum of **2i** (125 MHz, CDCl_3)



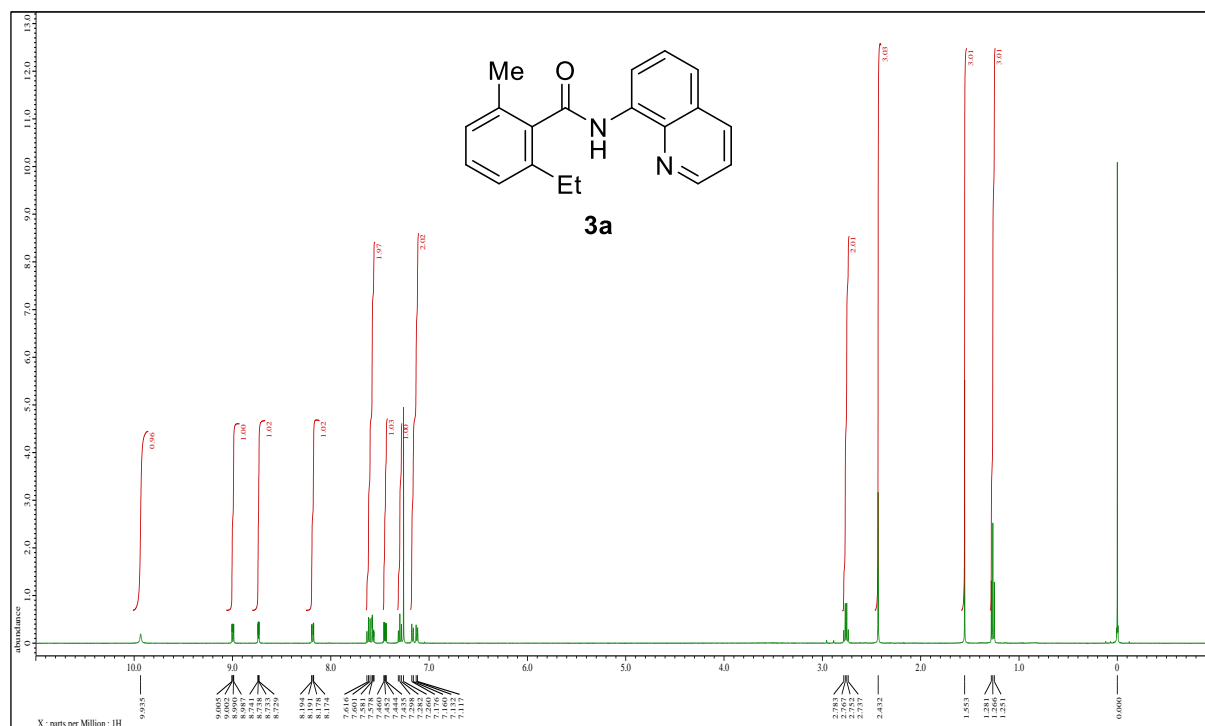
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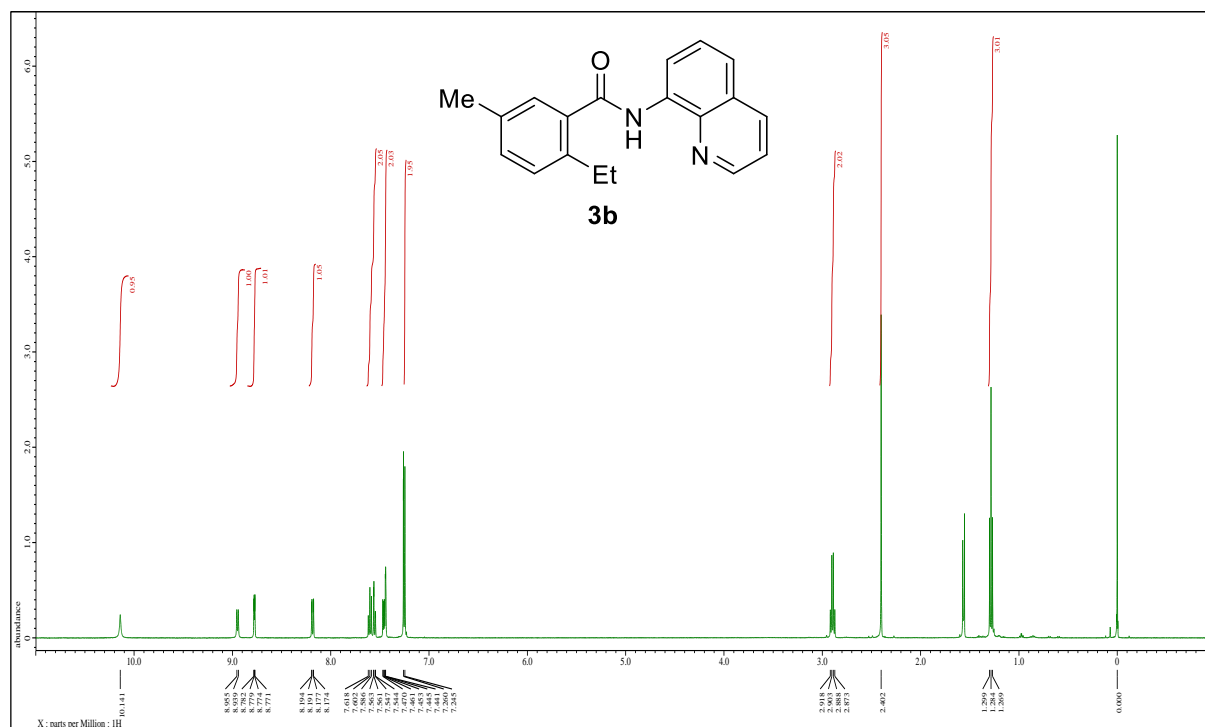
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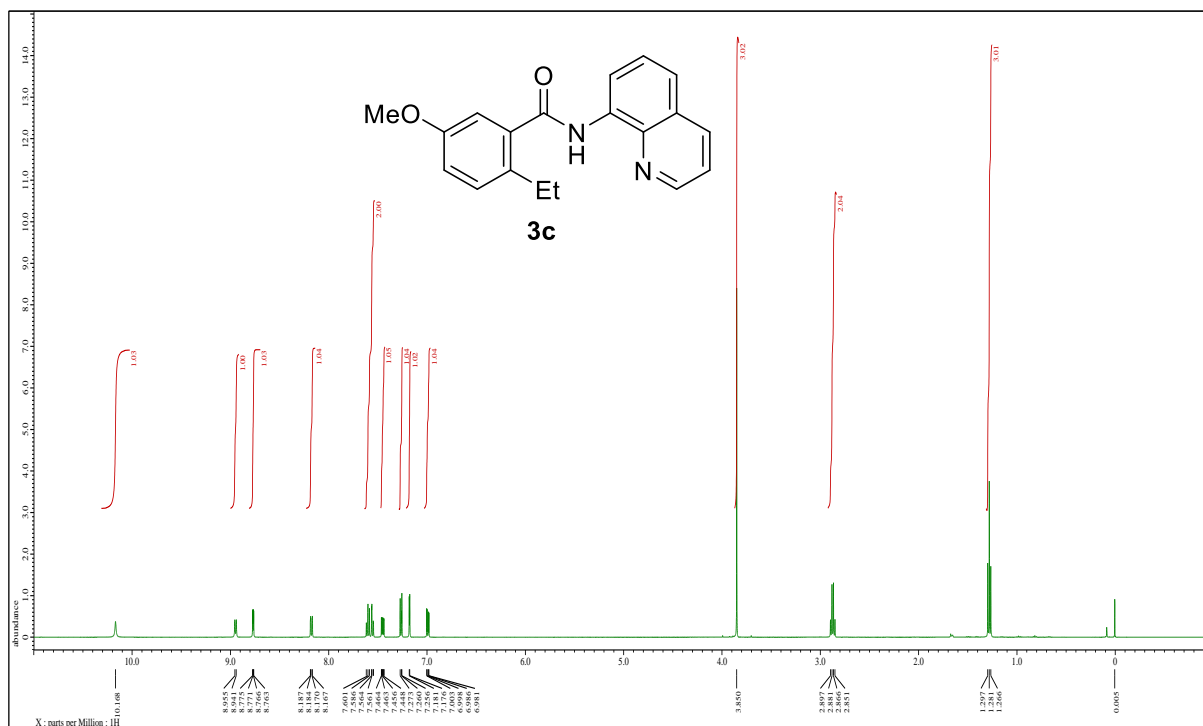
¹H NMR spectrum of **3a** (500 MHz, CDCl₃)



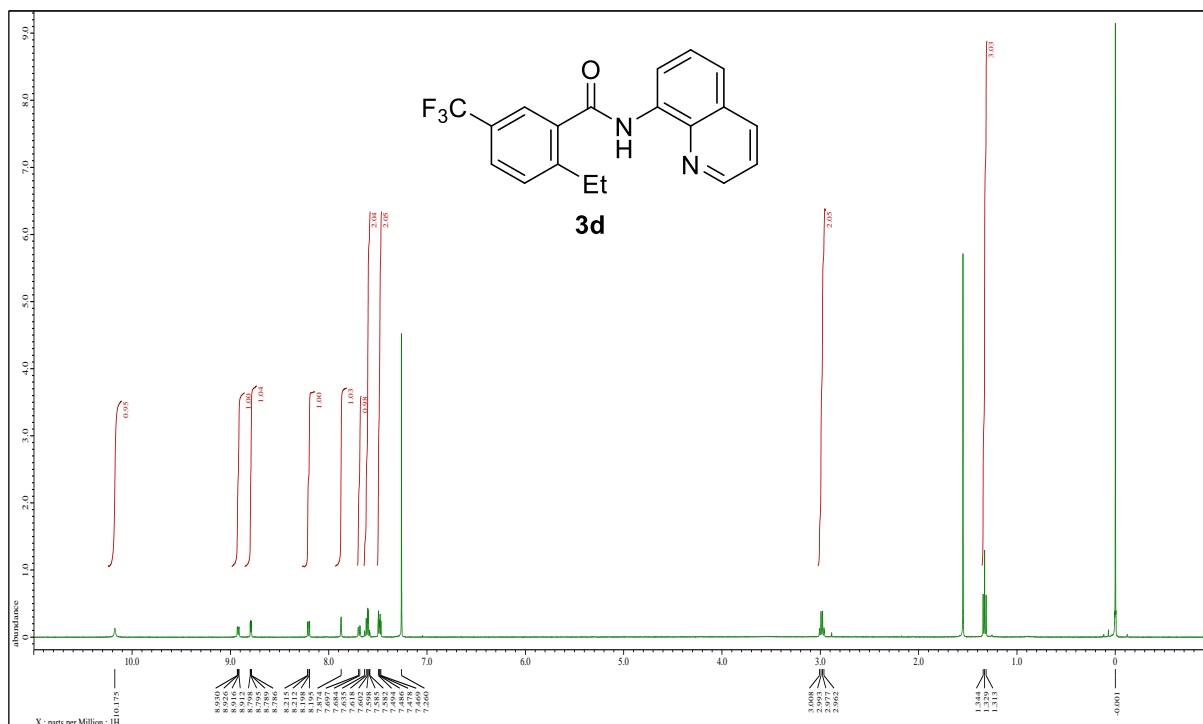
¹H NMR spectrum of **3b** (500 MHz, CDCl₃)



