Supporting Information

A Stepwise Dearomatization/nitration/enantioselective homoenolate reactions of quinolines to construct C_3-nitro-substituted tetrahydroquinolines

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Experimental Section

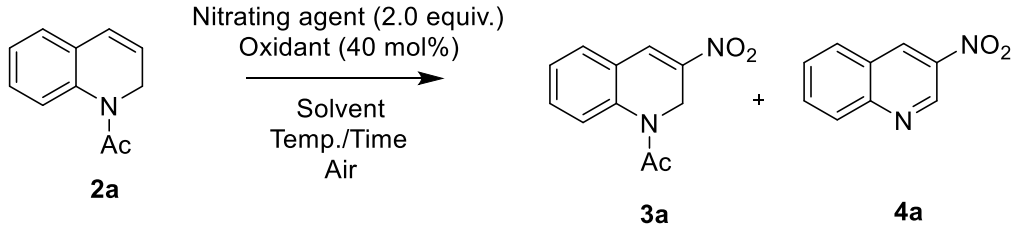
General information

All reactions were conducted using oven-dried glassware under an atmosphere of Argon (Ar). Commercial AR-grade reagents were used without further purification. Solvents were dried and distilled following usual protocols. Toluene was used as received. Flash column chromatography was performed in all cases using the indicated solvent system on silica gel (230-400 mesh). Analytical thin layer chromatography (TLC) was performed on aluminum-backed plates coated with Silica gel 60 with F_{254} indicator (Merck). The ^{1}H-NMR spectra were measured with 400 MHz, and ^{13}C-NMR spectra were recorded with 400 (100 MHz), using $CDCl_3$ as solvent. ^{1}H-NMR chemical shifts are expressed in parts per million (δ) downfield to $CHCl_3$ (δ = 7.26), ^{13}C-NMR chemical shifts are expressed in parts per million (δ) relative to the central $CDCl_3$ resonance (δ = 77.0). Coupling constants in ^{1}H-NMR are in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, dd = doublet of doublets, dt = doublet of triplet, td = triplet of doublet, ddd = doublet of doublet of doublet. Electro spray ionization (ESI) mass spectrometry (MS) experiments were performed on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. IR spectra were recorded using NICOLET IS5 FTIR with KBr window. Melting point was determined by Labtronics LT-115 digital melting/boiling point apparatus (Indian make). Specific rotation was recorded in Labman digital polarimeter.

All the cinnamaldehyde derivatives **(5)** were synthesized according to the reported literature procedure[1a]. All quinolines **(1)** were purchased from commercial suplier. NHC-cat. **6a**, **6b** and **6c** were prepared according to the standard literature procedure[2], [3].

Optimization Details:

Table 1: Optimization by varying different Nitrating agent, Oxidant and solvents[a]

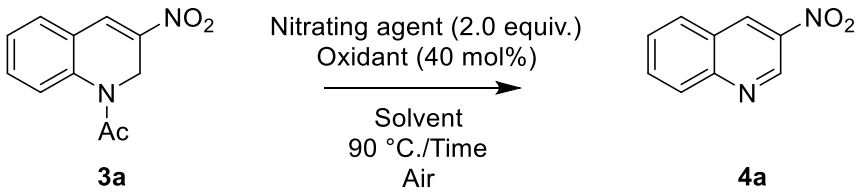


2a **3a** **4a**

Entry	Nitrating agent	Oxidant	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]	
						3a	**4a**
1	^{t}BuONO	TEMPO	1,4-dioxane	90	12	53	34
2	^{t}BuONO	TEMPO	1,4-dioxane	90	24	-	94
3	$AgNO_2$	TEMPO	1,4-dioxane	90	24	<10	54
4	$AgNO_3$	TEMPO	1,4-dioxane	90	24	NR	NR
5	$Fe(NO_3)_3.9H_2O$	TEMPO	1,4-dioxane	90	24	20	32
[6c]	^{t}BuONO	DDQ	1,4-dioxane	90	24	38	52
7[c]	^{t}BuONO	BPO	1,4-dioxane	90	24	15	35
8	^{t}BuONO	TEMPO	1,4-dioxane	rt	10	90	-
9	^{t}BuONO	TEMPO	DCM	rt	32	65	-
10	^{t}BuONO	TEMPO	CH_3CN	rt	36	60	Trace
11	^{t}BuONO	TEMPO	THF	rt	34	53	-
12	^{t}BuONO	TEMPO	Toluene	rt	29	40	-
13[c]	^{t}BuONO	DDQ	1,4-dioxane	rt	3	38	Trace
14[c]	^{t}BuONO	BPO	1,4-dioxane	rt	4	35	Trace
15	^{t}BuONO	4-oxo-TEMPO	1,4-dioxane	rt	24	48	-
16	^{t}BuONO	-	1,4-dioxane	rt	24	32	-
17[d]	^{t}BuONO	TEMPO	1,4-dioxane	rt	24	68	-

[a]Reaction conditions: unless indicated otherwise, 1,2-dihydroquinoline **2a** (0.17 mmol, 1.0 equiv.), nitrating agent (2.0 equiv.), oxidant (40 mol%), solvent (0.8 mL), 90 °C or rt (~30 °C) under open air conditions. [b]Isolated yield after column chromatography. [c]A non-desired and uncharacterized product was formed. [d] ^{t}BuONO was used 1.0 equiv. NR = No reaction. rt = Room temperature. TEMPO = (2,2,6,6-Tetramethylpiperidin-yl)oxyl. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. BPO = Benzoyl peroxide.

Table 2: Reaction with or without Nitrating agent or Oxidant[a]

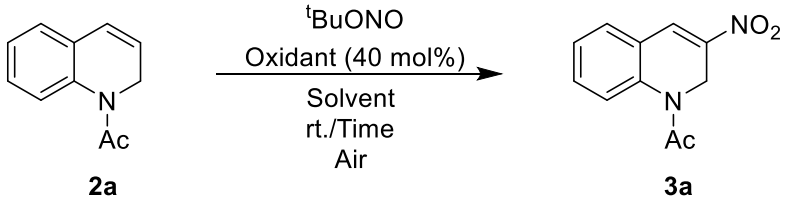


3a **4a**

Entry	Nitrating agent	Oxidant	Solvent	Time (h)	Yield (%)[b]
1[c]	-	-	1,4-dioxane	18	<10
2[c]	-	TEMPO	1,4-dioxane	18	<10
3	^{t}BuONO	-	1,4-dioxane	15	94
4	^{t}BuONO	TEMPO	1,4-dioxane	24	94

[a]Reaction conditions: unless indicated otherwise, 1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one **3a** (0.14 mmol, 1.0 equiv.), nitrating agent (2.0 equiv.), oxidant (40 mol%), solvent (0.7 mL), 90 °C under open air conditions. [b]Isolated yield after column chromatography. [c]1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one **3a** was not completely consumed (72% recovered).

Table 3: Optimization by varying amount of ^{t}BuONO[a]



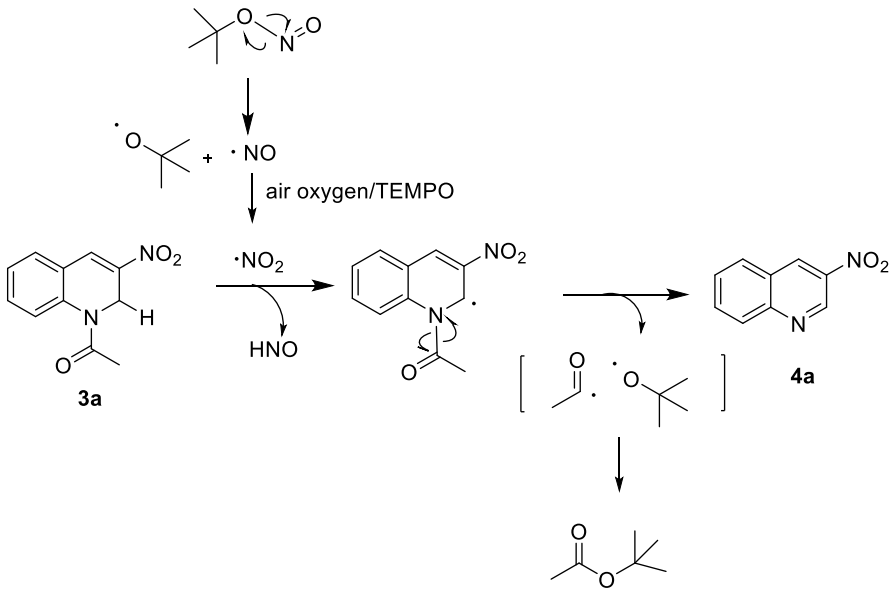
2a **3a**

Entry	^{t}BuONO (equiv.)	Oxidant	Solvent	Time (h)	Yield (%)[b]
1[c]	1.0	-	1,4-dioxane	24	45
2[c]	2.0	-	1,4-dioxane	20	47
3	1.0	TEMPO	1,4-dioxane	24	68

[a]Reaction conditions: unless indicated otherwise, 1-(quinolin-1(2*H*)-yl)ethan-1-one **2a** (0.17 mmol, 1.0 equiv.), nitrating agent, oxidant (40 mol%), solvent (0.8 mL), under open air conditions. [b]Isolated yield after column chromatography. [c]A non-desired and uncharacterized product was formed.

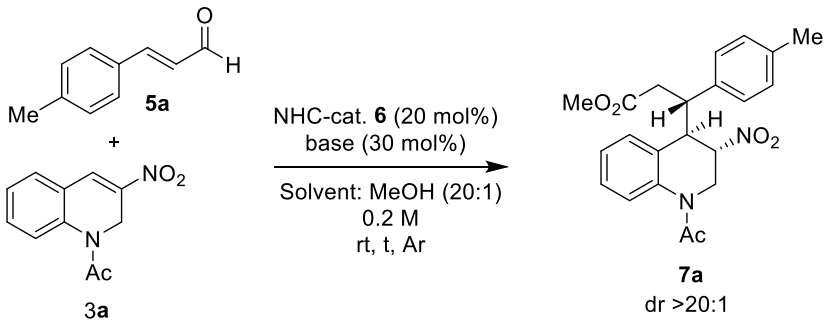
We observed a divergent nitration of 1,2-dihydroquinolines via control of temperature to give 3-nitro-1,2-dihydroquinolines (at room temperature) or 3-nitroquinolines (at elevated temperature) under the optimized conditions. To gain more insight into the mechanism, a few control experiments were conducted (**Table 2**). When, the substrate 3-nitro-1,2-dihydroquinoline (**3a**) was subjected to react in the presence of TBN (2.0 equiv), the 3-nitroquinoline (**4a**) was formed exclusively in 94% yield after 15 h (entry 3).

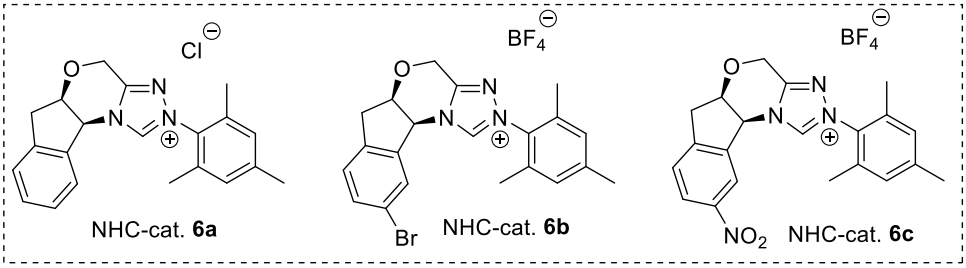
Probably, at high temperature (90 °C), the deacylation reaction takes place via the following reaction mechanism (Scheme 1). Under the optimized conditions (TBN/TEMPO and air oxygen), nitro radical abstracts C2-H to generate the intermediate I. Next, N-C bond cleavage forms acyl radical and affords 3-nitroquinoline. Finally, the recombination of acyl radical and *tert*-butoxide radical gives *tert* butyl acetate, which could be removed during work-up. However, we could not able to isolate any relevant intermediate or any by-product by NMR or GC-MS for direct proof. Thus, the probable deacylation mechanism is not included in the main draft. However, the control experiments including the plausible mechanism of deacylation reaction have been included in the ESI.



Scheme 1: Deacylation mechanism for the preparation of 3-nitroquinolines (plausible)

Table 4: Optimization of homoenolate addition reaction[a]

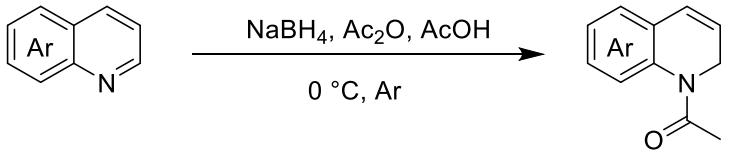




Entry	NHC cat. **6**	Base	Solvent	Time (t)	Yield (%)[b]	ee (%)[c]
1	**6a**	K_3PO_4	Toluene	12	73	85
2	**6b**	K_3PO_4	Toluene	15	78	87
3	**6c**	K_3PO_4	Toluene	24	51	81
4	**6b**	DBU	Toluene	18	72	41
5	**6b**	Et_3N	Toluene	18	41	43
6	**6b**	K_2CO_3	Toluene	14	72	64
7	**6b**	Cs_2CO_3	Toluene	15	61	65
8	**6b**	$KHCO_3$	Toluene	15	88	94
9	**6b**	$NaHCO_3$	Toluene	15	73	89
10	**6b**	KOAc	Toluene	16	70	88
11	**6b**	KCO_2Ph	Toluene	15	78	82
12	**6b**	$KHCO_3$	THF	18	78	82
13	**6b**	$KHCO_3$	DCM	16	80	78
14	**6b**	$KHCO_3$	Mesitylene	18	82	90
15	**6b**	$KHCO_3$	Et_2O	16	67	82
16	**6b**	$KHCO_3$	1,4-dioxane	16	71	83
17[d]	**6b**	$KHCO_3$	Toluene	20	68	93

[a]Reaction conditions: Unless indicated otherwise, the reaction of *p*-tolylcinnamaldehyde **5a** (40 mg, 0.27 mmol, 1.2 equiv), 3-nitro-1,2-dihydroquinoline **3a** (50 mg, 0.23 mmol, 1.0 equiv), NHC-cat. **6** (20 mol%) and base (30 mol%) was stirred in solvent:MeOH (0.2 M) at rt under Ar atmosphere. [b]Yield of the isolated product. [c]The ee values were determined by HPLC using a chiral stationary phase. [d]NHC-cat. **6b** was used in 15 mol%. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

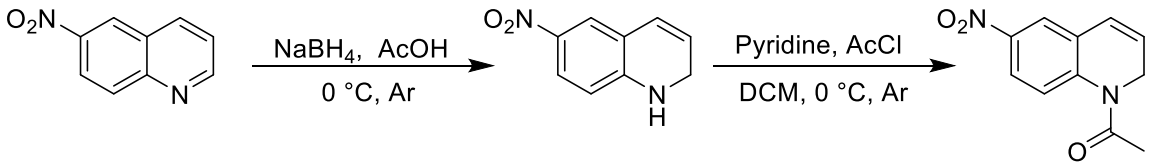
General procedure I: *Synthesis of substituted 1-(quinolin-1(2H)-yl)ethan-1-one[4]* ***(2)***



1 **2**

Sodium borohydride (4.0 equiv.) was gradually added to a mixture of quinoline **(1)** (1.0 equiv.), acetic anhydride (5.0 equiv.), and acetic acid (0.6 M) over a period of 1.5 h at 0 ˚C. After the addition was complete, the mixture was warmed to 50 ˚C for 30 min. The reaction mixture was concentrated under a vacuum, diluted with water (100 mL/gm), and neutralized with sodium carbonate. This was then extracted with DCM, and the organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude oil was purified by silica gel column chromatography (eluent: Petroleum ether:EtOAc).

Procedure for the synthesis of 1-(6-nitroquinolin-1(2H)-yl)ethan-1-one[4] (2f)

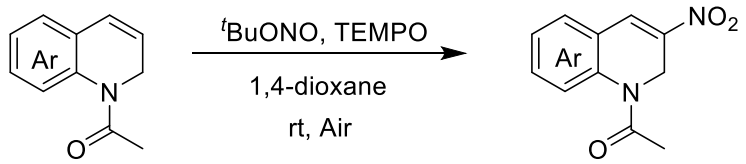


1f **2f**

To an ice-cold solution of 6-nitroquinoline **(1f)** (0.5 g, 2.87 mmol) in acetic acid (3 mL) was added sodium borohydride (0.108 g, 2.87 mmol) in small portions (reaction was monitored by TLC). Upon completion of the reaction, the mixture was carefully poured into crushed ice and filtered. The reddish-brown solid that was obtained, was dried well and used without purification for the next step (crude yield 85%).

To an ice-cold solution of 6-nitro-1, 2-dihydroqunoline (0.43 g, 2.44 mmol), pyridine (1.2 mL, 14.65 mmol) in DCM (8 mL) was added acetyl chloride (0.5 mL, 7.32 mmol), dropwise, and the resulting mixture was stirred for an hour at the same temperature before being warmed to room temperature and stirred for next 16 h. Upon dilution with EtOAc, the mixture was washed with water and brine. The organic fraction was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (30% Ethyl acetate in Petroleum ether, R_f = 0.2). Yield: 0.372 g, 70%; Physical appearance: Greenish-yellow solid.

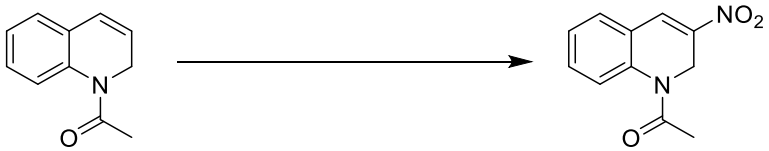
General procedure II: *Synthesis of substituted 1-(3-nitroquinolin-1(2H)-yl)ethan-1-one[5]* ***(3)***



2 **3**

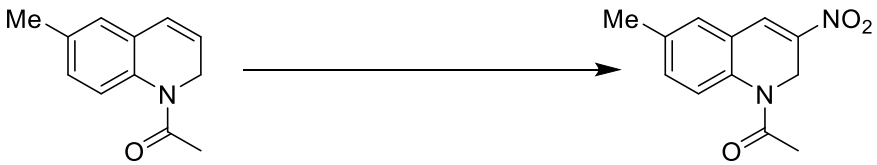
In an oven-dried round bottom flask, 1-(quinolin-1(2*H*)-yl)ethan-1-one **(2)** (1.0 equiv.) was dissolved in 1,4-dioxane (0.2 M) and added TEMPO (0.4 equiv.), and ^{t}BuONO (2.0 equiv.). The reaction mixture was stirred at room temperature in an open air. When the reaction was completed (checked by TLC), the reaction mixture was extracted with ethyl acetate, and the organic fraction was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography.

Spectral data of 1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one derivatives:



2a **3a**

1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3a)**: Prepared according to the general reaction procedure **II** using 1-(quinolin-1(2*H*)-yl)ethan-1-one **(2a)** (500 mg, 2.887 mmol), ^{t}BuONO (600 mg, 5.773 mmol) and TEMPO (180 mg, 1.154 mmol) in 1,4-dioxane at rt in 10 h to obtain **3a** (567 mg, 90%) as yellow solid (20% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 92-94 °C; **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ 7.82 (s, 1H), 7.46-7.24 (m, 4H), 5.00 (s, 2H), 2.25 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz): δ 169.9, 138.0, 131.6, 130.4, 129.4, 126.5, 125.2, 124.5, 40.8, 22.6; **HRMS** (EI) calcd for $C_{11}H_{10}N_2O_3$, 241.05891 *m/z* $(M+Na)^+$; Found, 241.05888 *m/z*; **FTIR (cm^{-1}):** 1644, 1564, 1491, 1373, 1321, 1250, 1228, 760.



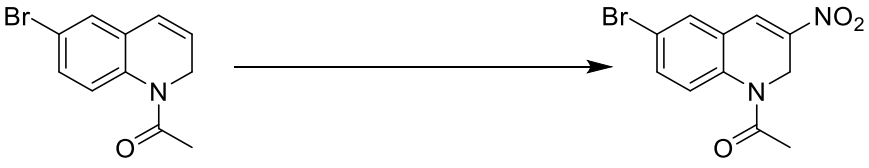
2b **3b**

1-(6-methyl-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3b)**: Prepared according to the general reaction procedure **II** using 1-(6-methylquinolin-1(2*H*)-yl)ethan-1-one **(2b)** (100 mg, 0.534

mmol), ^{t}BuONO (110 mg, 1.068 mmol) and TEMPO (33 mg, 0.214 mmol) in 1,4-dioxane at rt in 1 h to obtain **3b** (100 mg, 81%) as yellow solid (15% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 140-142 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.77 (s, 1H), 7.25-7.20 (m, 3H), 4.98 (s, 2H), 2.37 (s, 3H), 2.23 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ169.9, 136.5, 135.6, 132.3, 130.7. 124.3, 56.8, 35.1, 27.6, 22.5, 20.8; **HRMS** (EI) calcd for $C_{12}H_{12}N_2O_3$, 255.07456 *m/z* $(M+Na)^+$; Found, 255.07442 *m/z*; **FTIR (cm^{-1}):** 1659, 1509, 1321, 1239, 1205, 1072, 938, 831, 717.

2c **3c**

1-(6-methoxy-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3c)**: Prepared according to the general reaction procedure **II** using 1-(6-methoxyquinolin-1(2*H*)-yl)ethan-1-one **(2c)** (200 mg, 0.984 mmol), ^{t}BuONO (202 mg, 1.968 mmol) and TEMPO (62 mg, 0.394 mmol) in 1,4-dioxane at rt in 4 h to obtain **3c** (200 mg, 82%) as yellow solid (30% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 128-130 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.79 (s, 1H), 7.27 (s, 1H), 6.99 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.94 (d, *J* = 2.2 Hz, 1H), 5.00 (s, 2H), 3.85 (s, 3H), 2.22 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 169.8, 157.7, 131.3, 129.4, 125.6, 125.4, 117.2, 114.6, 55.8, 27.2, 24.0; **HRMS** (EI) calcd for $C_{12}H_{12}N_2O_4$, 271.06948 *m/z* $(M+Na)^+$; Found, 271.06950 *m/z*; **FTIR (cm^{-1}):** 1622, 1498, 1375, 1266, 1036, 845, 716.



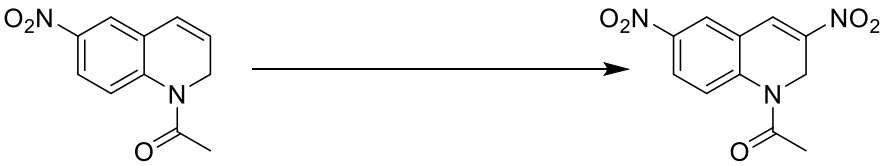
2d **3d**

1-(6-bromo-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3d)**: Prepared according to the general reaction procedure **II** using 1-(6-bromoquinolin-1(2*H*)-yl)ethan-1-one **(2d)** (100 mg, 0.397 mmol), ^{t}BuONO (81 mg, 0.793 mmol) and TEMPO (25 mg, 0.159 mmol) in 1,4-dioxane at rt in 1 h to obtain **3d** (100 mg, 85%) as yellow solid (20% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 115-117 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.68 (s, 1H), 7.49 (d, *J* = 6.4 Hz, 2H), 7.22 (m, 1H), 4.92 (s, 2H), 2.21 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ169.6, 136.8, 134.2, 132.6, 128.1. 126.9, 126.0, 119.3, 27.6, 22.6; **HRMS** (EI) calcd for $C_{11}H_9{}^{79}BrN_2O_3$, 318.96942

m/z (M+Na)$^+$; Found, 318.96922 *m/z*; **FTIR (cm^{-1}):** 1650, 1505, 1473, 1317, 1188, 1097, 929, 831, 717.

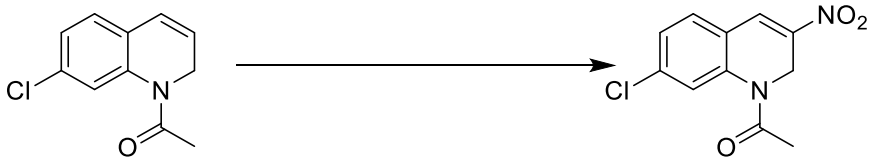
2e **3e**

1-(6-chloro-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3e)**: Prepared according to the general reaction procedure **II** using 1-(6-chloroquinolin-1(2*H*)-yl)ethan-1-one **(2e)** (100 mg, 0.481 mmol), ^{t}BuONO (99 mg, 0.963 mmol) and TEMPO (30 mg, 0.192 mmol) in 1,4-dioxane at rt in 2.5 h to obtain **3e** (109 mg, 90%) as yellow solid (20% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 109-111 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.75 (s, 1H), 7.45-7.41 (m, 1H), 7.40-7.39 (m, 2H), 4.98 (s, 2H), 2.27 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 169.7, 150.5, 135.6, 131.3, 130.7, 129.7, 126.6, 122.1, 56.7, 22.6; **HRMS** (EI) calcd for $C_{11}H_9ClN_2O_3$, 275.01994 *m/z* (M+Na)$^+$; Found, 275.01989 *m/z*; **FTIR (cm^{-1}):** 1675, 1510, 1262, 1080, 1011, 798, 720.



2f **3f**

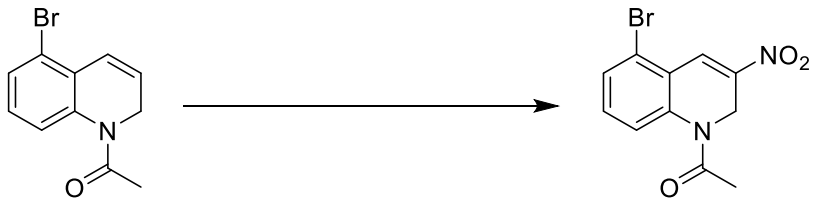
1-(3,6-dinitroquinolin-1(2*H*)-yl)ethan-1-one **(3f)**: Prepared according to the general reaction procedure **II** using 1-(6-nitroquinolin-1(2*H*)-yl)ethan-1-one **(2f)** (100 mg, 0.458 mmol), ^{t}BuONO (94 mg, 0.916 mmol) and TEMPO (29 mg, 0.183 mmol) in 1,4-dioxane at rt in 4 h to obtain **3f** (100 mg, 83%) as yellow solid (30% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 112-114 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 8.32-8.29 (m, 2H), 7.89 (s, 1H), 7.70 (d, *J* = 9.6 Hz, 1H), 5.03 (s, 2H), 2.38 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 169.6, 145.6, 145.0, 142.9, 127.8, 126.4, 125.4, 125.3, 124.9, 41.9, 23.1; **HRMS** (EI) calcd for $C_{11}H_9N_3O_5$, 286.04399 *m/z* (M+Na)$^+$; Found, 286.04390 *m/z*; **FTIR (cm^{-1}):** 1686, 1507, 1258, 1085, 1018, 795, 737.



2g **3g**

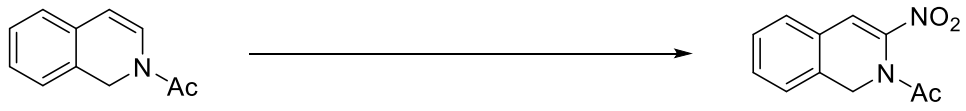
1-(7-chloro-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3g)**: Prepared according to the general reaction procedure **II** using 1-(7-chloroquinolin-1(2*H*)-yl)ethan-1-one **(2g)** (100 mg, 0.481

mmol), ^{t}BuONO (99 mg, 0.963 mmol) and TEMPO (30 mg, 0.192 mmol) in 1,4-dioxane at rt in 8 h to obtain **3g** (109 mg, 90%) as yellow solid (20% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 113-115 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.79 (s, 1H), 7.46-7.41 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.26 (dd, *J* = 8.2, 1.9 Hz, 1H), 4.97 (s, 2H), 2.30 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 169.7, 151.2, 136.5, 131.1, 129.2, 128.1, 128.0, 127.4, 126.7, 121.4, 22.7, 20.8; **HRMS** (EI) calcd for $C_{11}H_9ClN_2O_3$, 275.01994 *m/z* $(M+Na)^+$; Found, 275.01998 *m/z*; **FTIR (cm^{-1}):** 1673, 1505, 1268, 1075, 1016, 800, 735.



2h **3h**

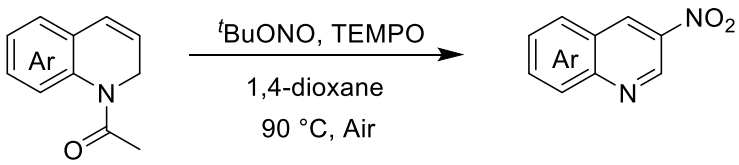
1-(5-bromo-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3h)**: Prepared according to the general reaction procedure **II** using 1-(5-bromoquinolin-1(2*H*)-yl)ethan-1-one **(2h)** (100 mg, 0.397 mmol), ^{t}BuONO (82 mg, 0.793 mmol) and TEMPO (25 mg, 0.159 mmol) in 1,4-dioxane at rt in 4 h to obtain **3h** (104 mg, 88%) as yellow solid (20% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 121-123 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 8.18 (s, 1H), 7.52 (d, *J* = 9.2 Hz, 1H), 7.34-7.28 (m, 2H), 4.97 (s, 2H), 2.26 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 169.7, 139.6, 131.8, 130.6, 128.4, 125.5, 125.1, 123.8, 40.7, 22.6; **HRMS** (EI) calcd for $C_{11}H_9{}^{79}Br\,N_2O_3$, 318.96942 *m/z* $(M+Na)^+$; Found, 318.96939 *m/z*; **FTIR (cm^{-1}):** 1655, 1510, 1480, 1320, 1175, 1080, 930, 798, 742.



2i **3i**

1-(3-nitroisoquinolin-2(1*H*)-yl)ethan-1-one **(3i)**: Prepared according to the general reaction procedure **II** using 1-(isoquinolin-2(1*H*)-yl)ethan-1-one **(2i)** (200 mg, 1.155 mmol), ^{t}BuONO (238 mg, 2.309 mmol) and TEMPO (72 mg, 0.462 mmol) in 1,4-dioxane at rt in 16 h to obtain **3i** (207 mg, 82%) as yellow solid (15% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 131-133 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.65 (s, 1H), 7.45-7.41 (m, 2H), 7.39-7.35 (m, 1H), 7.29-7.27 (d, *J* = 7.1 Hz, 1H), 4.97 (s, 2H), 2.07 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 170.4, 131.8, 129.2, 129.1, 128.7, 128.2, 126.8, 125.9, 121.7, 57.4, 21.8; **HRMS** (EI) calcd for $C_{11}H_{10}N_2O_3$, 241.05891 *m/z* $(M+Na)^+$; Found, 241.05888 *m/z*; **FTIR (cm^{-1}):** 1670, 1502, 1255, 1089, 1020, 790, 736.

General procedure III: *Synthesis of substituted 3-nitroquinoline* ***(4)***



2 **4**

In an oven-dried round bottom flask, 1-(quinolin-1(2*H*)-yl)ethan-1-one **(2)** (1.0 equiv.) was dissolved in 1,4-dioxane (0.2 M) and added TEMPO (0.4 equiv.), and ^{t}BuONO (2.0 equiv.). The round bottom flask was fitted with a condenser, and the reaction mixture was stirred at 90 °C in open air. When the reaction was completed (confirmed by TLC), the reaction mixture was washed with ethyl acetate, the organic part was concentrated under reduced pressure, and the crude oil was purified using silica gel (230-400) column chromatography.

Figure 1: Reaction set-up for the preparation of 3-nitroquinolines

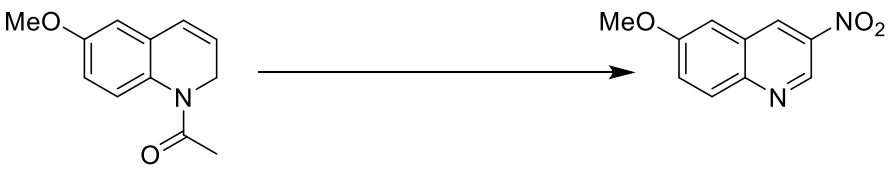
Spectral data of 3-nitroquinoline derivatives:

2a **4a**

3-nitroquinoline **(4a)**: Prepared according to the general reaction procedure **III** using 1-(quinolin-1(2*H*)-yl)ethan-1-one **(2a)** (370 mg, 2.136 mmol), ^{t}BuONO (433 mg, 4.272 mmol) and TEMPO (133 mg, 0.854 mmol) in 1,4-dioxane at 90 °C in 24 h to obtain **4a** (350 mg, 94%) as white solid (5% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 100-102 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 9.64 (d, *J* = 2.6 Hz, 1H), 9.03 (d, *J* = 2.2 Hz, 1H), 8.24 (dd, *J* = 8.6, 0.5 Hz, 1H), 8.05-8.03 (m, 1H), 7.97-7.92 (m, 1H), 7.75-7.71 (m, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 150.3, 144.2, 141.8, 133.5, 132.4, 130.0, 129.9, 129.0, 126.2; **HRMS** (EI) calcd for $C_9H_6N_2O_2$, 197.03270 *m/z* $(M+Na)^+$; Found, 197.03266 *m/z*; **FTIR (cm^{-1}):** 1605, 1519, 1346, 1316, 1129, 1086, 927, 892, 803, 787, 764.

2b **4b**

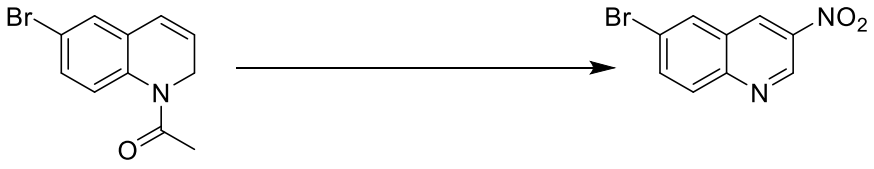
6-methyl-3-nitroquinoline **(4b)**: Prepared according to the general reaction procedure **III** using 1-(6-methylquinolin-1(2*H*)-yl)ethan-1-one **(2b)** (445 mg, 2.376 mmol), ^{t}BuONO (500 mg, 4.753 mmol) and TEMPO (150 mg, 0.950 mmol) in 1,4-dioxane at 90 °C in 17 h to obtain **4b** (371 mg, 83%) as white solid (5% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 174-176 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 9.58 (d, *J* = 2.5 Hz, 1H), 8.95 (d, *J* = 2.3 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 10.4, 8.6 Hz, 2H), 2.61 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 148.9, 143.2, 141.2, 139.3, 135.9, 131.6, 129.5, 128.5, 126.2, 21.7; **HRMS** (EI) calcd for $C_{10}H_8N_2O_2$, 211.04835 *m/z* $(M+Na)^+$; Found, 211.04840 *m/z*; **FTIR (cm^{-1}):** 1538, 1374, 1261, 1131, 1014, 926, 907.



