Supporting Information

Efficient synthesis of 2-acylquinolines based on an aza-vinylogous Povarov reaction

Giulia Bianchini,[a] Pascual Ribelles,[a] Diana Becerra,[a,b] M. Teresa Ramos[a] and J. Carlos Menéndez [a]

[a] Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad Complutense, 28040 Madrid, Spain.
[b] Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad del Valle, A. A. 25360 Cali, Colombia.

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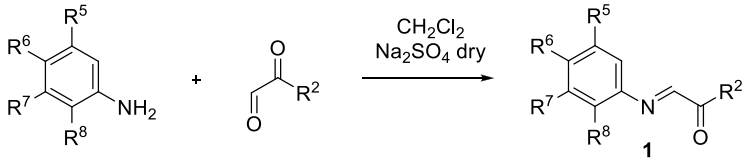
Experimental Section

EXPERIMENTAL SECTION

1. Synthesis of imines

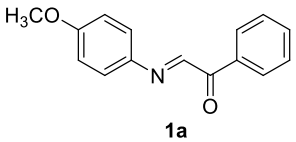
1.1 Synthesis of α-ketoimines 1a-h



Cmpd.	R^2	R^5	R^6	R^7	R^8
1a	C_6H_5	H	4-OCH_3	H	H
1b	4-FC_6H_4	H	4-OCH_3	H	H
1c	4-$OCH_3C_6H_4$	H	4-OCH_3	H	H
1d	4-FC_6H_4	CH_3	H	CH_3	H
1e	C_6H_5	H	CH_3	H	CH_3
1f	OEt	H	CH_3	H	CH_3
1g	OEt	H	4-OCH_3	H	H
1h	2-furyl	H	4-OCH_3	H	H

A solution of aniline (1 eq) and aldehyde (1 eq) in CH_2Cl_2 was stirred vigorously in the presence of anhydrous Na_2SO_4 (5 g) for 30 minutes and the filtrate was evaporated under reduced pressure affording the desired imines, which were used in the following reactions without further purification. Some commercially available glyoxals (4-methoxyphenyl and 4-fluorophenyl) are available as hydrates containing an unknown amount of water so the amount of aldehyde used in these cases was optimized by gradual addition of the glyoxal reagent until no aniline was detected by ^{1}H-NMR.

2-(4-Methoxyphenylimino)-1-phenylethanone (1a)[1]

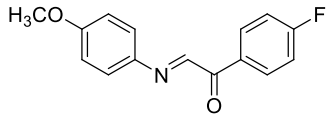


1a

^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 3.84 (s, 3H, OCH_3); 6.96 (d, *J* = 9.0 Hz, 2H, H-3 and H-5); 7.40 (d, *J* = 9.0 Hz, 2H, H-2 and H-6); 7.49-7.58 (m, 2H, H-3´ and H-5´); 7.62 (m, 1H, H-4´); 8.27-8.31 (m, 2H, H-2´ and H-6´); 8.35 (s, 1H, CH=N). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 55.8 (OCH_3); 114.9 (C-3 and C-5); 123.8 (C-2 and C-6); 128.6 (C-2´ and C-6´); 130.9 (C-3´ and C-5´); 133.7 (C-4´); 135.8 (C-1´); 141.9 (C-1); 154.4 (CH=N); 160.8 (C-4); 191.1 (CO). **IR** (NaCl) *v*: 1653.7 (C=O), 1595.9 (C=N) cm^{-1}.

[1] S. A. Kunzi; B. Morandi and E. Carreira, *Org. Lett*., 2012, **14**, 1900.

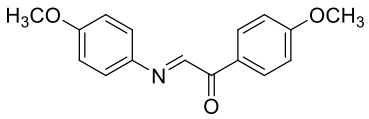
1-(4-Fluorophenyl)-2-(4-methoxyphenylimino)ethanone (1b)[1]



1b

^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 3.86 (s, 3H, OCH_3); 6.97 (d, *J* = 9.0 Hz, 2H, H-3 and H-5); 7.17 (t, *J* = 8.8 Hz, 2H, H-3´ and H-5´); 7.40 (d, *J* = 9.0 Hz, 2H, H-2 and H-6); 8.31 (s, 1H, CH=N); 8.39 (dd, *J* = 9.0, 5.6 Hz, 2H, H-2´ and H-6´). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 55.9 (OCH_3); 115.0 (C-3 and C-5); 115.9 (d, *J* = 23.5 Hz, C-3´ and C-5´); 123.9 (C-2 and C-6); 132.1 (d, *J* = 3.4 Hz, C-1'); 133.8 (d, *J* = 9.6 Hz, C-2´ and C-6´); 141.7 (C-1); 154.4 (CH=N); 161.0 (C-4); 166.4 (d, *J* = 280.4 Hz, C-4´); 189.6 (CO). **IR** (NaCl) *v*: 1654.9 (C=O), 1599.5 (C=N) cm^{-1}.

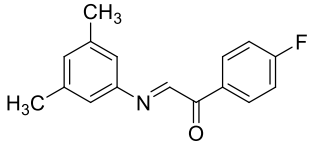
1-(4-Methoxyphenyl)-2-(4-methoxyphenylimino)ethanone (1c)[1]



1c

^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 3.85 (s, 3H, OCH_3); 3.89 (s, 3H, OCH_3); 6.96 (d, *J* = 9.0 Hz, 2H, H-3 and H-5); 6.98 (d, *J* = 9.1 Hz, 2H, H-3´ and H-5´); 7.39 (d, *J* = 9.0 Hz, 2H, H-2 and H-6); 8.33 (s, 1H, CH=N); 8.35 (d, *J* = 9.1 Hz, 2H, H-2´ and H-6´). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 55.8 (OCH_3); 55.8 (OCH_3); 114.0 (C-3´ and C-5´); 114.9 (C-3 and C-5); 123.7 (C-2 and C-6); 128.7 (C-1´); 133.4 (C-2´ and C-6´); 142.1 (C-1); 155.1 (CH=N); 160.6 (C-4); 164.3 (C-4´); 189.3 (CO). **IR** (NaCl) *v*: 1670.1 (C=O), 1597.7 (C=N) cm^{-1}.

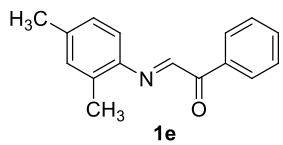
2-(3,5-Dimethylphenylimino)-1-(4-fluorophenyl)ethanone (1d)



1d

^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 2.37 (s, 6H, 2 x CH_3); 6.96 (s, 2H, H-2 and H-6); 7.01 (s, 1H, H-4); 7.18 (t, *J* = 8.7 Hz, 2H, H-3´ and H-5´); 8.26 (s, 1H, CH=N); 8.40 (d, *J* = 9.0 Hz, 2H, H-2´ and H-6´). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 21.6 (2 x CH_3); 116.0 (d, *J* = 24.1 Hz, C-3´ and C-5´); 119.5 (C-2 and C-6); 130.7 (C-4); 131.8 (d, *J* = 3.4 Hz, C-1´); 133.8 (d, *J* = 10.3 Hz, C-2´ and C-6´); 139.5 (C-3 and C-5); 149.3 (C-1); 157.0 (CH=N); 166.4 (d, *J* = 281.5 Hz, C-4'); 189.4 (C=O). **IR** (NaCl) *v*: 1654.4 (C=O), 1598.0 (C=N) cm^{-1}.

2-(2,4-Dimethylphenylimino)-1-phenylethanone (1e)

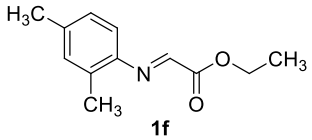


1e

^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 2.36 (s, 3H, CH_3); 2.40 (s, 3H, CH_3); 6.98-7.11 (m, 3H, H-3, H-5 and H-6); 7.47-7.54 (m, 2H, H-3' and H-5'); 7.61 (m, 1H, H-4'); 8.23 (s, 1H, CH=N); 8.33-8.36 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 18.3 (CH_3);

21.2 (CH_3); 116.9 (C-6); 127.7 (C-5); 128.4 (C-2' and C-6'); 130.8 (C-3' and C-5'); 131.7 (C-3); 133.5 (C-4'); 134.3 (C-2); 135.5 (C-4); 138.8 (C-1'); 145.7 (C-1); 155.6 (CH=N); 191.2 (C=O). **IR** (NaCl) *v*: 2924.7 (C-H), 1649.3 (C=O), 1580.8 (C=N) cm^{-1}.