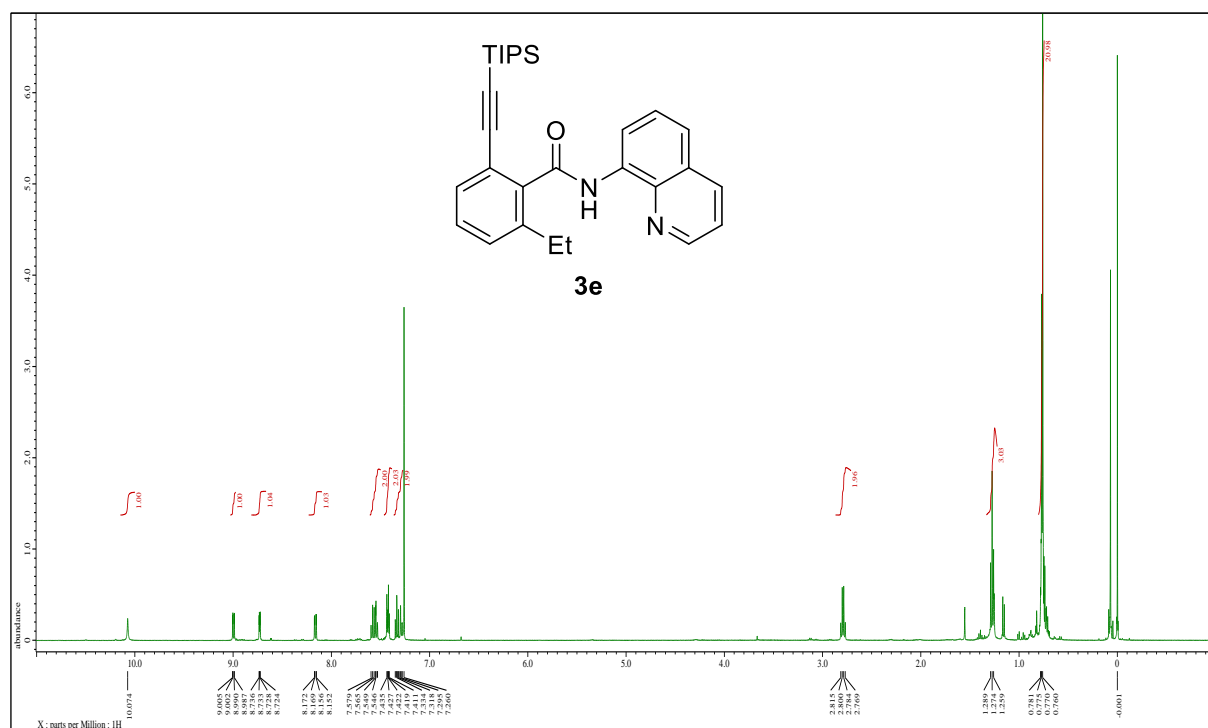
¹H NMR spectrum of **3c** (500 MHz, CDCl₃)



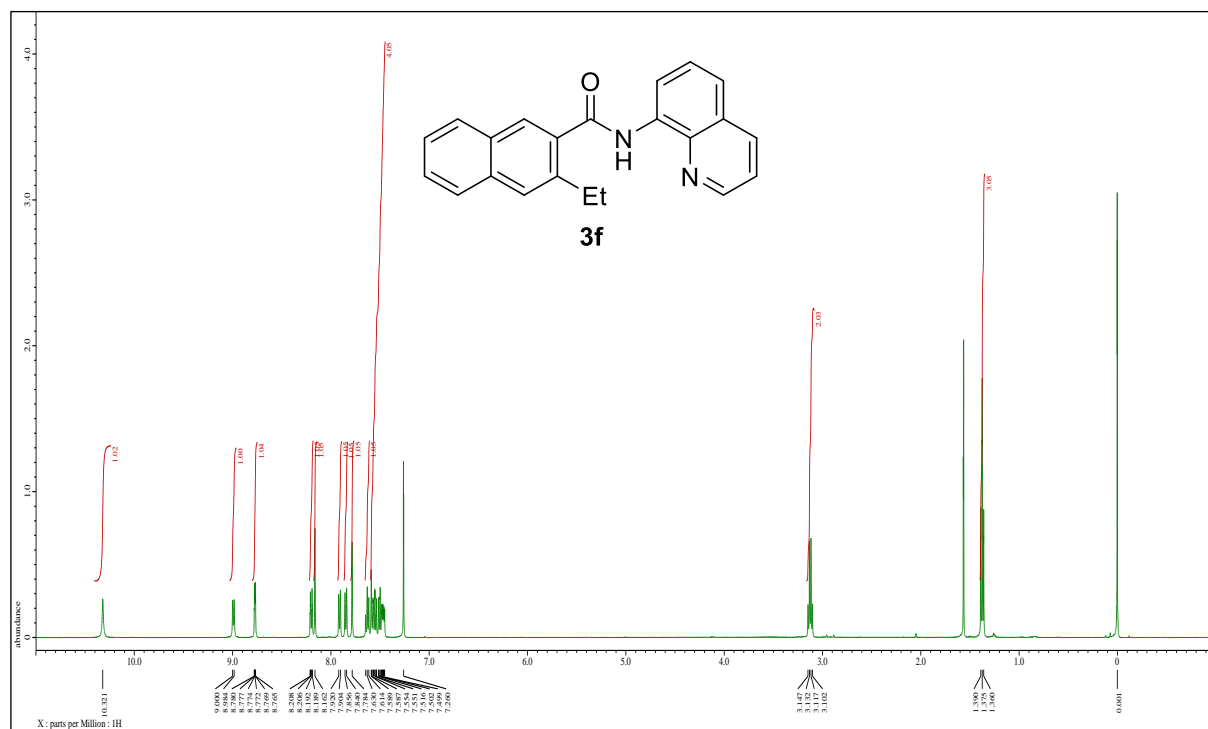
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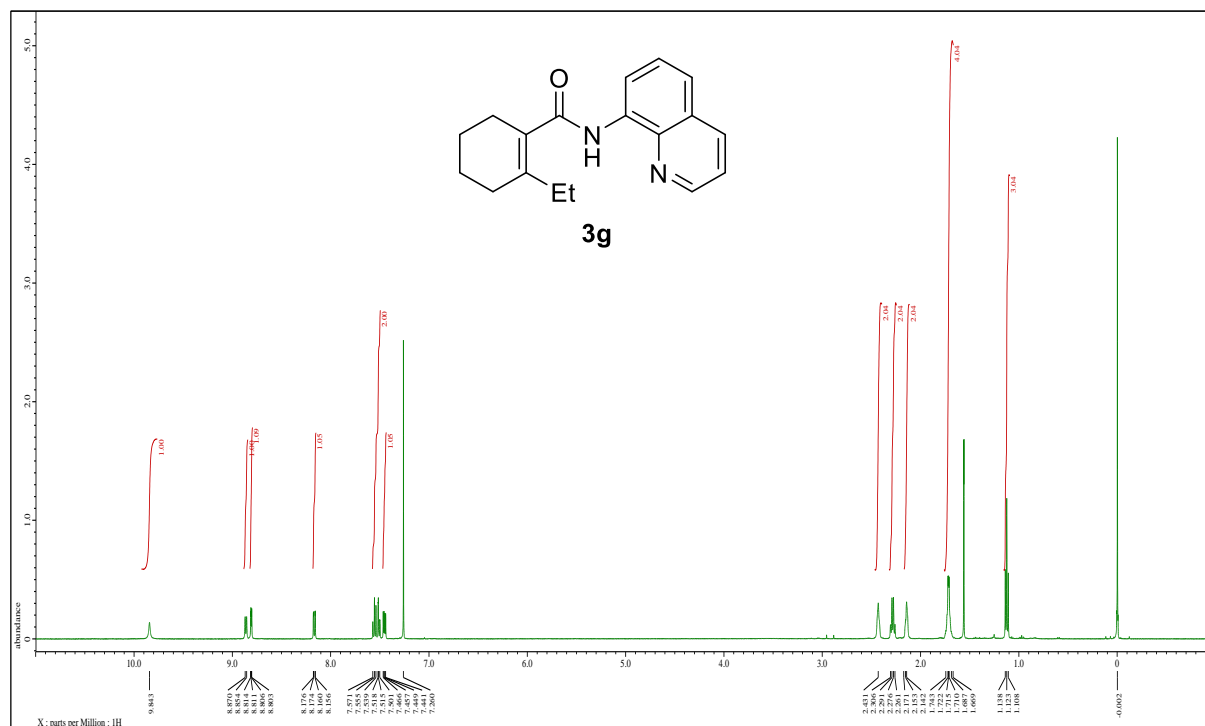
¹H NMR spectrum of **3e** (500 MHz, CDCl₃)