2c **4c**

6-methoxy-3-nitroquinoline **(4c)**: Prepared according to the general reaction procedure **III** using 1-(6-methoxyquinolin-1(2*H*)-yl)ethan-1-one **(2c)** (400 mg, 1.968 mmol), ^{t}BuONO (405

mg, 3.936 mmol) and TEMPO (122 mg, 0.787 mmol) in 1,4-dioxane at 90 °C in 17 h to obtain **4c** (354 mg, 88%) as white solid (8% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 120-122 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 9.47 (d, *J* =2.4 Hz, 1H), 8.91 (d, *J* = 2.3 Hz, 1H), 8.11 (d, *J* = 9.3 Hz, 1H), 7.56 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.23 (d, *J* = 2.8 Hz, 1H), 3.98 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 159.5, 146.5, 141.5, 131.2, 130.7, 127.7, 126.6, 106.5, 56.0; **HRMS** (EI) calcd for $C_{10}H_8N_2O_3$, 227.04326 *m/z* $(M+Na)^+$; Found, 227.04320 *m/z*; **FTIR (cm^{-1}):**.1548, 1537, 1519, 1341, 1230, 1129, 1024, 944, 910, 846, 830, 728.



2d **4d**

6-bromo-3-nitroquinoline **(4d)**: Prepared according to the general reaction procedure **III** using 1-(6-bromoquinolin-1(2*H*)-yl)ethan-1-one **(2d)** (250 mg, 0.992 mmol), ^{t}BuONO (173 mg, 1.983 mmol) and TEMPO (62 mg, 0.397 mmol) in 1,4-dioxane at 90 °C in 16 h to obtain **4d** (201 mg, 80%) as white solid (5% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 156-158 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 9.65 (d, *J* = 2.6 Hz, 1H), 8.95 (d, *J* = 2.8 Hz, 1H), 8.21 (d, *J* = 2.2 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 8.00 (dd, *J* = 9.0, 2.2 Hz, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz): 148.9, 144.5, 142.0, 137.0, 131.6, 131.5, 131.3, 127.4, 123.2; **HRMS** (EI) calcd for $C_9H_5{}^{79}BrN_2O_2$, 274.94321 *m/z* $(M+Na)^+$; Found, 274.94315 *m/z*; **FTIR (cm^{-1}):** 1595, 1523, 1216, 970, 926, 913, 835, 814, 736.

2e **4e**

6-chloro-3-nitroquinoline **(4e)**: Prepared according to the general reaction procedure **III** using 1-(6-chloroquinolin-1(2*H*)-yl)ethan-1-one **(2e)** (100 mg, 0.481 mmol), ^{t}BuONO (99 mg, 0.963 mmol) and TEMPO (30 mg, 0.192 mmol) in 1,4-dioxane at 90 °C in 16 h to obtain **4e** (75 mg, 75%) as white solid (5% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 155-157 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 9.62 (d, *J* = 2.5 Hz, 1H), 8.95 (d, *J* = 2.5 Hz, 1H), 8.18 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 2.3 Hz, 1H), 7.87 (dd, *J* = 9.0, 2.3 Hz, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 148.6, 144.3, 141.6, 135.1, 134.4, 131.5, 131.4, 128.2, 126.9; **HRMS** (EI) calcd for $C_9H_5ClN_2O_2$, 230.99372 *m/z* $(M+Na)^+$; Found, 230.99368 *m/z*; **FTIR (cm^{-1}):** 1592, 1518, 1215, 972, 924, 910, 830, 815, 734.

2f **4f**

3,6-dinitroquinoline **(4f)**: Prepared according to the general reaction procedure **III** using 1-(6-nitroquinolin-1(2*H*)-yl)ethan-1-one **(2f)** (460 mg, 2.108 mmol), ^{t}BuONO (433 mg, 4.216 mmol) and TEMPO (132 mg, 0.843 mmol) in 1,4-dioxane at 90 °C in 15 h to obtain **4f** (360 mg, 78%) as white solid (15% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 160-162 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 9.82 (d, *J* = 2.7 Hz, 1H), 9.24-9.23 (m, 1H), 9.01-9.00 (m, 1H), 8.70 (dd, *J* = 9.3, 2.6 Hz, 1H), 8.44-8.41 (m, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz): 151.9, 147.4, 142.5, 133.9, 132.1, 126.6, 126.2, 125.4; **HRMS** (EI) calcd for $C_9H_5N_3O_4$, 242.01778 *m/z* $(M+Na)^+$; Found, 242.01770 *m/z*; **FTIR (cm^{-1}):** 1725, 1550, 1513, 1345, 1320, 1298, 1259, 948, 859, 840, 806, 744.

2g **4g**

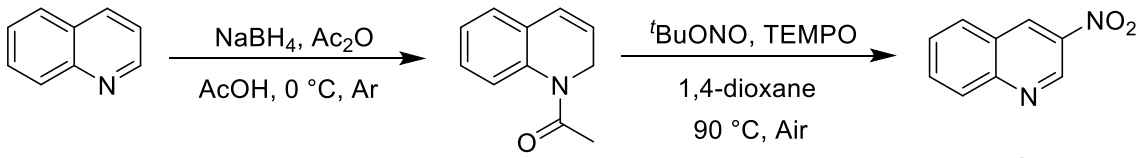
7-chloro-3-nitroquinoline **(4g)**: Prepared according to the general reaction procedure **III** using 1-(7-chloroquinolin-1(2*H*)-yl)ethan-1-one **(2g)** (100 mg, 0.481 mmol), ^{t}BuONO (99 mg, 0.963 mmol) and TEMPO (30 mg, 0.192 mmol) in 1,4-dioxane at 90 °C in 20 h to obtain **4g** (90 mg, 90%) as white solid (5% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 122-124 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 9.64 (d, *J* = 2.6 Hz, 1H), 9.02 (d, *J* = 2.5 Hz, 1H), 8.23 (d, *J* = 2.0 Hz, 1H), 9.98 (d, *J* = 8.8 Hz, 1H), 7.69 (dd, *J* = 8.8, 2.0 Hz, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 150.5, 145.3, 141.1, 140.0, 132.2, 130.9, 130.2, 129.1, 124.6; **HRMS** (EI) calcd for $C_9H_5ClN_2O_2$, 230.99372 *m/z* $(M+Na)^+$; Found, 230.99375 *m/z*; **FTIR (cm^{-1}):** 1590, 1524, 1212, 968, 920, 912, 831, 814, 730.

2h **4h**

5-bromo-3-nitroquinoline **(4h)**: Prepared according to the general reaction procedure **III** using 1-(5-bromoquinolin-1(2*H*)-yl)ethan-1-one **(2h)** (100 mg, 0.397 mmol), ^{t}BuONO (82 mg, 0.793 mmol) and TEMPO (25 mg, 0.159 mmol) in 1,4-dioxane at 90 °C in 20 h to obtain **4h** (78 mg,

78%) as white solid (5% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 116-118 °C; mg, 90%) as white solid (5% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 122-124 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 9.64 (d, *J* = 2.5 Hz, 1H), 9.39 (d, *J* = 2.5 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.79 (dd, *J* = 8.5, 8.0 Hz, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 151.0, 144.9, 142.0, 133.6, 132.6, 132.3, 129.7, 126.3, 123.8; **HRMS** (EI) calcd for $C_9H_5{}^{79}BrN_2O_2$, 274.94321 *m/z* $(M+Na)^+$; Found, 274.94318 *m/z*; **FTIR (cm^{-1}):** 1579, 1518, 1210, 965, 918, 905, 825, 810, 722.

Gram-scale reaction: Synthesis of 3-nitroquinlone **(4a)** from Quinoline **(1a)**



1a **2a** **4a**

In an oven dried round bottom flask, Sodium borohydride (1.2 gm, 30.97 mmol) was gradually added to a mixture of quinoline **1a** (1.0 gm, 7.74 mmol), acetic anhydride (3.6 mL, 38.71 mmol), and acetic acid (13 mL) over a period of 1.5 h at 0 ˚C. After the addition was complete, the mixture was warmed to 50 ˚C for 30 min. The reaction mixture was concentrated under a vacuum, diluted with water (100 mL), and neutralized with sodium carbonate. This was then extracted with DCM, and the organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude oil was purified by silica gel column chromatography (25% ethyl acetate in petroleum ether, R_f = 0.25) to afford the product **2a** (925 mg, 69%), off-white solid.

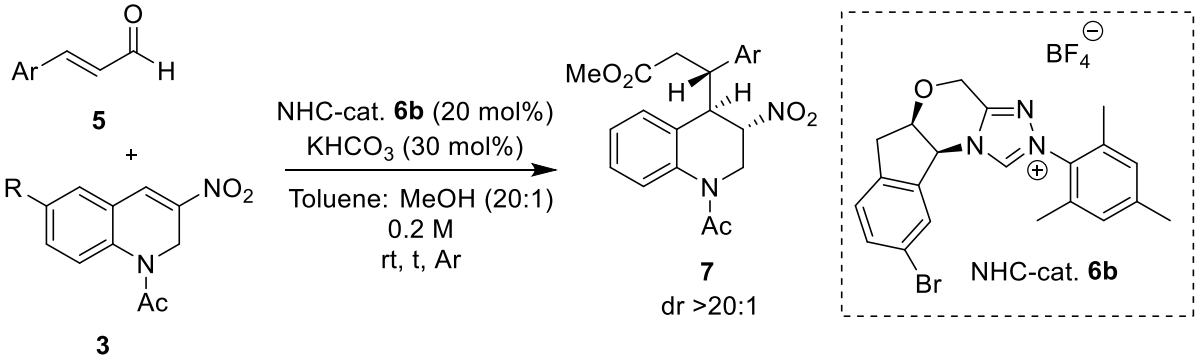
In an oven-dried round bottom flask, 1-(quinolin-1(2*H*)-yl)ethan-1-one **(2a)** (920 mg, 5.34 mmol) was dissolved in 1,4-dioxane (27 mL) and added TEMPO (0.33 mg, 2.14 mmol), and ^{t}BuONO (1.3 mL, 10.68 mmol). The reaction mixture was stirred for 22 h at 90 °C in an open air, the reaction was cooled to ambient temperature and concentrated under reduced pressure, the crude oil was purified using silica gel (230-400) column chromatography (5% ethyl acetate in petroleum ether, R_f = 0.25), to afford the product **4a** (1.09 gm, 94%), white solid.

Overall Yield = (multiply of all step %yield in fractions) X 100

= (0.69 X 0.94) X100

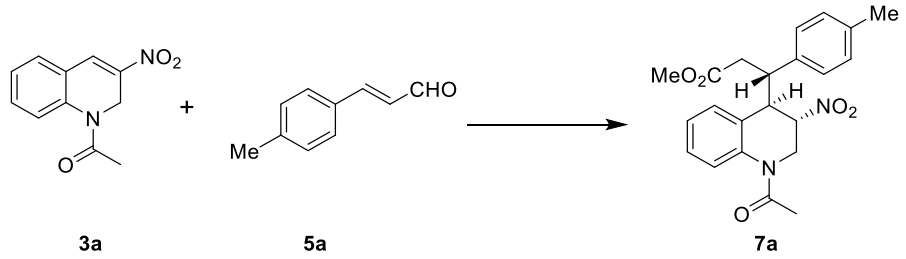
Overall Yield = 65%

General procedure IV: *Synthesis of 3-nitro-1,2,3,4-tetrahydroquinolin derivatives* ***(7)***



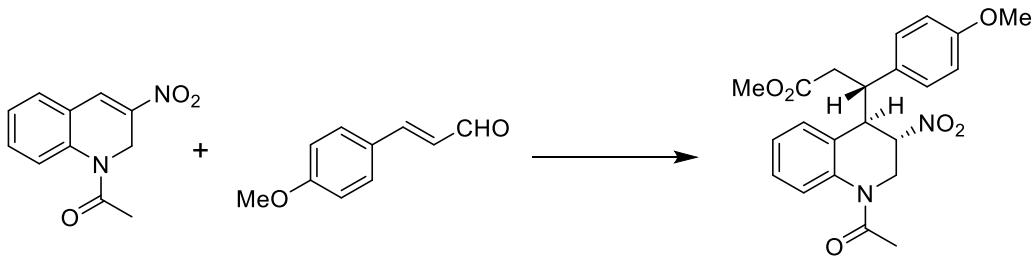
In an oven-dried round bottom flask, a solution of substituted 1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one **3** (1.0 equiv.), cinnamaldehyde derivative **5** (1.2 equiv.), $KHCO_3$ (30 mol%), and NHC-cat. **6b** (20 mol%) in toluene:MeOH (20:1, 0.2 M) was stirred overnight at room temperature under argon atmosphere. After complete consumption of 1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one (confirmed by TLC), reaction mixture was diluted with ethyl acetate and solvent was evaporated under reduced pressure. The residue was then subjected to purification by flash column chromatography using EtOAc and petroleum-ether mixture as an eluent to yield the desired product **7**.

Spectral data of 3-nitro-1,2,3,4-tetrahydroquinolin derivatives:



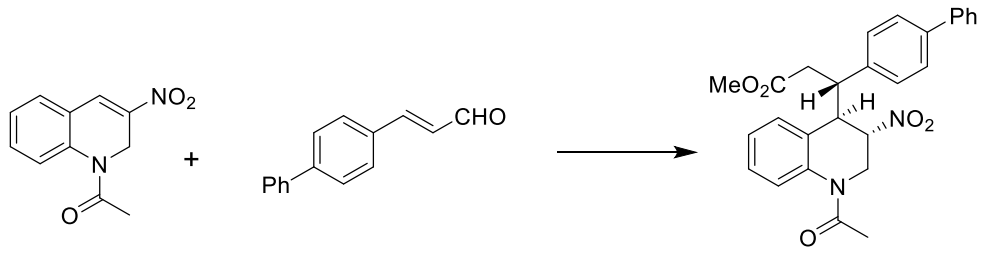
methyl 3-(1-acetyl-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(*p*-tolyl)propanoate **(7a)**: Prepared according to the general reaction procedure **IV** using 1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3a)** (100 mg, 0.458 mmol), 3-(*p*-tolyl)acrylaldehyde **(5a)** (80 mg, 0.550 mmol), NHC-cat. **(6b)** (46 mg, 0.092 mmol) and $KHCO_3$ (14 mg, 0.137 mmol) in toluene:MeOH (0.2 M) was stirred 15 h at room temperature to obtain **7a** (160 mg, 88%) as white solid (15% ethyl acetate in petroleum ether, R_f = 0.2); m.p. = 92-94 °C; $[\alpha]_D^{29}$ = +96.95 (c = 0.1 gm/100 ml, $CHCl_3$); **HPLC analysis of 7a:** *ee* = 94% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Minor: 7.6 min, Major: 8.4 min]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.35-7.32 (m, 1H), 7.31 (d, *J* = 2.0 Hz, 2H), 7.24-7.14 (m, 5H), 4.58 (t, *J* = 6.6 Hz, 2H), 4.01 (d, *J* = 12.5 Hz, 1H), 3.85 (d, *J* = 11.0 Hz, 1H), 3.36 (s, 3H), 3.17-3.13 (m, 1H), 2.60 (dq, *J* = 15.7, 6.2 Hz, 2H), 2.33 (s, 3H), 2.28 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.5, 170.3,

138.0, 136.6, 130.5, 130.2, 128.9, 127.5, 126.2, 125.3, 83.9, 51.6, 49.3, 43.2, 42.7, 40.1, 22.8, 21.1; **HRMS** (EI) calcd for $C_{22}H_{24}N_2O_5$, 419.15829 *m/z* $(M+Na)^+$; Found, 419.15835 *m/z*; **FTIR (cm^{-1}):** 1729, 1641, 1551, 1492, 1337, 1254, 1151, 842, 817, 763.



3a **5b** **7b**

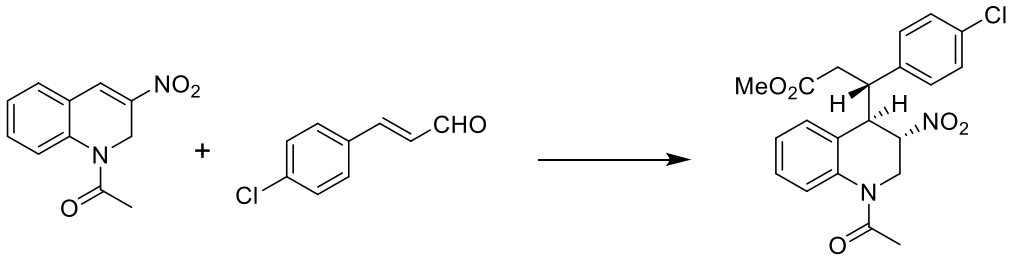
methyl 3-(1-acetyl-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(4-methoxyphenyl)propanoate **(7b)**: Prepared according to the general reaction procedure **IV** using 1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3a)** (70 mg, 0.321 mmol), 3-(4-methoxyphenyl)acrylaldehyde **(5b)** (62 mg, 0.385 mmol), NHC-cat. **(6b)** (32 mg, 0.064 mmol) and $KHCO_3$ (10 mg, 0.096 mmol) in toluene:MeOH (0.2 M) was stirred 14 h at room temperature to obtain **X** (95 mg, 72%) as pale-yellow solid (30% ethyl acetate in petroleum ether, R_f = 0.2); m.p. = 98-100 °C; $[\alpha]_D^{29}$ = +17.50 (c = 0.1 gm/100 ml, $CHCl_3$); **HPLC analysis of 7b:** *ee* > 99% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Minor: 11.4 min, Major: 12.6 min]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.32 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.24-7.20 (m, 2H), 7.18 (d, *J* = 8.7 Hz, 3H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.58 (s, 2H), 3.99 (d, *J* = 12.8 Hz, 1H), 3.82 (t, *J* = 2.2 Hz, 1H), 3.78 (s, 3H), 3.35 (s, 3H), 3.20-3.09 (m, 1H), 2.61 (dq, *J* = 15.7, 9.6 Hz, 2H), 2.27 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.5, 170.4, 159.4, 131.5, 130.5, 128.9, 128.7, 126.3, 125.4, 114.9, 83.9, 55.4, 51.7, 49.5, 43.2, 42.4, 40.2, 22.8; **HRMS** (EI) calcd for $C_{22}H_{24}N_2O_6$, 435.15321 *m/z* $(M+Na)^+$; Found, 435.15318 *m/z*; **FTIR (cm^{-1}):** 1728, 1639, 1551, 1512, 1492, 1338, 1253, 1179, 1012, 844, 760.



3a **5c** **7c**

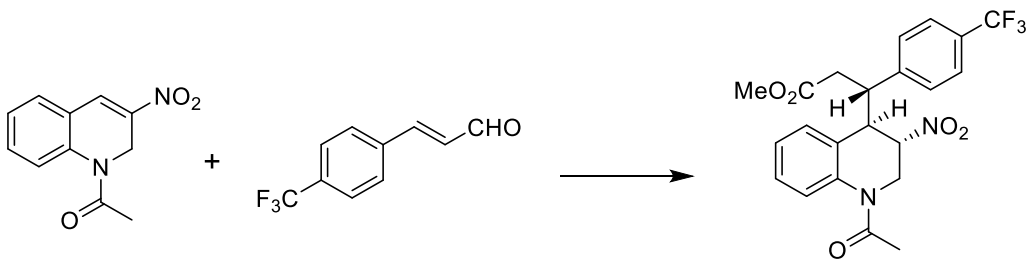
methyl 3-([1,1'-biphenyl]-4-yl)-3-(1-acetyl-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)propanoate **(7c)**: Prepared according to the general reaction procedure **IV** using 1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3a)** (70 mg, 0.321 mmol), 3-([1,1'-biphenyl]-4-yl)acrylaldehyde **(5c)** (80 mg, 0.385 mmol), NHC-cat. **(6b)** (31 mg, 0.064 mmol) and $KHCO_3$ (10 mg, 0.096 mmol) in

toluene:MeOH (0.2 M) was stirred 15 h at room temperature to obtain **7c** (112 mg, 76%) as yellow solid (30% ethyl acetate in petroleum ether, R_f = 0.2); m.p. = 120-122 °C; $[\alpha]_D^{29}$ = +94.82 (c = 0.1 gm/100 ml, $CHCl_3$); **HPLC analysis of 7c:** *ee* > 99% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Minor: 12.9 min, Major: 15.6 min]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.61 (s, 1H), 7.59-7.56 (m, 3H), 7.46-7.43 (m, 2H), 7.37-7.33 (m, 4H), 7.29 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.23 (td, *J* = 7.4, 6.3 Hz, 2H), 4.67 (d, *J* = 3.0 Hz, 2H), 4.03 (d, *J* = 13.2 Hz, 1H), 3.93 (d, 11.0 Hz, 1H), 3.39 (s, 3H), 3.28-3.23 (m, 1H), 2.67 (dq, *J* = 9.1, 6.3 Hz, 2H), 2.28 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.4, 170.4, 141.1, 140.3, 138.7, 130.6, 129.0, 128.9, 128.2, 128.2, 127.7, 127.1, 126.3, 125.4, 83.8, 51.8, 49.3, 43.2, 42.8, 40.0, 22.8; **HRMS** (EI) calcd for $C_{27}H_{26}N_2O_5$, 481.17394 *m/z* $(M+Na)^+$; Found, 481.17380 *m/z*; **FTIR (cm^{-1}):** 1736, 1650, 1547, 1489, 1373, 1336, 1156, 851, 765, 733, 697.



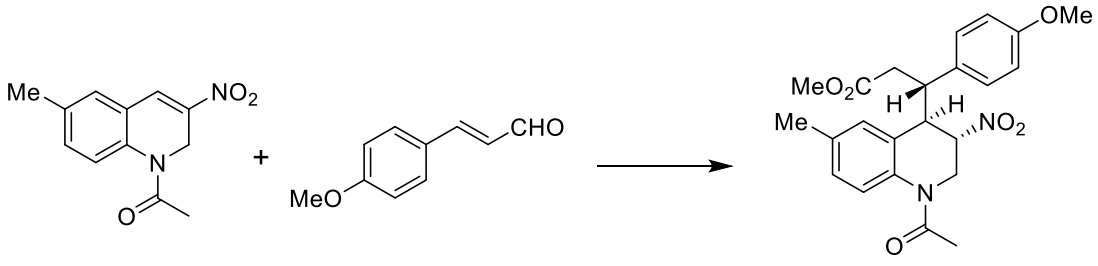
3a **5d** **7d**

methyl 3-(1-acetyl-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(4-chlorophenyl)propanoate **(7d)**: Prepared according to the general reaction procedure **IV** using 1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3a)** (70 mg, 0.321 mmol), 3-(4-chlorophenyl)acrylaldehyde **(5d)** (64 mg, 0.385 mmol), NHC-cat. **(6b)** (31 mg, 0.064 mmol) and $KHCO_3$ (10 mg, 0.096 mmol) in toluene:MeOH (0.2 M) was stirred 15 h at room temperature to obtain **7d** (94 mg, 70%) as off-white solid (30% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 98-100 °C; $[\alpha]_D^{29}$ = +115.08 (c = 0.1 gm/100 ml, $CHCl_3$); **HPLC analysis of 7d:** *ee* = 96% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Minor: 10.4 min, Major: 11.4 min]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.37-7.33 (m, 3H), 7.25-7.20 (m, 5H), 4.62-4.55 (m, 2H), 4.00 (d, *J* = 14.4 Hz, 1H), 3.85 (d, *J* = 10.7 Hz, 1H), 3.39 (s, 3H), 3.20-3.17 (m, 1H), 2.59 (dq, *J* = 15.5, 6.0 Hz, 2H), 2.27 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.2, 170.3, 138.2, 134.2, 130.6, 129.8, 129.1, 126.5, 125.5, 83.7, 51.8, 49.1, 43.1, 42.6, 39.9, 22.8; **HRMS** (EI) calcd for $C_{21}H_{21}ClN_2O_5$, 439.10367 *m/z* $(M+Na)^+$; Found, 439.10360 *m/z*; **FTIR (cm^{-1}):** 1729, 1667, 1552, 1490, 1367, 1325, 1308, 1254, 1161, 1012, 848, 764.



3a **5e** **7e**

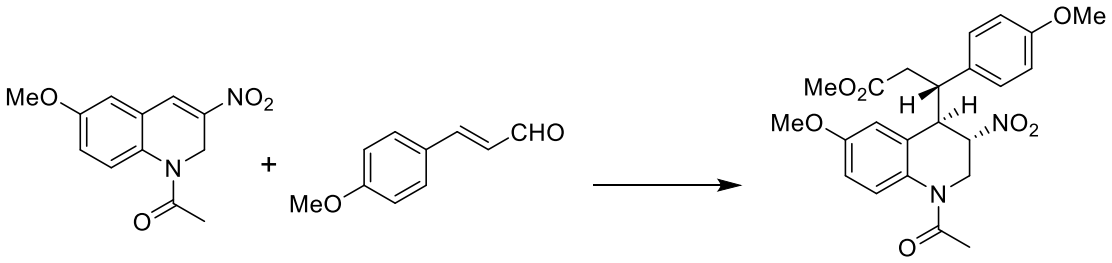
Methyl 3-(1-acetyl-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(4-(trifluoromethyl)phenyl)propanoate **(7e)**: Prepared according to the general reaction procedure **IV** using 1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3a)** (70 mg, 0.321 mmol), 3-(4-(trifluoromethyl)phenyl)acrylaldehyde **(5e)** (77 mg, 0.385 mmol), NHC-cat. **(6b)** (31 mg, 0.064 mmol) and $KHCO_3$ (10 mg, 0.096 mmol) in toluene:MeOH (0.2 M) was stirred 15 h at room temperature to obtain **7e** (116 mg, 80%) as white solid (30% ethyl acetate in petroleum ether, R_f = 0.25); m.p. = 92-94 °C; $[\alpha]_D^{29}$ = +67.90 (c = 0.1 gm/100 ml, $CHCl_3$); **HPLC analysis of 7e:** *ee* > 99% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Minor: 9.0 min, Major: 10.5 min]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.36-7.32 (m, 1H), 7.27-7.23 (m, 2H), 7.20 (dd, *J* = 7.3, 1.0 Hz, 1H), 4.63-4.50 (m, 2H), 3.98 (d, *J* = 15.0 Hz, 1H), 3.91 (dd, *J* = 11.0, 2.0 Hz, 1H), 3.37 (s, 3H), 3.29-3.26 (m, 1H), 2.61 (dq, *J* = 16.8, 6.0 Hz, 2H), 2.24 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.0, 170.3, 143.9 (d, $J_{C\text{-}F}$ = 1.4 Hz), 130.6 (t, $J_{C\text{-}F}$ = 19.9 Hz), 129.2, 128.3, 126.5 (t, $J_{C\text{-}F}$ = 3.8 Hz), 125.5, 125.3, 122.6, 83.5, 51.9, 48.9, 43.0, 39.7, 22.7; **^{19}F-NMR** ($CDCl_3$, 376 MHz): δ -62.6; **HRMS** (EI) calcd for $C_{22}H_{21}F_3N_2O_5$, 473.13003 *m/z* $(M+Na)^+$; Found, 473.13000 *m/z*; **FTIR (cm^{-1}):** 1730, 1673, 1555, 1369, 1327, 1164, 1112, 1068, 858, 764.



3b **5b** **7f**

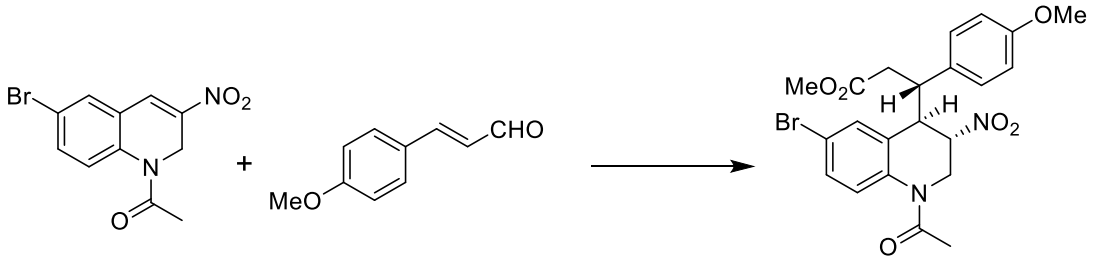
methyl 3-(1-acetyl-6-methyl-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(4-methoxyphenyl)propanoate **(7f)**: Prepared according to the general reaction procedure **IV** using 1-(6-methyl-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3b)** (30 mg, 0.129 mmol), 3-(4-methoxyphenyl)acrylaldehyde **(5b)** (25 mg, 0.155 mmol), NHC-cat. **(6b)** (13 mg, 0.026 mmol) and $KHCO_3$ (4 mg, 0.039 mmol) in toluene:MeOH (0.2 M) was stirred 15 h at room temperature to obtain **7f** (51 mg, 92%) as colorless liquid (25% ethyl acetate in petroleum ether, R_f = 0.20); $[\alpha]_D^{29}$ = +51.13 (c = 0.1 gm/100 ml, $CHCl_3$); **HPLC analysis of 7f:** *ee* = 96% [Daicel

CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Minor: 8.6 min, Major: 8.8 min]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.21-7.17 (m, 2H), 7.13-7.11 (m, 1H), 7.12 (s, 2H), 7.03-6.88 (m, 2H), 4.66-4.55 (m, 2H), 3.98 (d, *J* = 14.5 Hz, 1H), 3.80 (s, 3H), 3.76 (d, *J* = 10.9 Hz, 1H), 3.38 (s, 3H), 3.12-3.08 (m, 1H), 2.59 (dq, *J* = 14.8, 5.9 Hz, 2H), 2.34 (s, 3H), 2.26 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.6, 159.4, 141.7, 132.1, 131.6, 131.0, 129.6, 128.7, 126.5, 125.2, 114.9, 84.1, 57.5, 55.4, 51.7, 42.4, 40.3, 22.7, 21.0, 18.0; **HRMS** (EI) calcd for $C_{23}H_{26}N_2O_6$, 449.16886 *m/z* $(M+Na)^+$; Found, 449.16886 *m/z*; **FTIR (cm^{-1}):** 1731, 1654, 1550, 1510, 1372, 1247, 1159, 1028, 827.



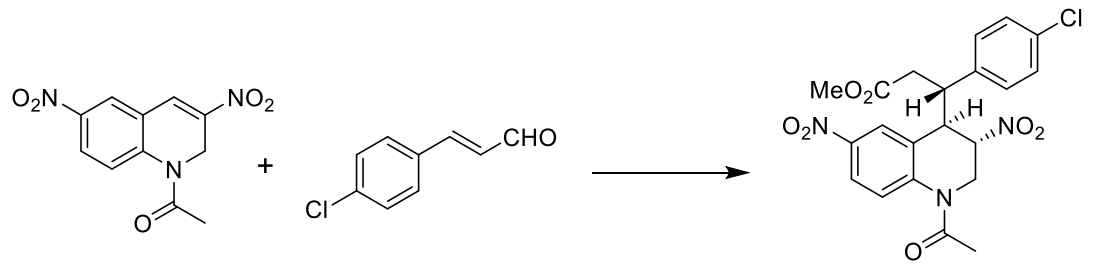
3c **5b** **7g**

methyl 3-(1-acetyl-6-methoxy-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(4-methoxyphenyl)propanoate **(7g)**: Prepared according to the general reaction procedure **IV** using 1-(6-methoxy-3-nitroquinolin-1(2H)-yl)ethan-1-one **(3c)** (30 mg, 0.121 mmol), 3-(4-methoxyphenyl)acrylaldehyde **(5b)** (24 mg, 0.145 mmol), NHC-cat. **(6b)** (12 mg, 0.024 mmol) and $KHCO_3$ (4 mg, 0.036 mmol) in toluene:MeOH (0.2 M) was stirred 15 h at room temperature to obtain **7g** (51 mg, 95%) as colorless liquid (30% ethyl acetate in petroleum ether, R_f = 0.20); $[\alpha]_D^{29}$ = +46.90 (c = 0.1 gm/100 ml, $CHCl_3$); **HPLC analysis of 7g:** *ee* = 94% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Minor: 10.4 min, Major: 10.9 min]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.19 (dt, *J* = 8.7, 3.1 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 1H), 6.40 (dt, *J* = 8.7, 3.0 Hz, 2H), 6.85 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.77 (d, *J* = 2.8 Hz, 1H), 4.67 (dd, *J* = 15.3, 7.5 Hz, 1H), 4.58-4.54 (m, 1H), 3.93 (d, *J* = 15.0 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.77-3.76 (m, 1H), 3.39 (s, 3H), 3.14-3.07 (m, 1H), 2.63 (dq, *J* = 15.6, 5.9 Hz, 2H), 2.24 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.5, 159.4, 157.8, 145.9, 131.5, 128.8, 126.5, 115.7, 114.9, 114.0, 100.0, 84.0, 55.7, 55.4, 51.7, 49.9, 43.1, 42.4, 40.3, 22.6; **HRMS** (EI) calcd for $C_{23}H_{26}N_2O_7$, 465.16377 *m/z* $(M+Na)^+$; Found, 465.16370 *m/z*; **FTIR (cm^{-1}):** 1730, 1658, 1556, 1508, 1375, 1233, 1168, 1148, 1029, 862, 840, 829.