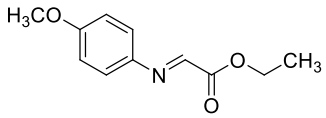
Ethyl 2-(2,4-dimethylphenylimino)acetate (1f)



1f

^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 1.41 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); 2.33 (s, 3H, CH_3); 2.35 (s, 3H, CH_3); 4.41 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3); 6.83 (d, *J* = 8.0 Hz, 1H, H-6); 7.00 (m, 1H, H-5); 7.06 (s, 1H, H-3); 7.81 (s, 1H, CH=N). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 14.3 (OCH_2CH_3); 17.9 (CH_3); 21.2 (CH_3); 63.0 (OCH_2CH_3); 117.2 (C-6); 127.4 (C-5); 131.6 (C-3); 133.4 (C-4); 138.3 (C-2); 146.0 (C-1); 150.1 (CH=N); 163.5 (C=O). **IR** (NaCl) *v*: 2922.4 (C-H), 1741.8 (C=O), 1624.3 (C=N) cm^{-1}.

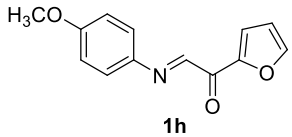
Ethyl 2-(4-methoxyphenylimino)acetate (1g)[1]



1g

^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 1.35 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); 3.77 (s, 3H, OCH_3); 4.35 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3); 6.88 (d, *J* = 8.9 Hz, 2H, H-3 and H-5); 7.32 (d, *J* = 8.9 Hz, 2H, H-2 and H-6); 7.89 (CH=N). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 15.5 (OCH_2CH_3); 55.8 (OCH_3); 62.2 (OCH_2CH_3); 114.8 (C-3 and C-5); 124.0 (C-2 and C-6); 141.6 (C-1); 148.3 (CH=N); 160.9 (C-4); 163.9 (CO_2Et). **IR** (NaCl) *v*: 2838.4 (C-H), 1740.1 (C=O), 1622.5 (C=N) cm^{-1}.

1-(2-Furyl)-2-(4-methoxyphenylimino)ethanone (1h)



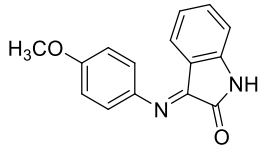
1h

^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 3.89 (s, 3H, OCH_3); 6.65 (dd, *J* = 3.6, 1.7 Hz, 1H, H-4´); 7.01 (d, *J* = 9.0 Hz, 2H, H-3 and H-5); 7.44 (d, *J* = 9.0 Hz, 2H, H-2 and H-6); 7.78 (dd, *J* = 1.6, 0.7 Hz, 1H, H-5´); 8.00 (dd, *J* = 3.5, 0.7 Hz, 1H, H-3´); 8.29 (s, 1H, CH=N). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 55.5 (OCH_3); 112.5 (C-4´); 114.6 (C-3 and C-5); 123.1 (C-3´); 123.7 (C-2 and C-6); 141.3 (C-1); 147.9 (C-5´); 150.6 (C-2´); 153.0 (CH=N); 160.7 (C-4); 177.6 (CO). **IR** (NaCl) *v*: 2854.3 (C-H), 1642.4 (C=O); 1578.2 (C=N) cm^{-1}.

1.2 Synthesis of α-ketoimines 1i-j

A solution of *p*-anisidine (1 eq) and the corresponding isatin (1 eq) in EtOH and acetic acid (0.2 mL) was refluxed until the starting material disappeared. The reaction mixture was kept at room temperature overnight. The resultant solid was filtrated and washed with cold ethanol affording imines **1i-j**.

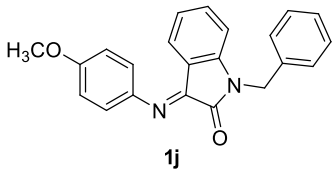
3-(4-Methoxyphenylimino)indolin-2-one (1i)[2]



1i

Reaction time: 3 h. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 3.90 (s, 3H, OCH_3); 6.82 (t, *J* = 7.7 Hz, 1H, H-5); 6.91-7.16 (m, 6H, H-4, H-7, H-2', H-3', H-5' and H-6'); 7.35 (t, *J* = 7.7 Hz, 1H, H-6); 9.28 (bs, 1H, NH).

1-Benzyl-3-(4-methoxyphenylimino)indolin-2-one (1j)

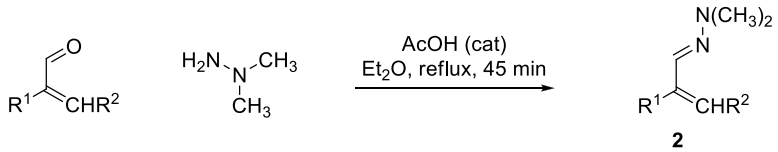


1j

Reaction time: 2 h. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 3.87 (s, 3H, OCH_3); 5.02 (s, 2H, CH_2); 6.69-6.80 (m, 2H, H-3' and H-5'); 6.93-7.00 (m, 3H, H-2', H-6' and H-5); 7.04-7.09 (m, 2H, H-2'' and H-6''); 7.19-7.38 (m, 6H, H-4, H-6, H-7, H-3'', H-4'', H-5''). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 44.1 (CH_2); 55.6 (OCH_3); 110.4 (C-7); 114.7 (C-3' and C-5'); 116.1 (C-3a); 120.3 (C-2' and C-6'); 122.7 (C-5); 125.8 (C-4); 127.6 (C-2'' and C-6''); 128.0 (C-4''); 129.0 (C-3'' and C-5''); 133.9 (C-6); 135.3 (C-1''); 143.2 (C-1'); 147.1 (C-7a); 153.8 (C-4'); 158.0 (C-3); 163.7 (CO).

[2] K. M. Khan, U. R. Mughal, S. S. Perveen and M. I. Choudhary, *Lett. Drug Design Discov*. 2008, **5**, 243.

2. Synthesis of α,β-unsaturated *N*,*N*-dimethylhydrazones 2a-e



2

Hydrazone	R^1	R^2	Yield (%)
2a	CH_3	H	95
2b	CH_2CH_3	H	90
2c	H	H	95
2d	H	CH_2CH_3	95
2e	CH_3	CH_2CH_3	90

To a stirred solution of the corresponding acrolein derivative (1 eq, 60 mmol) in diethyl ether (50 mL) was added *N*,*N*-dimethylhydrazine (2 eq, 120 mmol) and acetic acid (1 mL) dropwise and the resulting yellow solution was reflux for 45 minutes. After cooling at room temperature, it was washed successively with saturated $NaHCO_3$ (2 x 50 mL) and water (2 x 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated on a water bath keeping the temperature below 60°C, to avoid volatilization of the resulting hydrazone. The crude product thus obtained was used in subsequent reactions with no further purification.

Spectral data of compounds **2** were in agreement with those reported in the literature.[3,4,5,6]

[3] E. Gómez-Bengoa and A. M. Echavarren, *J. Org. Chem*., 1991, **56**, 3497.

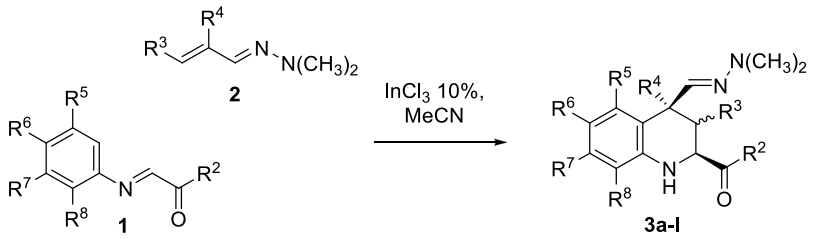
[4] R. Habernegg, *Chem. Ber.*, 1986, **119**, 2397

[5] A. Waldner, *Helv. Chim. Acta*, 1988, **71**, 486.

[6] J. M. Pérez, C. Avendaño and J. C. Menéndez, *Tetrahedron*, 1995, **51**, 6573.

3. Synthesis of tetrahydroquinoline derivatives 3a-l

3.1 Synthesis of 2-acyl-1,2,3,4-tetrahydroquinoline derivatives 3a-l

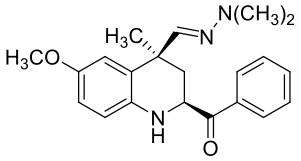


To a stirred solution of imine **1** (1 eq, 1.0 mmol) and $InCl_3$ (10 mol %) in acetonitrile (20 ml) was added hydrazone **2** (1.2 eq, 1.2 mmol). Stirring was continued for the time period specified in the compound data sheet and after completion of the reaction, as indicated by TLC, the reaction mixture was diluted with water (10 ml), extracted with CH_2Cl_2 (4 x 10 ml), dried and evaporated. Purification of the resulting crude was achieved through flash chromatography using a Combiflash Teledyne automated chromatograph, eluting with a gradient from neat petroleum ether to 9:1 petroleum ether-ethyl acetate. This purification afforded *cis-trans* mixtures, with the dr values specified in the table below, which were used as such for the subsequent reactions. The major *cis* isomers were isolated and characterized in most cases, and to this end the mixtures were purified by silica gel column chromatography, using the mixture of solvents specified in each case.