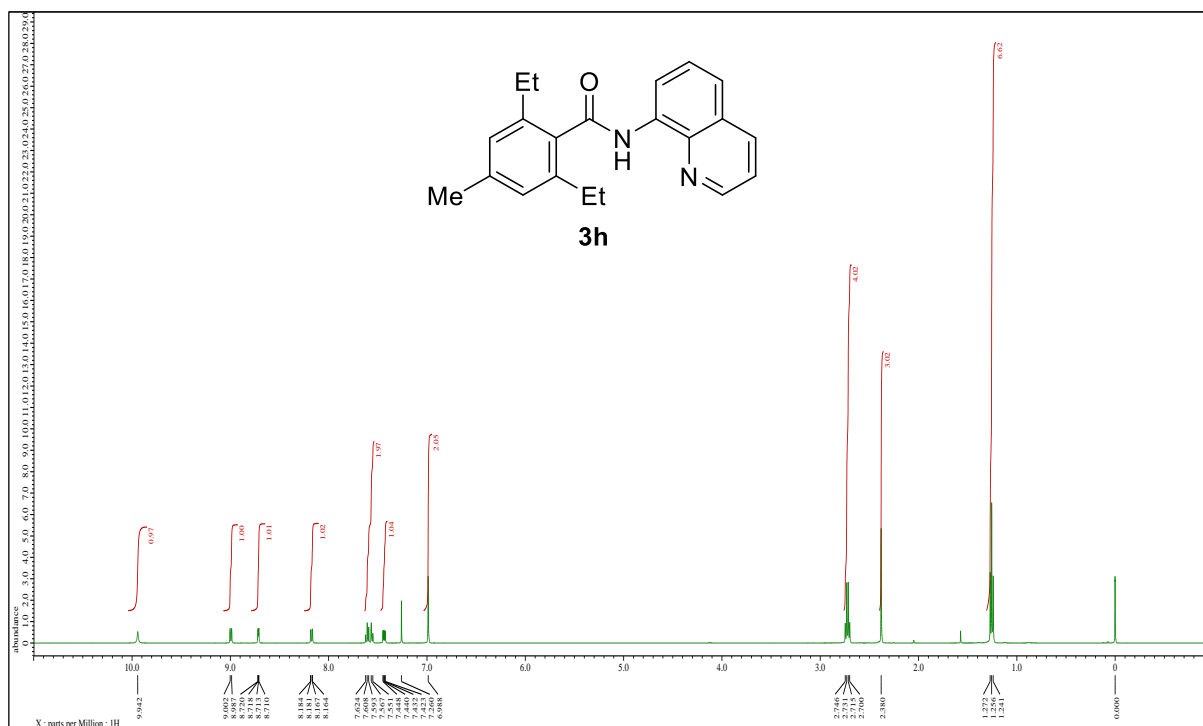
¹H NMR spectrum of **3f** (500 MHz, CDCl₃)



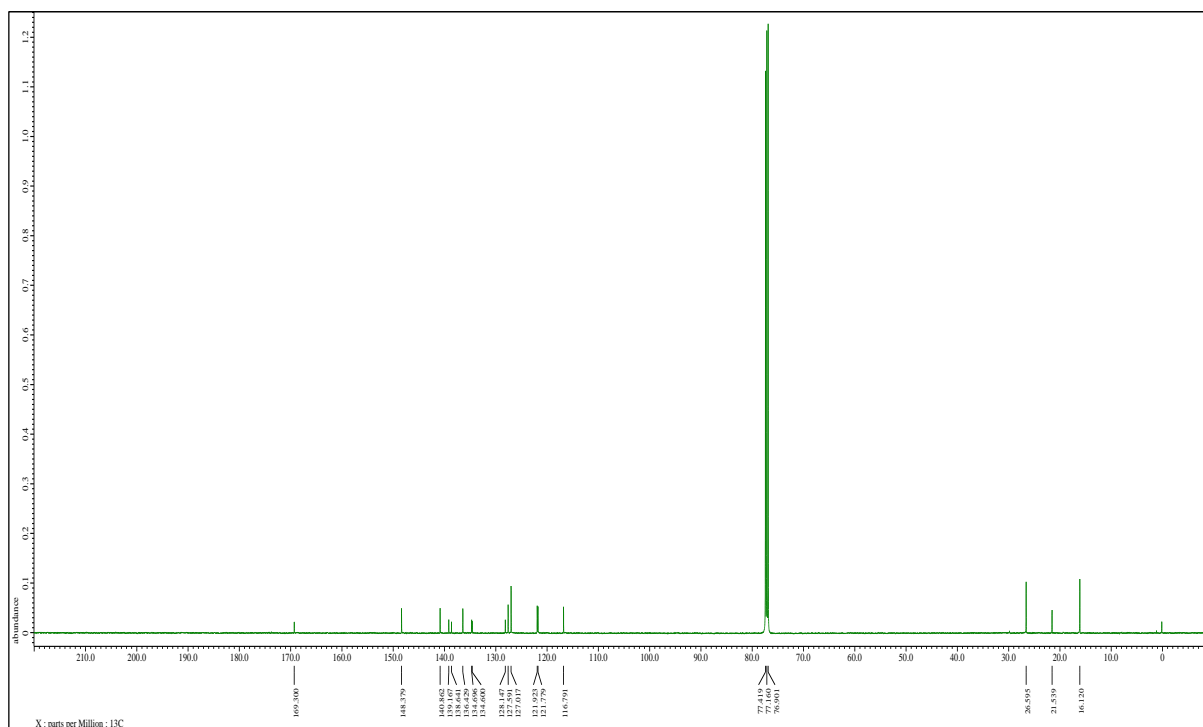
^1H NMR spectrum of **3g** (500 MHz, CDCl_3)



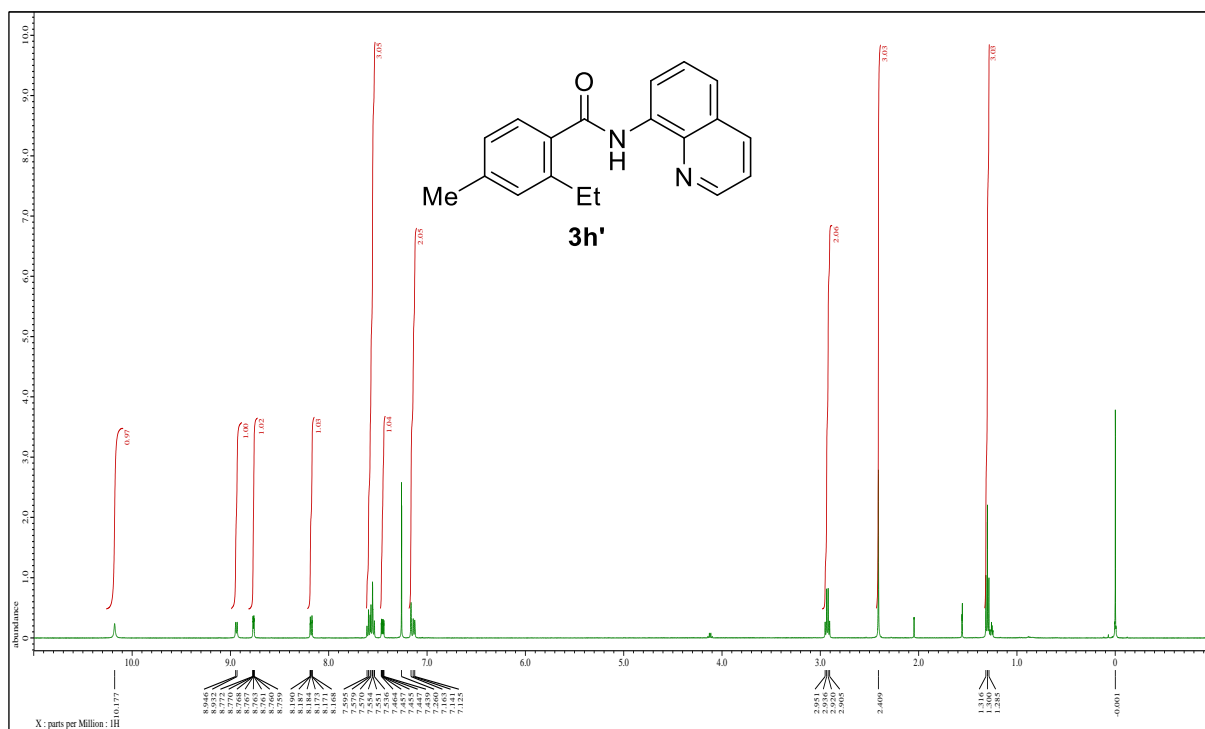
¹H NMR spectrum of **3h** (500 MHz, CDCl₃)



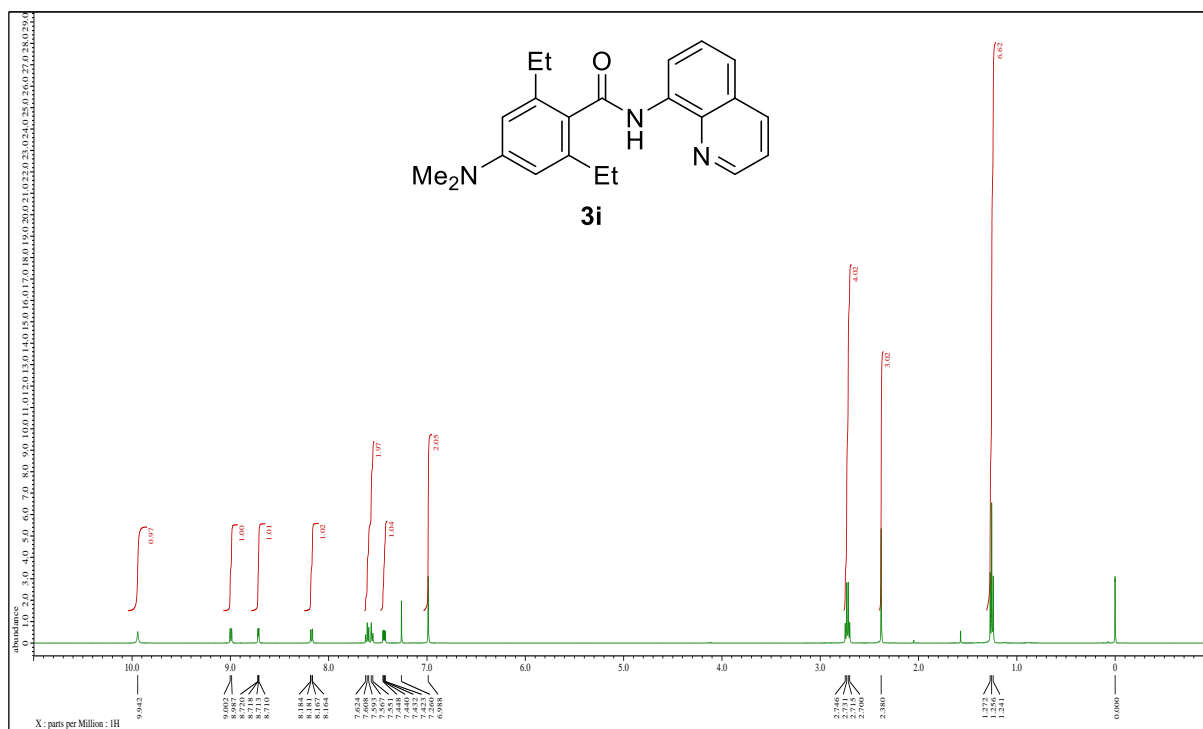
¹³C NMR spectrum of **3h** (125 MHz, CDCl₃)