3d **5b** **7h**

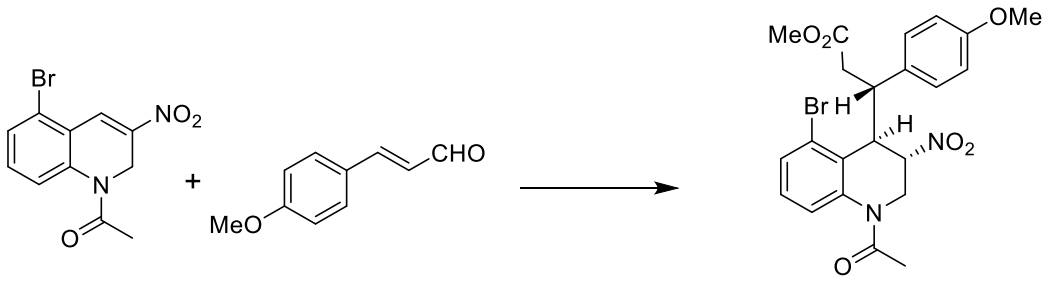
methyl 3-(1-acetyl-6-bromo-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(4-methoxyphenyl)propanoate **(7h)**: Prepared according to the general reaction procedure **IV** using 1-(6-bromo-3-nitroquinolin-1(2H)-yl)ethan-1-one **(3d)** (30 mg, 0.101 mmol), 3-(4-methoxyphenyl)acrylaldehyde **(5b)** (20 mg, 0.121 mmol), NHC-cat. **(6b)** (10 mg, 0.020 mmol) and $KHCO_3$ (3 mg, 0.030 mmol) in toluene:MeOH (0.2 M) was stirred 15 h at room temperature to obtain **7h** (42 mg, 85%) as colorless liquid (20% ethyl acetate in petroleum ether, R_f = 0.25); $[\alpha]_D^{29}$ = +77.08 (c = 0.1 gm/100 ml, $CHCl_3$); **HPLC analysis of 7h:** *ee* = 96% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Minor: 10.0 min, Major: 11.0 min]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.45 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.41-7.40 (m, 1H), 7.19-6.88 (m, 5H), 4.66-4.56 (m, 2H), 4.02 (d, *J* = 13.9 Hz, 1H), 3.80 (s, 3H), 3.41 (s, 3H), 3.16-3.11 (m, 1H), 2.60 (dq, *J* = 16.8, 6.6 Hz, 2H), 2.28 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.4, 159.5, 133.1, 132.1, 131.9, 131.2, 129.6, 129.4, 129.2, 128.7, 126.7, 126.5, 121.5, 115.0, 78.3, 61.4, 57.4, 55.4, 51.8, 40.2, 21.2, 17.9; **HRMS** (EI) calcd for $C_{22}H_{23}{}^{79}BrN_2O_6$, 513.06372 *m/z* $(M+Na)^+$; Found, 513.06370 *m/z*; **FTIR (cm^{-1}):** 1735, 1640, 1559, 1537, 1341, 1230, 1150, 1148, 1024, 855, 845, 830, 728.



3f **5d** **7i**

methyl 3-(1-acetyl-3,6-dinitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(4-chlorophenyl)propanoate **(7i)**: Prepared according to the general reaction procedure **IV** using 1-(3,6-dinitroquinolin-1(2*H*)-yl)ethan-1-one **(3f)** (30 mg, 0.114 mmol), 3-(4-chlorophenyl)acrylaldehyde **(5d)** (23 mg, 0.137 mmol), NHC-cat. **(6b)** (11 mg, 0.023 mmol) and $KHCO_3$ (3 mg, 0.034 mmol) in toluene:MeOH (0.2 M) was stirred 15 h at room temperature to obtain **7i** (45 mg, 85%) as off-white solid (30% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 152-154 °C; $[\alpha]_D^{29}$ = +9.17 (c = 0.1 gm/100 ml, $CHCl_3$); **HPLC analysis of 7i:** *ee* = 95% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Minor: 13.7 min, Major: 14.9 min]; **^{1}H-NMR (**$CDCl_3$,

400 MHz**):** δ 8.23 (dd, *J* = 8.9, 2.6 Hz, 1H), 8.17 (d, *J* = 2.6 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.25 (t, *J* = 2.6 Hz, 2H), 4.62-4.59 (m, 1H), 4.38 (dd, *J* = 15.3, 6.8 Hz, 1H), 4.21 (d, *J* = 15.2 Hz, 1H), 3.99 (dd, *J* = 11.0, 1.5 Hz, 1H), 3.37 (s, 3H), 3.26-3.20 (m, 1H), 2.68 (dq, *J* = 16.2, 6.7 Hz, 2H), 2.37 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.0, 170.1, 144.7, 143.5, 137.6, 134.6, 130.1, 128.9, 125.6, 125.4, 124.5, 82.7, 51.9, 48.7, 43.5, 42.1, 39.7, 23.3; **HRMS** (EI) calcd for $C_{21}H_{20}ClN_3O_7$, 484.08875 *m/z* $(M+Na)^+$; Found, 484.08870 *m/z*; **FTIR (cm^{-1}):** 1732, 1675, 1510, 1260, 1092, 1030, 860, 795, 758, 737.

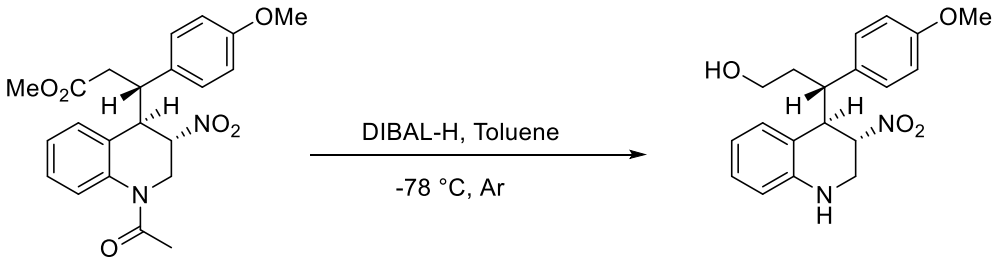


3h **5b** **7j**

methyl 3-(1-acetyl-5-bromo-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(4-methoxyphenyl)propanoate **(7j)**: Prepared according to the general reaction procedure **IV** using 1-(5-bromo-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(3h)** (50 mg, 0.168 mmol), 3-(4-methoxyphenyl)acrylaldehyde **(5b)** (33 mg, 0.202 mmol), NHC-cat. **(6b)** (17 mg, 0.034 mmol) and $KHCO_3$ (5 mg, 0.050 mmol) in toluene:MeOH (0.2 M) was stirred 15 h at room temperature to obtain **7j** (68 mg, 82%) as off-white solid (30% ethyl acetate in petroleum ether, R_f = 0.20); m.p. = 141-143 °C; $[\alpha]_D^{29}$ = +62.09 (c = 0.1 gm/100 ml, $CHCl_3$); **HPLC analysis of 7j:** *ee* = 98% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Minor: 10.1 min, Major: 11.4 min]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.49 (d, *J* = 9.1 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.20 (q, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.68-4.65 (m, 1H), 4.58-4.48 (m, 2H), 4.01 (d, *J* = 14.2 Hz, 1H), 3.81 (s, 3H), 3.38 (s, 3H), 3.16-3.10 (m, 1H), 2.76 (dq, *J* = 36.8, 9.3 Hz, 2H), 2.31 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.6, 170.3, 159.5, 139.7, 131.6, 130.7, 129.7, 128.8, 125.9, 125.1, 115.0, 84.1, 55.4, 51.7, 48.1, 43.0, 42.3, 39.8, 22.8; **HRMS** (EI) calcd for $C_{22}H_{23}{}^{79}BrN_2O_5$, 513.06372 *m/z* $(M+Na)^+$; Found, 513.06368 *m/z*; **FTIR (cm^{-1}):** 1724, 1680, 1545, 1230, 1091, 1032, 861, 790, 750, 720.

Transformation of product:

*Reaction procedure for the synthesis of **8**:[6]*



7b **8**

To an oven dried round bottom flask, **7b** (100 mg, 0.242 mmol, 1.0 equiv.) was dissolved in toluene (2 mL, 0.1 M) under inert atmosphere and the solution was cooled to -78 °C for 20 minutes. Then, the DIBAL-H (1.0 M in toluene) (847 µL, 0.847 mmol, 3.5 equiv.) was added dropwise in 1-2 minutes. After addition, immediately TLC was checked to confirm the completion of reaction. After completion (checked *via* TLC) the reaction was quenched with water and extracted 3-5 times with ethyl acetate. The combined organic layers were dried using Na_2SO_4. After removal of the combined organic layers under reduced pressure, the crude mixture was subjected to purification by column chromatography directly using (30% EtOAc/petroleum ether, R_F = 0.2) as eluent to afford **8** in (60 mg, 73%) yield as yellow solid; m.p. = 128-130 °C; $[\alpha]_D^{27}$ = –15.30 (*c* = 0.05 gm/100 ml, $CHCl_3$); **HPLC analysis of 8:** *ee* > 99% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane,1.0 ml/min, 254 nm, Major: 13.1 min, Minor: 20.8 min]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.36-7.31 (m, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.08-7.04 (m, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.68 (td, *J* = 7.4, 1.0 Hz, 1H), 6.53 (dd, *J* = 8.3, 0.8 Hz, 1H), 4.29-4.27 (m, 1H), 4.06-3.99 (m, 1H), 3.88-3.83 (m, 1H), 3.81 (s, 3H), 3.80-3.77 (m, 1H), 3.51 (dd, *J* = 14.2, 4.0 Hz, 1H), 3.42-3.36 (m, 1H), 3.25-3.19 (m, 1H), 2.71 (td, *J* = 11.4, 3.7 Hz, 1H), 2.14-2.06 (m, 1H), 1.85-1.76 (m, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 159.0, 142.1, 139.6, 132.6, 131.7, 129.8, 128.9, 128.7, 117.4, 117.1, 114.9, 114.5, 79.3, 60.8, 55.4, 46.9, 45.2, 39.5, 37.3; **HRMS** (EI) calcd for $C_{19}H_{22}N_2O_4$, 365.14773 *m/z* $(M+Na)^+$; Found, 365.14768 *m/z*; **FTIR (cm^{-1}):** 3298, 1674, 1605, 1498, 1435, 1261, 1175, 1024, 817, 749.

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[1] (a) Battistuzzi, G.; Cacchi, S.; Fabrizi, G. An Efficient Palladium-Catalyzed Synthesis of Cinnamaldehydes from Acrolein Diethyl Acetal and Aryl Iodides and Bromides. *Org. Lett.* **2003**, *5*, 777.

[2] (a) Hsieh, S.Y.; Binanzer, M.; I.; Kreitussa, Bode, J. W. Expanded Substrate Scope and Catalyst Optimization for the Catalytic Kinetic Resolution of N-heterocycles. *Chem. Commun.* **2012**, *48*, 8892. (b) Zhao, C.; Li, F.; Wang, J. *N*-Heterocyclic Carbene Catalyzed Dynamic Kinetic Resolution of Pyranones. *Angew. Chem. Int. Ed.* **2016**, *55*, 1820; (c) Struble, J. R.; Bode, J. W. Synthesis of a N-mesityl Substituted Aminoindanol-Derived Triazolium Salt. *Org. Synth.* **2010**, *87*, 362; (d) Vora, H. U.; Lathrop, S. P.; Reynolds, N. T.; Kerr, M. S.; Alaniz, J. R. de.; Rovis, T. Preparation of Chiral and Achiral Triazolium Salts: Carbene Precursors with Demonstrated Synthetic Utility. *Org. Synth.* **2010**, *87*, 350.

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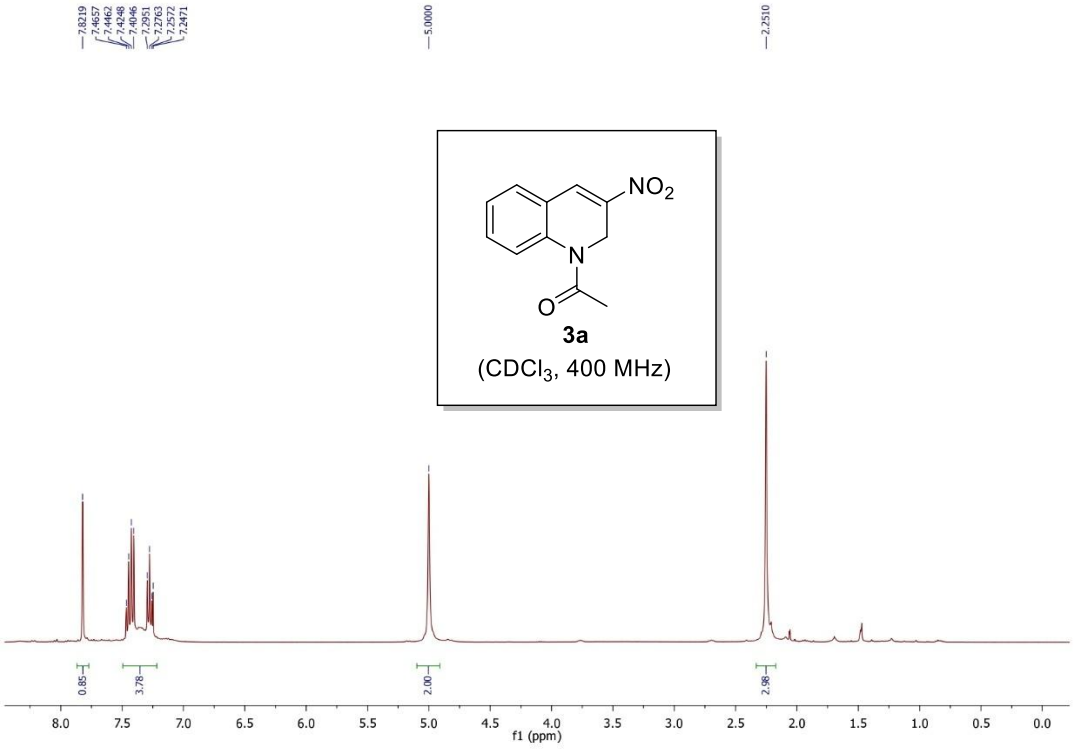
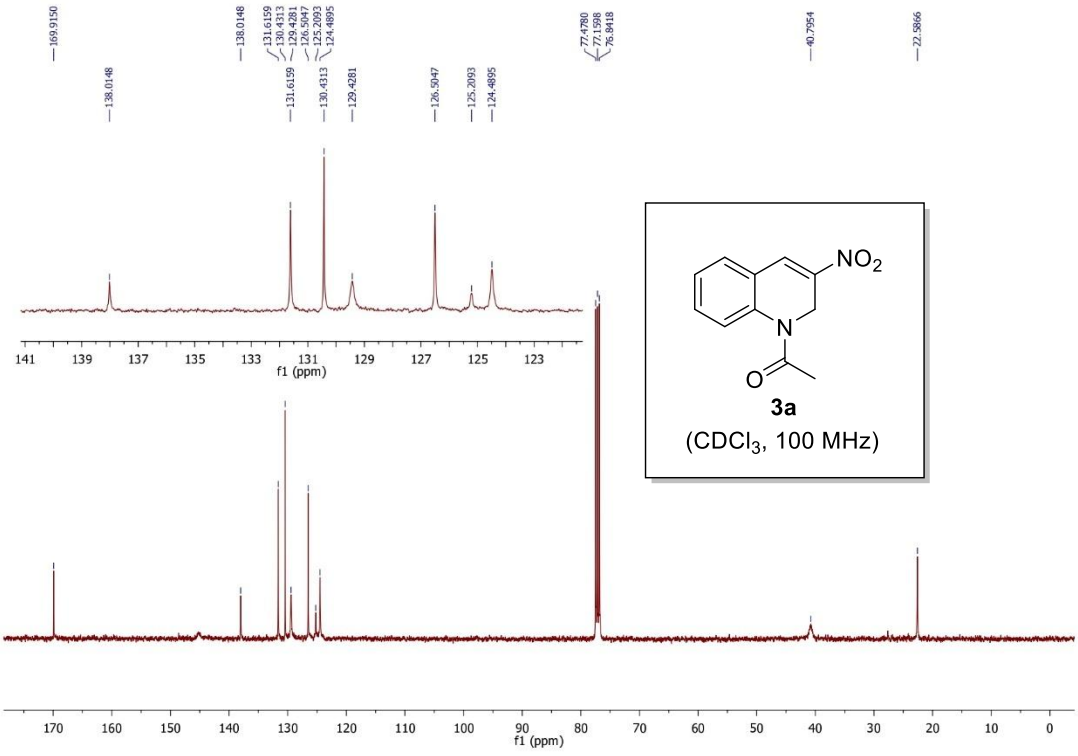
^{1}H and ^{13}C NMR spectra of 1-(3-nitroquinolin-1(2*H*)-yl)ethan-1-one derivatives (3):

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



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



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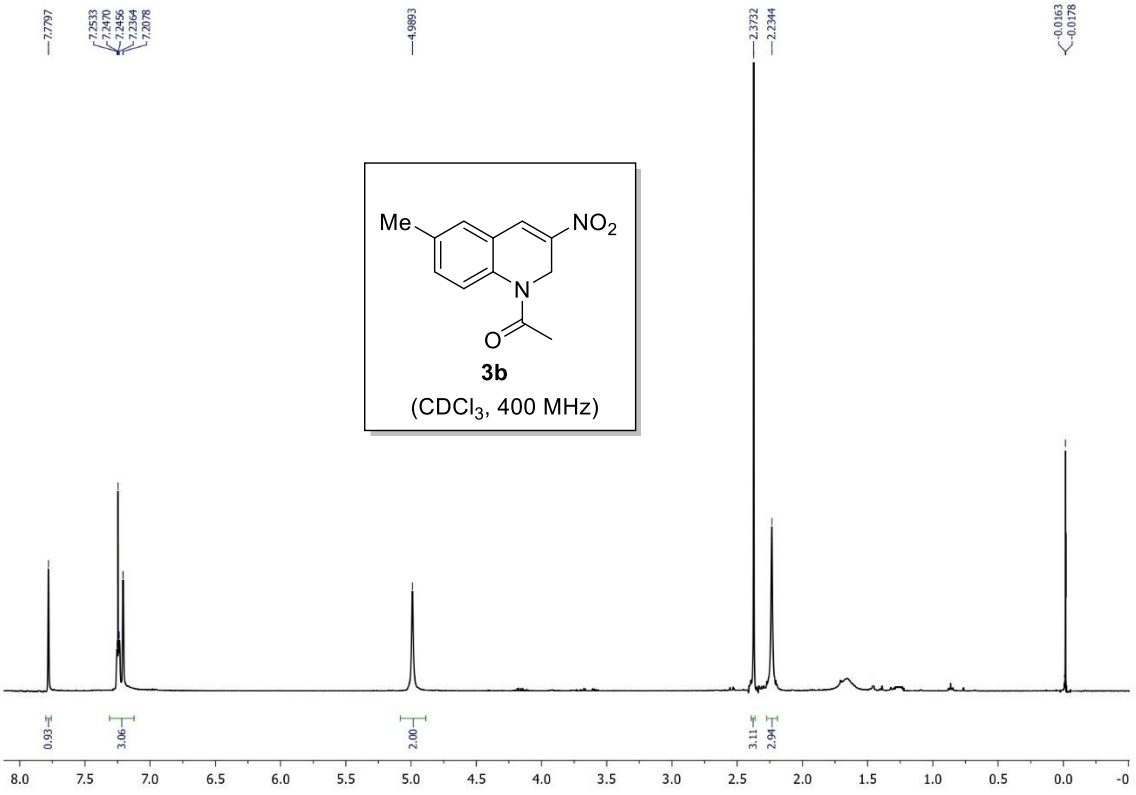
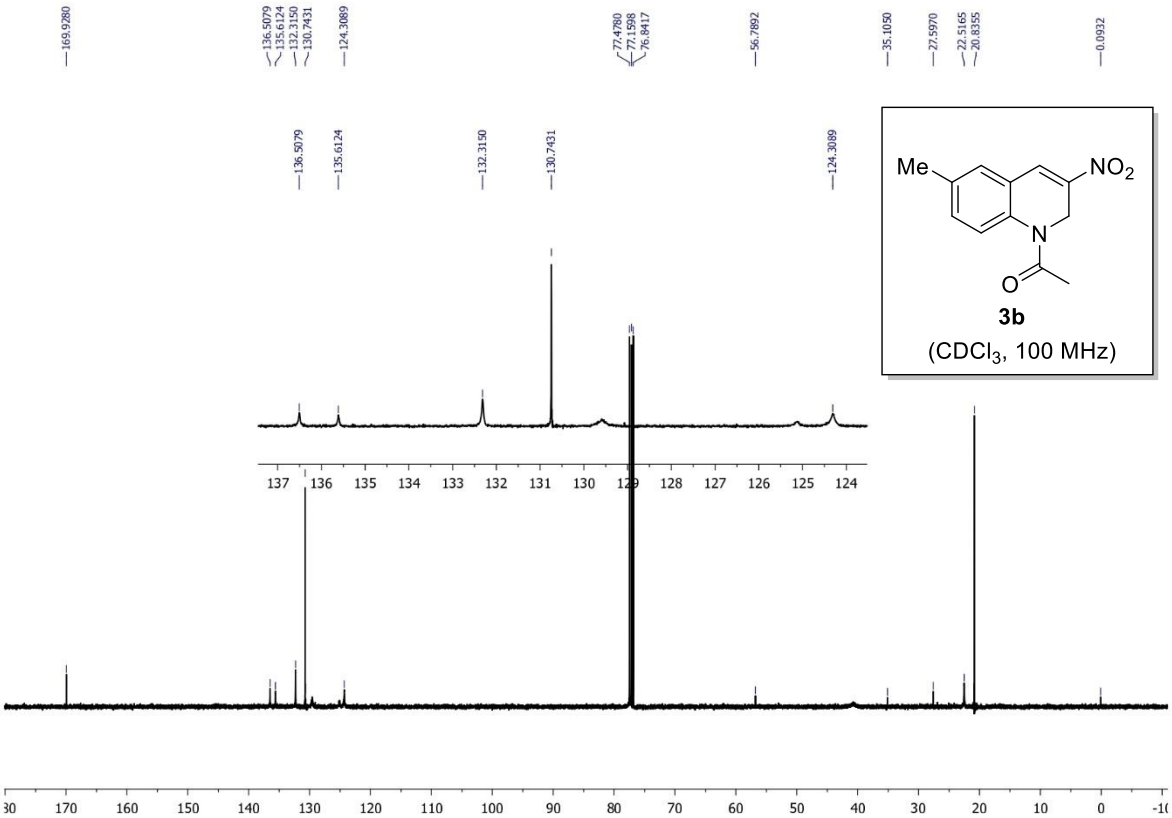
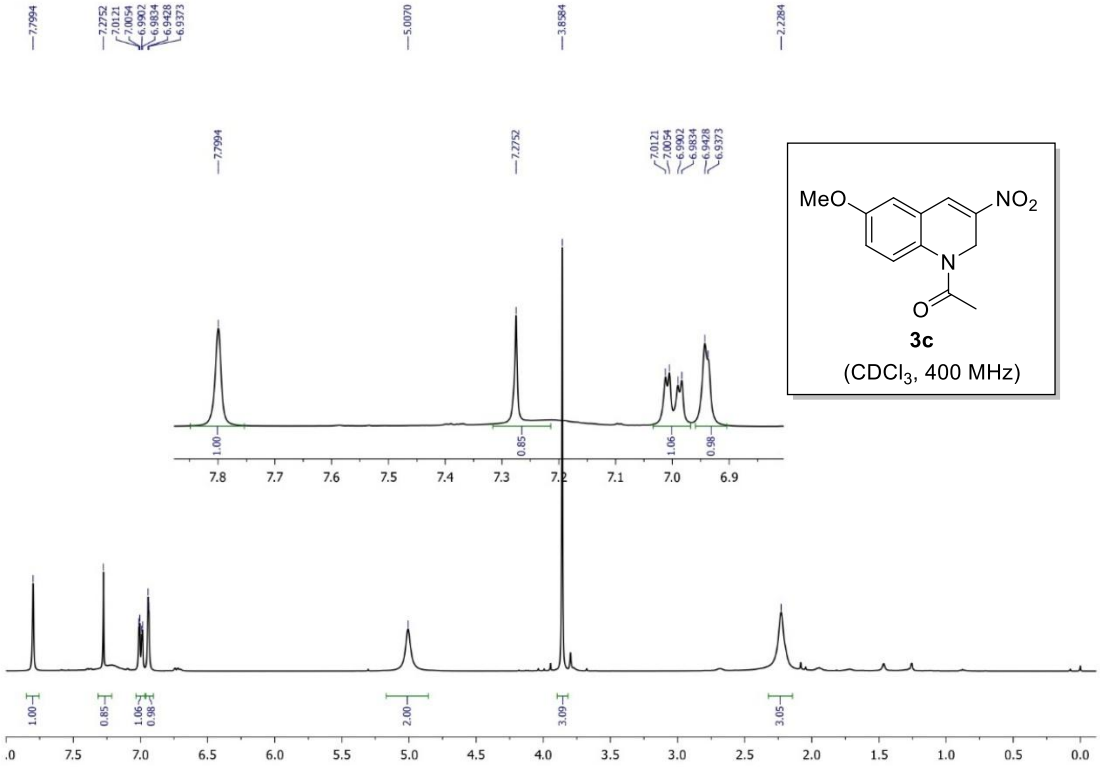


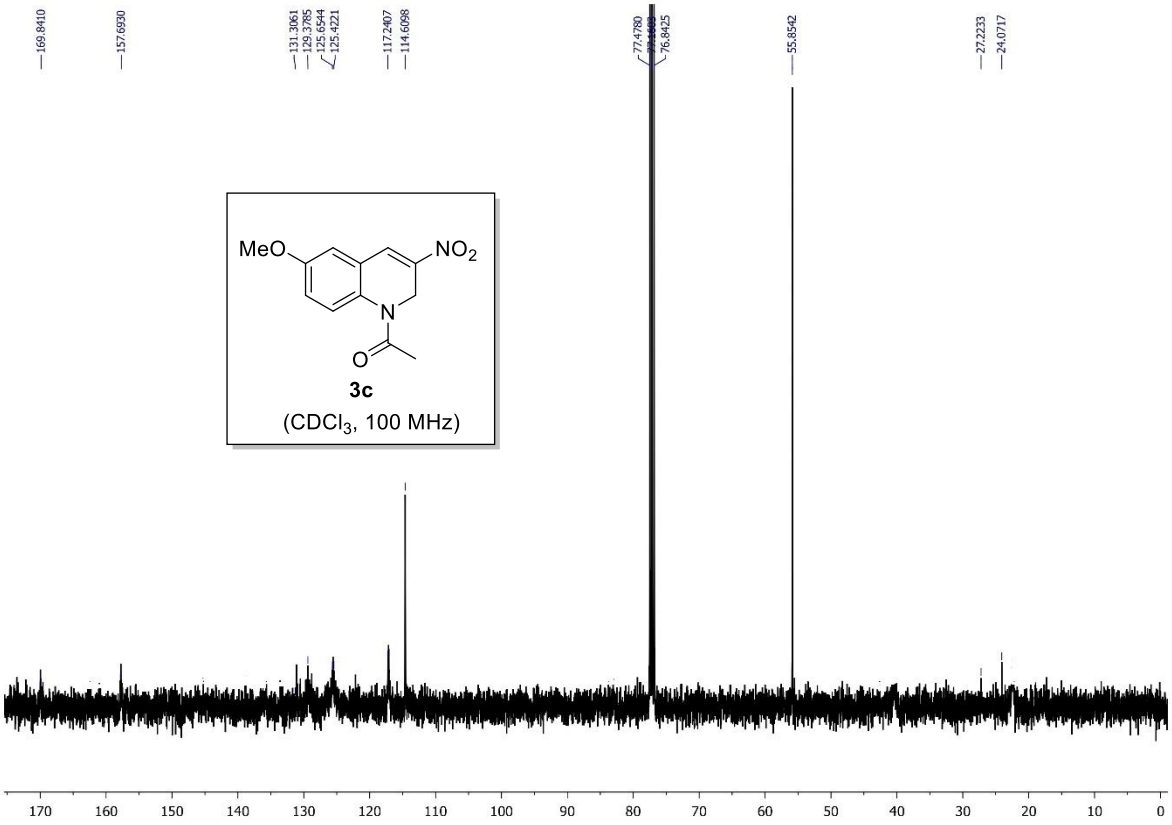
^{13}C NMR of 3b ($CDCl_3$, 100 MHz)



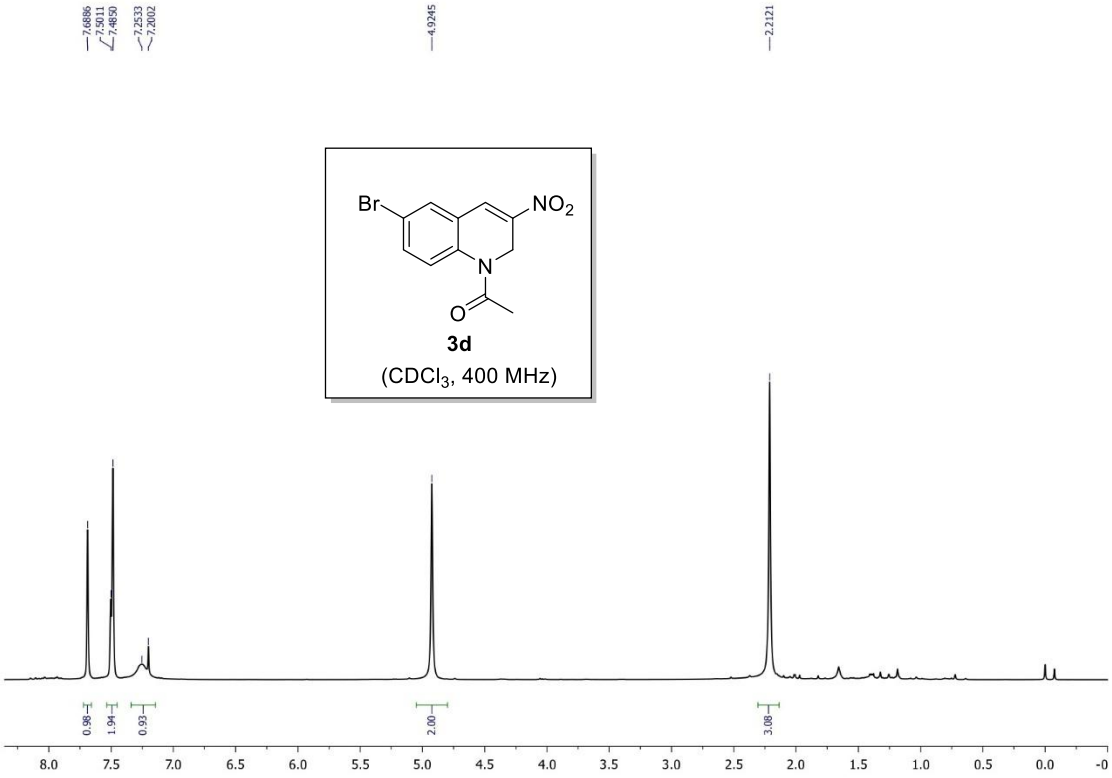
^{1}H NMR of 3c ($CDCl_3$, 400 MHz)