Cmpd.	R^2	R^3	R^4	R^5	R^6	R^7	R^8	Yield 3 (%)	Cis : Trans
3a	C_6H_5	H	CH_3	H	6-OCH_3	H	H	72	82 : 18 [a]
3b	4-FC_6H_4	H	CH_3	H	6-OCH_3	H	H	75	84 : 16 [a]
3c	4-$OCH_3C_6H_4$	H	CH_3	H	6-OCH_3	H	H	70	83 : 17 [a]
3d	C_6H_5	H	CH_2CH_3	H	6-OCH_3	H	H	63	91 : 09 [a]
3e	C_6H_5	H	CH_3	H	CH_3	H	CH_3	95	98 : 02 [a]
3f	4-FC_6H_4	H	CH_3	CH_3	H	CH_3	H	50	50 : 50 [a]
3g	OEt	H	CH_3	H	6-OCH_3	H	H	88	100 : 0 [a]
3h	OEt	H	CH_3	H	CH_3	H	CH_3	86	84 : 16 [a]
3i	OEt	H	CH_2CH_3	H	6-OCH_3	H	H	74	87 : 13 [a]
3j	2-furyl	H	CH_3	H	6-OCH_3	H	H	88	100 : 0 [a]
3k	C_6H_5	CH_2CH_3	H	H	6-OCH_3	H	H	66	50 : 50 [b]
3l	C_6H_5	H	H	H	6-OCH_3	H	H	72	100 : 0 [a]
3m	C_6H_5	CH_2CH_3	CH_3	H	6-OCH_3	H	H	73	57 : 43 [b]

[a] *Cis*:*trans* diastereoselection in 2,4-disubstituted compounds. [b] The C-2 and C-4 substituents are *cis*, and the group at C-3 can be *cis* or *trans* with regard to them with no selectivity.

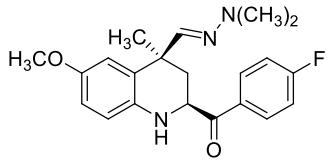
(±)-(2*S,4*S**)-2-Benzoyl-4-[(2,2-dimethylhydrazono)methyl]-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline (3a)**



3a

Reaction time: 3 h. Purification of the *cis* isomer: chromatography with petroleum ether:ethyl acetate (10:1, v/v). Yellow solid, mp: 130-131 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.65 (s, 3H, CH_3); 1.73 (t, *J* = 12.6 Hz, 1H, H-3ax); 2.07 (dd, *J* = 13.0, 2.8 Hz, 1H, H-3eq); 2.72 (s, 6H, $N(CH_3)_2$); 3.73 (s, 3H, OCH_3); 4.60 (br s, 1H, NH); 5.09 (dd, *J* = 12.2, 2.7 Hz, 1H, H-2); 6.53 (s, 1H, CH=N); 6.64-6.66 (m, 1H, H-5); 6.70-6.73 (m, 2H, H-7 and H-8); 7.49 (t, *J* = 7.4 Hz, 2H, H-3´ and H-5´); 7.61 (t, *J* = 7.4 Hz, 1H, H-4´); 7.92-7.98 (m, 2H, H-2´ and H-6´). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 26.6 (CH_3); 39.2 (C-3); 41.4 (C-4); 43.6 ($N(CH_3)_2$); 54.6 (C-2); 56.1 (OCH_3); 113.8 (C-5); 113.9 (C-7); 117.4 (C-8); 128.5 (C-4a); 128.6 (C-2´ and C-6´); 129.2 (C-3´ and C-5´); 133.9 (C-4´); 135.0 (C-1´); 136.8 (C-8a); 143.6 (CH=N); 152.5 (C-6); 199.9 (CO). **IR** (NaCl) *v*: 3370.9 (N-H), 2954.1 (C-H), 1685.3 (C=O), 1597.0 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{21}H_{25}N_3O_2$ (M = 351.44): C, 71.77; H, 7.17; N, 11.96. Found: C, 71.48; H, 7.03; N, 11.80.

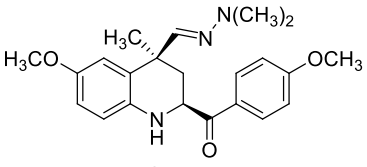
(±)-(2S*,4S*)-4-[(2,2-Dimethylhydrazono)methyl]-2-(4-fluorobenzoyl)-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline (3b)



3b

Purification of the *cis* isomer: chromatography with petroleum ether:ethyl acetate (20:1, v/v). Reaction time: 3 h. Yellow solid, mp: 121-122 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.63 (s, 3H, CH_3); 1.74 (t, *J* = 12.6 Hz, 1H, H-3ax); 2.04 (dd, *J* = 13.0, 2.8 Hz, 1H, H-3eq); 2.72 (s, 6H, $N(CH_3)_2$); 3.73 (s, 3H, OCH_3); 5.04 (dd, *J* = 12.2, 2.8 Hz, 1H, H-2); 6.53 (s, 1H, CH=N); 6.64-6.66 (m, 1H, H-5); 6.70-6.72 (m, 2H, H-7 and H-8); 7.17 (t, *J* = 8.6 Hz, 2H, H-3´ and H-5´); 7.98 (dd, *J* = 8.8, 5.4 Hz, 2H, H-2´ and H-6´). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 26.7 (CH_3); 39.3 (C-3); 41.3 (C-4); 43.6 ($N(CH_3)_2$); 54.6 (C-2); 56.1 (OCH_3); 113.9 (C-5); 114.0 (C-7); 116.4 (d, *J* = 24.1 Hz, C-3´ and C-5´); 117.5 (C-8); 128.6 (C-4a); 131.3 (d, *J* = 10.2 Hz, C-2´ and C-6´); 131.3 (d, *J* = 3.6 Hz, C-1´); 136.7 (C-8a); 143.1 (CH=N); 152.6 (C-6); 166.2 (d, *J* = 280.8 Hz, C-4´); 198.3 (CO). **IR** (NaCl) *v*: 3358.2 (N-H), 2960.2 (C-H), 1686.1 (C=O), 1597.4 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{21}H_{24}FN_3O_2$ (M = 369.43): C, 68.27; H, 6.55; N, 11.37. Found: C, 68.53; H, 6.29; N, 10.98.

(±)-(2*S,4*S**)-4-[(2,2-Dimethylhydrazono)methyl]-6-methoxy-2-(4-methoxybenzoyl)-4-methyl-1,2,3,4-tetrahydroquinoline (3c)**

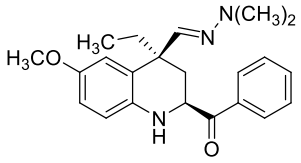


3c

Reaction time: 3 h. Purification of the *cis* isomer: chromatography with petroleum ether:ethyl acetate (20:1, v/v). Yellow solid, mp: 127-128 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.64 (s, 3H, CH_3); 1.72 (t, *J* = 12.7 Hz, 1H, H-3ax); 2.06 (dd, *J* = 13.0, 2.8

Hz, 1H, H-3eq); 2.73 (s, 6H, $N(CH_3)_2$); 3.73 (s, 3H, OCH_3); 3.88 (s, 3H, OCH_3); 4.58 (bs, 1H, NH); 5.04 (dd, *J* = 12.3, 2.7 Hz, 1H, H-2); 6.53 (s, 1H, CH=N); 6.63-6.66 (m, 1H, H-5); 6.69-6.73 (m, 2H, H-7 and H-8); 6.96 (d, *J* = 9.0 Hz, 2H, H-3´ and H-5´); 7.94 (d, *J* = 9.0 Hz, 2H, H-2´ and H-6´). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 26.5 (CH_3); 39.5 (C-3); 41.4 (C-4); 43.6 ($N(CH_3)_2$); 54.1 (C-2); 55.9 (OCH_3); 56.1 (OCH_3); 113.9 (C-5); 113.9 (C-7); 114.4 (C-3´ and C-5´); 117.5 (C-8); 127.8 (C-1´); 128.6 (C-4a); 131.0 (C-2´ and C-6´); 137.0 (C-8a); 143.4 (CH=N); 152.5 (C-6); 164.1 (C-4´); 198.2 (CO). **IR** (NaCl) *v*: 3375.9 (N-H), 2960.7 (C-H), 1676.3 (C=O), 1600.5 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{22}H_{27}N_3O_3$ (M = 381.47): C, 69.27; H, 7.13; N, 11.02. Found: C, 68.90; H, 6.90; N, 10.77.