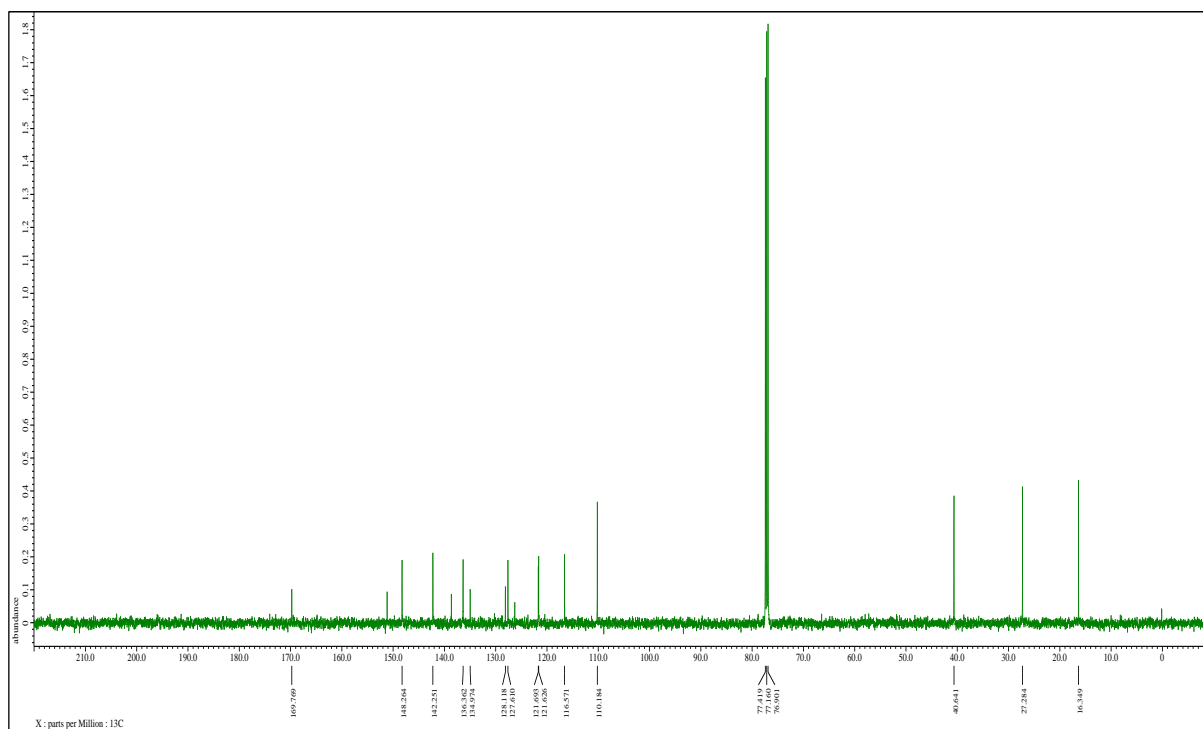
^1H NMR spectrum of **3h'** (500 MHz, CDCl_3)



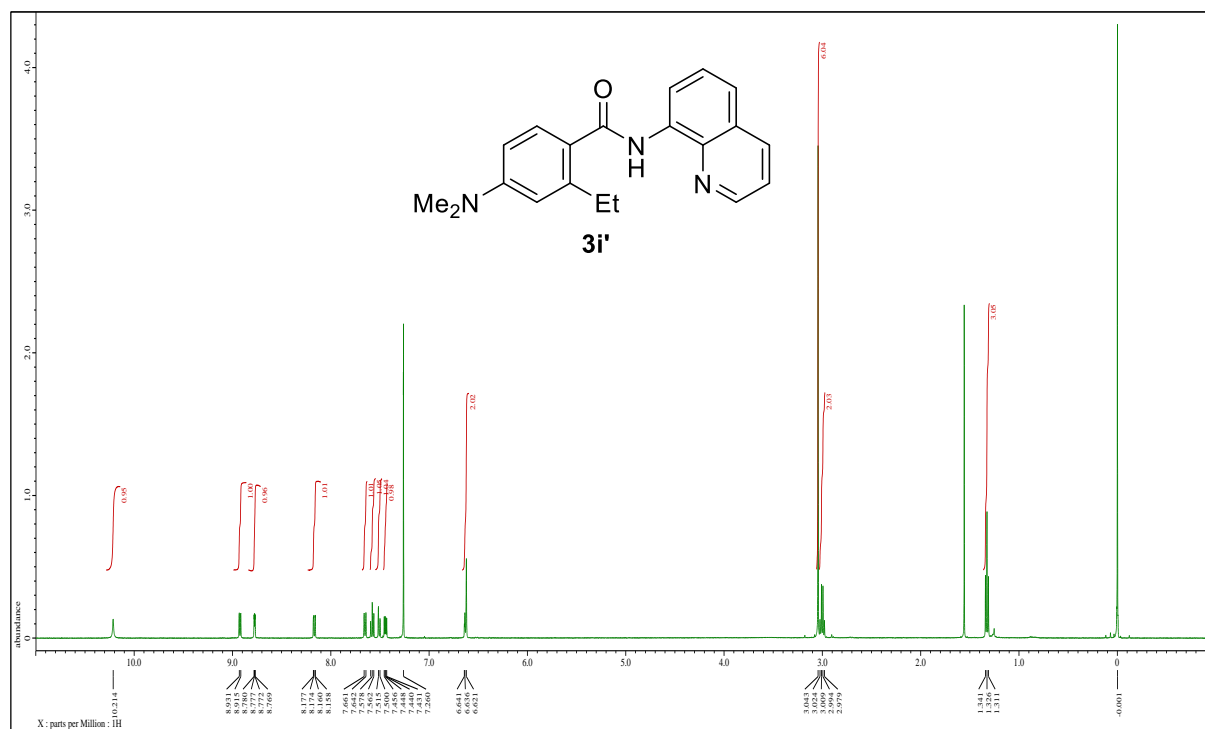
¹H NMR spectrum of **3i** (500 MHz, CDCl₃)



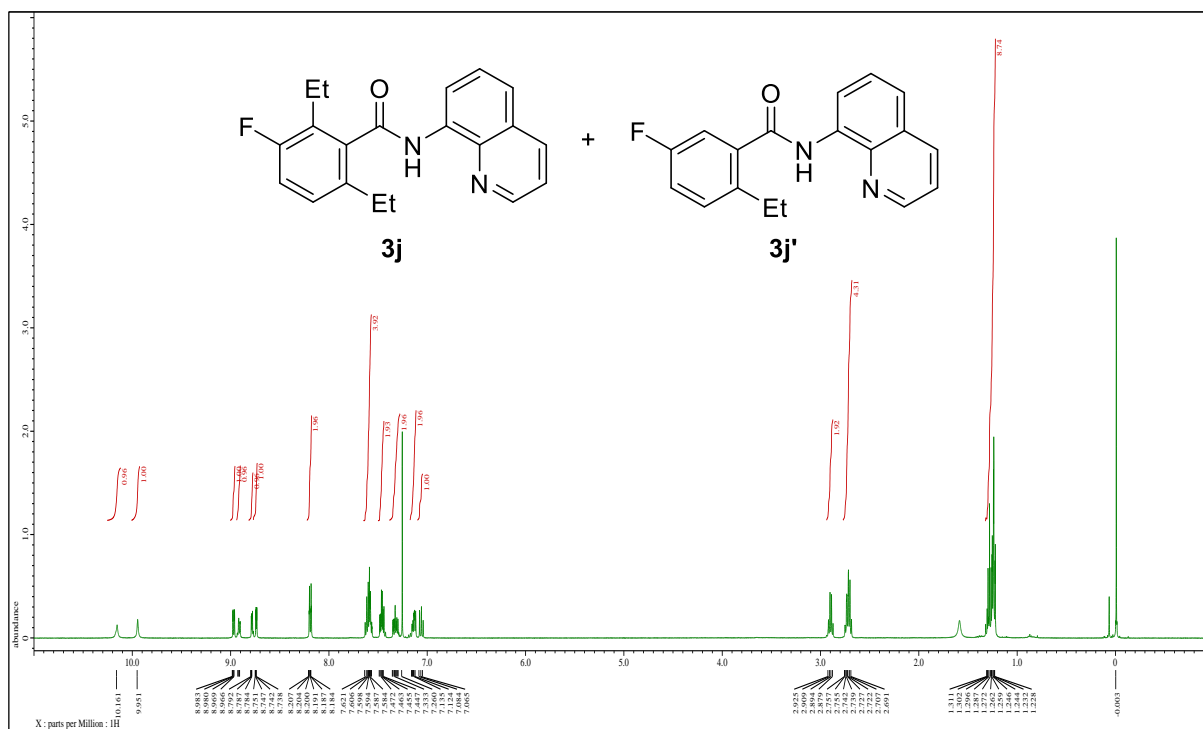
¹³C NMR spectrum of **3i** (125 MHz, CDCl₃)