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



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



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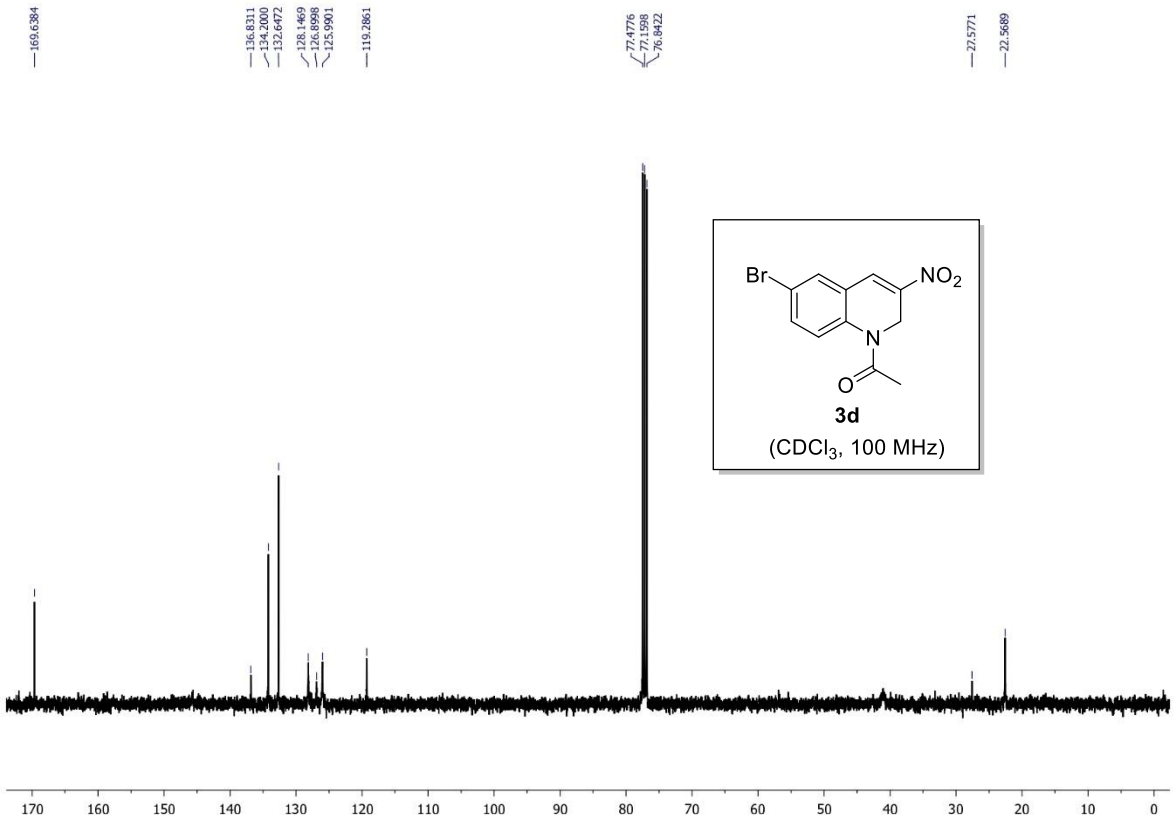
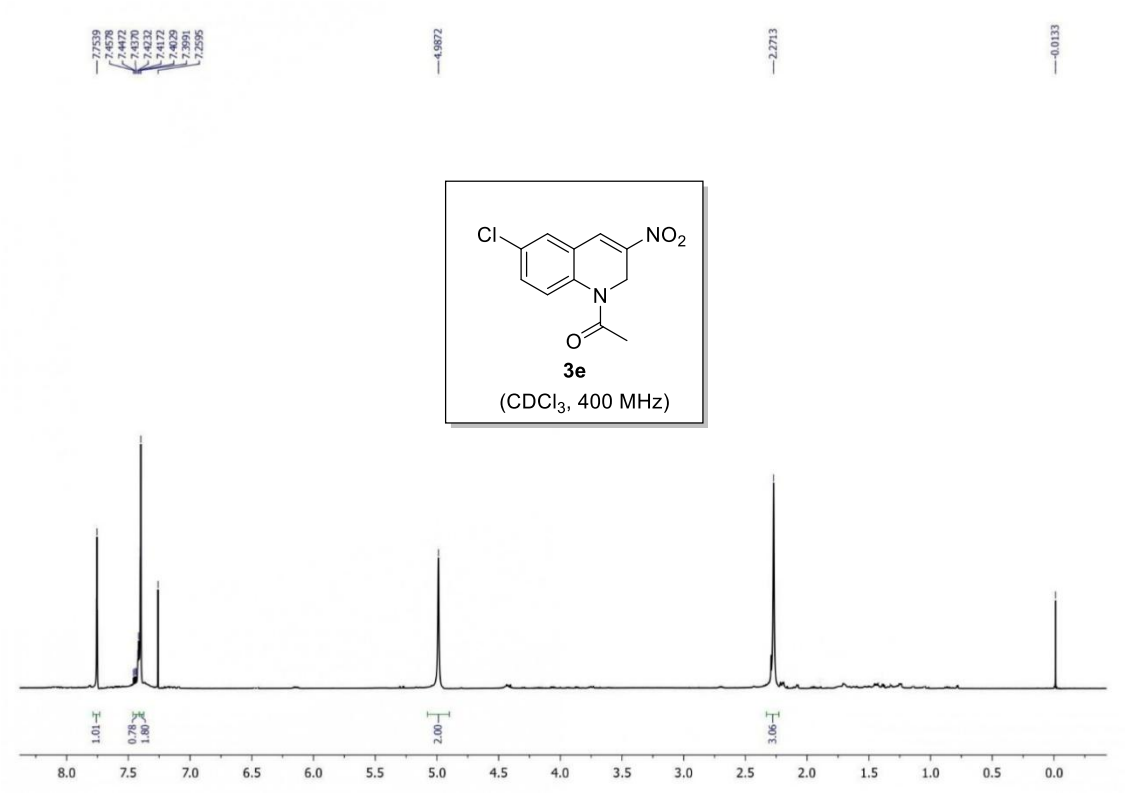
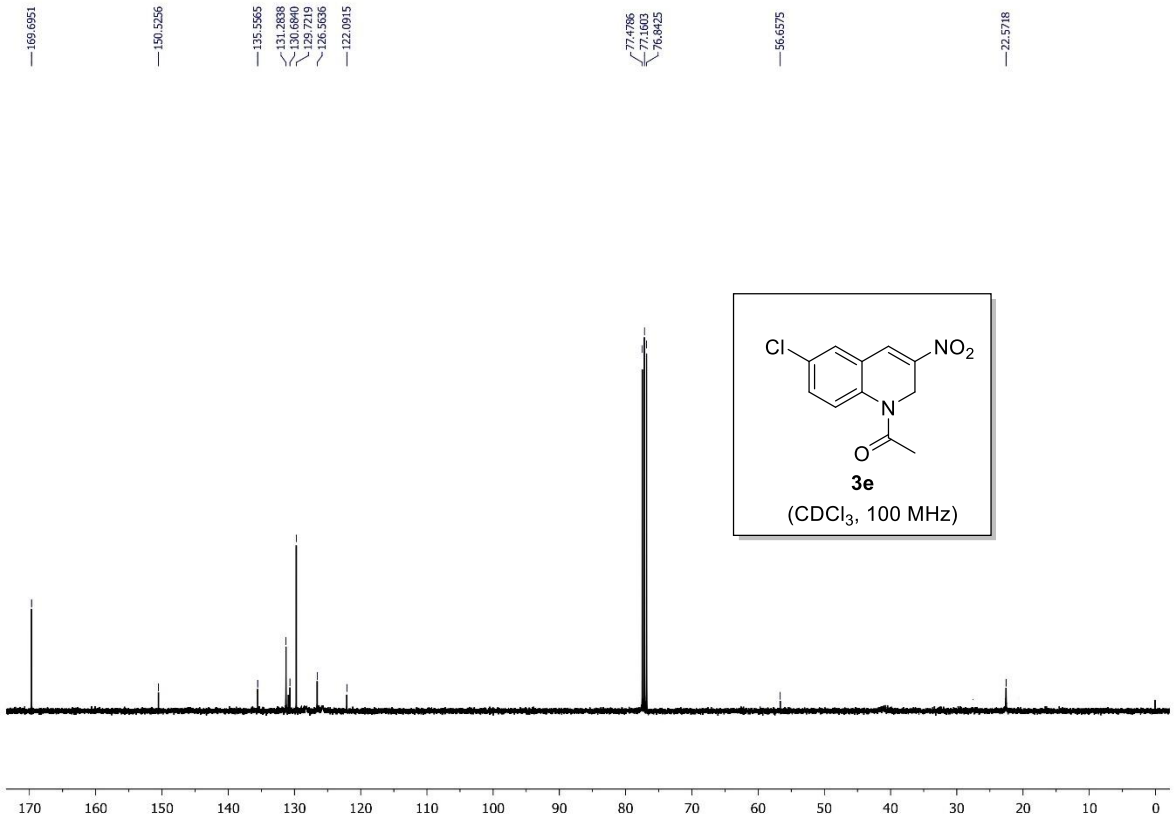


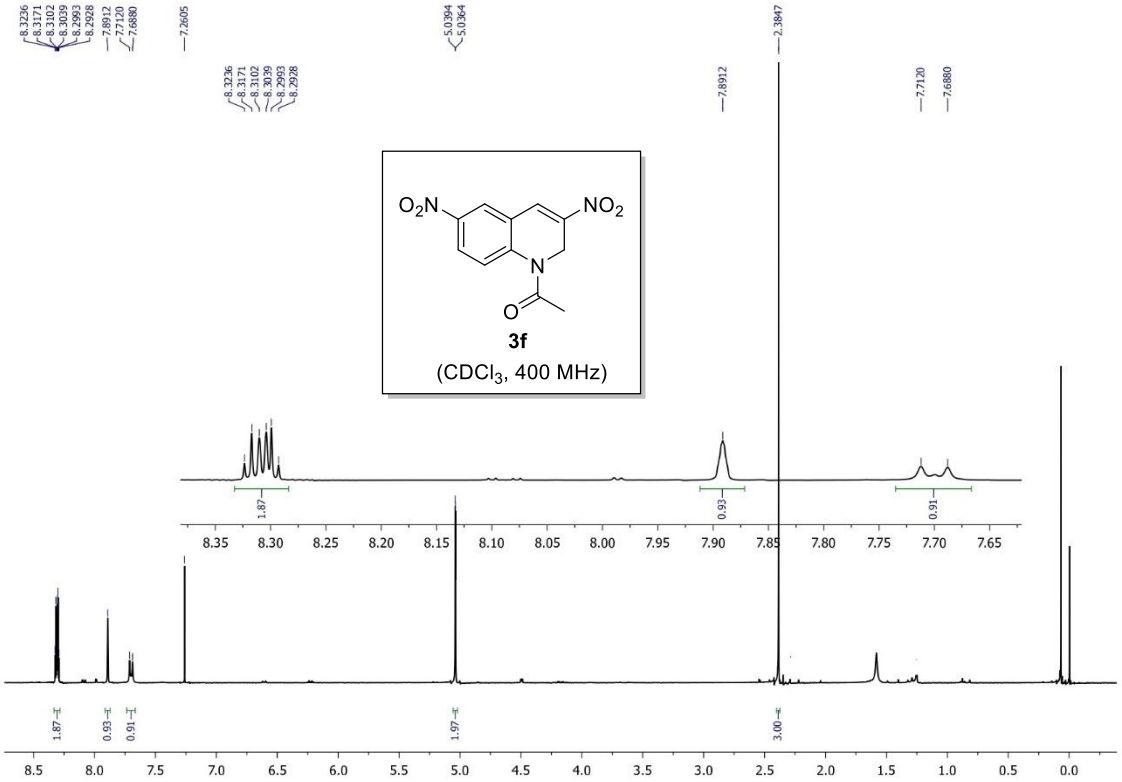
^{1}H NMR of 3e ($CDCl_3$, 400 MHz)



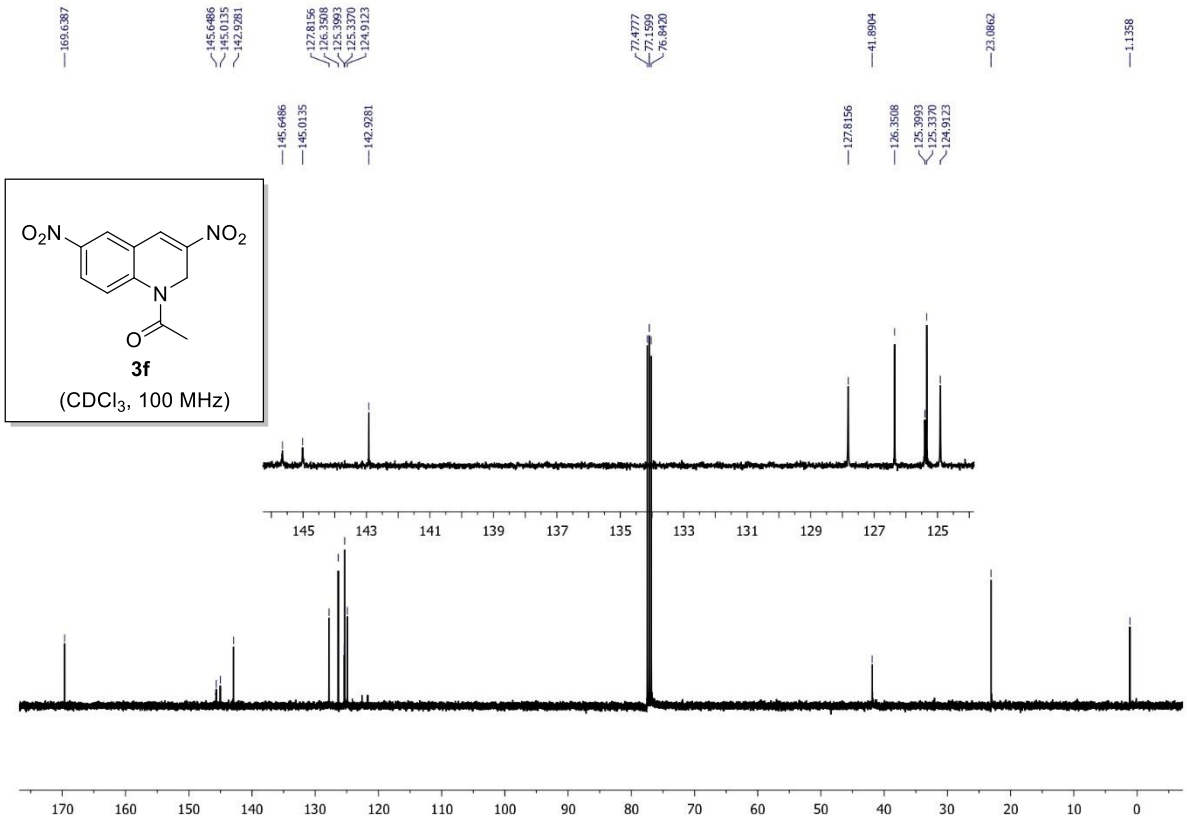
^{13}C NMR of 3e ($CDCl_3$, 100 MHz)



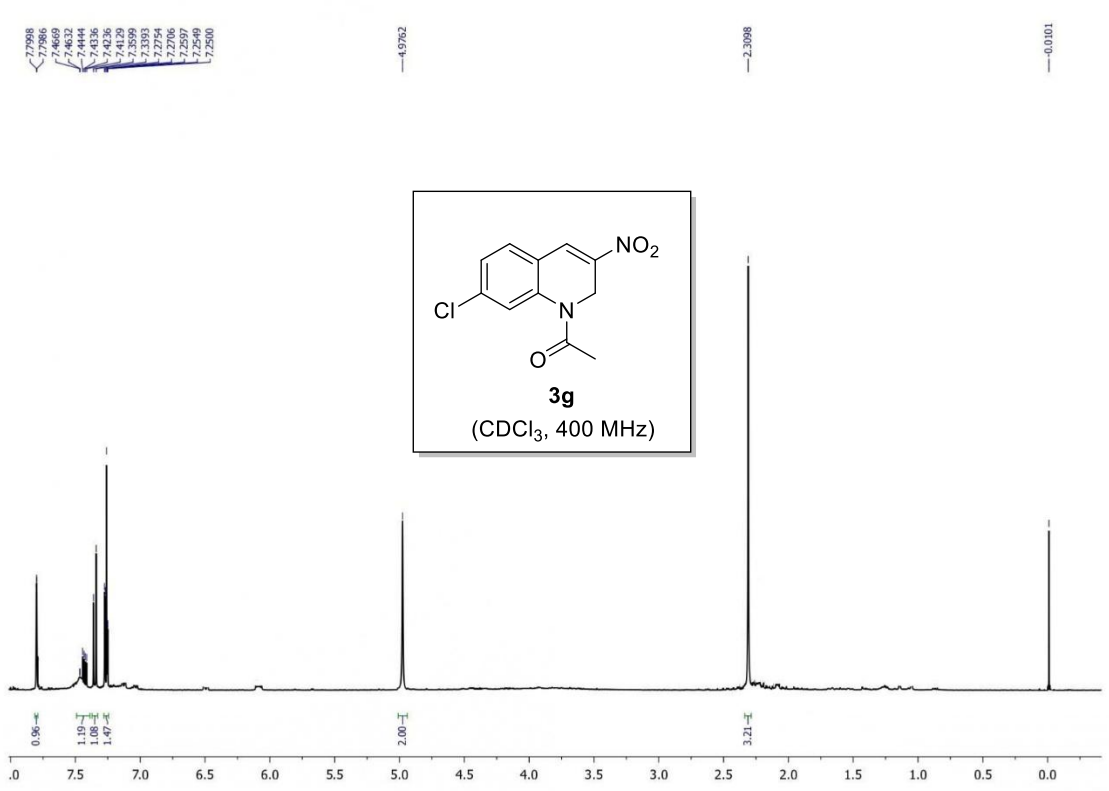
^{1}H NMR of 3f ($CDCl_3$, 400 MHz)



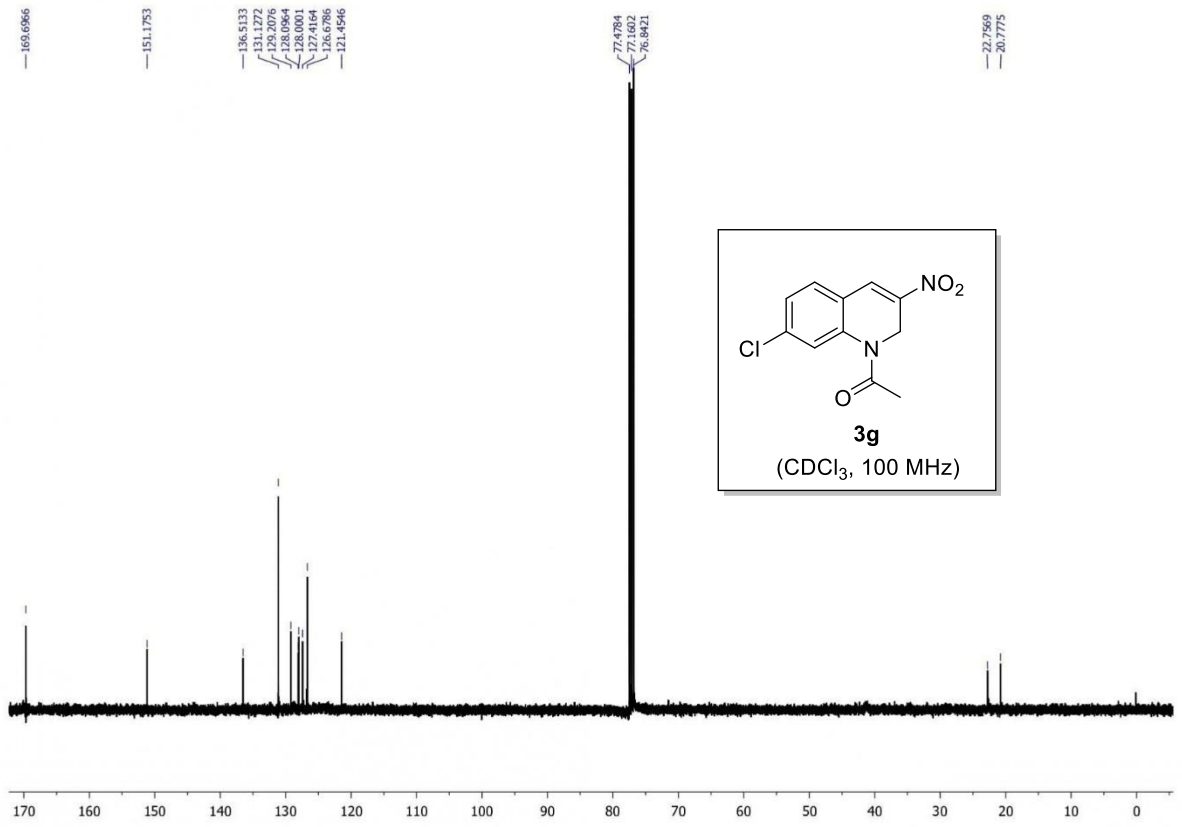
^{13}C NMR of 3f ($CDCl_3$, 100 MHz)



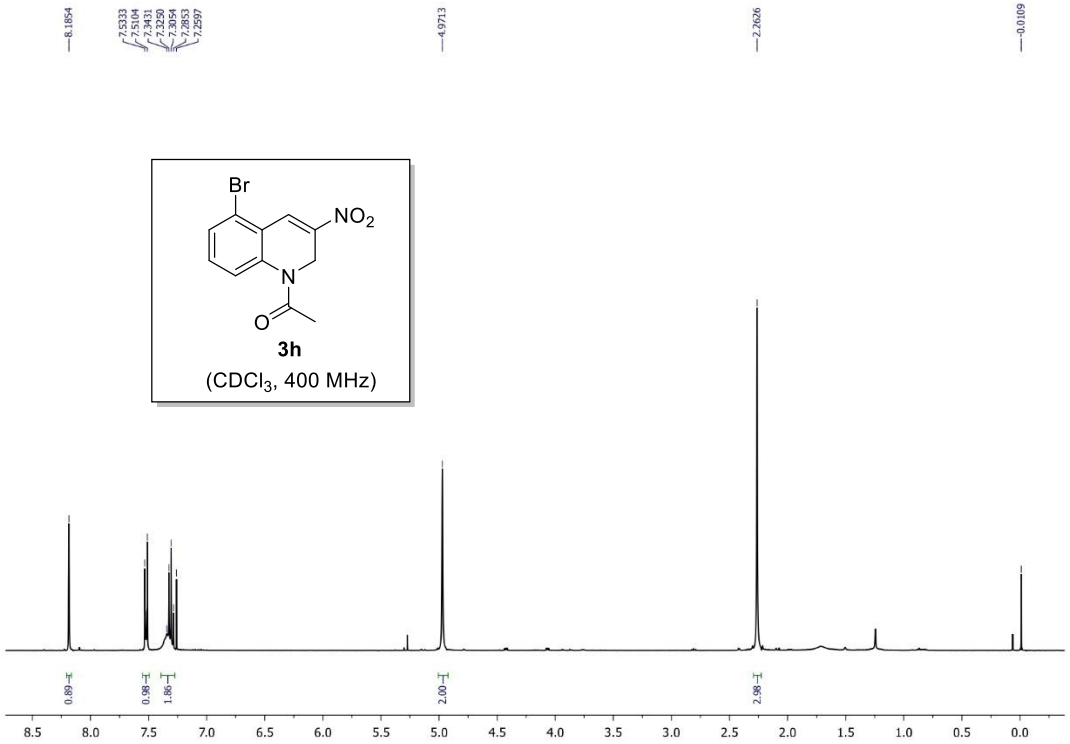
^{1}H NMR of 3g ($CDCl_3$, 400 MHz)



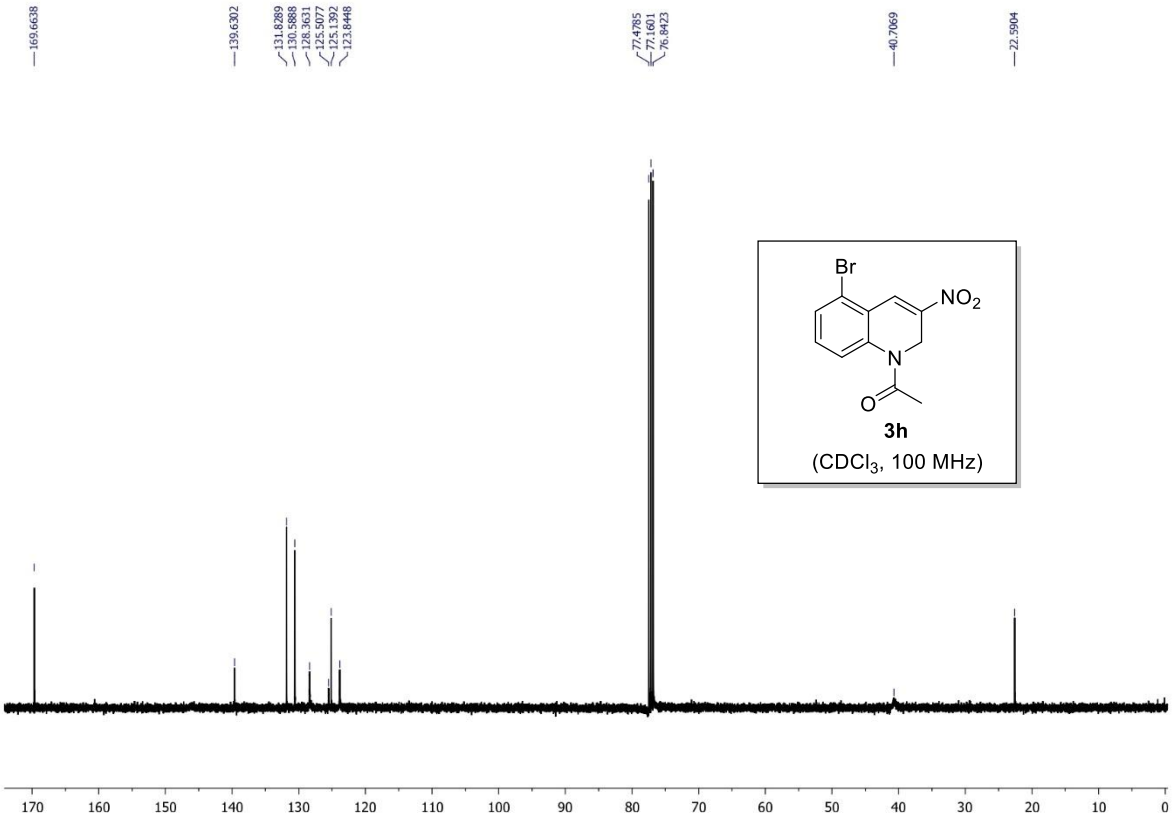
^{13}C NMR of 3g ($CDCl_3$, 100 MHz)



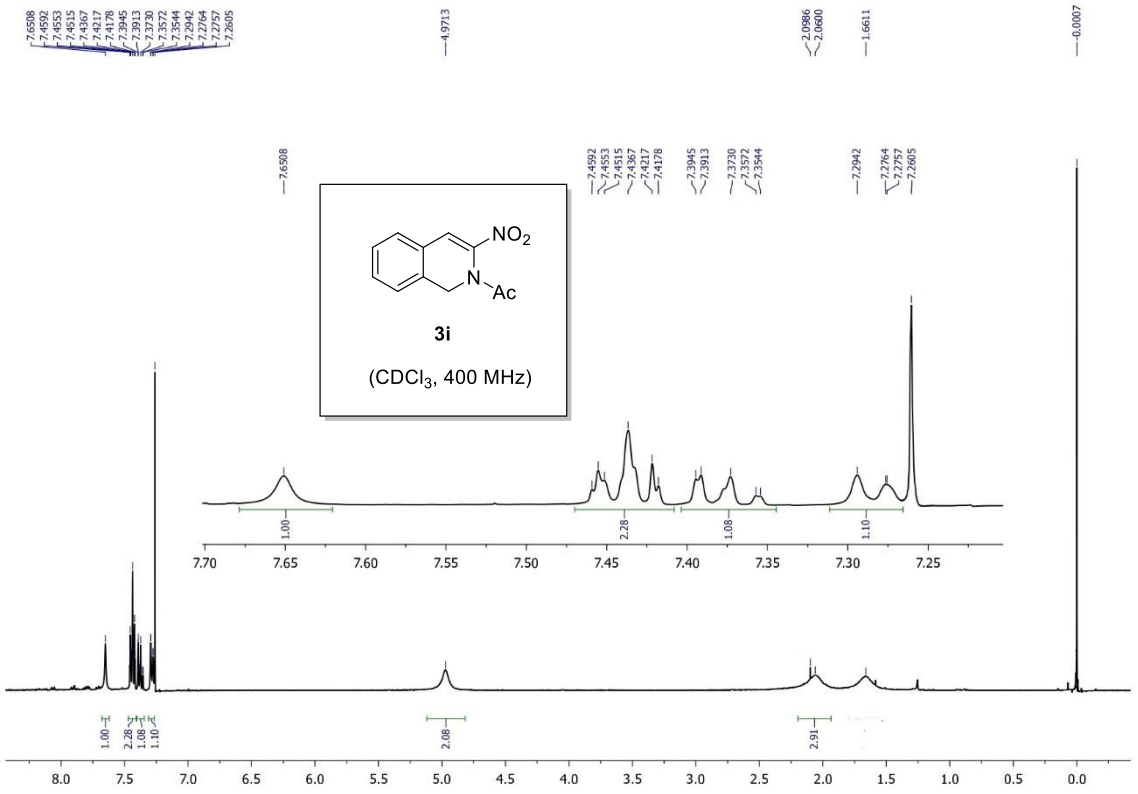
^{1}H NMR of 3h ($CDCl_3$, 400 MHz)



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



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



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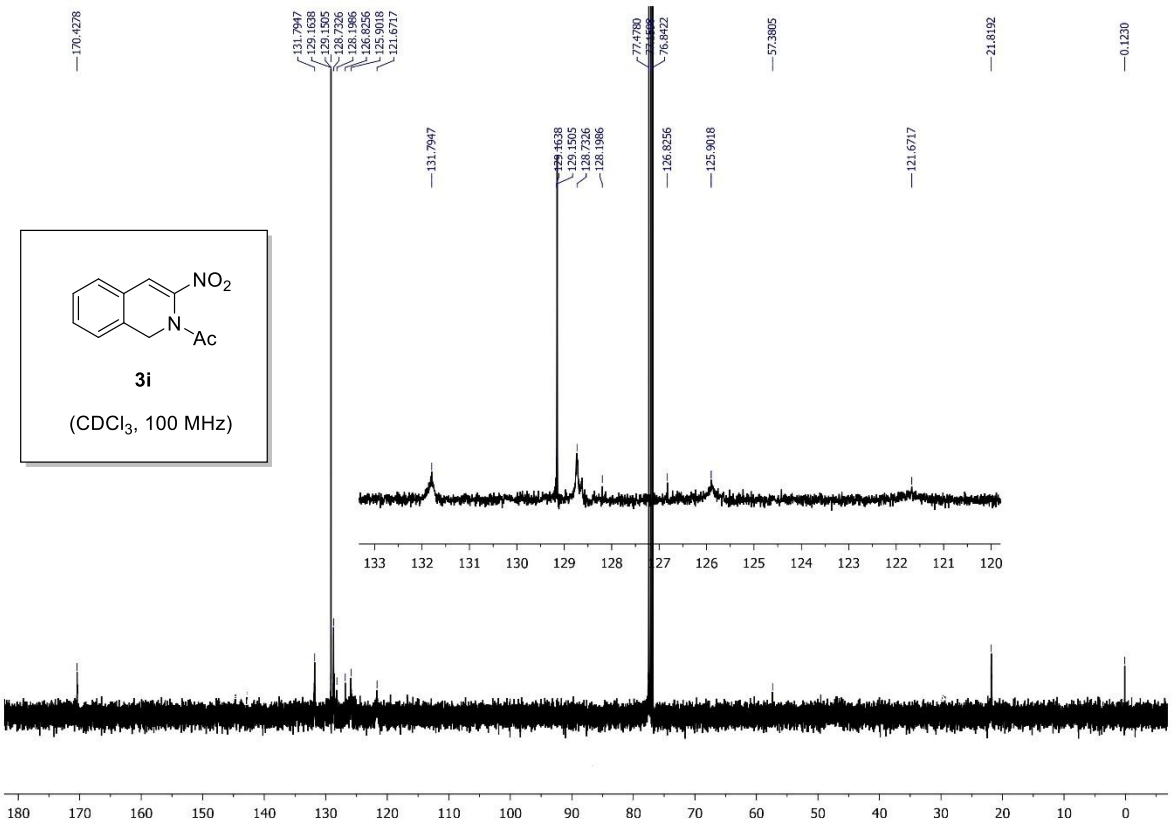
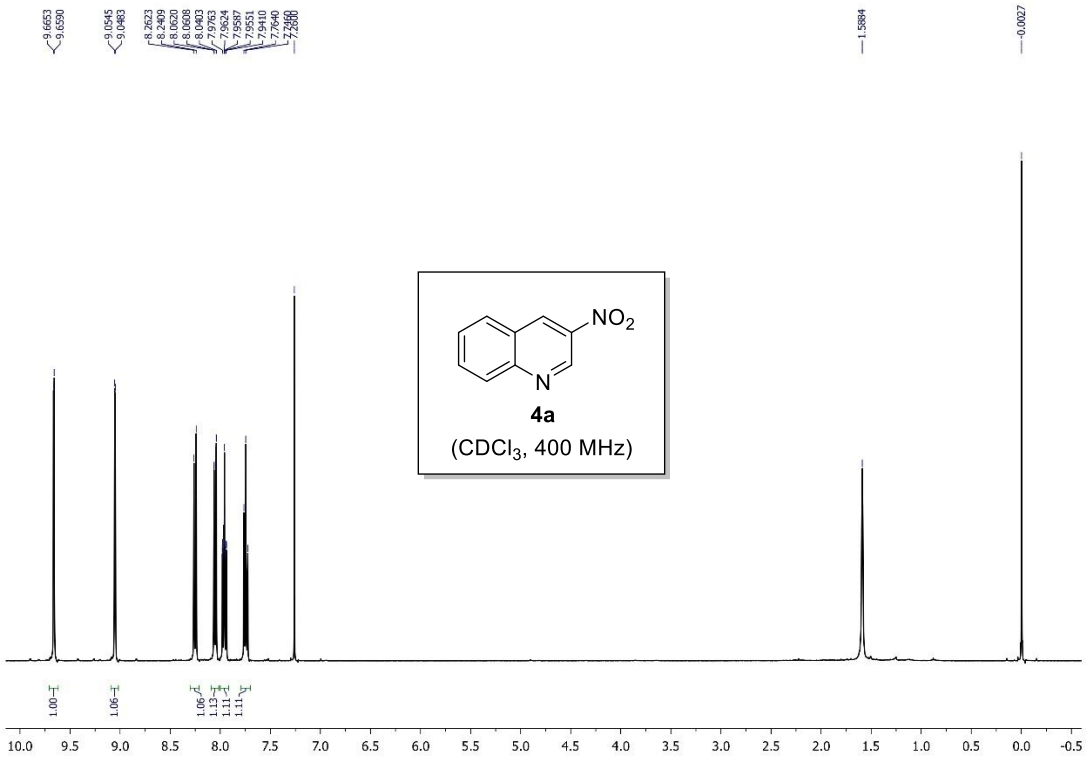
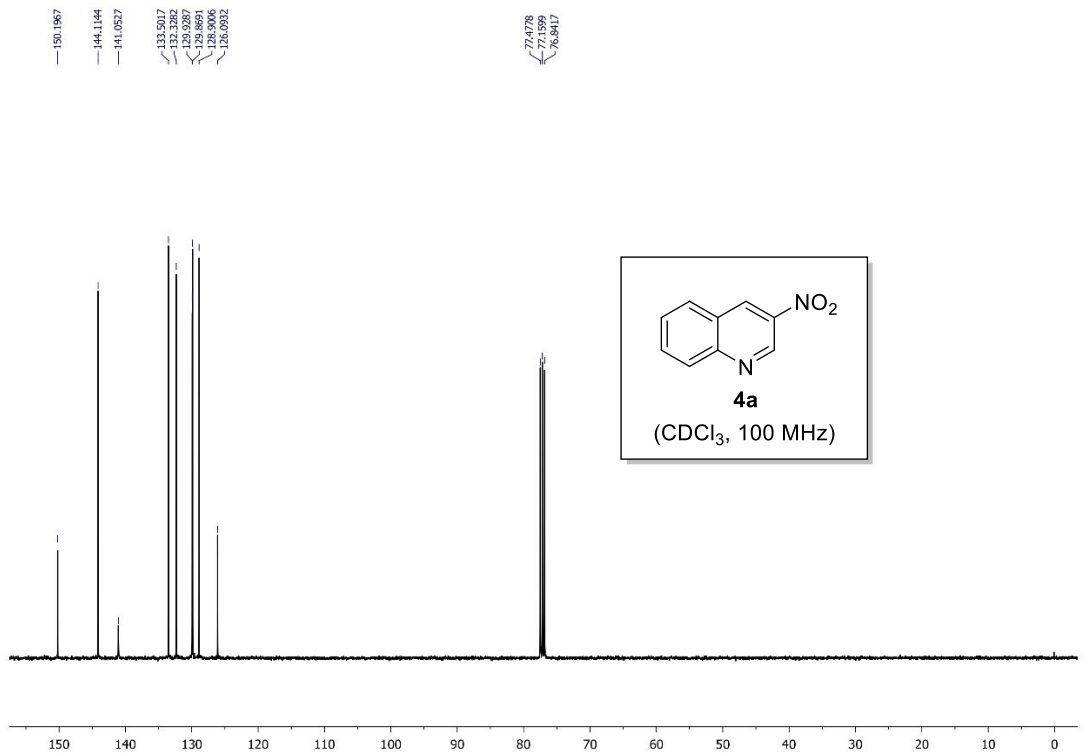


^{1}H and ^{13}C NMR spectra of 3-nitroquinoline derivatives (4):