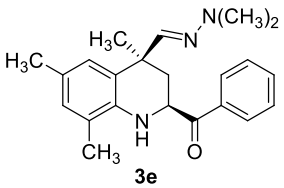
(±)-(2*S,4*S**)-2-Benzoyl-4-[(2,2-dimethylhydrazono)methyl]- 4-ethyl-6-methoxy-1,2,3,4-tetrahydroquinoline (3d)**



3d

Reaction time: 3 h. Purification of the *cis* isomer: chromatography with petroleum ether:ethyl acetate (20:1, v/v). Orange oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.00 (t, *J* = 7.3 Hz, 3H, CH_2CH_3); 1.71 (t, *J* = 12.5 Hz, 1H, H-3ax); 2.06 (q, *J* = 7.3 Hz, 2H, CH_2CH_3); 2.23 (dd, *J* = 13.3, 3.3 Hz, 1H, H-3eq); 2.69 (s, 6H, $N(CH_3)_2$); 3.73 (s, 3H, OCH_3); 5.05 (dd, *J* = 12.4, 3.3 Hz, 1H, H-2); 6.51 (s, 1H, CH=N); 6.68 (m, 3H, H-7, H-5 and H-8); 7.45-7.51 (m, 2H, H-3' and H-5'); 7.56-7.59 (m, 1H, H-4'); 7.93 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 9.3 (CH_2CH_3); 30.8 (CH_2CH_3); 35.2 (C-3); 43.3 ($N(CH_3)_2$); 43.8 (C-4); 54.1 (C-2); 56.0 (OCH_3); 113.3 (C-5); 114.5 (C-7); 116.8 (C-8); 127.4 (C-4a); 128.3 (C-2' and C-6'); 129.0 (C-3' and C-5'); 133.6 (C-4'); 135.2 (C-1'); 136.9 (C-8a); 141.2 (CH=N); 151.8 (C-6); 200.4 (C=O). **IR** (NaCl) *v*: 3375 (N-H), 2925 (C-H), 1620 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{22}H_{27}N_3O_2$ (M= 365.47): C, 72.30; H, 7.45; N, 11.50. Found: C, 72.01; H, 7.23; N, 11.25.

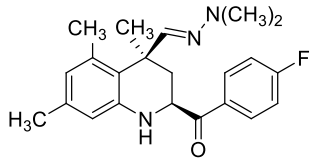
(±)-(2S*,4S*)-2-Benzoyl-4-[(2,2-dimethylhydrazono)methyl]-4,6,8-trimethyl-1,2,3,4-tetrahydroquinoline (3e)



3e

Reaction time: 4 h. Purification of the *cis* isomer: chromatography with petroleum ether:ethyl acetate (20:1, v/v). White solid, mp: 136-138 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.64-1.74 (m, 4H, CH_3 and H-3ax); 2.06 (dd, *J* = 12.9, 2.9 Hz, 1H, H-3eq); 2.21 (s, 3H, CH_3); 2,22 (s, 3H, CH_3); 2.73 (s, 6H, $N(CH_3)_2$); 4.57 (s, 1H, NH); 5.13 (d, *J* = 12.4 Hz, 1H, H-2); 6.55 (s, 1H, CH=N); 6.75 (s, 1H, H-7); 6.82 (s, 1H, H-5); 7.47-7.51 (m, 2H, H-3' and H-5'); 7.53-7.61 (m, 1H, H-4'); 7.94-7.97 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 17.7 ($ArCH_3$); 20.6 ($ArCH_3$); 26.3 (CH_3); 39.0 (C-3); 41.1 (C-4); 43.5 ($N(CH_3)_2$); 54.4 (C-2); 123.4 (C-4a); 126.2 (C-5); 126.4 (C-8); 126.4 (C-6); 128.5 (C-3' and C-5'); 129.0 (C-2' and C-6'); 129.7 (C-7); 133.7 (C-4'); 134.8 (C-1'); 138.2 (C-8a); 143.9 (CH=N); 199.7 (C=O). **IR** (NaCl) *v*: 3346.8 (N-H), 2918.2 (C-H), 1627.5 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{22}H_{27}N_3O$ (M= 349.47): C, 75.61; H, 7.79; N, 12.02. Found: C, 75.31; H, 7.79; N, 11.90.

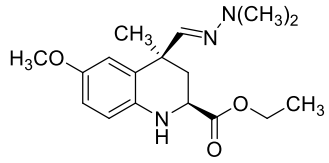
(±)-(2S*,4S*)-4-[(2,2-Dimethylhydrazono)methyl]-2-(4-fluorobenzoyl)-4,5,7-trimethyl-1,2,3,4-tetrahydroquinoline (3f).



3f

Reaction time: 5 h. Purification of the *cis* isomer: chromatography with petroleum ether:ethyl acetate (20:1, v/v). Yellow solid, mp: 145-147 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.66 (t, *J* = 12.6 Hz, 1H, H-3ax); 1.72 (s, 3H, CH_3); 1.91 (dd, *J* = 12.8, 2.5 Hz, 1H, H-3eq); 2.21 (s, 3H, CH_3); 2.22 (s, 3H, CH_3); 2.71 (s, 6H, $N(CH_3)_2$); 4.99 (dd, *J* = 12.2, 2.6 Hz, 1H, H-2); 6.37 (s, 1H, H-8); 6.47 (s, 1H, H-6); 6.62 (s, 1H, CH=N); 7.18 (t, *J* = 8.6 Hz, 2H, H-3´ and H-5´); 7.99 (dd, *J* = 8.8, 5.4 Hz, 2H, H-2´ and H-6´). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 21.1 (CH_3); 22.2 (CH_3); 23.4 (CH_3); 41.3 (C-4); 42.2 (C-3); 43.5 ($N(CH_3)_2$); 53.9 (C-2); 114.8 (C-8); 116.4 (d, *J* = 24.0 Hz, C-3´ and C-5´); 121.5 (C-4a); 122.9 (C-6); 131.2 (d, *J* = 2.8 Hz, C-1´); 131.3 (d, *J* = 10.1 Hz, C-2´ and C-6´); 137.6 (C-7); 137.7 (C-5); 143.5 (C-8a); 145.3 (CH=N); 166.2 (d, *J* = 280.6 Hz, C-4´); 197.9 (CO). **IR** (NaCl) *v*: 3332.4 (N-H), 2961.6 (C-H), 1686.9 (C=O), 1596.8 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{22}H_{26}FN_3O$ (M = 367.46): C, 71.91; H, 7.13; N, 11.44. Found: C, 71.79; H, 6.88; N, 11.05.

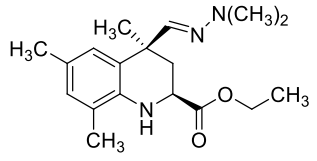
(±)-(2*S,4*S**)-Ethyl 4-[(2,2-dimethylhydrazono)methyl]-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline-2-carboxylate (3g)**



3g

Reaction time: 2 h. Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Pale yellow viscous liquid. Spectra data are identical to those found in the literature.[7] **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.34 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); 1.52 (s, 3H, CH_3); 1.98 (t, *J* = 12.0 Hz, 1H, H-3ax); 2.12 (dd, *J* = 12.9, 3.3 Hz, 1H, H-3eq); 2.80 (s, 6H, $N(CH_3)_2$); 3.74 (s, 3H, OCH_3); 4.14 (dd, *J* = 11.6, 3.2 Hz, 1H, H-2); 4.28 (q, *J* = 7.0 Hz, 2H, OCH_2CH_3); 4.29 (bs, 1H, NH); 6.60-6.73 (m, 4H, H-5, H-7, H-8 and CH=N).

(±)-(2*S,4*S**)-Ethyl 4-[(2,2-dimethylhydrazono)methyl]-4,6,8-trimethyl-1,2,3,4-tetrahydroquinoline-2-carboxylate (3h).**



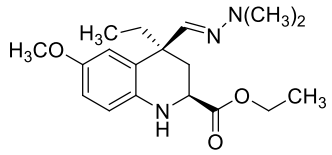
3h

Reaction time: 2 h. Purification: flash chromatography with petroleum ether:ethyl acetate (10:1, v/v). Yellow oil, consisting of a *ca.* 9:1 mixture of the *cis* and *trans* diastereomers. Spectral data correspond to the major *cis* compound. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.34 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); 1.51 (s, 3H, CH_3); 1.93 (t, *J* = 12.4 Hz, 1H, H-3ax); 2.10 (dd, *J* = 13.2, 4.0 Hz, 1H, H-3eq); 2.18 (s, 3H, CH_3); 2.21 (s, 3H, CH_3); 2.79 (s, 6H, $N(CH_3)_2$); 4.19 (m, 1H, H-2); 4.24-4.32 (m, 3H, OCH_2CH_3 and NH); 6.64 (s, 1H, CH=N); 6.75 (s, 1H, H-7); 6.79 (s, 1H, H-5). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 14.3 (CH_2CH_3); 17.4 ($ArCH_3$);

[7] V. Sridharan, P. Ribelles, V. Estévez, M. Villacampa, M. T. Ramos, P. T. Perumal and J. C. Menéndez. *Chem*. *Eur*. *J*., 2012, **18**, 5056.

20.5 ($ArCH_3$); 26.8 (CH_3); 37.3 (C-3); 40.2 (C-4); 43.5 ($N(CH_3)_2$); 51.1 (C-2); 61.5 (CH_2CH_3); 122.2 (C-4a); 126.1 (C-8); 126.3 (C-6); 126.4 (C-5); 129.6 (C-7); 138.1 (C-8a); 144.3 (CH=N); 173.6 (C=O). **IR** (NaCl) *v*: 3405 (N-H), 2930 (C-H), 1730 (C=O) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{18}H_{27}N_3O_2$ (M= 317.43): C, 68.11; H, 8.57; N, 13.24. Found: C, 67.98; H, 8.32; N, 12.99.