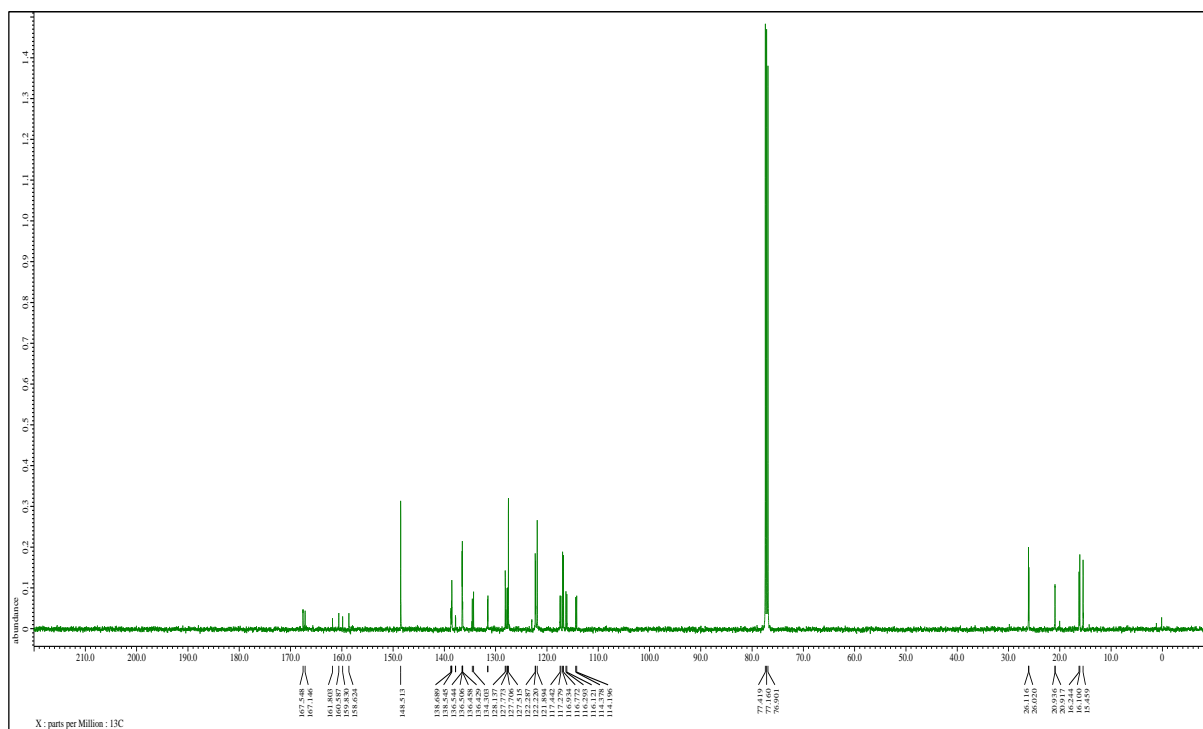
^1H NMR spectrum of **3i'** (500 MHz, CDCl_3)



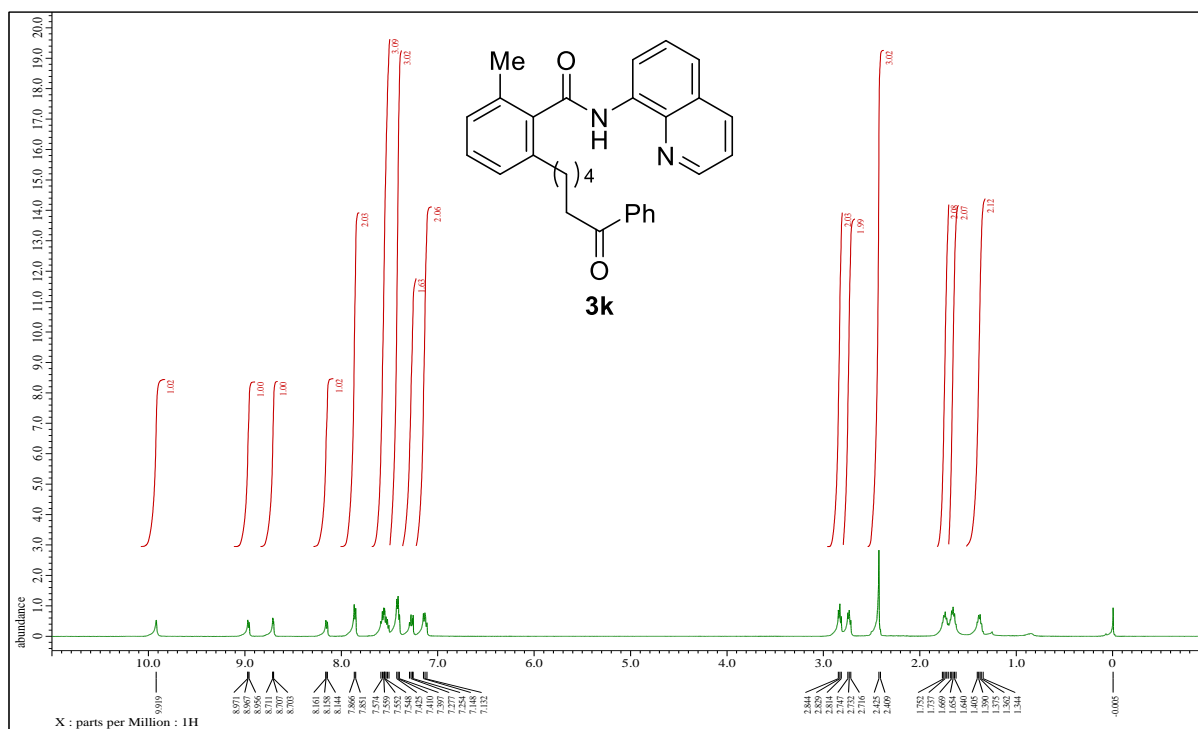
^1H NMR spectrum of **3j** and **3j'** (500 MHz, CDCl_3) (**3j** / **3j'** = 1.0 / 0.96)



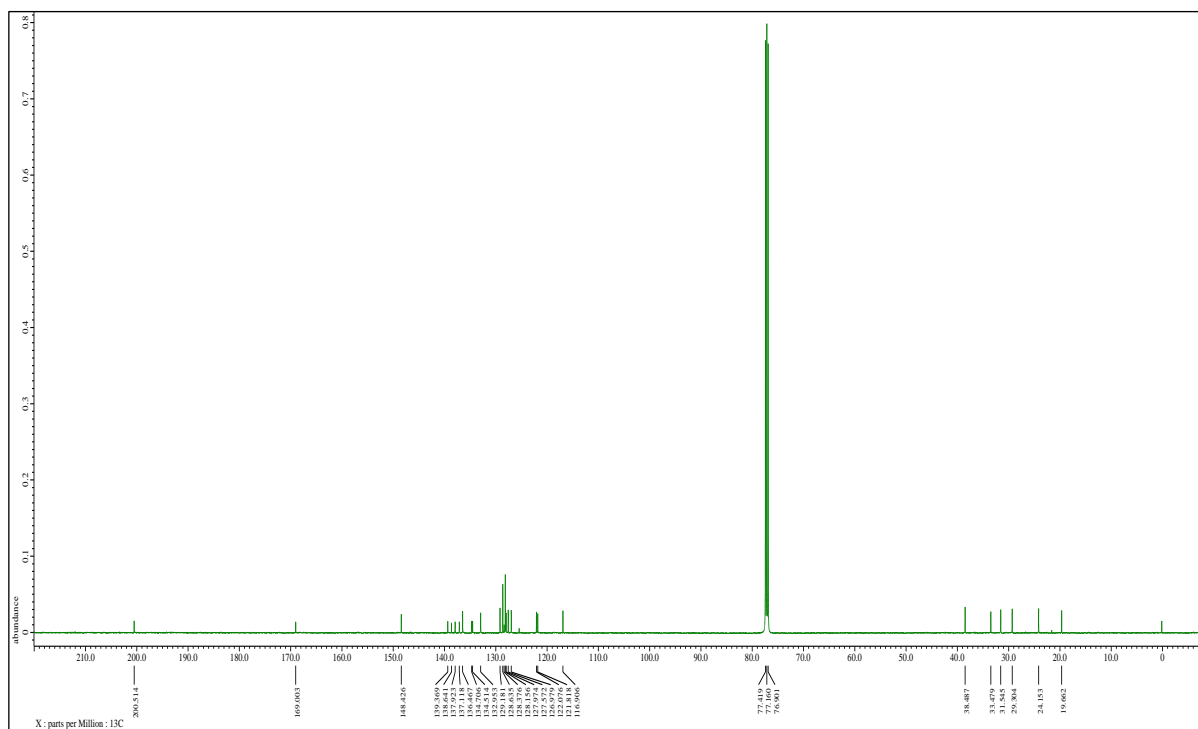
^{13}C NMR spectrum of **3j** and **3j'** (125 MHz, CDCl_3)



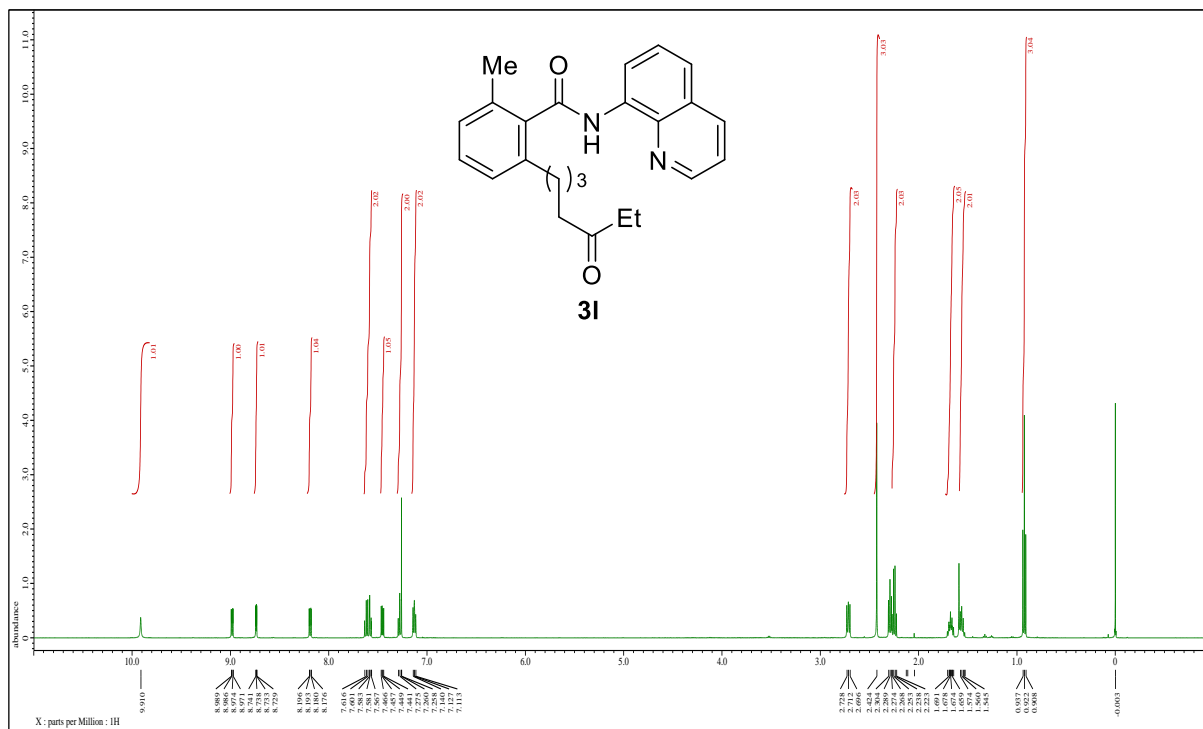
^1H NMR spectrum of **3k** (500 MHz, CDCl_3)