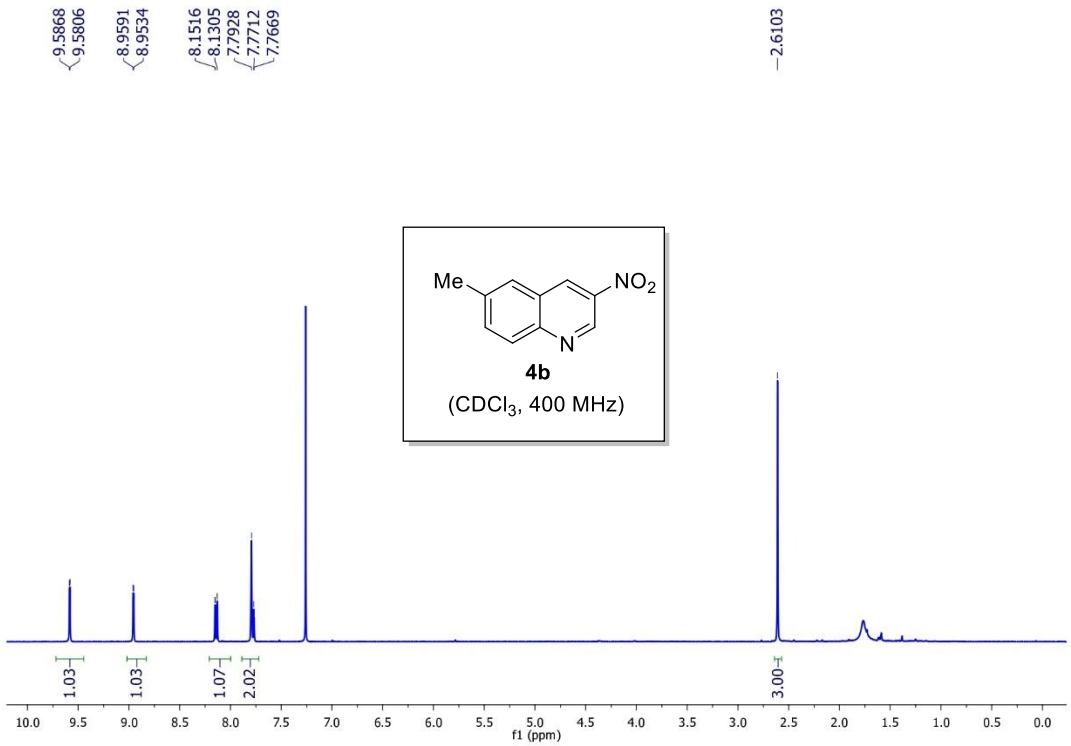
^{1}H NMR of 4a ($CDCl_3$, 400 MHz)



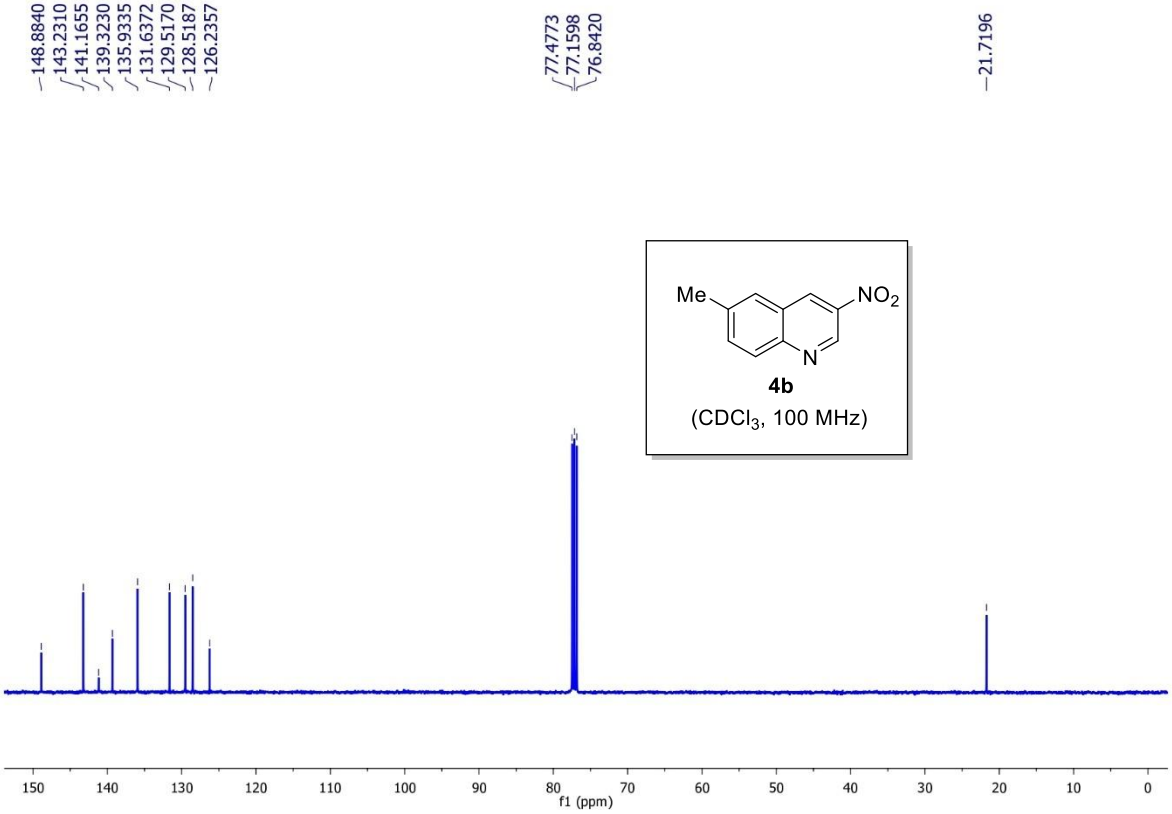
^{13}C NMR of 4a ($CDCl_3$, 100 MHz)



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



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



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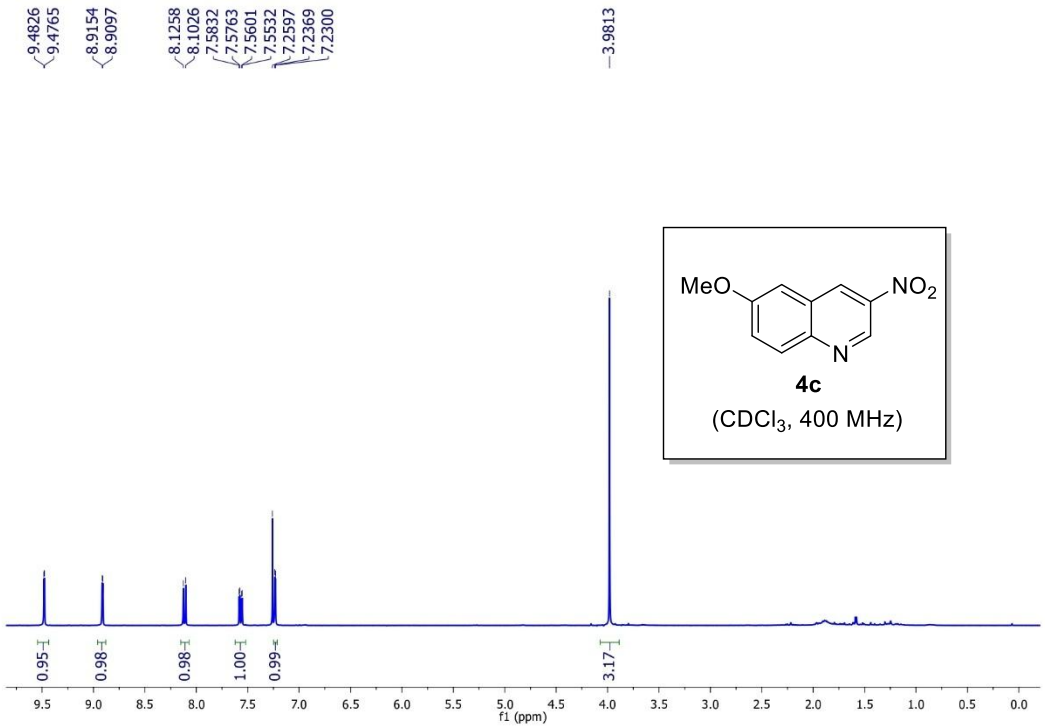
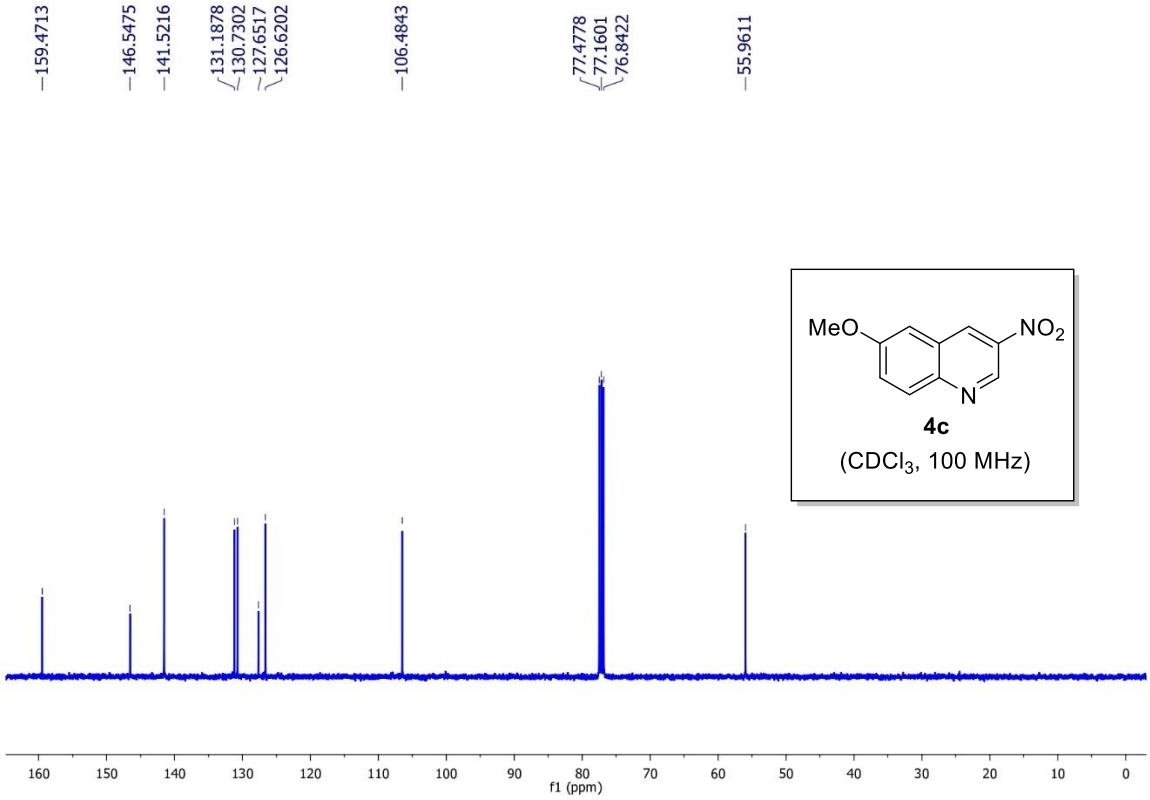
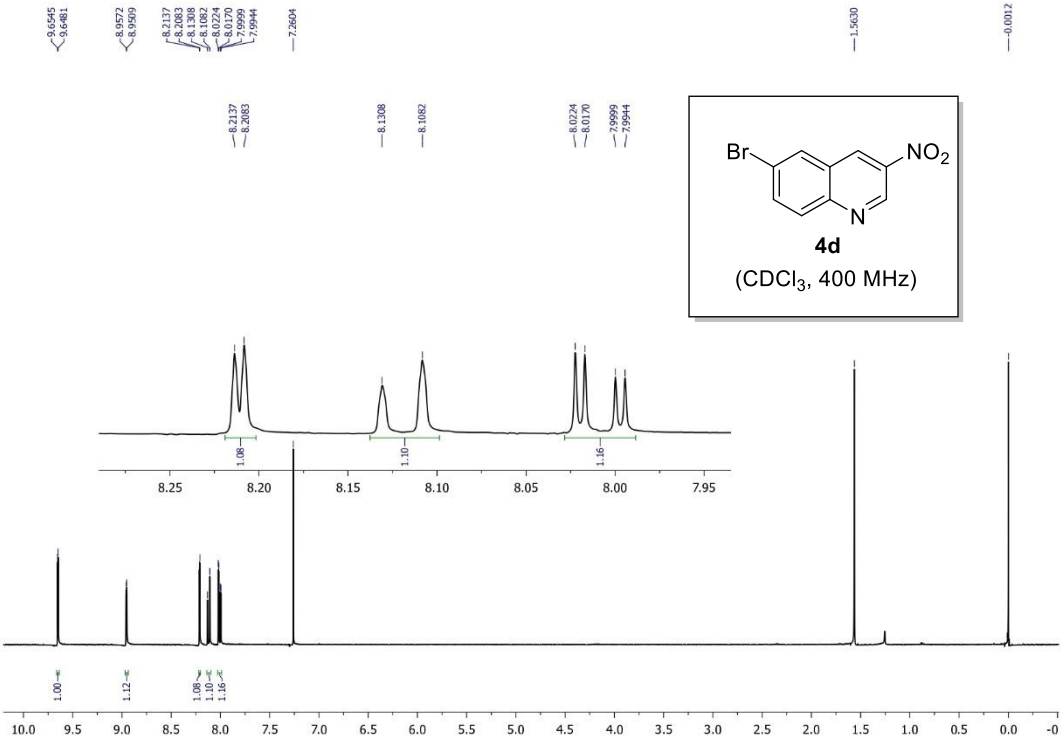


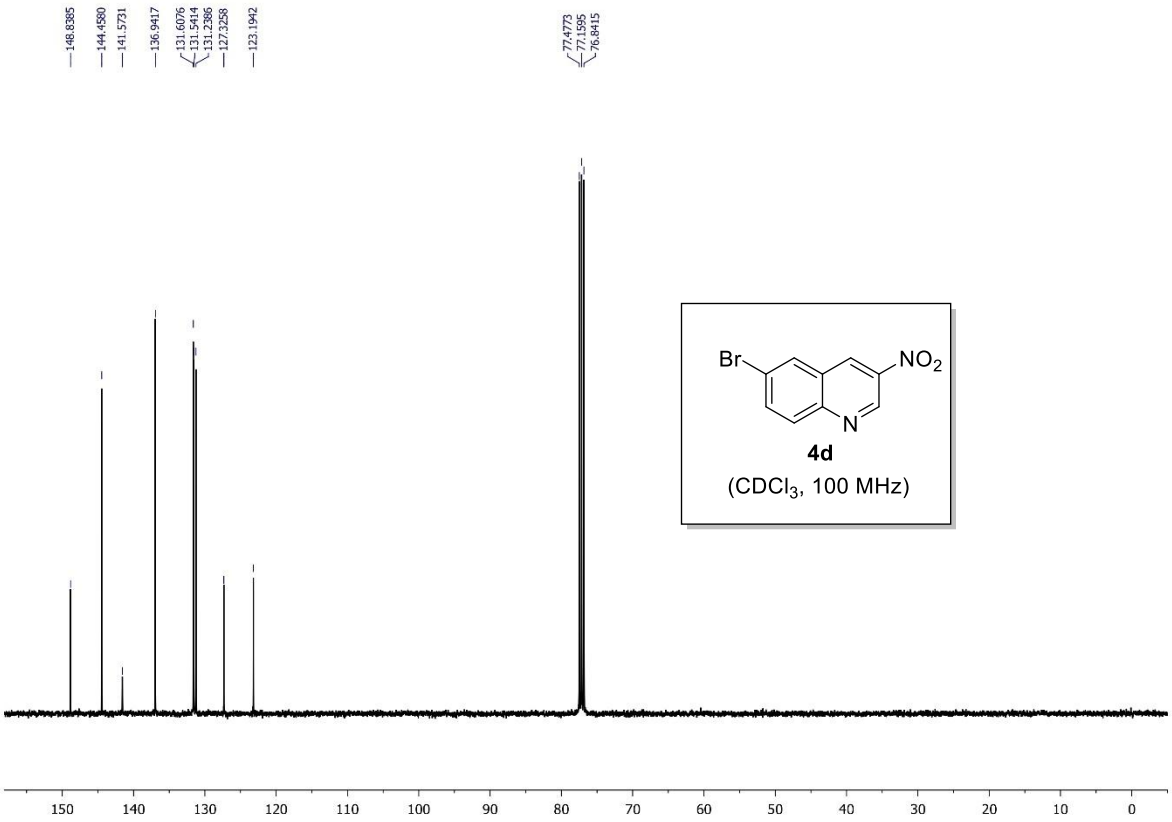
^{13}C NMR of 4c ($CDCl_3$, 100 MHz)



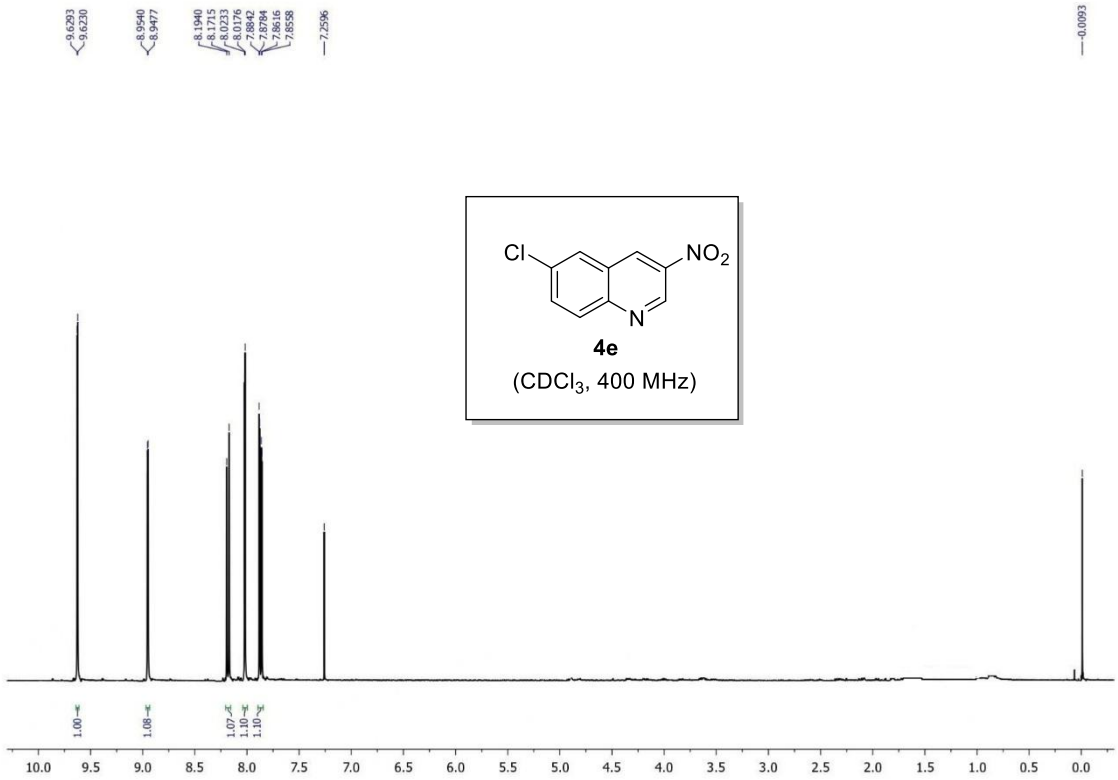
^{1}H NMR of 4d ($CDCl_3$, 400 MHz)



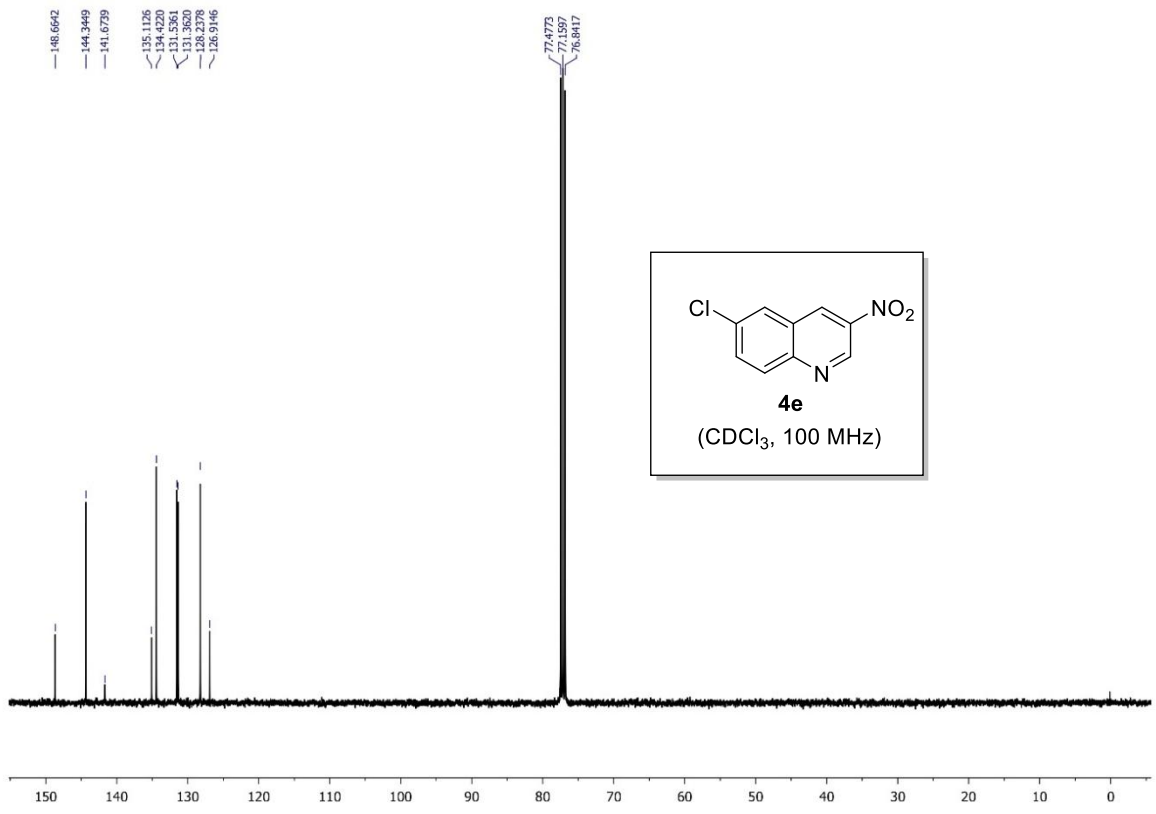
^{13}C NMR of 4d ($CDCl_3$, 100 MHz)



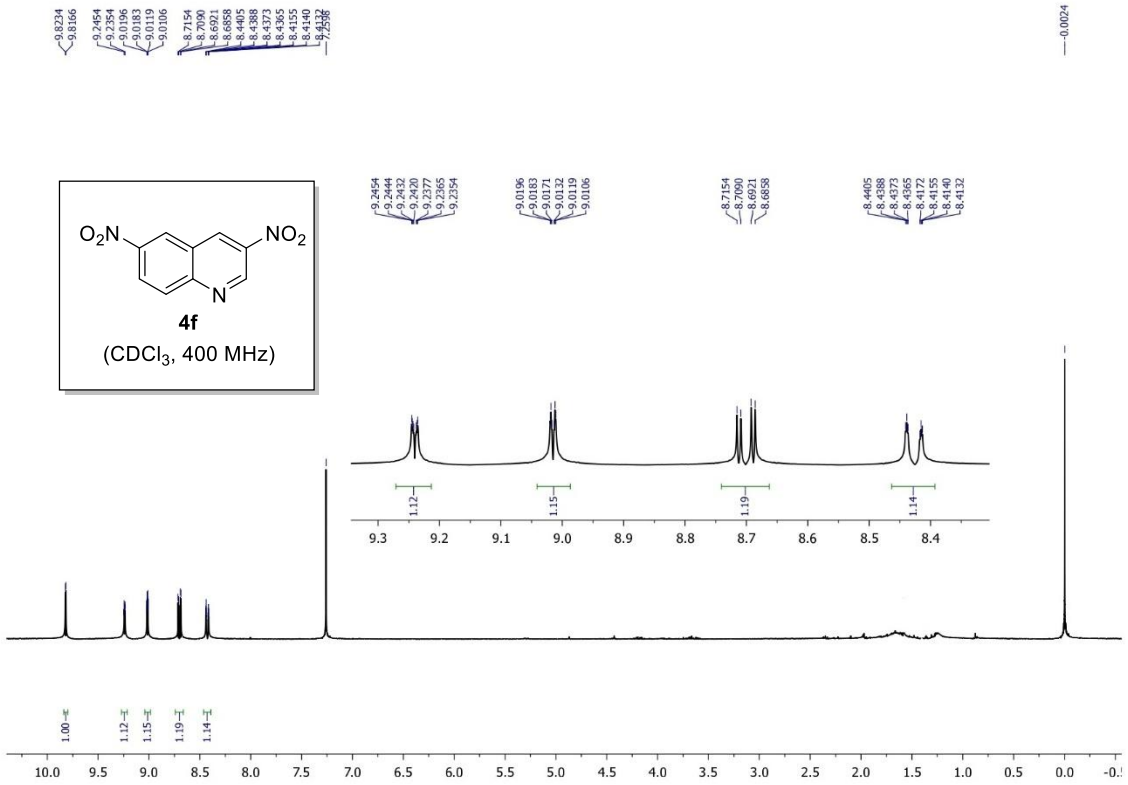
^{1}H NMR of 4e ($CDCl_3$, 400 MHz)



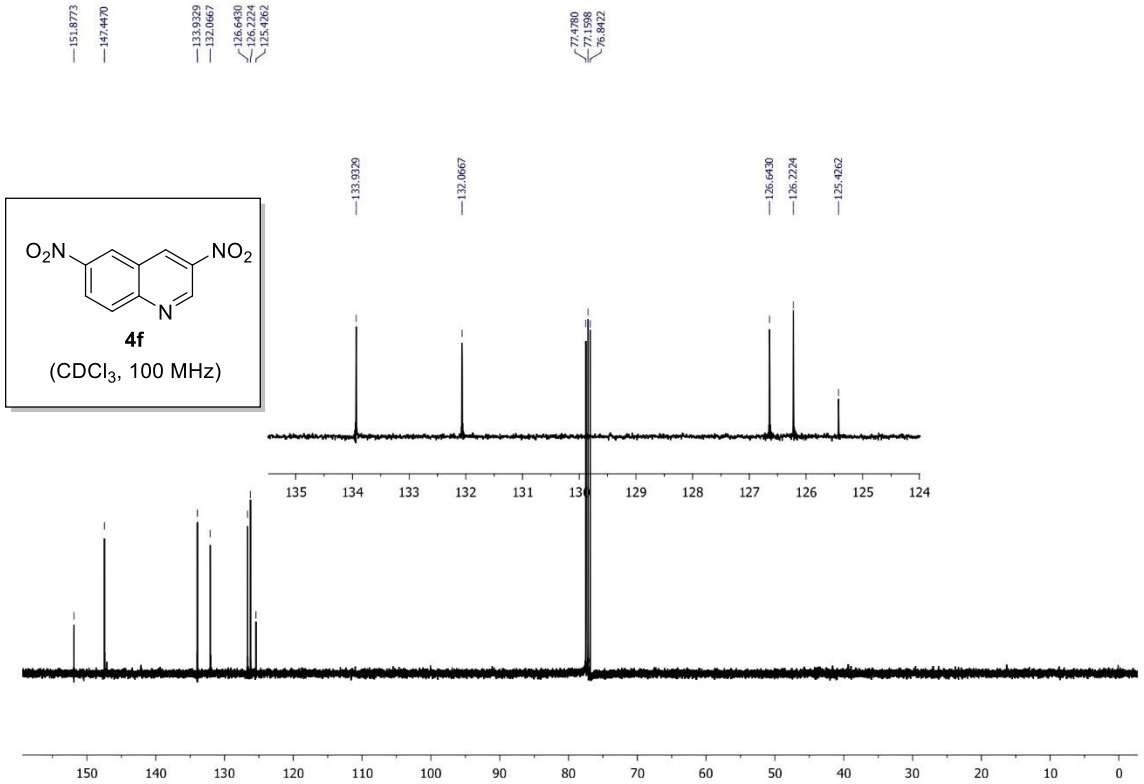
^{13}C NMR of 4e ($CDCl_3$, 100 MHz)



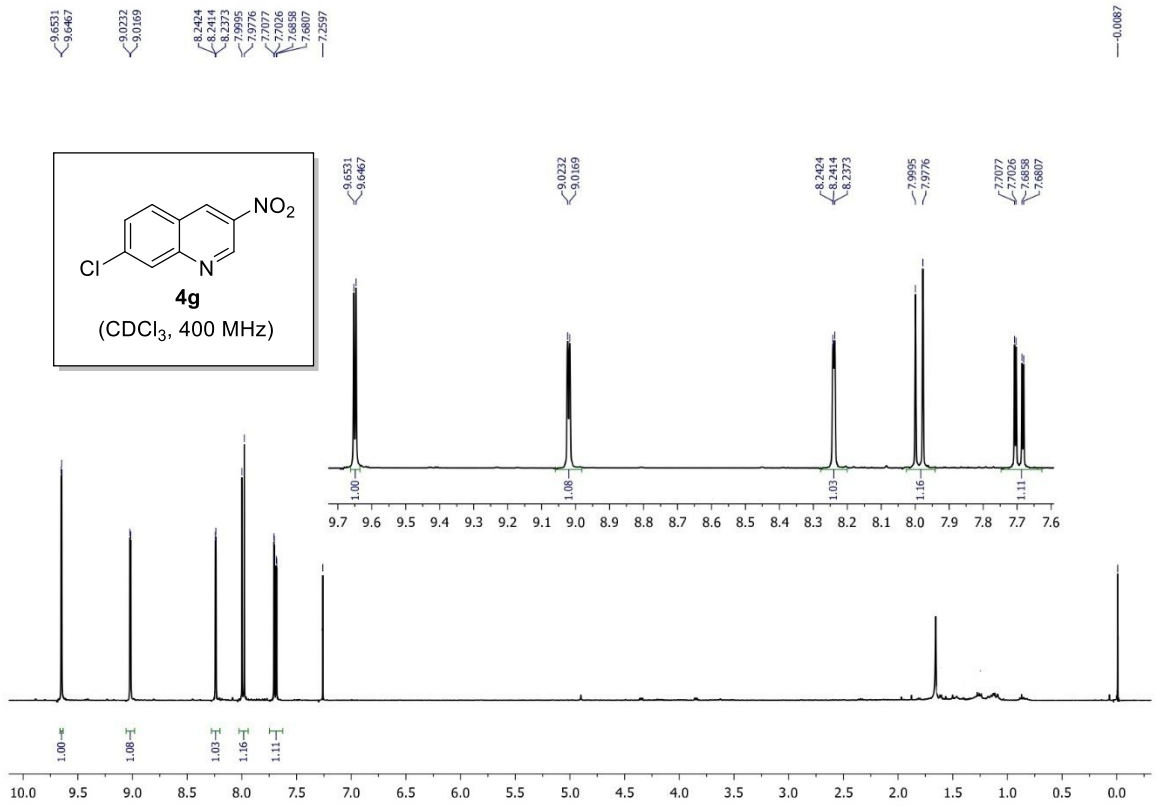
^{1}H NMR of 4f ($CDCl_3$, 400 MHz)



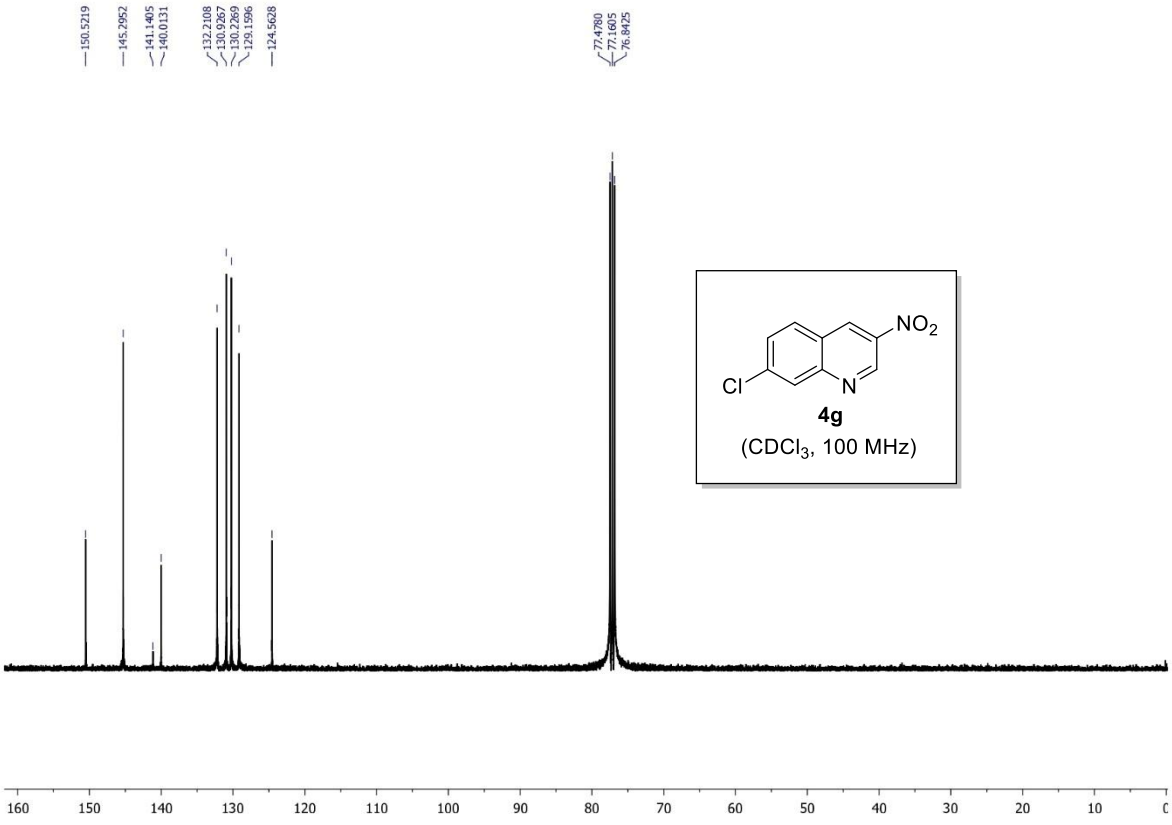
^{13}C NMR of 4f ($CDCl_3$, 100 MHz)