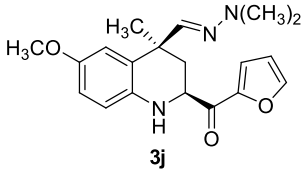
(±)-(2*S,4*S**)-Ethyl-4-[(2,2-dimethylhydrazono)methyl]-4-ethyl-6-methoxy-1,2,3,4-tetrahydroquinoline-2-carboxylate (3i)**



3i

Reaction time: 2 h. Purification of the *cis* isomer: flash chromatography with petroleum ether:ethyl acetate (10:1, v/v). Orange oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.30 (t, *J* = 7.1 Hz, 6H, 2 x CH_3); 1.81-2.0 (m, 3H, CH_2CH_3 and H-3ax); 2.29 (dd, *J* = 13.3, 3.6 Hz, 1H, H-3eq); 2.75 (s, 6H, $N(CH_3)_2$); 3.71 (s, 3H, OCH_3); 4.08 (dd, *J* = 11.9, 3.6 Hz, 1H, H-2); 4.23 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3); 6.55-6.68 (m, 4H, H-5, H-7, H-8 and CH=N). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 8.8 (CH_2CH_3); 14.3 (OCH_2CH_3); 33.4 (C-3 and CH_2CH_3); 43.1 (C-4); 43.4 ($N(CH_3)_2$); 51.0 (OCH_3); 55.9 (C-2); 61.5 (CH_2CH_3); 113.2 (C-5); 114.3 (C-7); 115.9 (C-8); 127.3 (C-4a); 136.6 (C-8a); 141.8 (CH=N); 151.8 (C-6); 173.8 (C=O). **IR** (NaCl) *v*: 3395.4 (N-H), 2927.3 (C-H), 1743.8 (C=O), 1117.3 (C-O) cm^{-1}. This compound was contaminated with *ca.* 13% of the corresponding quinoline 4i and could not be purified further.

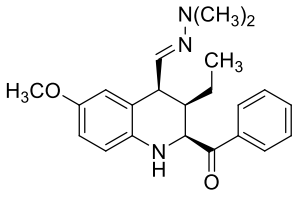
(±)-(2*S,4*S**)-4-[(2,2-Dimethylhydrazono)methyl]-2-(2-furylcarbonyl)-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline (3j)**



3j

Reaction time: 3 h. Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Yellow solid, mp: 113-114 °C. Spectra data are identical to those found in the literature.[7] **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.64 (s, 3H, CH_3); 1.86 (t, *J* = 12.3, 1H, H-3ax); 2.22 (dd, *J* = 12.7, 3.0 Hz, 1H, H-3eq); 2.77 (s, 6H, $N(CH_3)_2$); 3.75 (s, 3H, OCH_3); 4.87 (dd, *J* = 11.9, 2.9 Hz, 1H, H-2); 6.58-6.62 (m, 2H, H-4´ and CH=N); 6.66-6.73 (m, 3H, H-5, H-7 and H-8); 7.34 (dd, *J* = 3.6, 0.5 Hz, 1H, H-3´); 7.65 (dd, *J* = 1.6, 0.7 Hz, 1H, H-5´).

(±)-(2*S,3*R**,4*S**)-2-Benzoyl-4-[(2,2-dimethylhydrazono)methyl]-3-ethyl-6-methoxy-1,2,3,4-tetrahydroquinoline (3ka)**

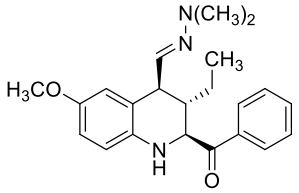


3ka

Reaction time: 1.30 h. Purification of the (2*S**,3*R**,4*S**) isomer (**3ka**) was achieved by flash chromatography eluting with petroleum ether:ethyl acetate (97:3, v/v). Yellow solid, mp: 79-81 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 0.67 (t, *J* = 7.4 Hz, 3H, CH_2CH_3); 0.97-1.05 (m, 2H, CH_2CH_3); 2.80-2.87 (m, 7H, $N(CH_3)_2$ and H-3); 3.61 (bs, 1H, H-4); 3.77 (s, 3H, OCH_3); 4.69 (br s,

1H, NH); 5.17 (d, *J* = 2.7 Hz, 1H, H-2); 6.72-6.73 (m, 3H, H-5, H-7 and H-8); 6.85 (d, *J* = 3.5 Hz, 1H, CH=N); 7.49 (t, *J* = 7.4 Hz, 2H, H-3' and H-5'); 7.58-7.61 (m, 1H, H-4'); 8.20 (d, *J* = 7.2 Hz, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 11.9 (CH_3); 19.9 (CH_2); 37.8 (C-3); 43.4 ($N(CH_3)_2$); 44.2 (C-4); 55.9 (OCH_3); 57.6 (C-2); 114.1 (C-5*); 115.5 (C-7*); 116.6 (C-8*); 121.0 (C-4a); 128.7 (C-3' and C-5'); 128.8 (C-2' and C-6'); 133.5 (C-4'); 135.0 (C-1'); 136.9 (C-8a); 140.3 (CH=N); 152.1 (C-6); 200.1 (C=O). **IR** (NaCl) *v*: 3375.5 (N-H), 2914.7 (C-H), 1677.2 (C=O), 1502.2 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{22}H_{27}N_3O_2$ (M = 365.47): C, 72.30; H, 7.45; N, 11.50. Found: C, 72.42; H, 7.29; N, 11.29.

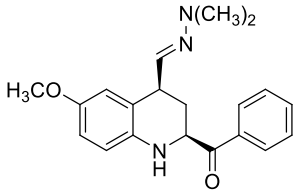
(±)-(2*S,3*S**,4*S**)-2-Benzoyl-4-[(2,2-dimethylhydrazono)methyl]-3-ethyl-6-methoxy-1,2,3,4-tetrahydroquinoline (3kb)**



3kb

Purification of the (2*S**,3*S**,4*S**) isomer (**3kb**) was achieved by flash chromatography, eluting with petroleum ether:ethyl acetate (97:3, v/v), afforded a yellow solid that was judged to be sufficiently pure for NOE studies. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.09 (t, *J* = 7.4 Hz, 3H, CH_2CH_3); 1.55-1.70 (m, 2H, CH_2CH_3); 2.49 (s, 6H, $N(CH_3)_2$); 2.57-2.61 (m, 1H, H-3); 3.43 (dd, *J* = 6.1, 3.8 Hz, 1H, H-4); 3.72 (s, 3H, OCH_3); 4.74 (d, *J* = 3.7 Hz, 1H, H-2); 6.26 (d, *J* = 6.3 Hz, 1H, H-8); 6.59 (d, *J* = 2.6 Hz, 1H, H-5); 6.68-6.70 (m, 2H, H-7 and CH=N); 7.45-7.46 (m, 2H, H-3' and H-5'); 7.49-7.57 (m, 1H, H-4'); 7.90-7.94 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 12.2 (CH_3); 26.9 (CH_2); 42.1 (C-3); 43.2 ($N(CH_3)_2$); 45.3 (C-4); 56.1 (OCH_3); 59.1 (C-2); 114.3 (C-5*); 115.3 (C-7*); 116.2 (C-8*); 121.4 (C-4a); 128.6 (C-3' and C-5'); 128.9 (C-2' and C-6'); 133.4 (C-4'); 135.6 (C-1'); 137.1 (C-8a); 140.2 (CH=N); 152.4 (C-6); 202.0 (C=O). **IR** (NaCl) *v*: 3375.2 (N-H), 2929.1 (C-H), 1682.8 (C=O), 1501.4 (C=N) cm^{-1}.