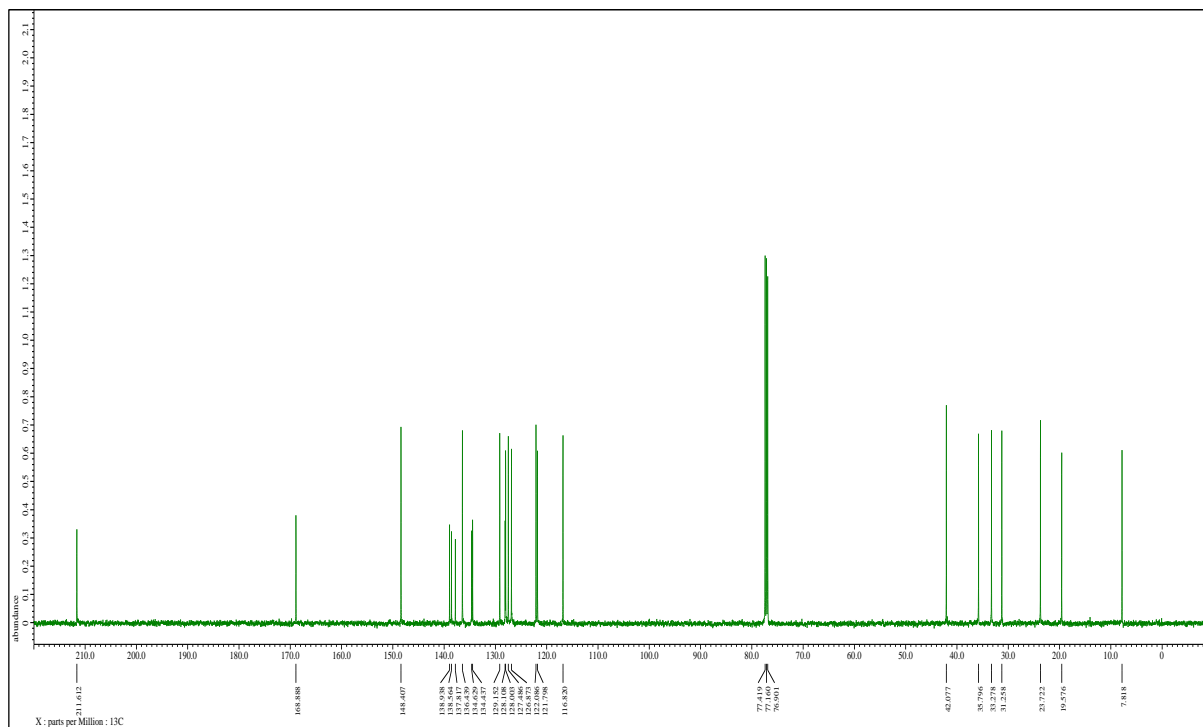
^{13}C NMR spectrum of **3k** (125 MHz, CDCl_3)



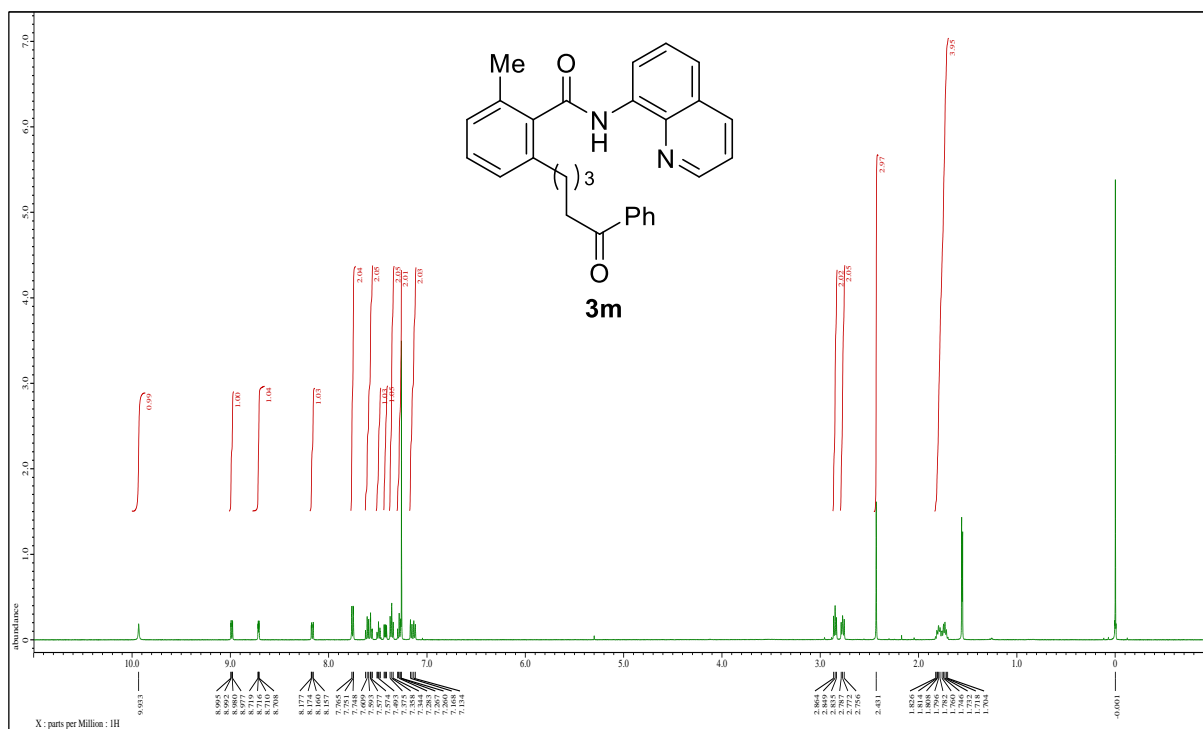
¹H NMR spectrum of **31** (500 MHz, CDCl₃)



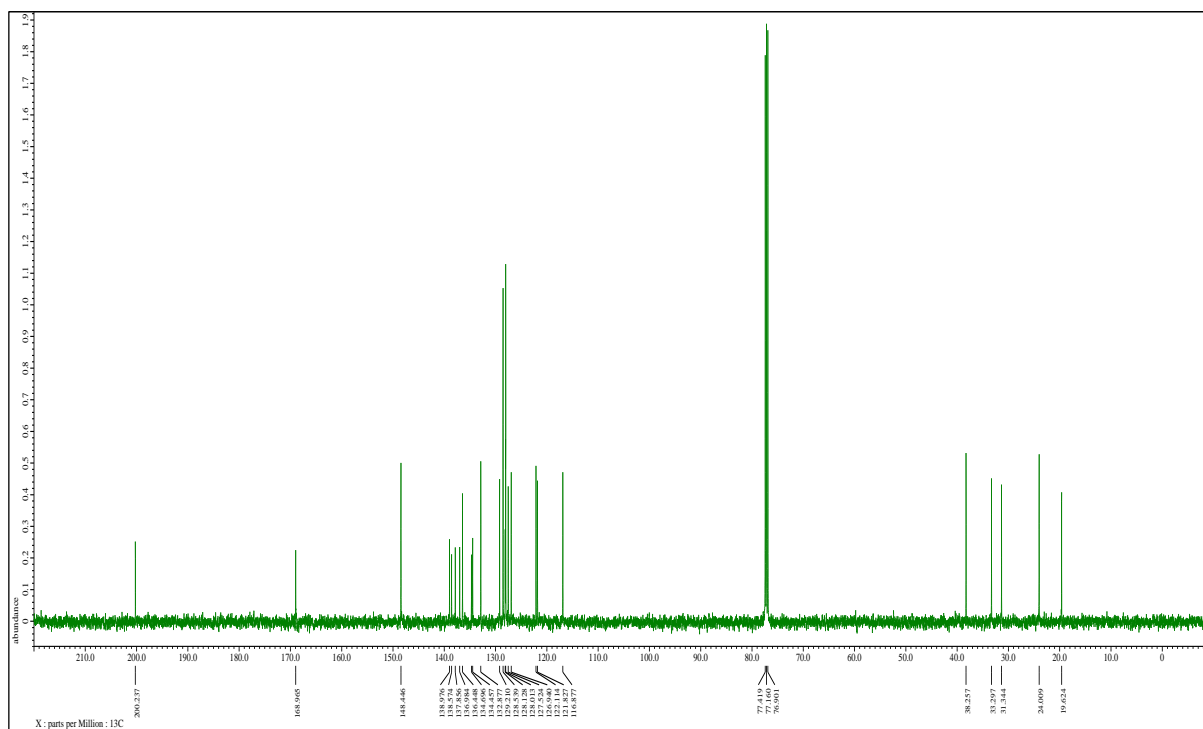
¹³C NMR spectrum of **31** (125 MHz, CDCl₃)