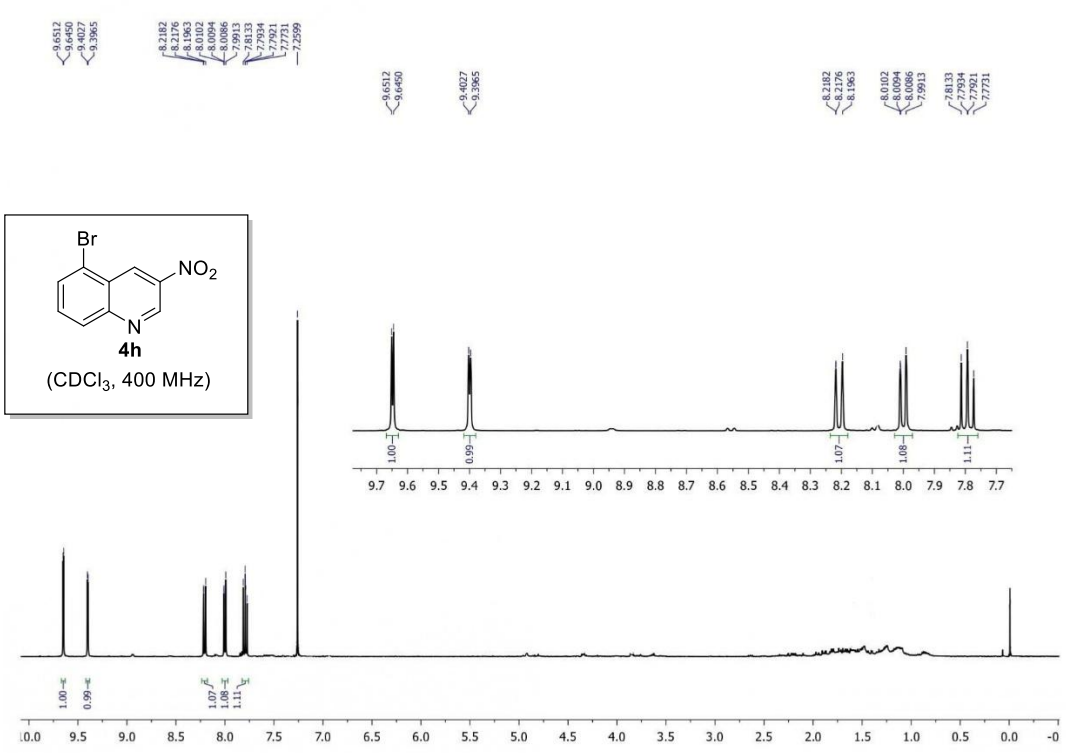
^{1}H NMR of 4g ($CDCl_3$, 400 MHz)



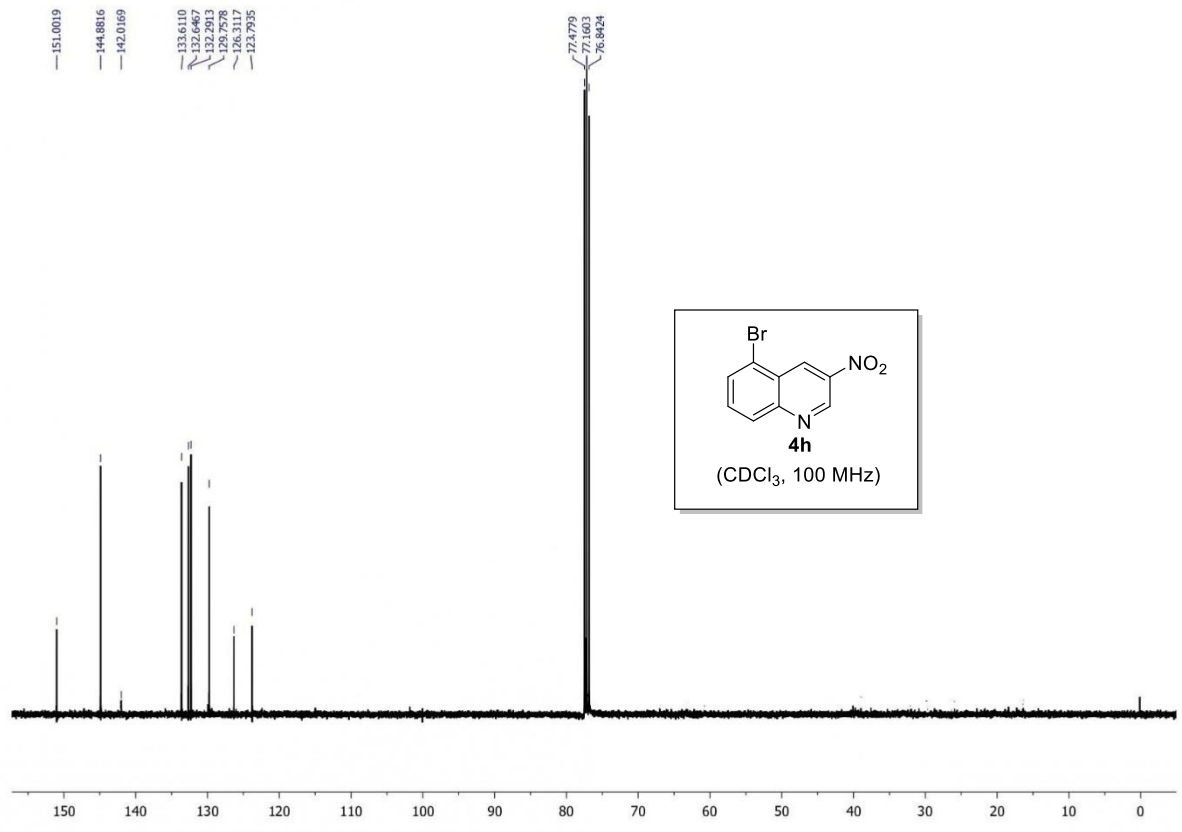
^{13}C NMR of 4g ($CDCl_3$, 100 MHz)



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

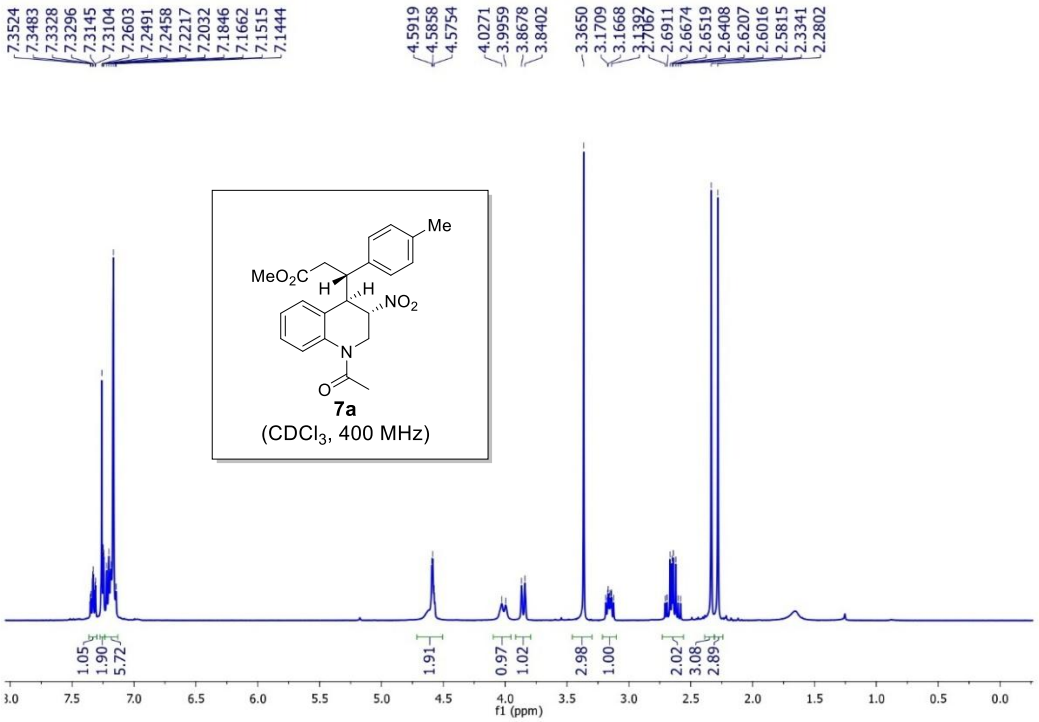


^{13}C NMR of 4h ($CDCl_3$, 100 MHz)

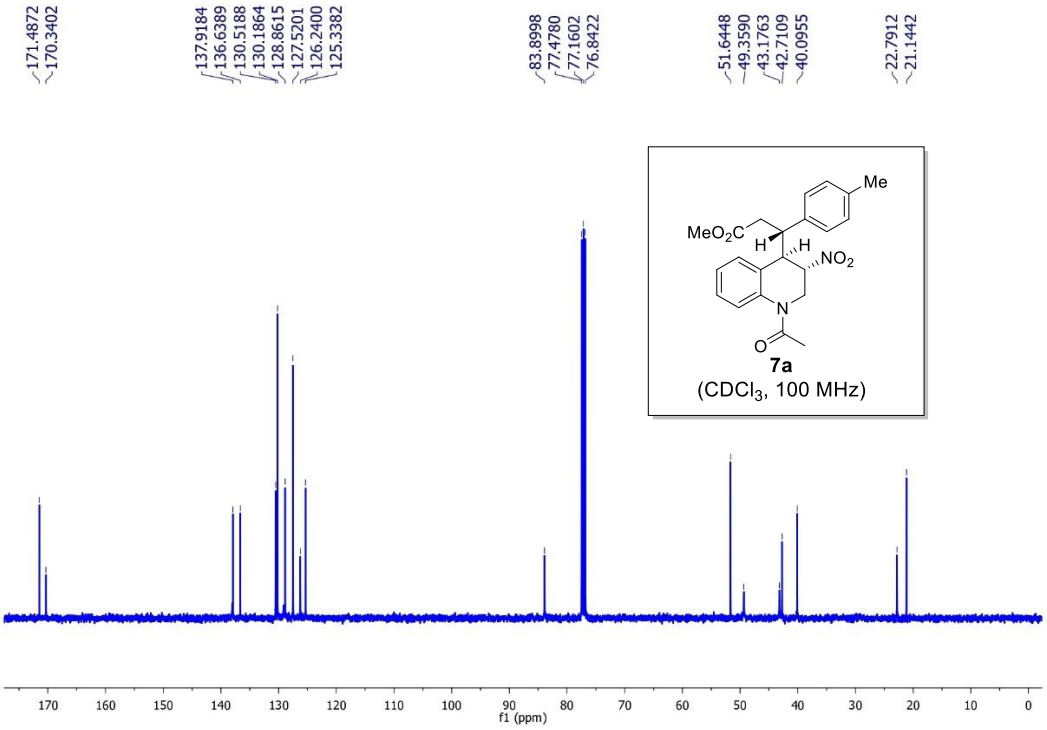


^{1}H and ^{13}C NMR spectra & HPLC chromatogram of 3-nitro-1,2,3,4-tetrahydroquinolin derivatives (7):

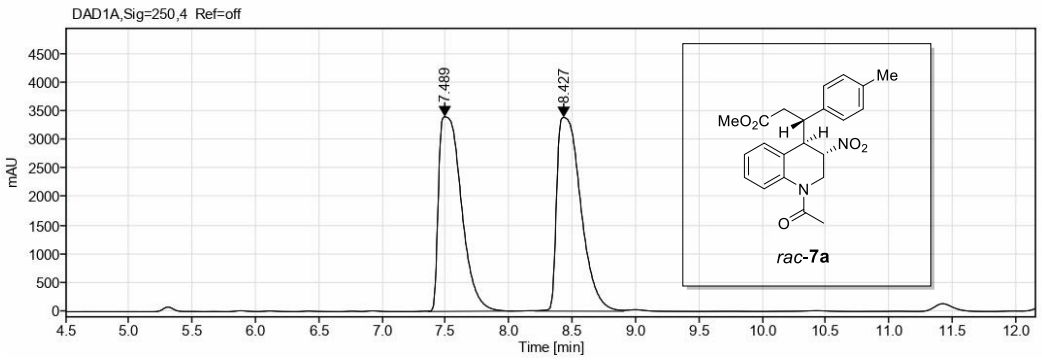
^{1}H NMR of 7a ($CDCl_3$, 400 MHz)



^{13}C NMR of 7a ($CDCl_3$, 100 MHz)



HPLC chromatogram of *rac*-7a



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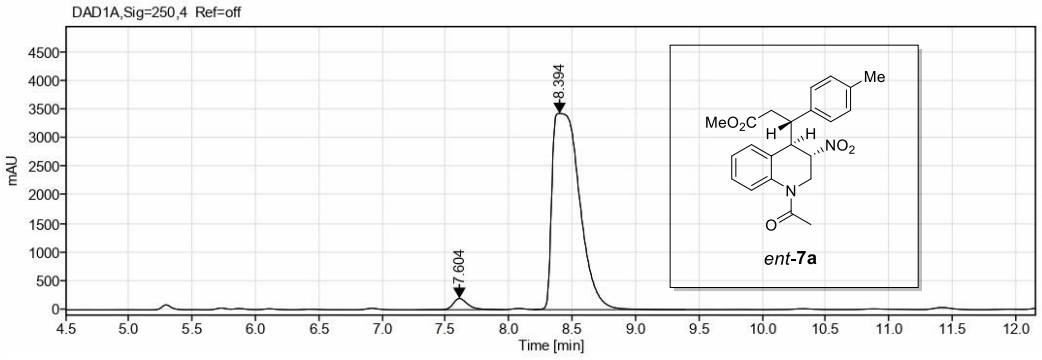
		Sum	87155.33			

HPLC chromatogram of *ent*-7a



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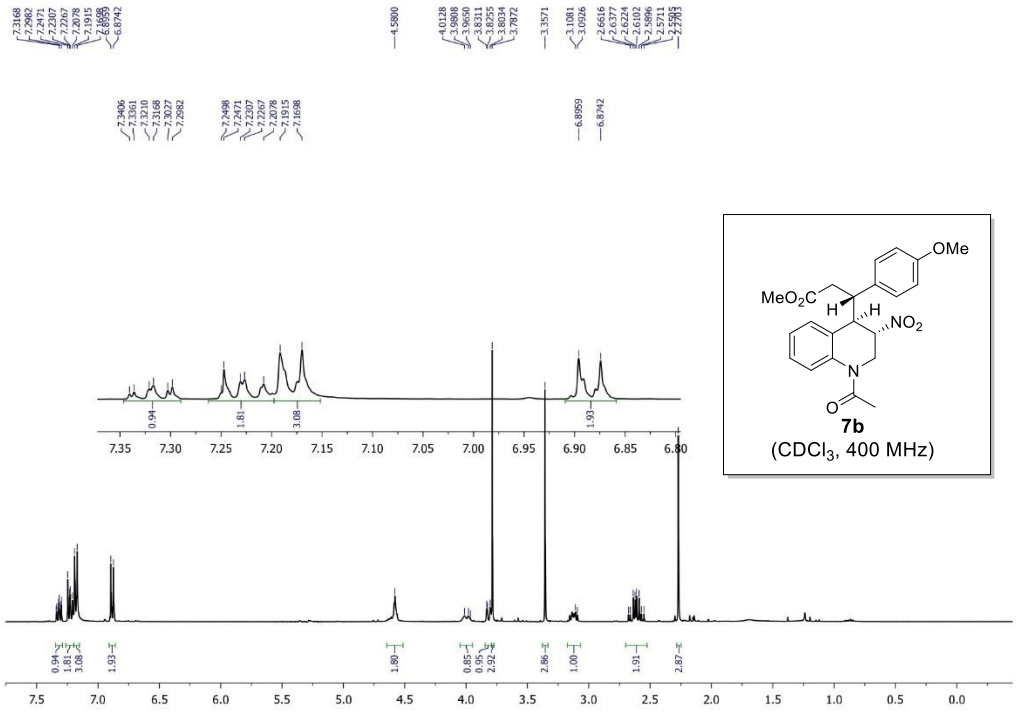
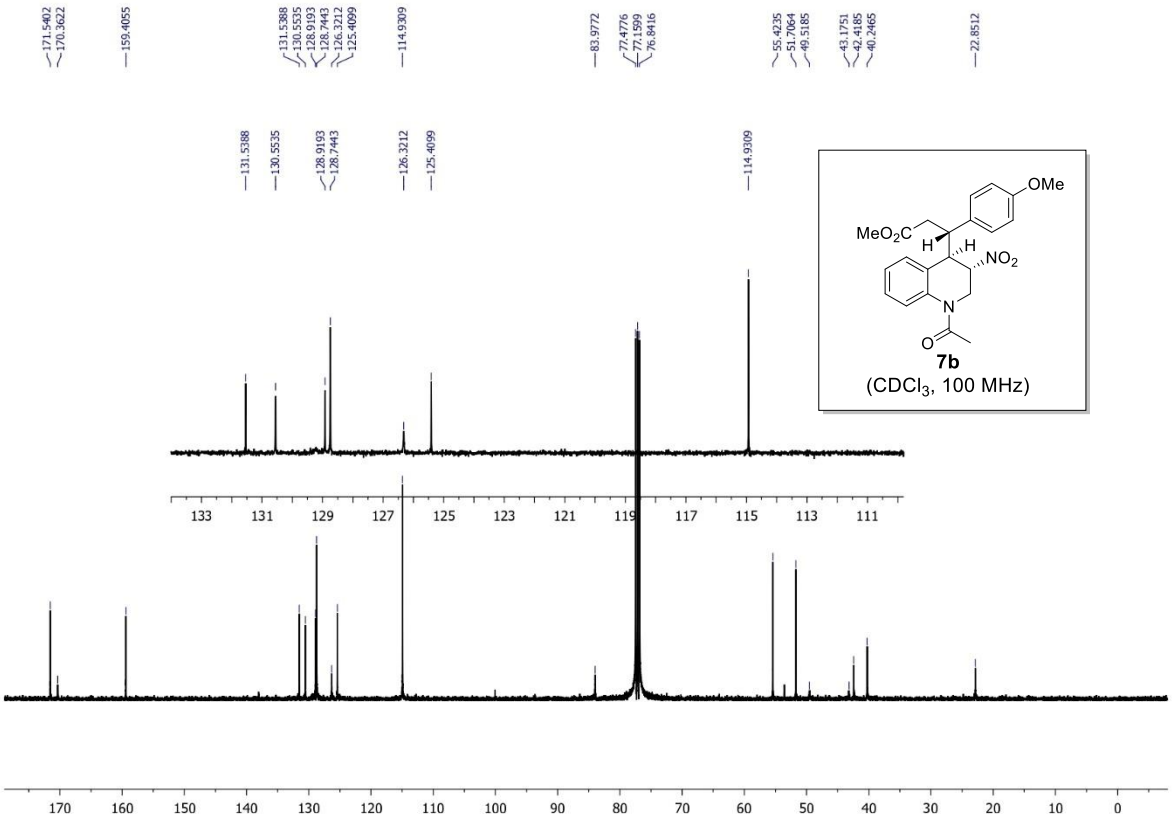
		Sum	53394.27			

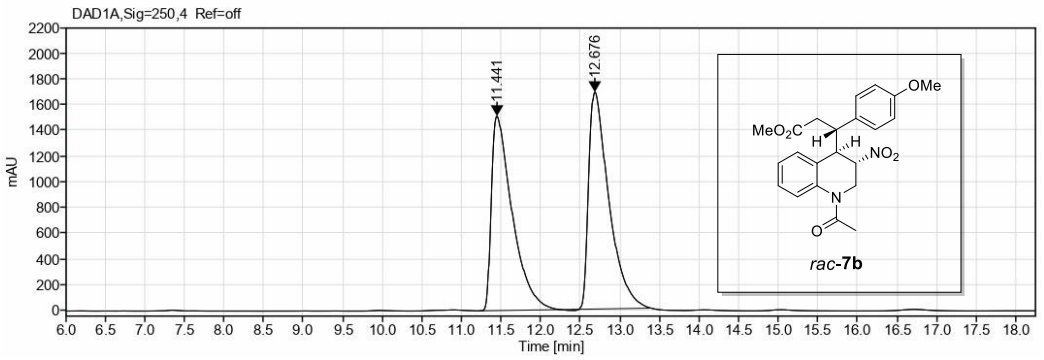
^{1}H NMR of 7b ($CDCl_3$, 400 MHz)



^{13}C NMR of 7b ($CDCl_3$, 100 MHz)



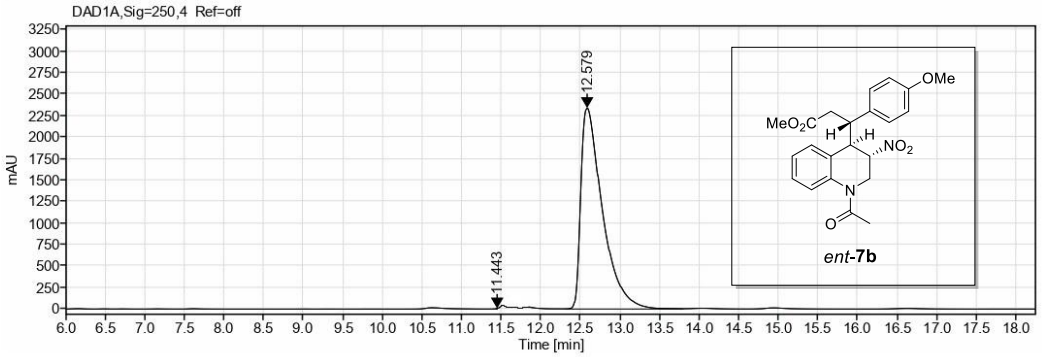
HPLC chromatogram of *rac*-7b



Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.441	BM m	1.20	27574.12714	1512.03808	47.86668	1
12.676	MM m	0.98	30031.97603	1686.73373	52.13332	2
		Sum	57606.10			

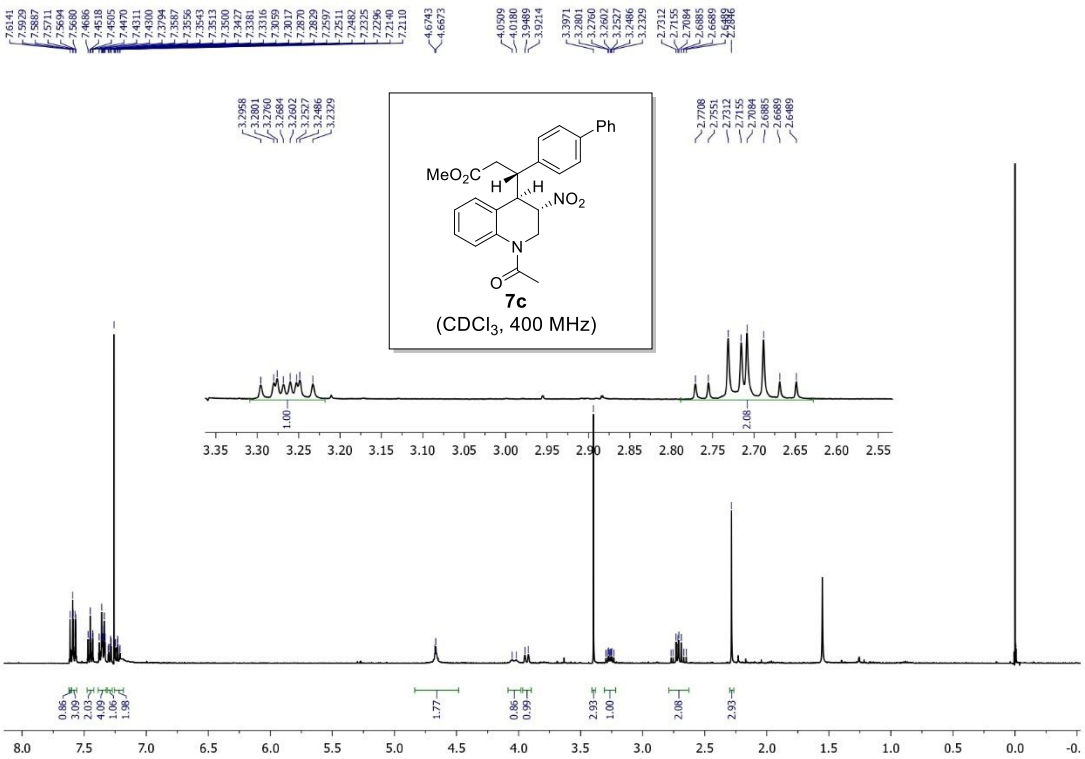
HPLC chromatogram of *ent*-7b



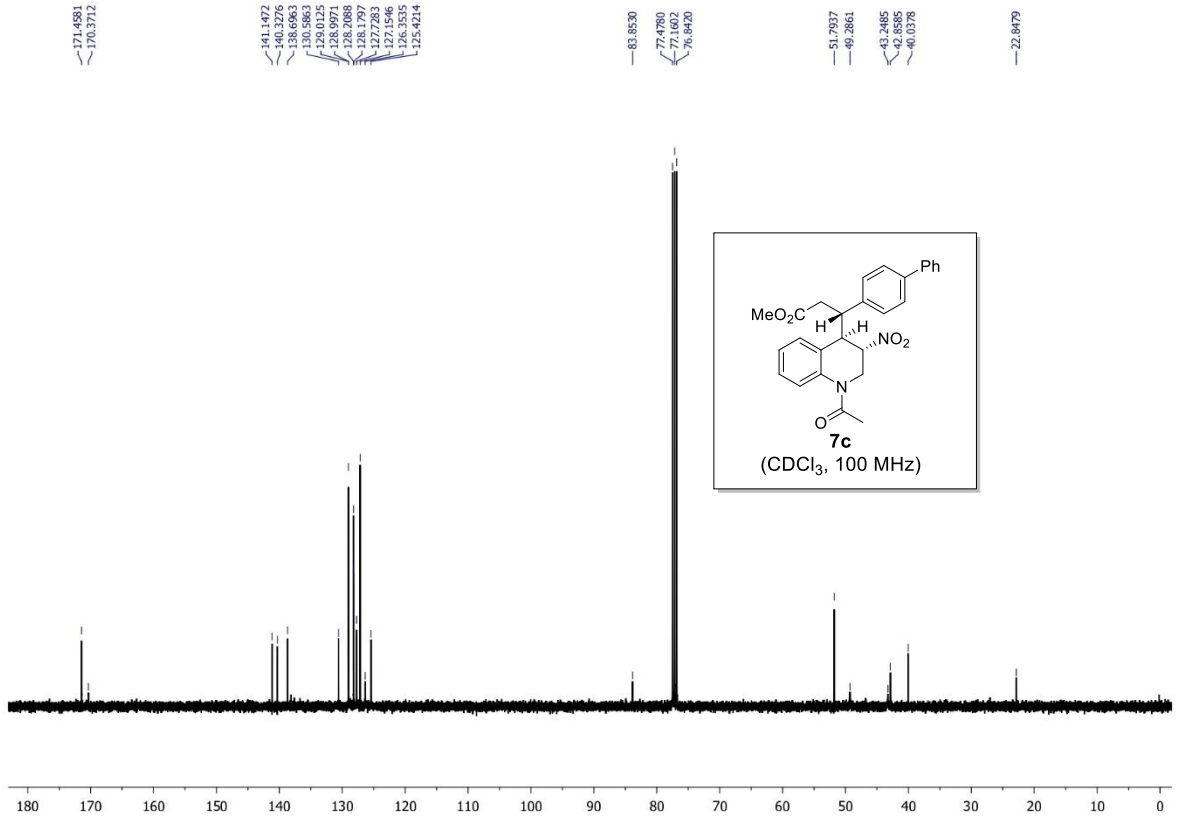
Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.443	MM m	0.02	7.06547	10.04088	0.01589	1
12.579	VV	1.50	44450.85731	2342.64491	99.98411	2
		Sum	44457.92			

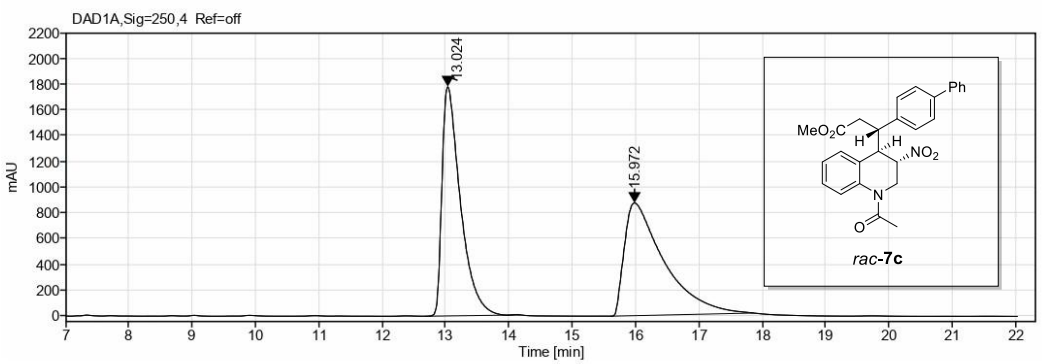
^{1}H NMR of 7C ($CDCl_3$, 400 MHz)



^{13}C NMR of 7C ($CDCl_3$, 100 MHz)



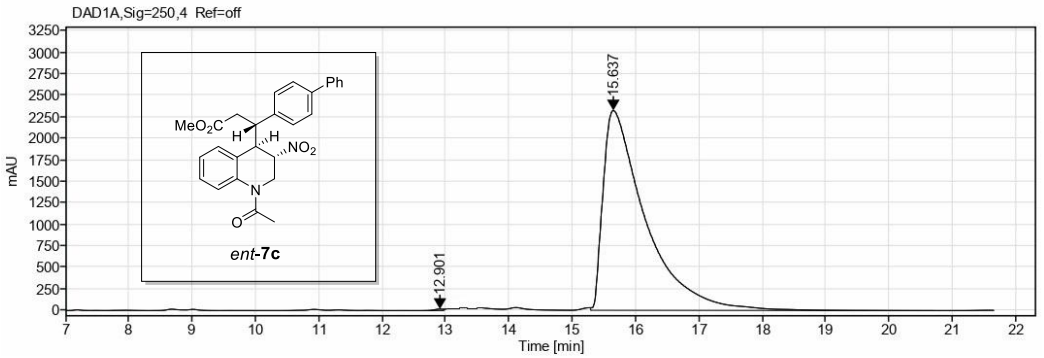
HPLC chromatogram of *rac*-7c



Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.024	VM m	1.51	35990.79755	1781.54943	48.61641	1
15.972	VM m	2.26	38039.34539	875.47273	51.38359	2
		Sum	74030.14			

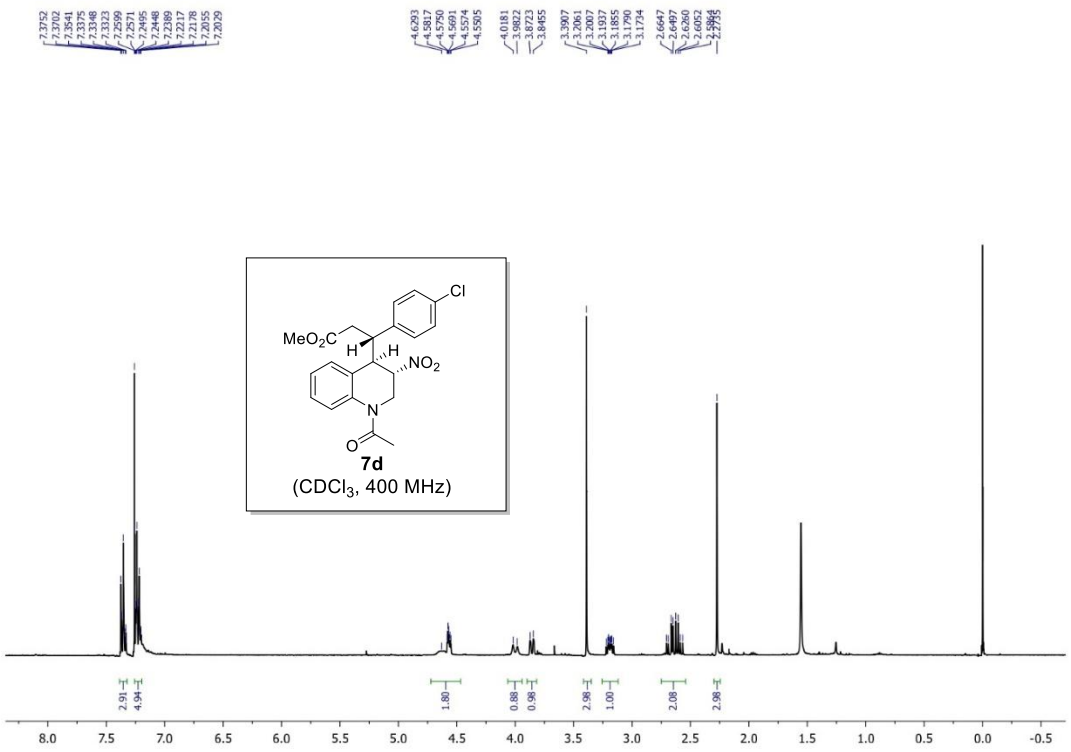
HPLC chromatogram of *ent*-7c



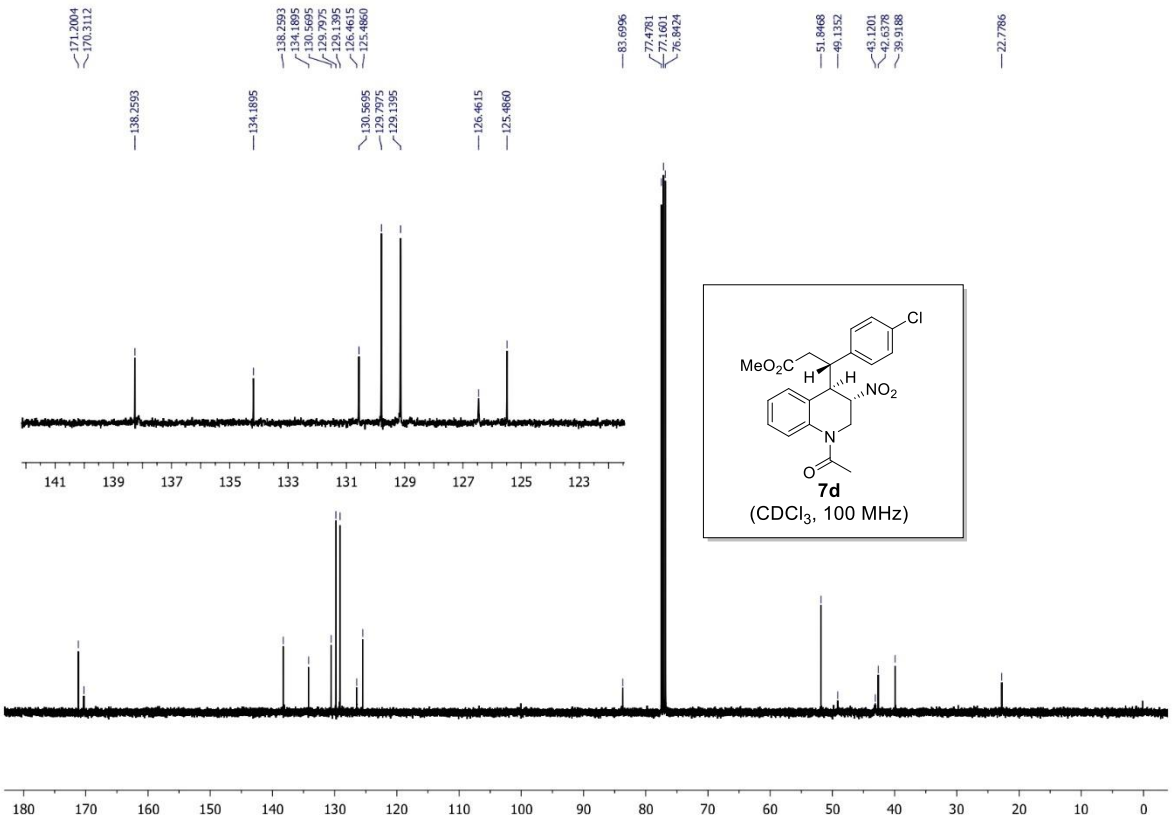
Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.901	BV	0.33	166.05496	17.38407	0.15355	1
15.637	VB	5.42	107981.00378	2326.10517	99.84645	2
		Sum	108147.06			