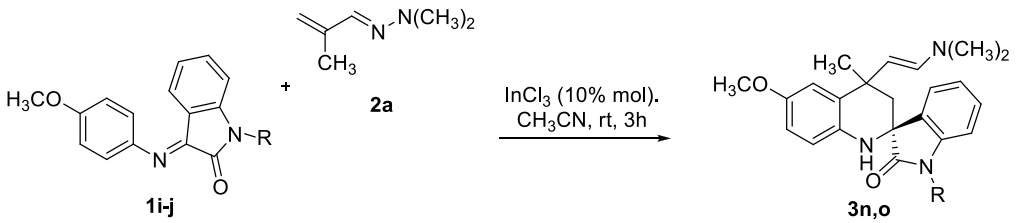
(±)-(2*S,4*S**)-2-Benzoyl-4-[(2,2-dimethylhydrazono)methyl]-6-methoxy-1,2,3,4-tetrahydroquinoline (3l)**



3l

Reaction time: 1 h. Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Red solid, mp: 95-97 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.64 (q, *J* = 12.5 Hz, 1H, H-3ax); 2.39 (ddd, *J* = 12.7, 5.5, 2.7 Hz, 1H, H-3eq); 2.77 (s, 6H, $N(CH_3)_2$); 3.73 (s, 3H, OCH_3); 3.96 (m, 1H, H-4); 4.61 (bs, 1H, NH); 5.0 (dd, *J* = 12.0, 2.7 Hz, 1H, H-2); 6.42 (d, *J* = 7.3 Hz, 1H, H-8); 6.66 (m, 1H, H-5); 6.72-6.73 (m, 2H, H-7 and CH=N); 7.43-7.55 (m, 2H; H-3' and H-5'); 7.61 (m, 1H, H-4'); 7.93-7.96 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 33.0 (C-3); 41.9 (C-4); 43.3 ($N(CH_3)_2$); 56.0 (OCH_3); 57.0 (C-2); 114.0 (C-5); 114.1 (C-7); 117.1 (C-8); 123.1 (C-4a); 128.5 (C-3' and C-5'); 129.0 (C-2' and C-6'); 133.7 (C-4'); 134.7 (C-1'); 137.4 (C-8a); 139.1 (CH=N); 152.3 (C-6); 199.3 (C=O). **IR** (NaCl) *v*: 3300.5 (N-H), 2949.1 (C-H), 1683.1 (C=O), 1503.0 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{20}H_{23}N_3O_2$ (M = 337.42): C, 71.19; H, 6.87; N, 12.45. Found: C, 70.86; H, 6.57; N, 12.25.

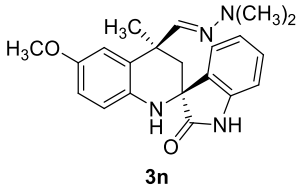
3.2 Synthesis of spiro[indoline-3,2'-quinoline] derivatives 3n and 3o



The reaction conditions are the same described in section 3.1 above.

Cmpd.	R	Yield (%)	dr
3o	H	51	1:0
3n	Bn	44	1:0

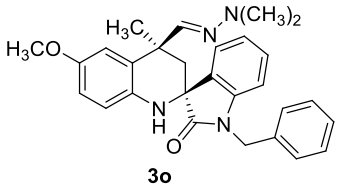
(±)-(2'*S,4'*S**) 4'-[(-(2,2-Dimethylhydrazono)-methyl]-6'-methoxy-4'-methyl-3',4'-dihydro-1'*H*-spiro[indoline-3,2'-quinolin]-2-one (3n)**



3n

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Orange solid, mp: 168-170 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.58 (s, 3H, CH_3); 2.25 (d, *J* = 14.0 Hz, 1H, H-3´); 2.60 (s, 6H, $N(CH_3)_2$); 2.61 (d, *J* = 15.0 Hz, 1H, H-3´); 3.78 (s, 3H, OCH_3); 3.91 (bs, 1H, NH); 6.57 (d, *J* = 8.6 Hz, 1H, H-8´); 6.68 (dd, *J* = 8.6, 2.8 Hz, 1H, H-7´); 6.71 (s, 1H, H-5´); 6.84-6.89 (m, 3H, H-4, H-5 and CH=N*); 7.07 (d, *J* = 7.1 Hz, 1H, H-7*); 7.16 (t, *J* = 7.7 Hz, 1H, H-6*). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 29.3 (CH_3); 39.6 (C-4´); 43.2 ($N(CH_3)_2$); 43.6 (C-3´); 55.8 (OCH_3); 60.9 (C-2´); 110.2 (C-5´*); 113.1 (C-7´*); 113.9 (C-8´*); 116.7 (C-7*); 122.4 (C-4*); 125.6 (C-6*); 129.0 (C-5 and C-4a´); 133.3 (C-8a´*); 136.4 (C-7a*); 139.9 (C-3a*); 143.7 (CH=N); 153.2 (C-6´); 181.1 (C=O). **IR** (NaCl) *v*: 3177.1 (N-H), 2920.9 (C-H), 1713.5 (C=O) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{21}H_{24}N_4O_2$ (M = 364.44): C, 69.21; H, 6.64; N, 15.37. Found: C, 68.89; H, 6.39; N, 15.01.

(±)-(2'*S,4'*S**)-1-Benzyl-4'-[(2,2-dimethylhydrazono)methyl]-6'-methoxy-4'-methyl-3',4'-dihydro-1'*H*-spiro[indoline-3,2'-quinolin]-2-one (3o)**

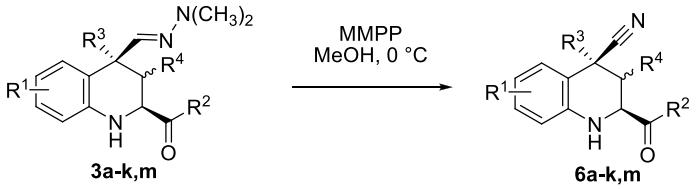


3o

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Orange solid, mp: 173-174 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.60 (s, 3H, CH_3); 2.30 (d, *J* = 13.6 Hz, 1H, CH_2Ph); 2.59 (s, 6H, $N(CH_3)_2$); 2.64 (d, *J* = 13.6 Hz, 1H, CH_2Ph);

3.79 (s, 3H, OCH_3); 3.87 (br s, 1H, NH); 4.70 (d, *J* = 15.6 Hz, 1H, H-3´); 5.09 (d, *J* = 15.6 Hz, 1H, H-3´); 6.58 (d, *J* = 8.6 Hz, 1H, H-8´); 6.67-6.74 (m, 3H, H-4, H-5 and H-6); 6.85-6.89 (m, 2H, H-5´ and H-7´); 7.07-7.12 (m, 2H, H-7 and H-4''); 7.30-7.33 (m, 5H, H-2'', H-3'', H-5'', H-6'' and CH=N). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 29.3 (CH_3); 39.6 (C-4´); 43.2 ($N(CH_3)_2$); 43.9 (C-3´); 55.9 (OCH_3); 60.7 (CH_2Ph); 77.4 (C-2´); 109.3 (C-5´*); 113.1 (C-7´*); 114.0 (C-8´*); 116.8 (C-7*); 122.4 (C-4*); 125.2 (C-6*); 127.4 (C-2'' and C-6''); 127.8 (C-5); 128.9 (C-4''); 129.0 (C-3'' and C-5''); 132.9 (C-4a´); 136.0 (C-8a´*); 136.5 (C-7a*); 141.9 (C-3a); 143.7 (CH=N); 145.2 (C-1´´*); 153.2 (C-6´); 178.8 (C=O). **IR** (NaCl) *v*: 3332.1 (N-H), 2927.0 (C-H), 1709.6 (C=O) cm^{-1}.
Elemental analysis (%): Calc. for $C_{28}H_{30}N_4O_2$ (M = 454.56): C, 73.98; H, 6.65; N, 12.33. Found: C, 73.58; H, 6.38; N, 12.09.

4. Synthesis of 2-acyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile derivatives 6a-k and m

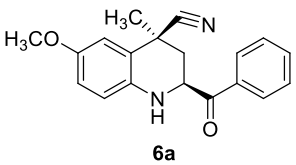


To a solution of the suitable hydrazone **3** (0.5 mmol, 1 eq, as a *cis-trans* mixture) in methanol (10 mL) was added dropwise a suspension of MMPP·$6H_2O$ (0.62 mmol, 1.25 eq) in methanol (5 mL), and the mixture was stirred until consumption of the starting material. The mixture was then diluted with water (20 mL) and extracted with CH_2Cl_2 (3 X 20 mL). The organic layer was washed with water (20 mL) and brine (20 mL), dried (Na_2SO_4), concentrated and the crude residue was regarded to be sufficiently pure to be used for the next step without further purification. The major *cis* compounds were purified by flash chromatography on silica gel, eluting with a mixture of petroleum ether:ethyl acetate (9:1, v/v), and their characterization data follow. Compound **6d** could not be isolated, as it spontaneously aromatized to quinoline **4d**. Flash chromatography on alumina of derivatives **6k** and **6l**, eluting with a mixture of petroleum ether:ethyl acetate (9,5:0,5, v/v), afforded directly the aromatic derivatives **7a** and **7b**.

Cmpd.	R^2	R^3	R^4	R^5	R^6	R^7	R^8	Yield 6 (%)
6a	C_6H_5	H	CH_3	H	OCH_3	H	H	72
6b	4-FC_6H_4	H	CH_3	H	OCH_3	H	H	70[a]
6c	4-$OCH_3C_6H_4$	H	CH_3	H	OCH_3	H	H	89
6d	C_6H_5	H	CH_2CH_3	H	OCH_3	H	H	NR
6e	C_6H_5	H	CH_3	H	CH_3	H	CH_3	98
6f	4-FC_6H_4	H	CH_3	CH_3	H	CH_3	H	93
6g	OEt	H	CH_3	H	OCH_3	H	H	60
6h	OEt	H	CH_3	H	CH_3	H	CH_3	83
6i	OEt	H	CH_2CH_3	H	OCH_3	H	H	63[b]
6j	2-furyl	H	CH_3	H	OCH_3	H	H	78
6k	C_6H_5	CH_2CH_3	H	H	OCH_3	H	H	NR
6l	C_6H_5	CH_2CH_3	H	H	OCH_3	H	H	NR
6m	C_6H_5	CH_2CH_3	CH_3	H	OCH_3	H	H	69

[a]Together with 14% of compound **4b**. [b] Together with 32% of compound **4i**.