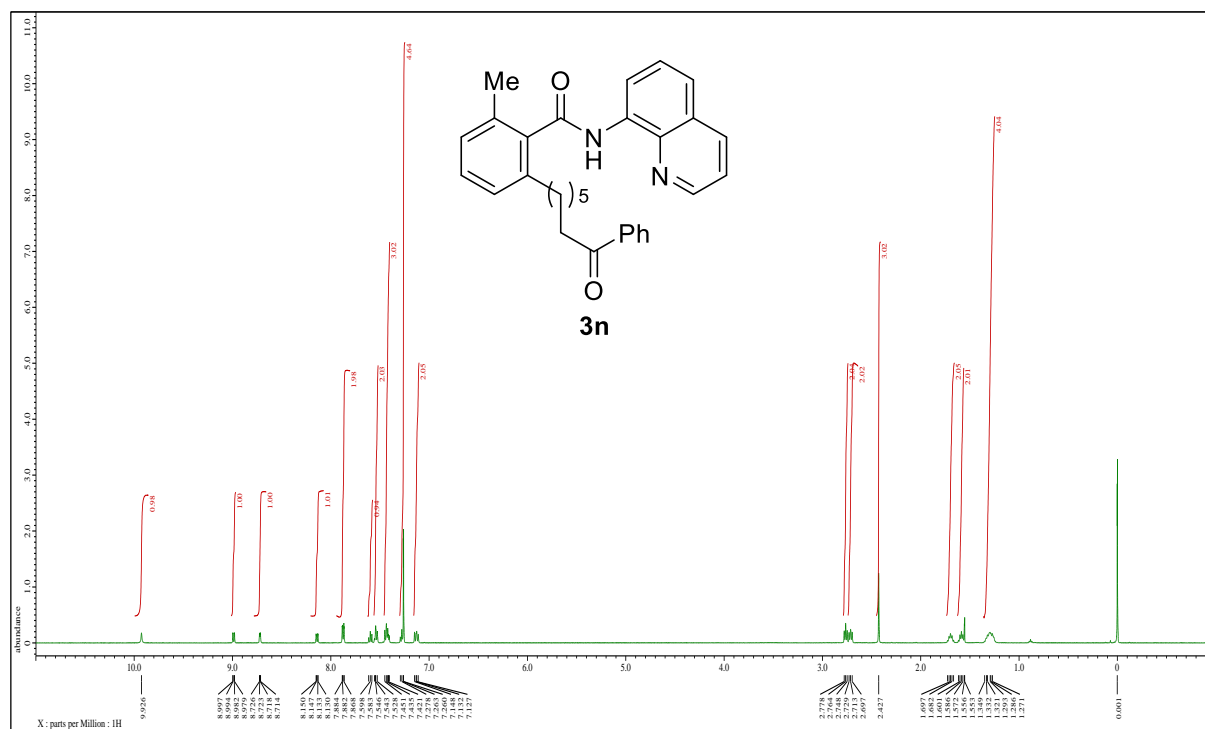
¹H NMR spectrum of **3m** (500 MHz, CDCl₃)



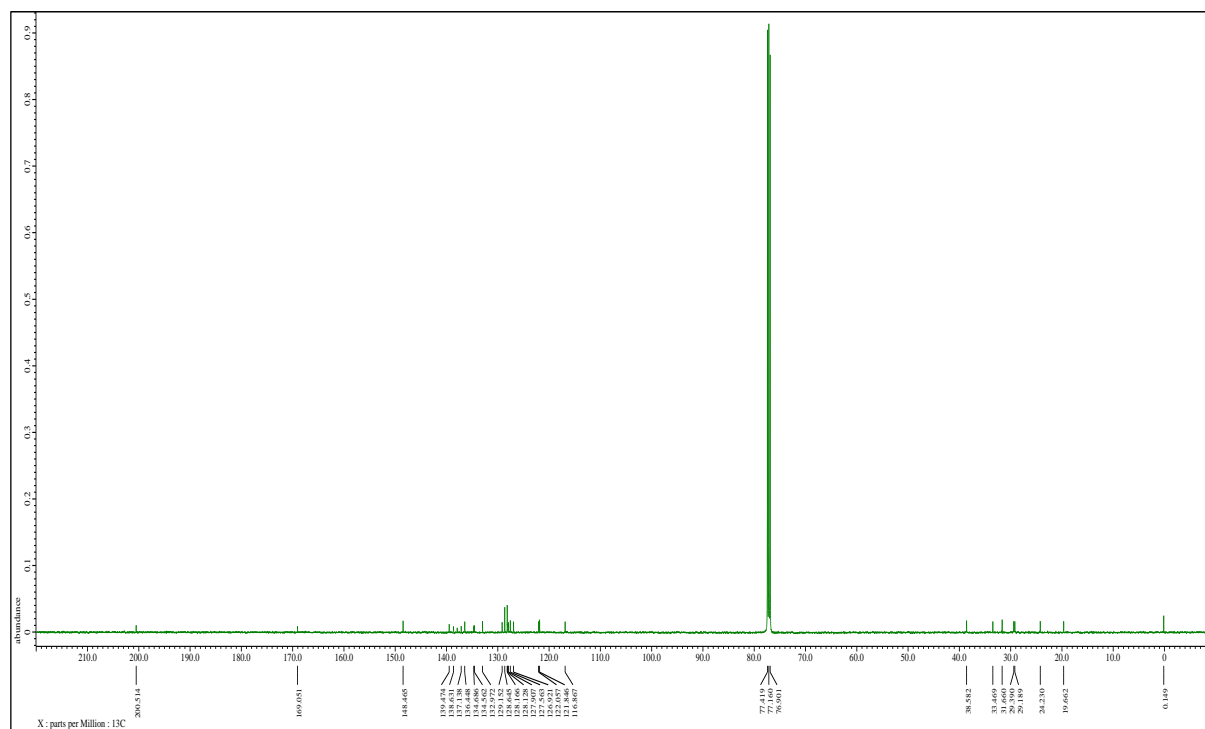
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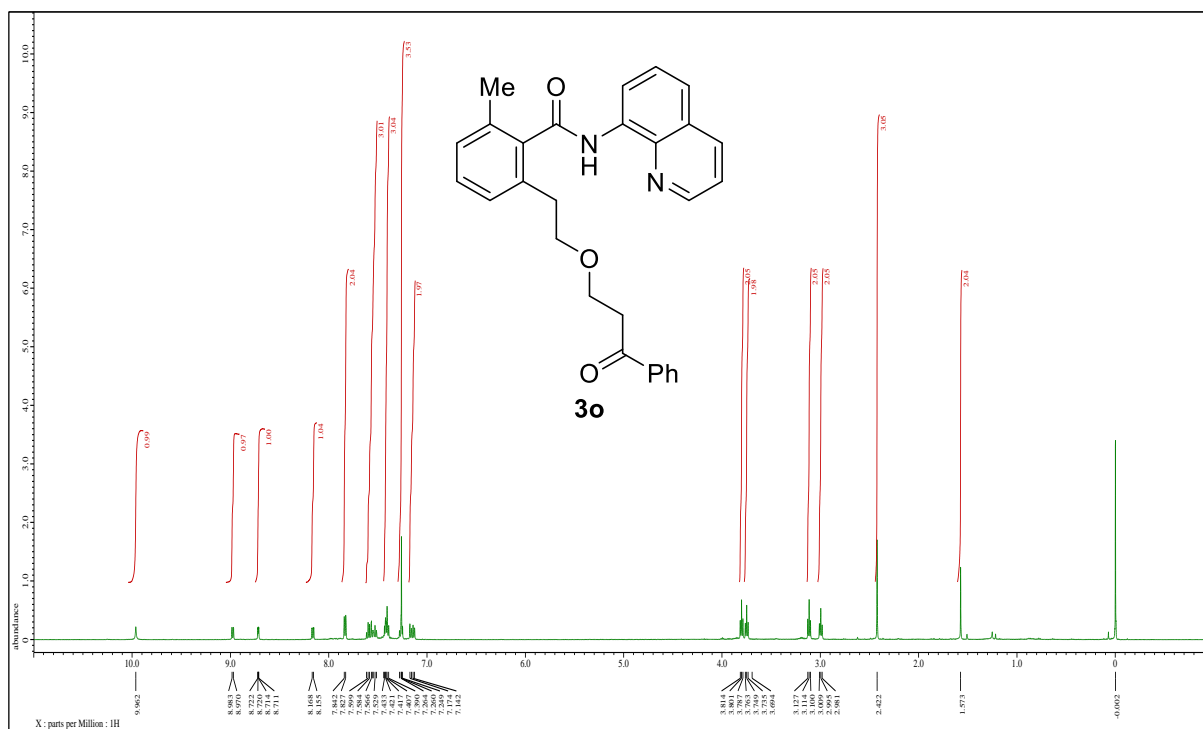
¹H NMR spectrum of **3n** (500 MHz, CDCl₃)



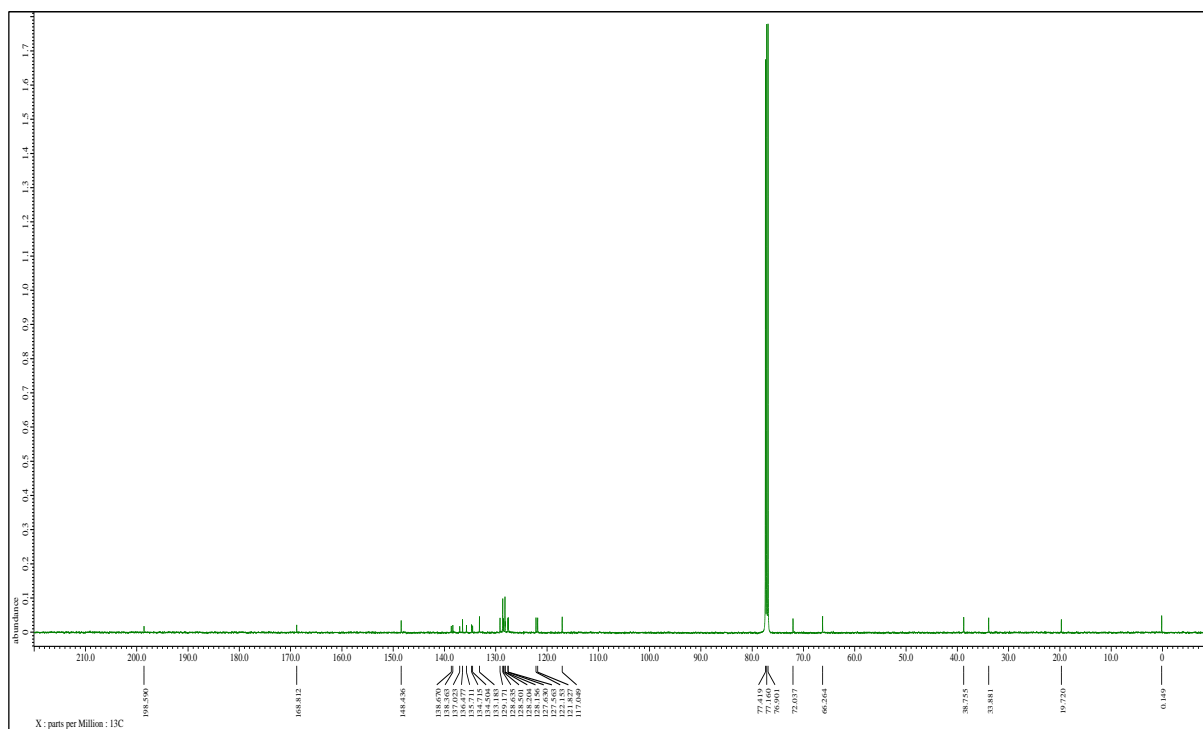
¹³C NMR spectrum of **3n** (125 MHz, CDCl₃)