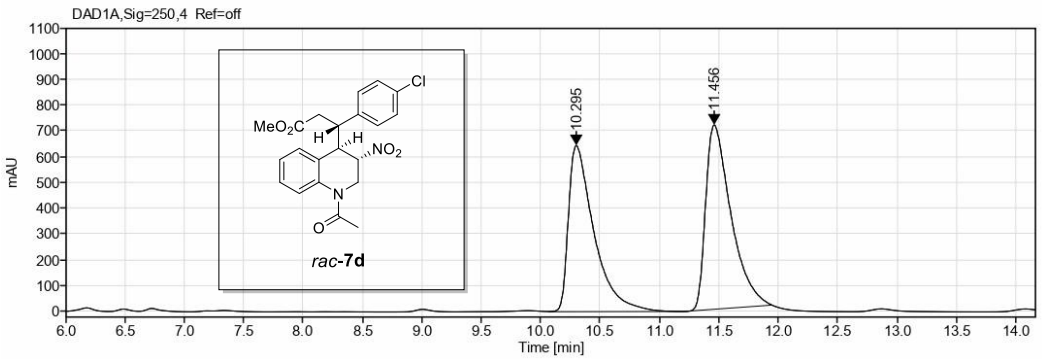
^{1}H NMR of 7d ($CDCl_3$, 400 MHz)



^{13}C NMR of 7d ($CDCl_3$, 100 MHz)



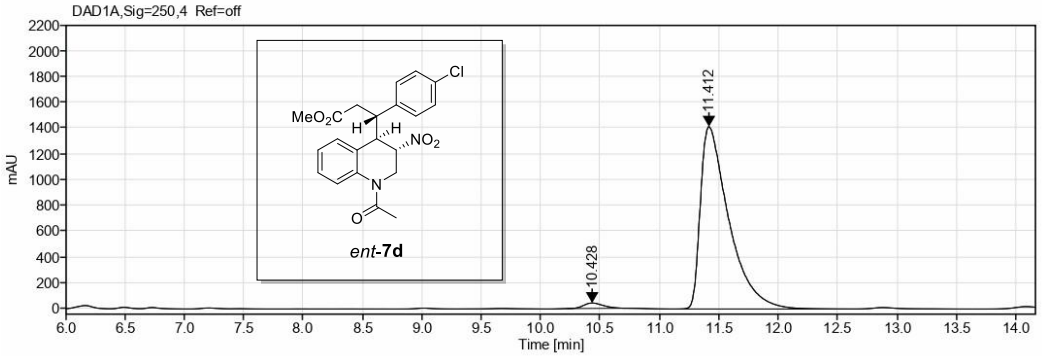
HPLC chromatogram of *rac*-7d



Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.295	VM m	1.13	9645.59892	645.01591	47.66539	1
11.456	MM m	0.75	10590.46422	715.30331	52.33461	2
		Sum	20236.06			

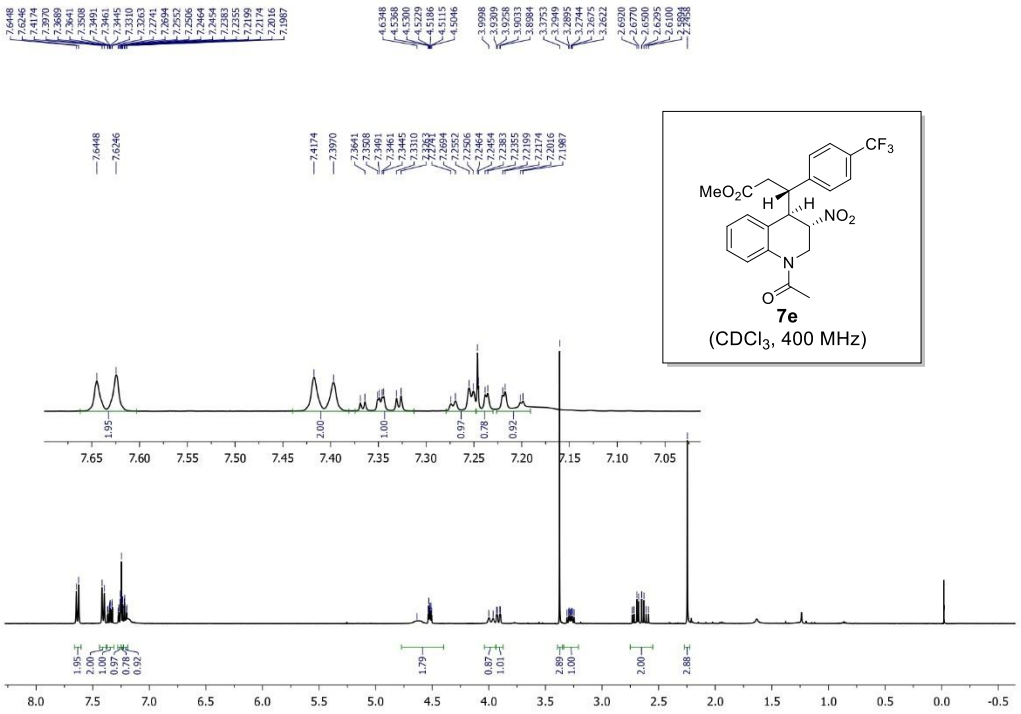
HPLC chromatogram of *ent*-7d



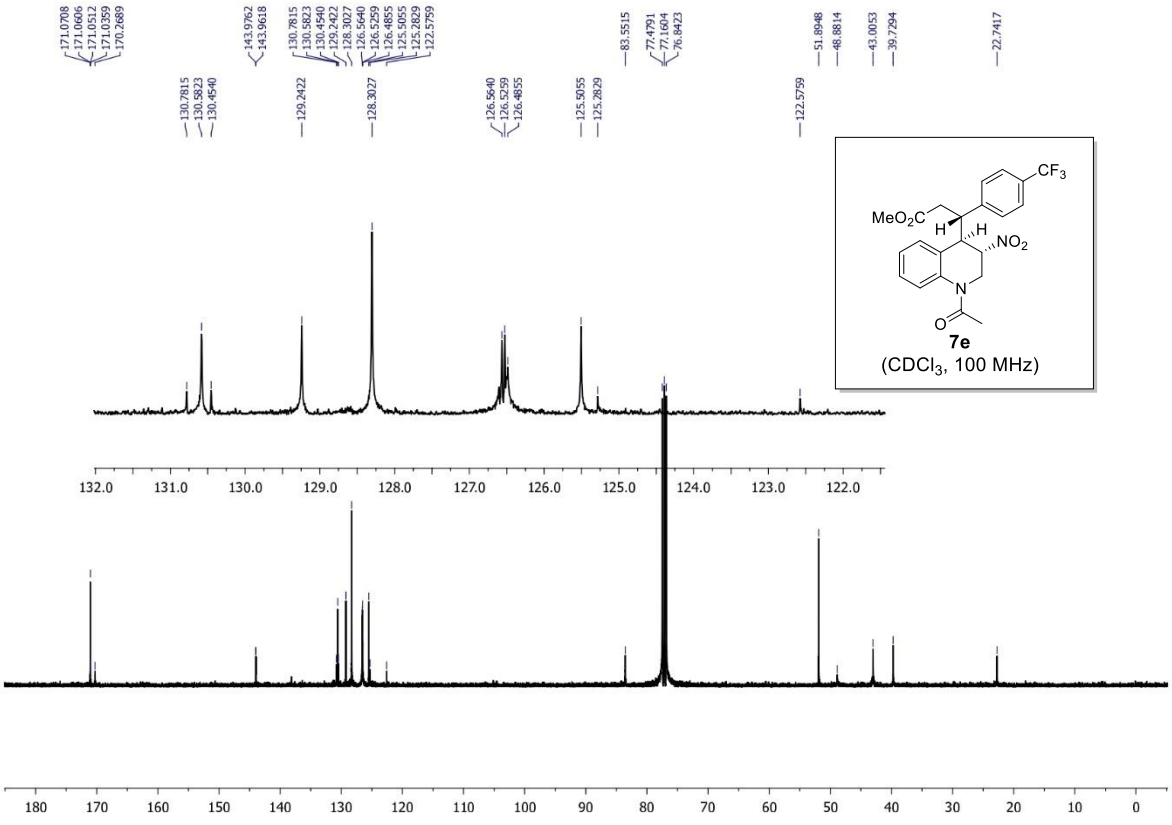
Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.428	MM m	0.49	484.74393	42.22906	2.01409	1
11.412	MV m	1.50	23582.92228	1415.02248	97.98591	2
		Sum	24067.67			

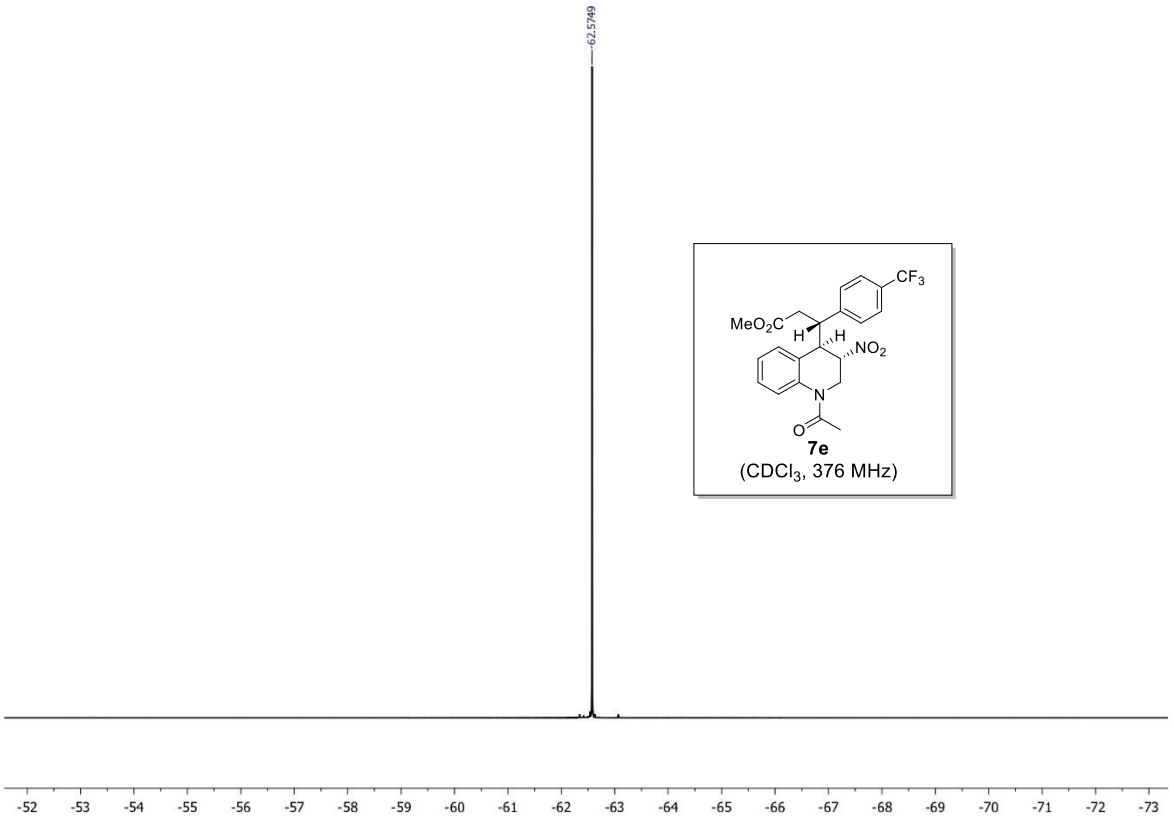
^{1}H NMR of 7e ($CDCl_3$, 400 MHz)



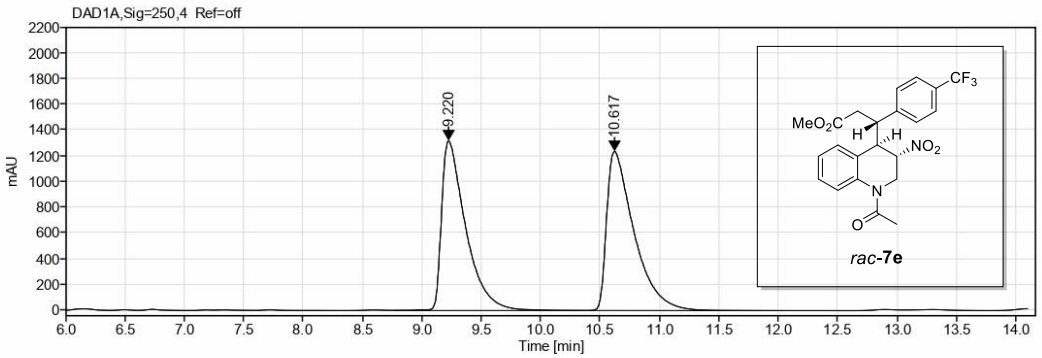
^{13}C NMR of 7e ($CDCl_3$, 100 MHz)



^{19}F NMR of 7e ($CDCl_3$, 376 MHz)

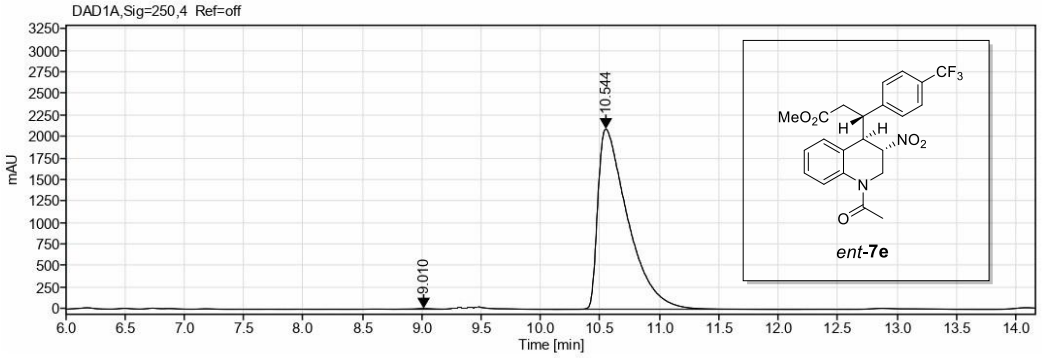


HPLC chromatogram of *rac*-7e



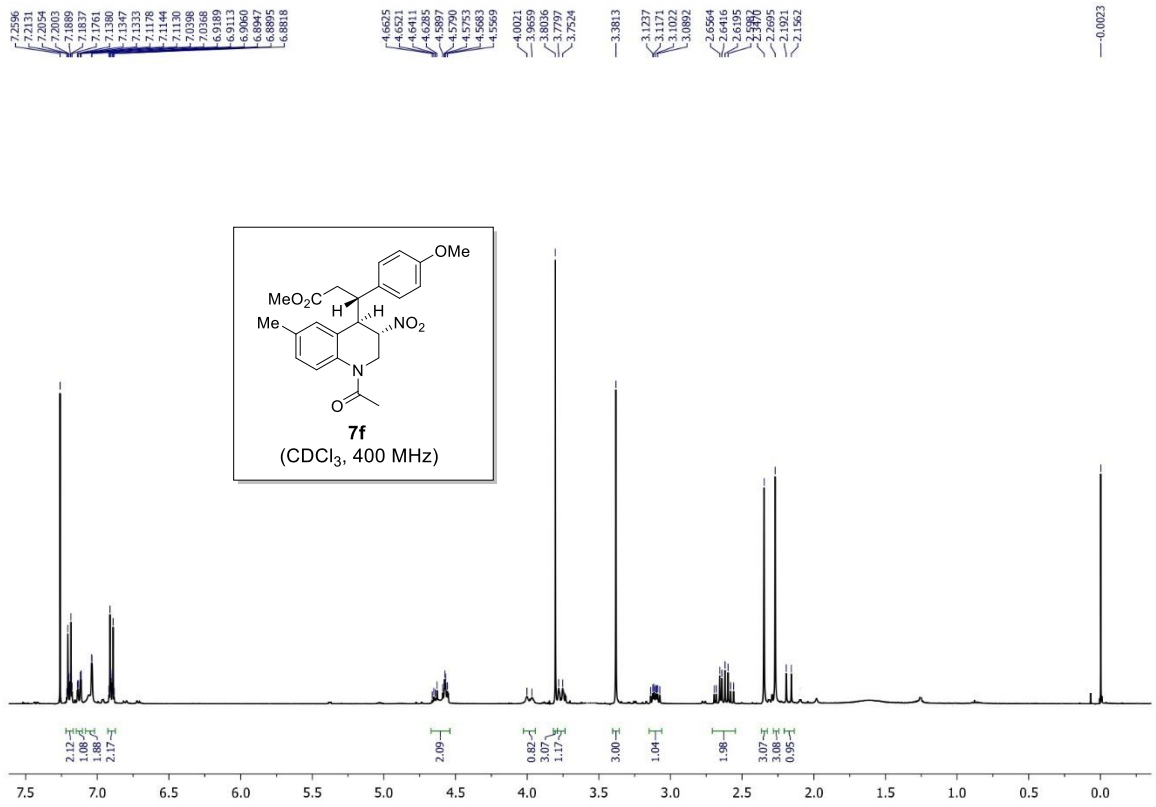
Signal:	DAD1A,Sig=250,4 Ref=off					
RT [min]	**Type**	**Width [min]**	**Area**	**Height**	**Area%**	**Name**
9.220	VB	1.61	18637.78658	1319.73126	48.49502	1
10.617	BB	1.77	19794.58666	1236.71258	51.50498	2
		Sum	38432.37			

HPLC chromatogram of *ent*-7e

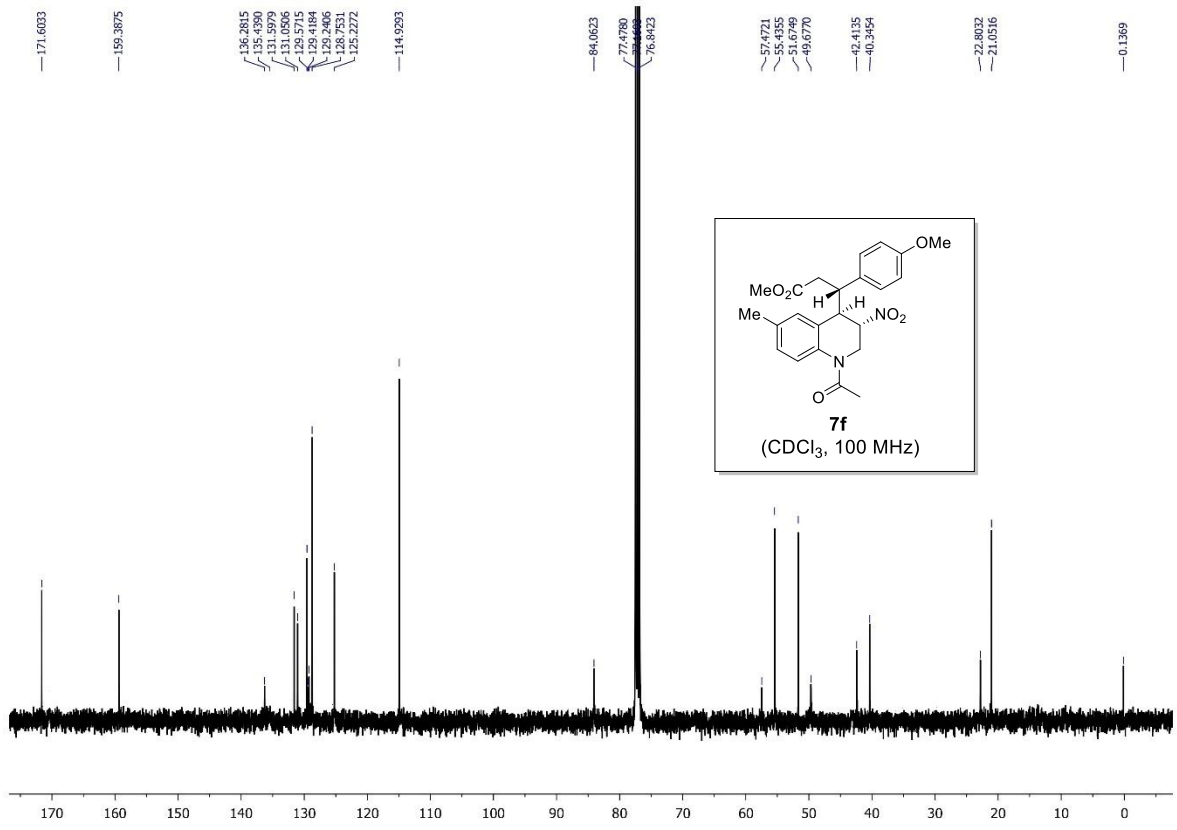


Signal:	DAD1A,Sig=250,4 Ref=off					
RT [min]	**Type**	**Width [min]**	**Area**	**Height**	**Area%**	**Name**
9.010	VV	0.43	93.92940	8.48858	0.25484	1
10.544	BB	2.10	36763.69214	2096.86510	99.74516	2
		Sum	36857.62			

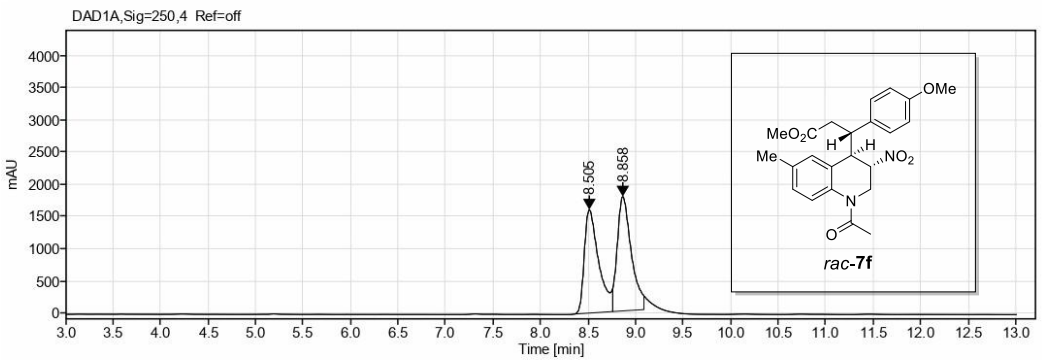
^{1}H NMR of 7f ($CDCl_3$, 400 MHz)



^{13}C NMR of 7f ($CDCl_3$, 100 MHz)



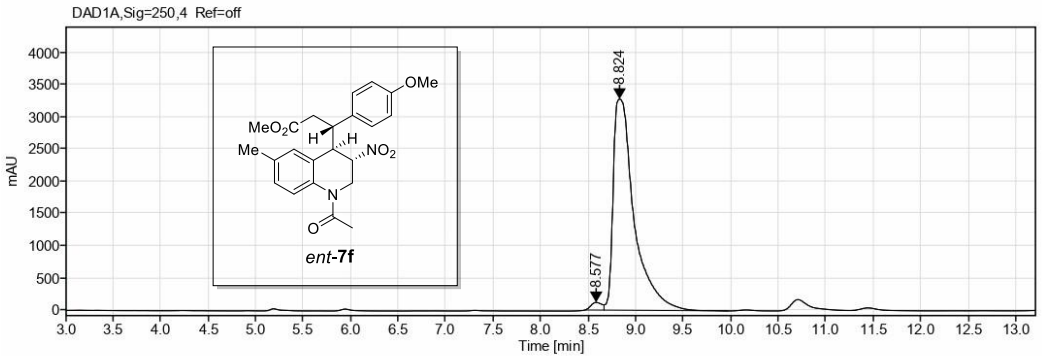
HPLC chromatogram of *rac*-7f



Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.505	MM m	0.40	16997.58347	1605.21754	48.18263	1
8.858	MM m	0.33	18279.82451	1775.19165	51.81737	2
		Sum	35277.41			

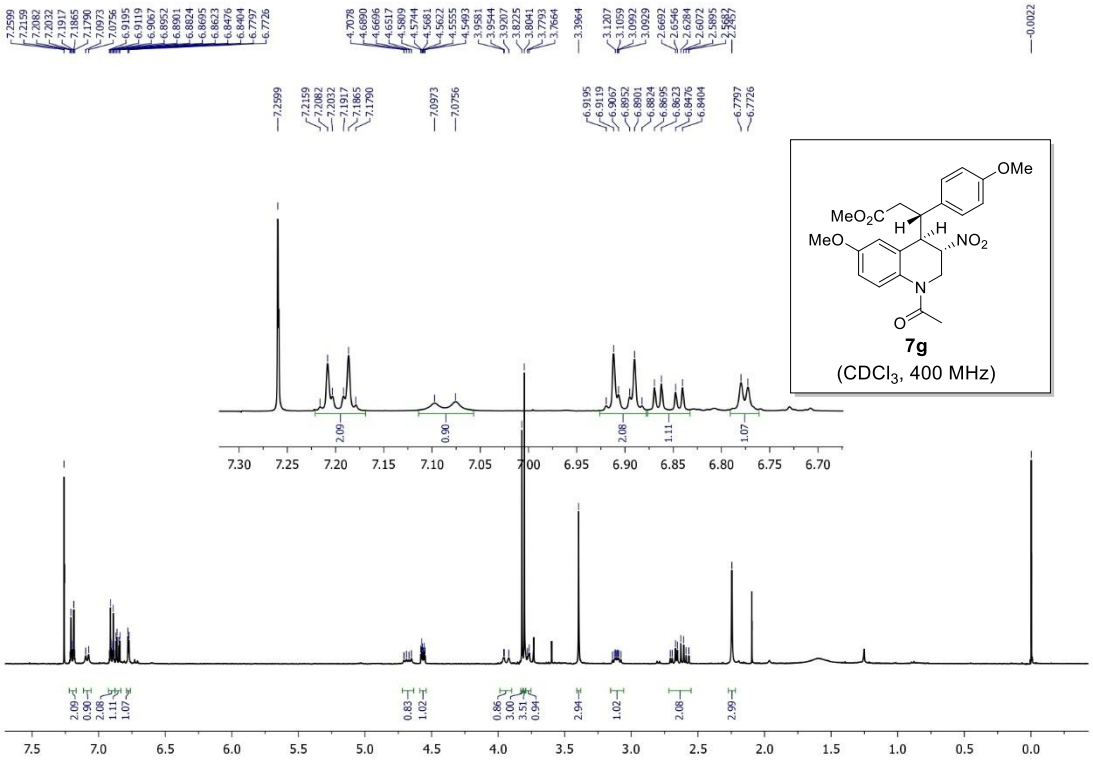
HPLC chromatogram of *ent*-7f



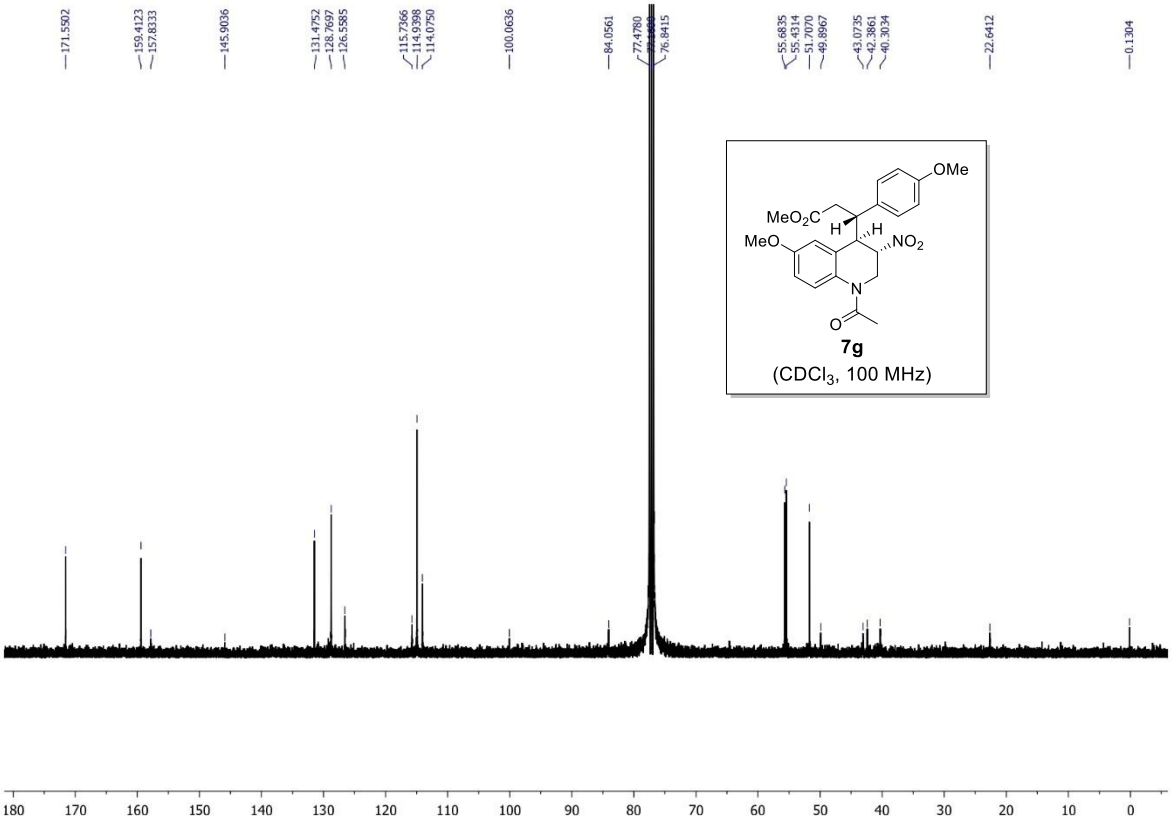
Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.577	MM m	0.20	948.37491	119.34821	1.85296	1
8.824	MB m	1.31	50233.36093	3277.82186	98.14704	2
		Sum	51181.74			

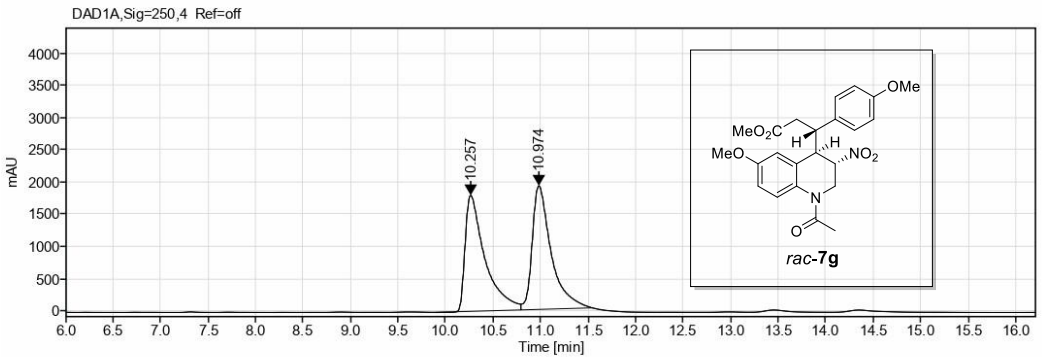
^{1}H NMR of 7g ($CDCl_3$, 400 MHz)



^{13}C NMR of 7g ($CDCl_3$, 100 MHz)



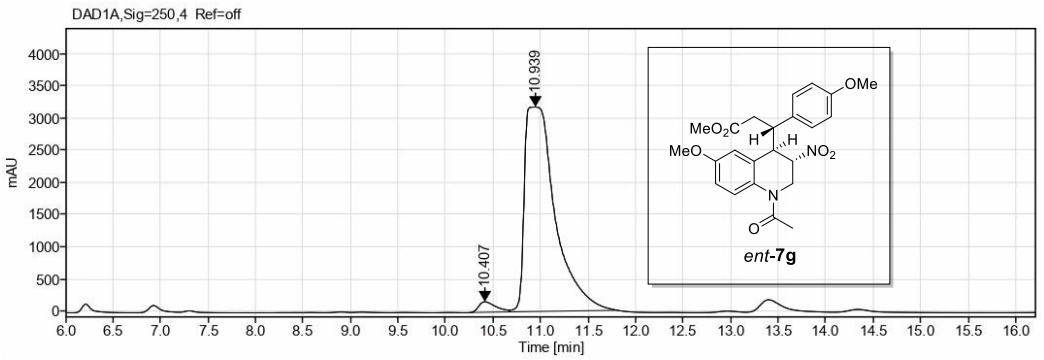
HPLC chromatogram of *rac*-7g



Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.257	BM m	0.90	26090.52064	1801.47946	49.42392	1
10.974	MM m	0.75	26698.73744	1919.66505	50.57608	2
		Sum	52789.26			