(±)-(2'*S,4'*S**)-2-Benzoyl-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (6a)**

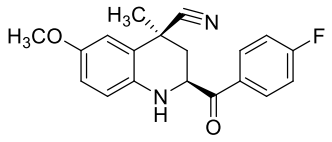


6a

Reaction time: 2 h. Yellow oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.87 (s, 3H, CH_3); 2.07 (t, *J* = 12.7 Hz, 1H, H-3ax); 2.50 (dd, *J* = 13.0, 3.2 Hz, 1H, H-3eq); 3.78 (s, 3H, OCH_3); 4.97 (dd, *J* = 12.5, 3.2 Hz, 1H, H-2); 6.72 (d, *J* = 8.7 Hz, 1H, H-8); 6.80 (dd, *J* = 8.8, 2.7 Hz, 1H, H-7); 6.97 (d, *J* = 2.6 Hz, 1H, H-5); 7.48-7.59 (m, 2H, H-3' and H-5'); 7.62-7.72 (m, 1H, H-4'); 7.87-7.96 (m,

2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 28.6 (CH_3); 35.6 (C-4); 36.7(C-3); 52.9 (OCH_3); 56.0 (C-2); 112.2 (C-7); 116.5 (C-5); 117.8 (C-8); 120.6 (CN); 123.7 (C-4a); 128.3 (C-2' and C-6'); 129.3 (C-3' and C-5'); 134.1 (C-4´); 134.4 (C-1´); 135.2 (C-8a); 152.7 (C-6); 198.0 (C=O). **IR** (NaCl) *v*: 3373.4 (C-N), 2926.2 (C-H), 2235.0 (CN), 1691.6 (C=O) cm^{-1}. **Elemental analysis (%)**: Calcd. for $C_{19}H_{18}N_2O_2$ (M = 306.36): C, 74.49; H, 5.92; N, 9.14. Found: C, 74.23; H, 5.75; N, 8.98.

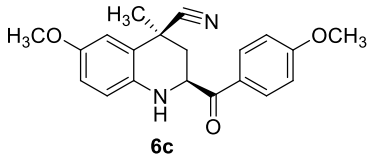
(±)-(2'S*,4'S*)-2-(4-Fluorobenzoyl)-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (6b)



6b

Reaction time: 2 h. Yellow solid, mp: 119-120 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.86 (s, 3H, CH_3); 2.10 (t, *J* = 12.5 Hz, 1H, H-3ax); 2.46 (dd, *J* = 13.0, 3.2 Hz, 1H, H-3eq); 3.78 (s, 3H, OCH_3); 4.58 (s, 1H, NH); 4.92 (m, 1H, H-2); 6.71 (d, *J* = 8.8 Hz, 1H, H-8); 6.80 (dd, *J* = 8.8, 2.7 Hz, 1H, H-7); 6.96 (d, *J* = 2.7 Hz, 1H, H-5); 7.22 (t, *J* = 8.6 Hz, 2H, H-3' and H-5'); 7.92-7.99 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 28.7 (CH_3); 35.5 (C-4); 36.8 (C-3); 52.9 (C-2); 56.0 (OCH_3); 112.2 (C-7); 116.4 (d, *J* = 12.7 Hz, C-3' and C-5'); 116.8 (C-5); 117.9 (C-8); 120.5 (CN); 123.7 (C-4a); 130.7 (d, *J* = 3.1 Hz, C-1'); 131.1 (d, *J* = 9.4 Hz, C-2' and C-6'); 135.1 (C-8a); 152.8 (C-6); 166.5 (d, *J* = 257 Hz, C-4'); 196.4 (C=O). **IR** (NaCl) *v*: 3345.2 (N-H), 2923.1 (C-H), 2232.1 (CN), 1684.4 (C=O) cm^{-1}. **Elemental analysis (%)**: Calcd. for $C_{19}H_{17}FN_2O_2$ (M = 324.35): C, 70.36; H, 5.28; N, 8.64. Found: C, 70.12; H, 5.03; N, 8.45.

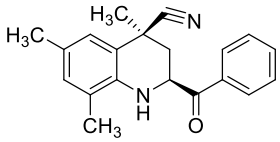
(±)-(2'S*,4'S*)-2-(4-Methoxybenzoyl)-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (6c)



6c

Reaction time: 2 h. Yellow oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.87 (s, 3H, CH_3); 2.07 (t, *J* = 12.8 Hz, 1H, H-3ax); 2.49 (dd, *J* = 13.0, 3.0 Hz, 1H, H-3eq); 3.78 (s, 3H, OCH_3); 3.91 (s, 3H, OCH_3); 4.61 (bs, 1H, NH); 4.91 (d, *J* = 10.7 Hz, 1H, H-2); 6.71 (d, *J* = 8.8 Hz, 1H, H-8); 6.79 (dd, *J* = 8.8, 2.6 Hz, 1H, H-7); 6.96-7.02 (m, 3H, H-5, H-3' and H-5'); 7.92 (d, *J* = 8.9 Hz, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 28.7 (CH_3); 35.6 (C-4); 37.0 (C-3); 52.4 (C-2); 55.8 (OCH_3); 56.0 (OCH_3); 112.2 (C-7*); 114.5 (C-3' and C-5'); 116.5 (C-5*); 118.0 (C-8*); 120.6 (CN*); 123.8 (C-4a*); 127.1 (C-1'); 130.8 (C-2' and C-6'); 135.4 (C-8a); 152.7 (C-6); 164.4 (C-4'); 196.2 (C=O). **IR** (NaCl) *v*: 3362.8 (N-H), 2924.9 (C-H), 2234.4 (CN), 1680.4 (C=O) cm^{-1}. **Elemental analysis (%)**: Calcd. for $C_{20}H_{20}N_2O_3$: (M = 336.38): C, 71.41; H, 5.99; N, 8.33. Found: C, 71.23; H, 5.78; N, 8.17.

(±)-(2'S*,4'S*)-2-Benzoyl-4,6,8-trimethyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (6e)

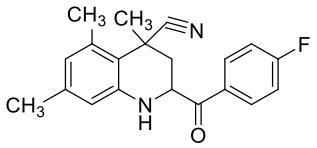


6e

Reaction time: 0.5 h. Orange solid, mp: 113-115 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.87 (s, 3H, CH_3); 2.04 (t, *J* = 12.8 Hz, 1H, H-3ax); 2.21 (s, 3H, CH_3); 2.26 (s, 3H, CH_3); 2.51 (dd, *J* = 12.9, 3.2 Hz, 1H, H-3eq); 4.61 (s, 1H, NH); 5.01 (d, *J* = 12.6 Hz, 1H, H-2); 6.90 (s, 1H, H-7); 7.13 (s, 1H, H-5); 7.51-7.58 (m, 2H, H-3' and H-5'); 7.67 (m, 1H, H-4'); 7.91-7.94 (m, 2H, H-2' and H-

6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 17.5 ($ArCH_3$); 20.5 ($ArCH_3$); 28.7 (CH_3); 35.6 (C-4); 36.7 (C-3); 52.9 (C-2); 119.2 (CN*); 123.8 (C-4a*); 124.1 (C-8); 125.6 (C-6); 127.3 (C-5); 128.3 (C-3' and C-5'); 129.3 (C-2' and C-6'); 131.3 (C-7); 134.2 (C-4'); 134.4 (C-1'); 136.9 (C-8a); 198.0 (C=O). **IR** (NaCl) *v*: 3386.3 (N-H), 2921.7 (C-H), 2234.8 (CN), 1680.4 (C=O) cm^{-1}. **Elemental analysis (%)**: Calcd. for $C_{20}H_{20}N_2O$ (M = 304.39): C, 78.92; H, 6.62; N, 9.20. Found: C, 78.67; H, 6.45; N, 9.01.