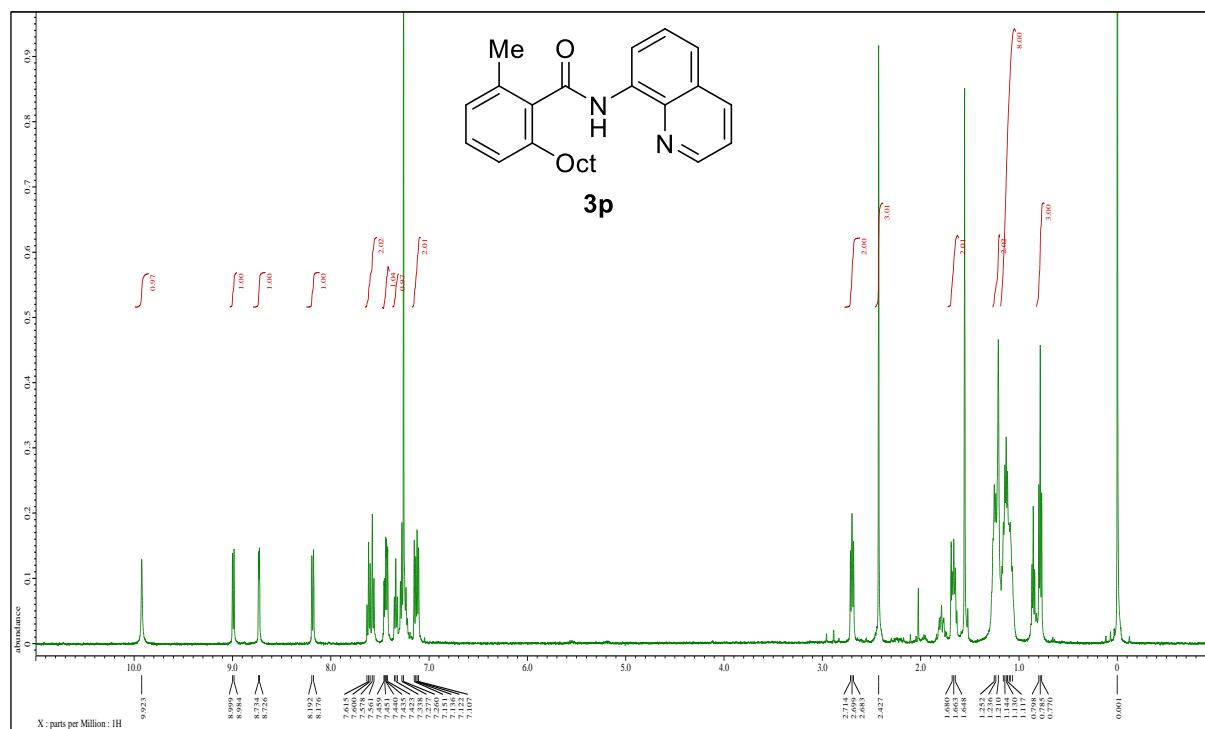
^1H NMR spectrum of **3o** (500 MHz, CDCl_3)



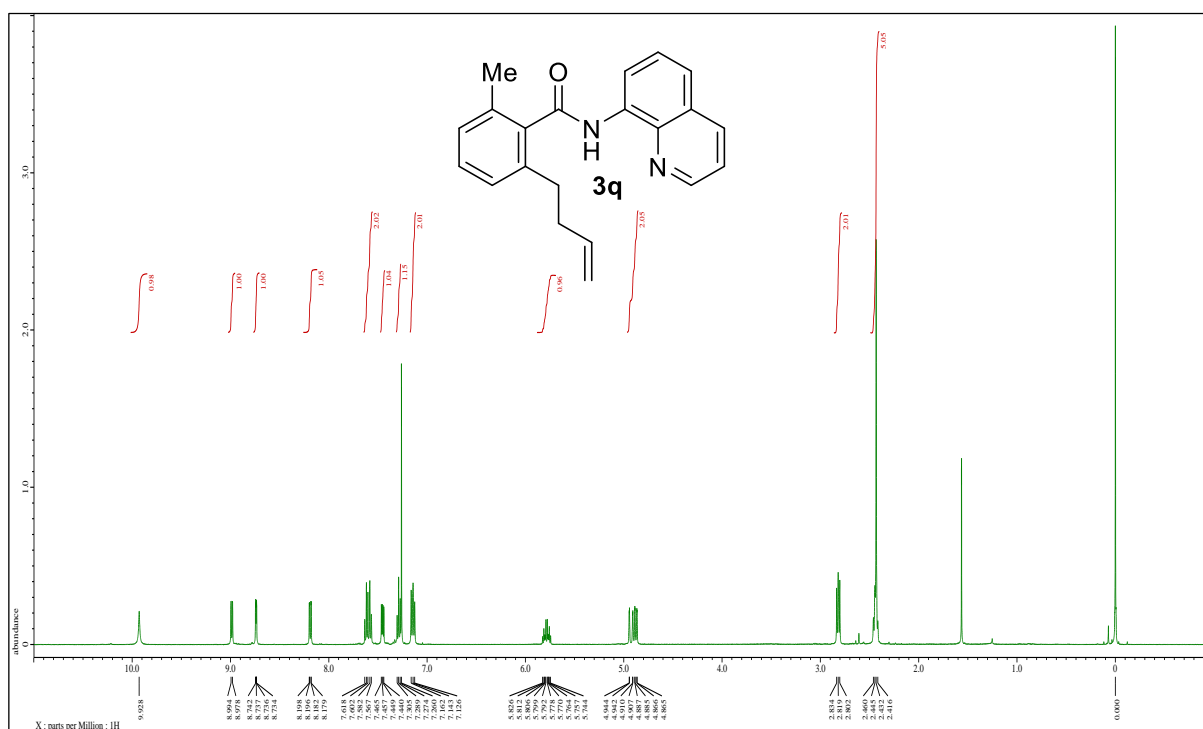
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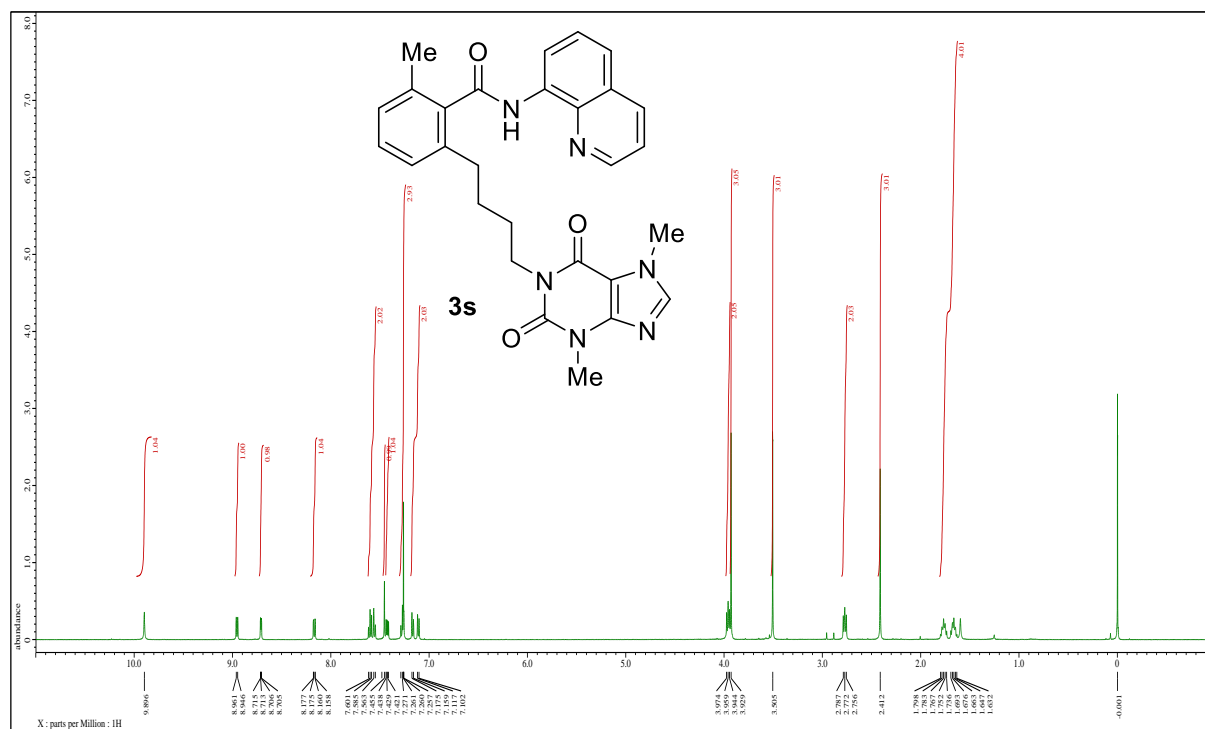
^1H NMR spectrum of **3p** (500 MHz, CDCl_3)



^1H NMR spectrum of **3q** (500 MHz, CDCl_3)



¹H NMR spectrum of **3s** (500 MHz, CDCl₃)



¹³C NMR spectrum of **3s** (125 MHz, CDCl₃)