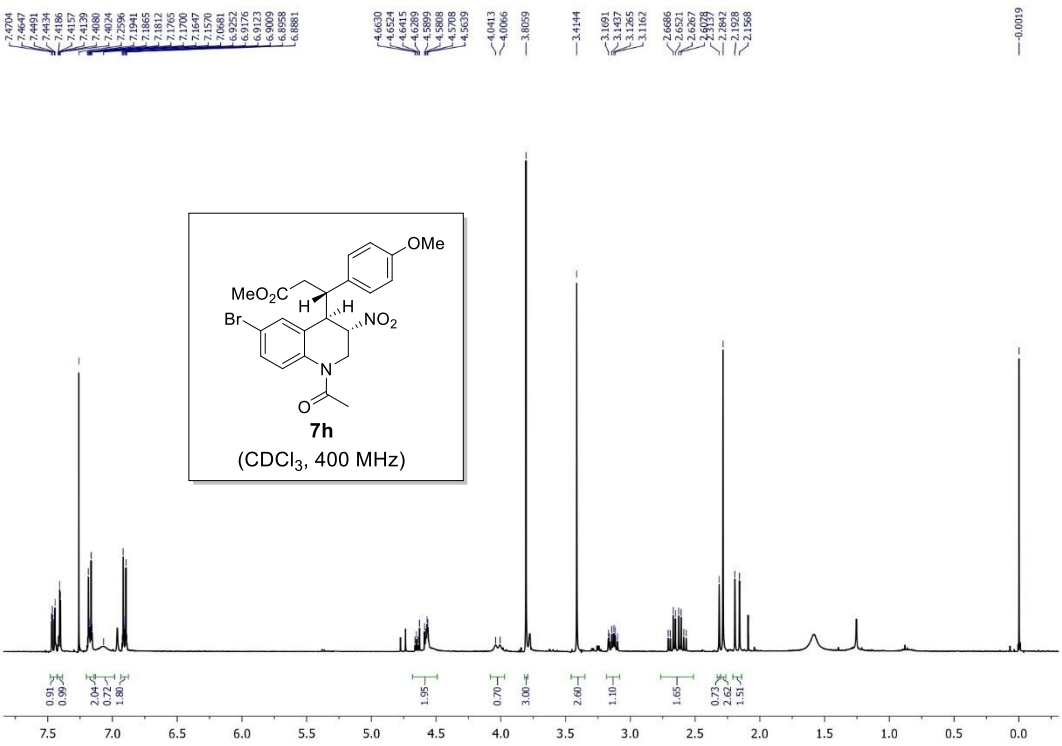
HPLC chromatogram of *ent*-7g



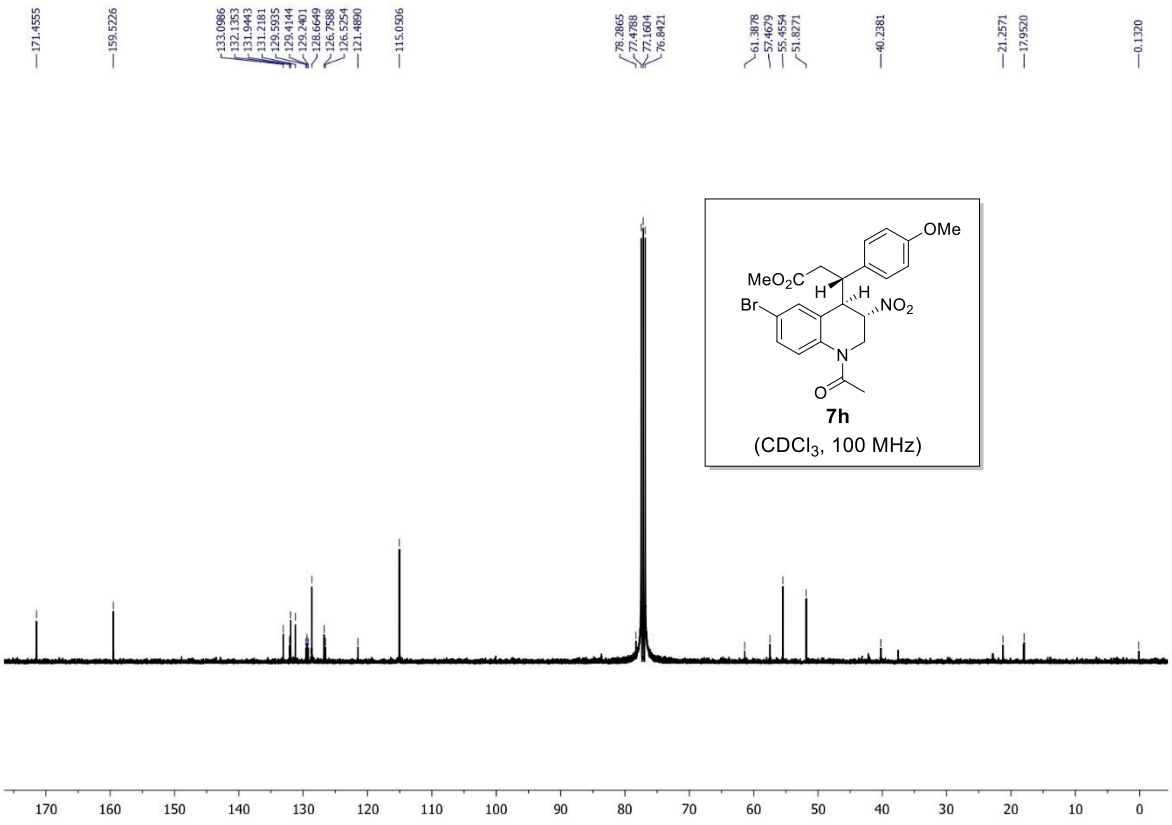
Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.407	MM m	0.41	2036.44478	163.27759	2.78070	1
10.939	MM m	1.13	71198.53776	3177.98404	97.21930	2
		Sum	73234.98			

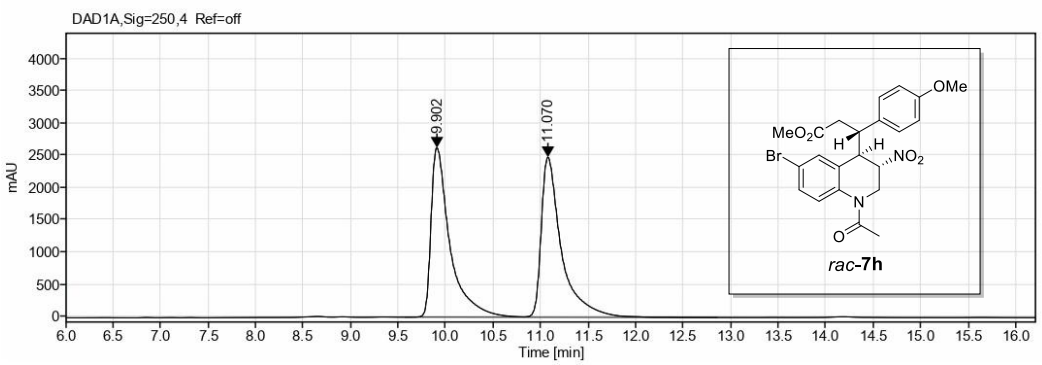
^{1}H NMR of 7h ($CDCl_3$, 400 MHz)



^{13}C NMR of 7h ($CDCl_3$, 100 MHz)



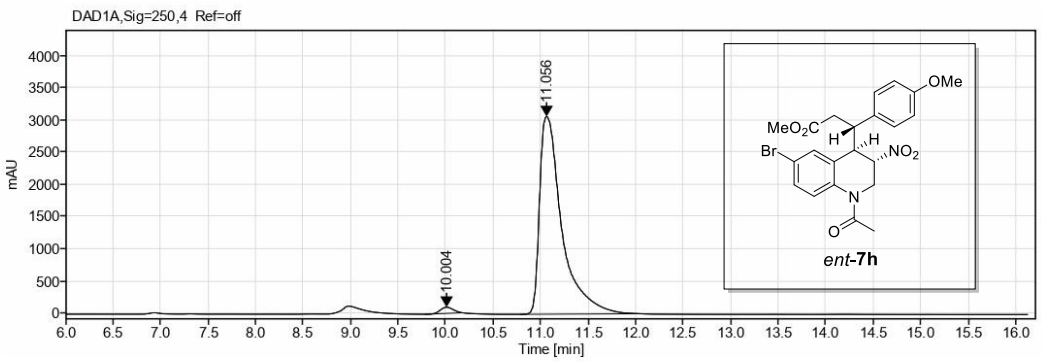
HPLC chromatogram of *rac*-7h



Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.902	BV	1.25	36327.45873	2627.96954	49.61489	1
11.070	VB	2.05	36891.40859	2482.56547	50.38511	2
		Sum	73218.87			

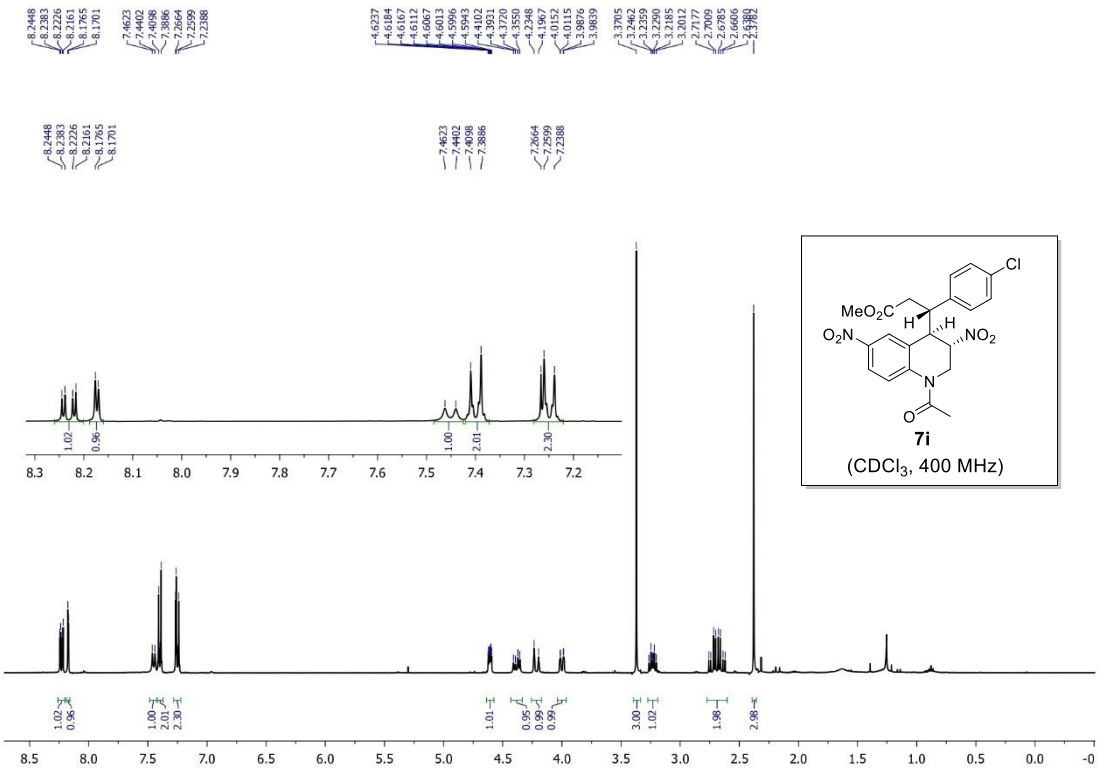
HPLC chromatogram of *ent*-7h



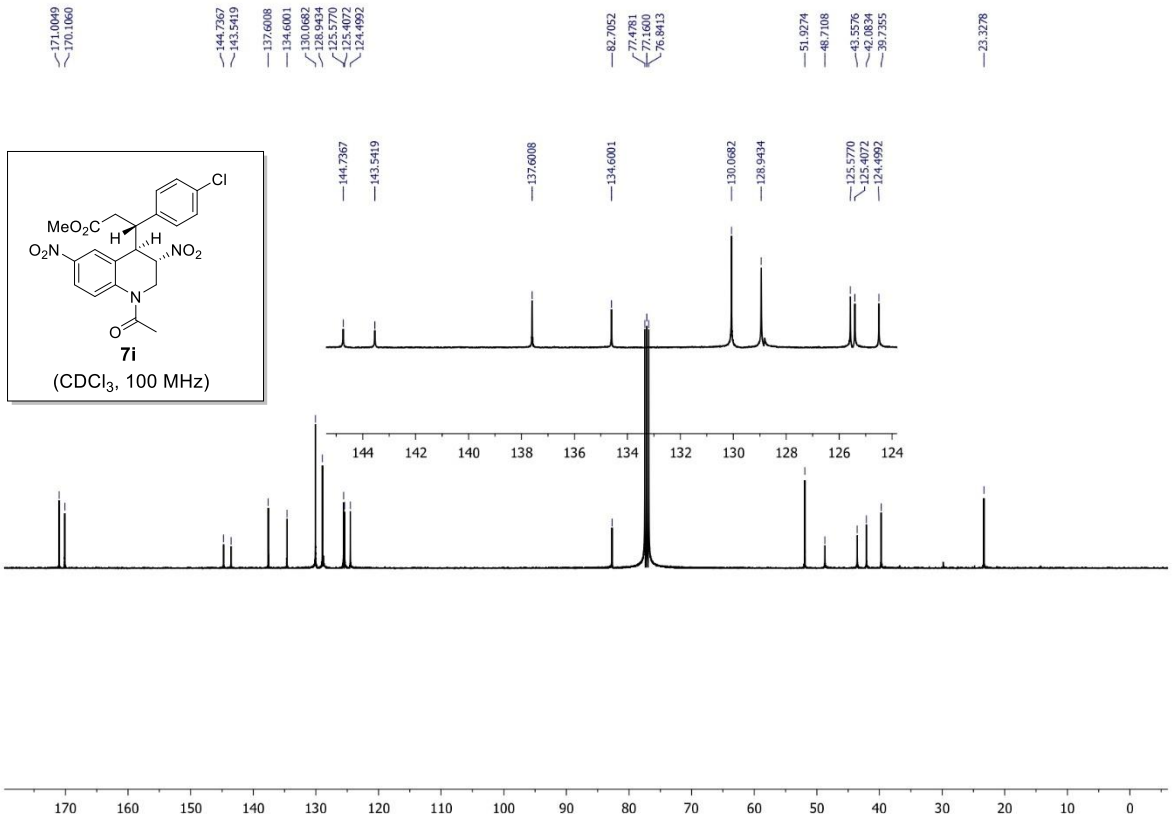
Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.004	VM m	0.40	895.00640	96.11014	1.76050	1
11.056	BM m	1.27	49943.24576	3069.37224	98.23950	2
		Sum	50838.25			

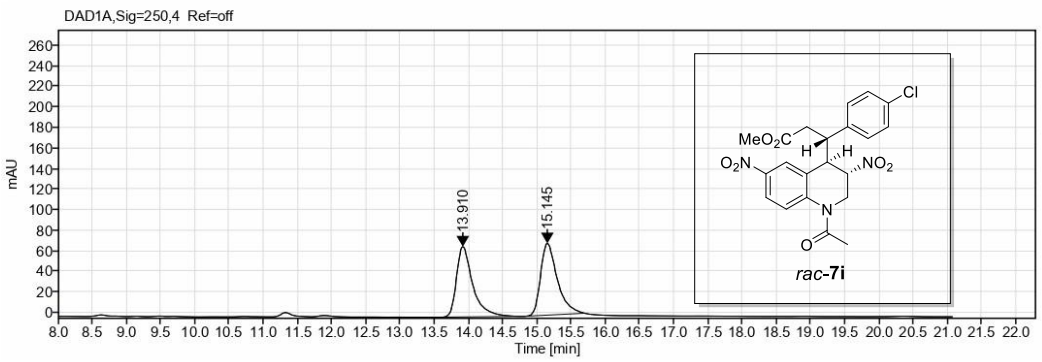
^{1}H NMR of 7i ($CDCl_3$, 400 MHz)



^{13}C NMR of 7i ($CDCl_3$, 100 MHz)



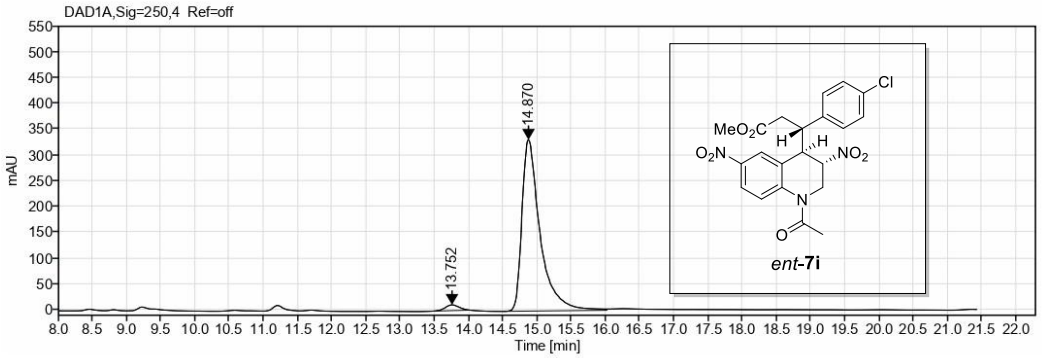
HPLC chromatogram of *rac*-7i



Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.910	MM m	1.18	1128.03080	68.23082	48.72918	1
15.145	MM m	0.89	1186.86724	69.64154	51.27082	2
	Sum		2314.90			

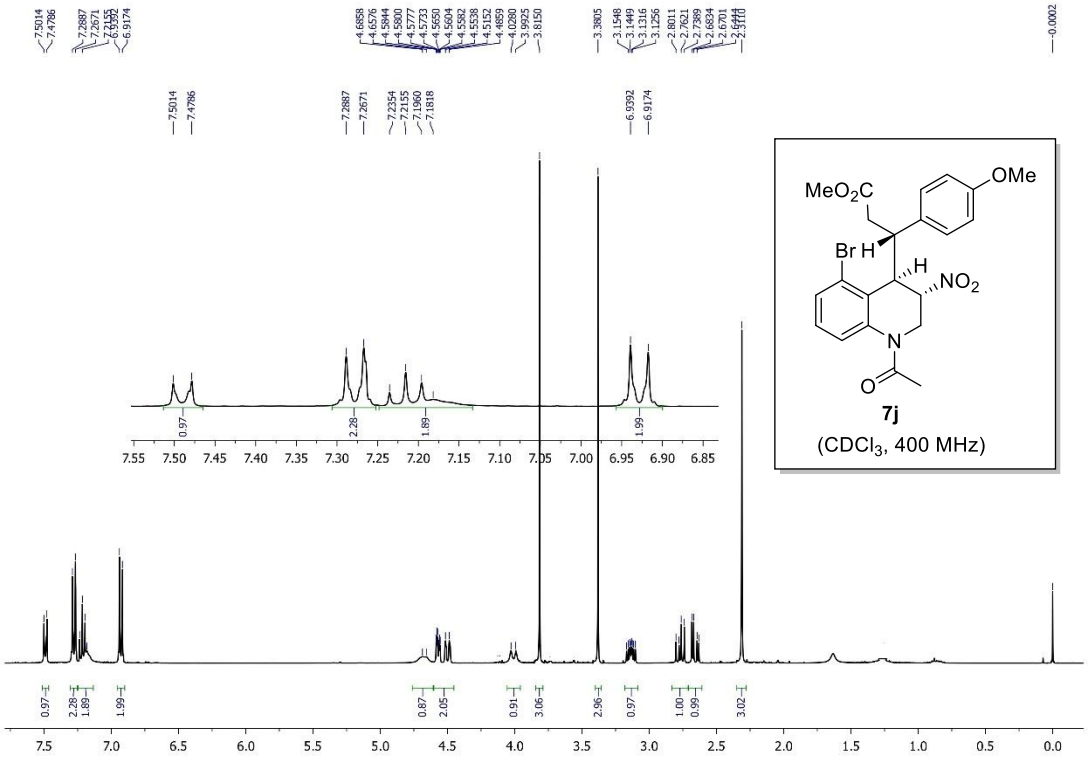
HPLC chromatogram of *ent*-7i



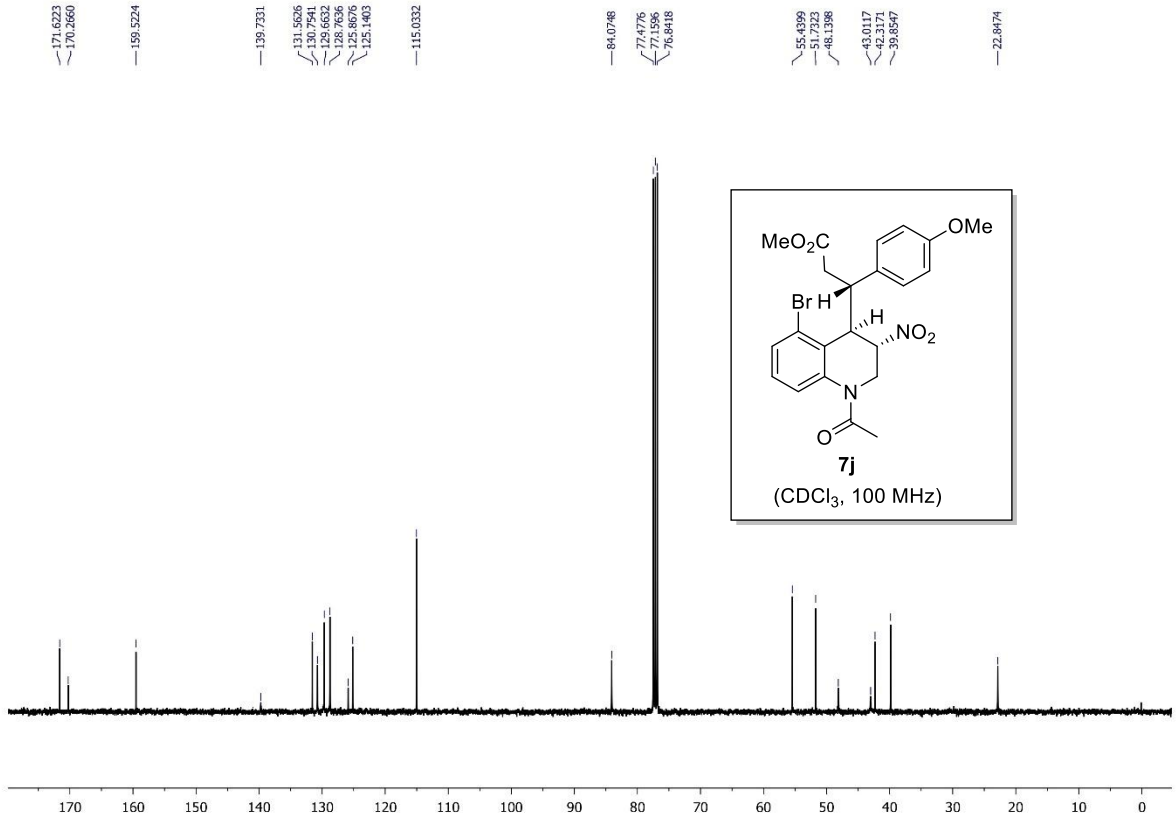
Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.752	MM m	0.54	155.94988	11.10677	2.47999	1
14.870	BV	1.51	6132.38351	331.91268	97.52001	2
	Sum		6288.33			

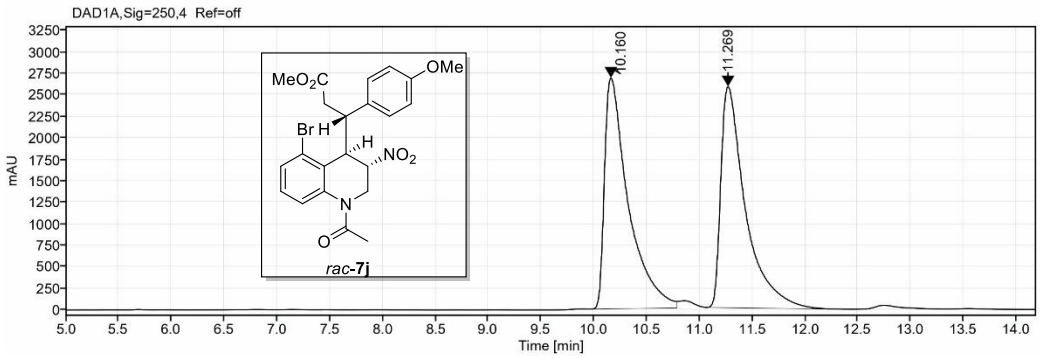
^{1}H NMR of 7j ($CDCl_3$, 400 MHz)



^{13}C NMR of 7j ($CDCl_3$, 100 MHz)

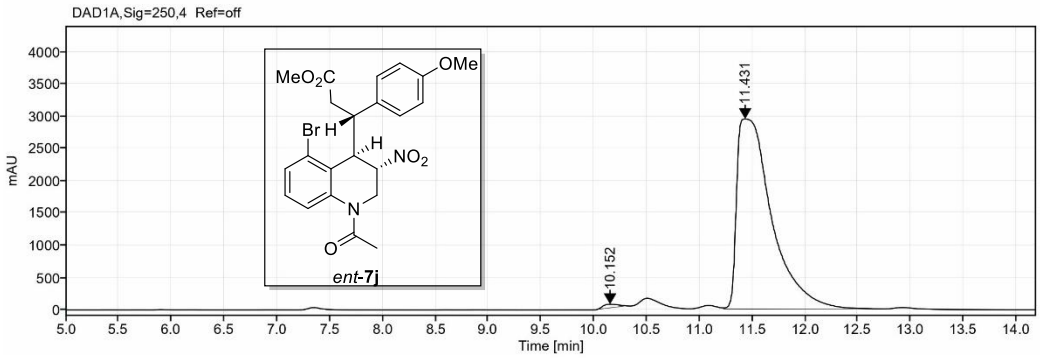


HPLC chromatogram of *rac*-7j



Signal:	DAD1A,Sig=250,4 Ref=off					
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.160	BV	0.82	41914.59059	2689.73576	50.20611	1
11.269	BB	1.30	41570.45347	2575.17735	49.79389	2
		Sum	83485.04			

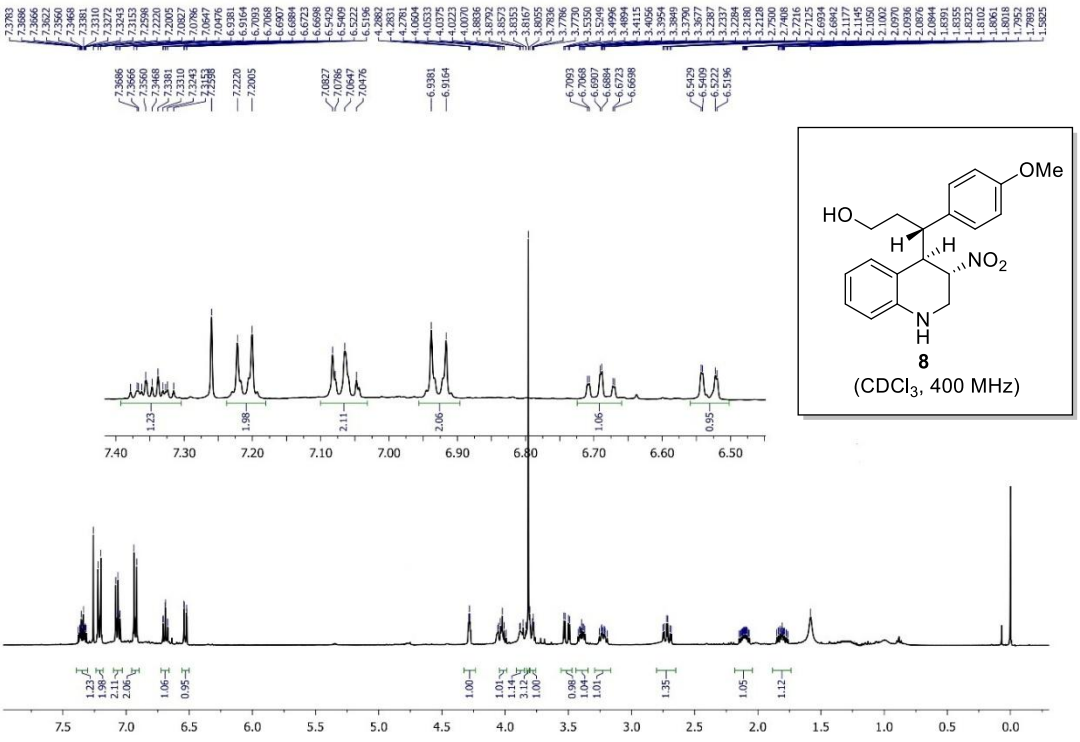
HPLC chromatogram of *ent*-7j



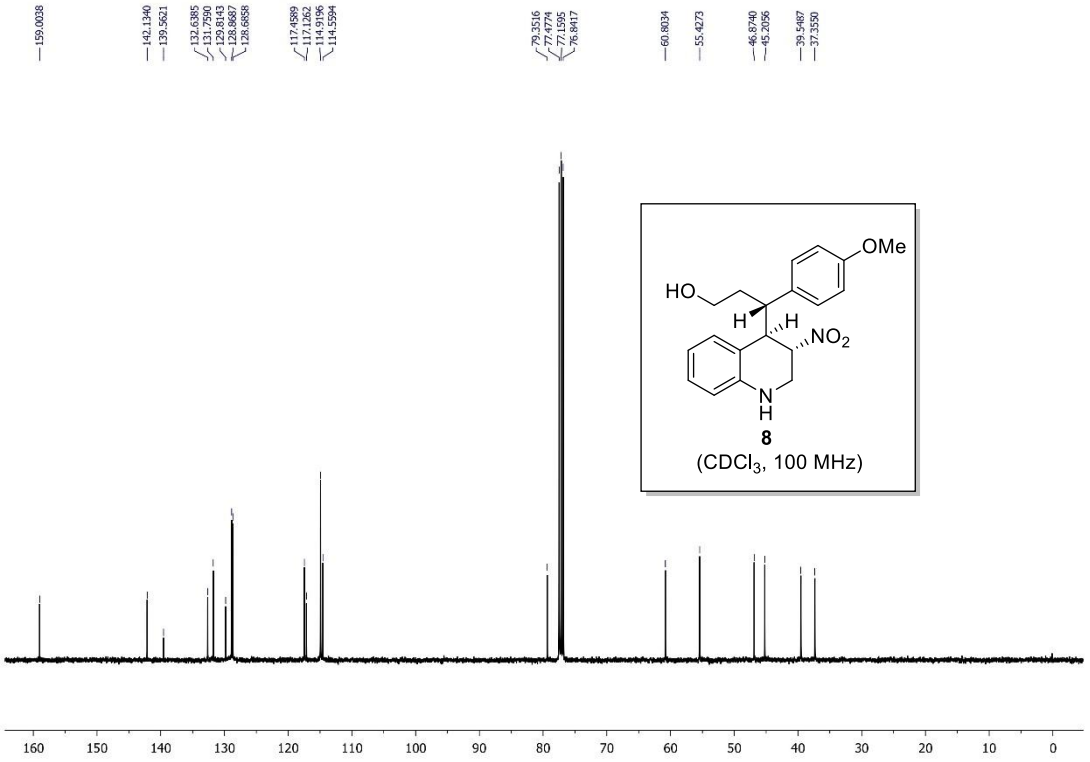
Signal:	DAD1A,Sig=250,4 Ref=off					
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.152	BM m	0.33	525.83048	55.01549	0.76797	1
11.431	VV	1.51	67944.66406	2946.02318	99.23203	2
		Sum	68470.49			

^{1}H and ^{13}C NMR spectra & HPLC chromatogram of 3-(4-methoxyphenyl)-3-(3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)propan-1-ol (8):

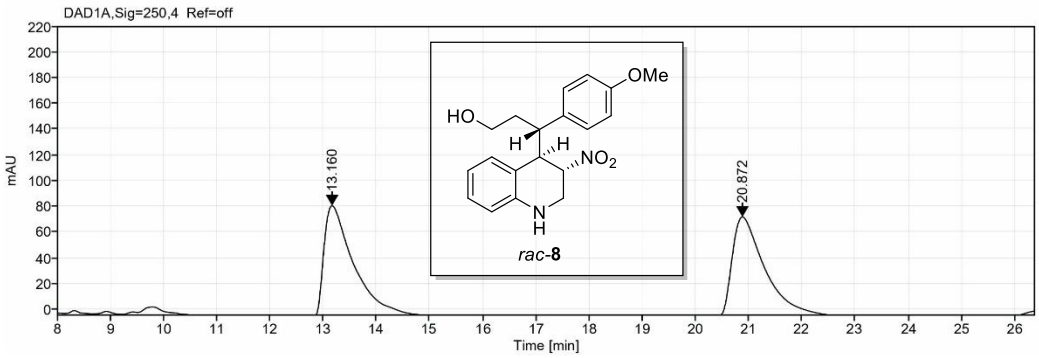
^{1}H NMR of 8 ($CDCl_3$, 400 MHz)



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



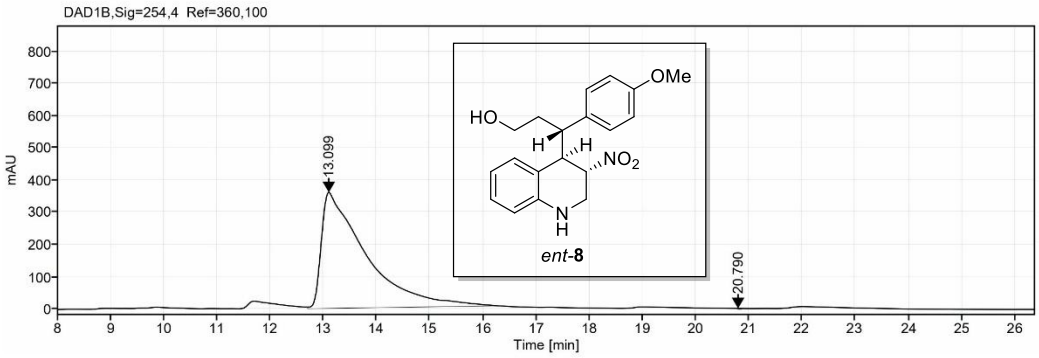
HPLC chromatogram of *rac*-8



Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.160	BB	2.53	3312.87751	85.66078	48.92230	1
20.872	VB	3.62	3458.83454	77.98838	51.07770	2
		Sum	6771.71			

HPLC chromatogram of *ent*-8



Signal: DAD1B,Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.099	VM m	3.58	20874.42325	360.28596	99.95436	1
20.790	MM m	0.06	9.53111	2.58730	0.04564	2
		Sum	20883.95			