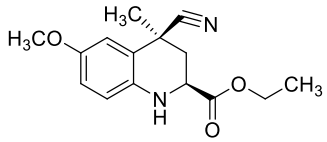
(±)-2-(4-Fluorobenzoyl)-4,5,7-trimethyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (6f)



6f

Reaction time: 1 h. Orange oil, as a 1:1 mixture of the *cis* and *trans* isomers. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.76 (s, 3H, CH_3); 1.88 (s, 3H, CH_3); 1.98 (t, *J* = 12.5 Hz, 1H, H-3ax); 2.21-2.22 (m, 7H, $ArCH_3$, $ArCH_3$ and H-3ax); 2.52-2.56 (m, 7H, $ArCH_3$, $ArCH_3$ and H-3eq); 2.73 (dd, *J* = 13.4, 1.9 Hz, 1H, H-3eq); 4.87 (dd, *J* = 12.6, 2.6 Hz, 1H, H-2); 5.03 (dd, *J* = 11.7, 1.9 Hz, 1H, H-2); 6.42-6.45 (m, 4H, H-6 and H-8); 7.19-7.25 (m, 4H, H-2' and H-6'); 7.97 (dd, *J* = 8.9; 5.3 Hz, 2H, H-3' and H-5'); 8.07 (dd, *J* = 8.9, 5.3 Hz, 2H, H-3' and H-5'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 20.9, 21.0, 21.0, 22.1, 26.4 and 26.5 (6 x CH_3); 33.5 and 33.8 (C-4 x 2); 40.0 and 44.0 (C-3 x 2); 52.2 and 54.9 (C-2 x 2); 114.2 and 115.8 (C-4a x 2); 115.0 and 115.3 (C-8 x 2); 116.4 and 116.8 (C-6 x 2); 123.1 and 123.8 ((C-2'and C-6' X 2) and CN); 124.0 (CN); 130.5 (d, *J* = 3.1 Hz, C-1'); 130.6 (d, *J* = 3.2 Hz, C-1'); 131.1 (d, *J* = 9.4 Hz, C-3' and C-5'); 131.3 (d, *J* = 9.4 Hz, C-3' and C-5'); 137.0 and 138.1 (C-7 x 2); 138.9 and 139.0 (C-5 x 2); 142.0 and 143.7 (C-8a x 2); 166.2 (d, *J* = 255.5 Hz, C-4'); 166.3 (d, *J* = 255.3 Hz, C-4'); 195.7 and 196.0 (C=O). **IR** (NaCl) *v*: 3361.5 (N-H), 2923.4 (C-H), 2237.1 (CN), 1689.3 (C=O) cm^{-1}. **Elemental analysis (%)**: Calcd. for $C_{20}H_{19}FN_2O$ (M = 322.38): C, 74.51; H, 5.94; N, 8.69. Found: C, 74.23; H, 5.75; N, 8.44.

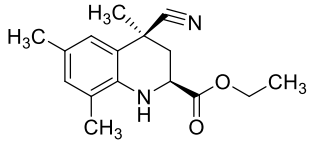
(±)-(2'S*,4'S*)-Ethyl 4-cyano-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline-2-carboxylate (6g)



6g

Reaction time: 1 h. Orange oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.32 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); 1.73 (s, 3H, CH_3); 2.34 (t, *J* = 12.5 Hz, 1H, H-3ax); 2.48 (dd, *J* = 13.1, 3.8 Hz, 1H, H-3eq); 3.76 (s, 3H, OCH_3); 4.02 (dd, *J* = 10.9, 3.8 Hz, 1H, H-2); 4.29 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3); 6.60 (d, *J* = 8.8 Hz, 1H, H-8); 6.74 (dd, *J* = 8.8, 2.8 Hz, 1H, H-7); 6.91 (d, *J* = 2.8 Hz, 1H, H-5). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 14.3 (OCH_2CH_3); 29.0 (CH_3); 34.5 (C-4); 35.6 (C-3); 50.1 (C-2); 56.0 (OCH_3); 62.1 (OCH_2CH_3); 112.4 (C-7*); 116.3 (C-5*); 116.9 (C-8*); 120.3 (CN); 123.9 (C-4a); 135.2 (C-8a); 152.6 (C-6); 171.8 (C=O). **IR** (NaCl) *v*: 3341.3 (N-H), 2922.7 (C-H), 2231.5 (CN), 1738.9 (C=O) cm^{-1}. **Elemental analysis (%)**: Calcd. for $C_{15}H_{18}N_2O_3$ (M = 274.32): C, 65.68; H, 6.61; N, 10.21. Found: C, 65.36; H, 6.43; N, 10.02.

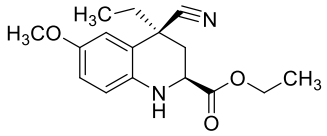
(±)-(2'*S,4'*S**)-Ethyl 4-cyano-4,6,8-trimethyl-1,2,3,4-tetrahydroquinoline-2-carboxylate (6h)**



6h

Reaction time: 2 h. Yellow oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.34 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); 1.72 (s, 3H, CH_3); 2.15 (s, 3H, $ArCH_3$); 2.24 (s, 3H, $ArCH_3$); 2.31 (t, *J* = 10.0 Hz, 1H, H-3ax); 2.50 (dd, *J* = 13.3, 3.6 Hz, 1H, H-3eq); 4.08 (ddd, *J* = 11.5, 3.7, 1.6 Hz, 1H, H-2); 4.33 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3 and NH); 6.86 (s, 1H, H-7); 7.08 (s, 1H, H-5). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 14.3 (OCH_2CH_3); 17.3 (CH_3); 20.5 (CH_3); 29.0 (CH_3); 34.7 (C-4); 35.4 (C-3); 50.0 (C-2); 62.2 (OCH_2CH_3); 119.0 (CN); 122.7 (C-4a); 124.2 (C-8); 125.7 (C-5); 127.2 (C-6); 131.3 (C-7); 136.9 (C-8a); 172.0 (C=O). **IR** (NaCl) *v*: 3348.9 (N-H), 2921.4 (C-H), 2241.9 (CN), 1733.2 (C=O) cm^{-1}. **Elemental analysis (%)**: Calcd. for $C_{16}H_{20}N_2O_2$ (M = 272.34): C, 70.56; H, 7.40; N, 10.29. Found: C, 70.43; H, 7.18; N, 10.12.

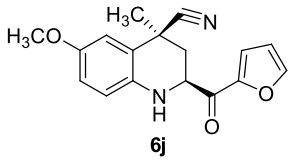
(±)-(2'*S,4'*S**)-Ethyl 4-cyano-4-ethyl-6-methoxy-1,2,3,4-tetrahydroquinoline-2-carboxylate (6i).**



6i

Reaction time: 1 h. Orange oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.17 (t, *J* = 7.4 Hz, 3H, CH_2CH_3); 1.32 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); 1.93 (m, 2H, CH_2CH_3); 2.19 (t, *J* = 12.5 Hz, 1H, H-3ax); 2.60 (dd, *J* = 13.2, 3.9 Hz, 1H, H-3eq); 3.76 (s, 3H, OCH_3); 4.01 (dd, *J* = 11.8, 3.9 Hz, 1H, H-2); 4.27 (qd, *J* = 7.1, 1.3 Hz, 2H, OCH_2CH_3); 6.59 (d, *J* = 8.7 Hz, 1H, H-8); 6.75 (dd, *J* = 8.8, 2.8 Hz, 1H, H-7); 6.89 (d, *J* = 2.8 Hz, 1H, H-5). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 9.3 (CH_2CH_3); 14.3 (OCH_2CH_3); 32.3 (CH_2CH_3); 32.9 (C-3); 40.2 (C-4); 49.9 (C-2); 56.0 (OCH_3); 62.1 (OCH_2CH_3); 112.9 (C-7*); 116.2 (C-5*); 116.6 (C-8); 119.5 (CN); 122.6 (C-4a); 135.2 (C-8a); 152.3 (C-6); 172.1 (C=O). **IR** (NaCl) *v*: 3350 (N-H), 2910 (C-H), 1739 (C=O) cm^{-1}. **Elemental analysis (%)**: Calcd. for $C_{16}H_{20}N_2O_3$ (M = 288.34): 66.65; H, 6.99; N, 9.72. Found: C, 66.42; H, 6.78; N, 9.59.

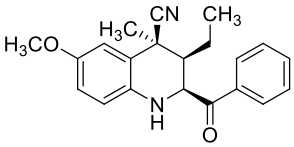
(±)-(2'S*,4'S*)-2-(2-Furylcarbonyl)-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (6j)



6j

Reaction time: 0.4 h. Yellow solid, mp: 101-102 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.87 (s, 3H, CH_3); 2.15 (t, *J* = 12.5, 1H, H-3ax); 2.71 (dd, *J* = 12.7, 3.2 Hz, 1H, H-3eq); 3.81 (s, 3H, OCH_3); 4.57 (bs, 1H, NH); 4.76 (dd, *J* = 12.3, 3.0 Hz, 1H, H-2); 6.66 (dd, *J* = 3.6, 1.7 Hz, 1H, H-4´); 6.72 (d, *J* = 8.7 Hz, 1H, H-8); 6.81 (dd, *J* = 8.8, 2.7 Hz, 1H, H-7); 6.99 (d, *J* = 2.7 Hz, 1H, H-5); 7.41 (dd, *J* = 3.6, 0.6 Hz, 1H, H-3´); 7.69 (dd, *J* = 1.7, 0.6 Hz, 1H, H-5´). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 28.4 (CH_3); 35.3 (C-4); 35.7 (C-3); 53.3 (C-2); 55.8 (OCH_3); 111.9 (C-4´); 112.8 (C-7); 116.2 (C-5); 117.5 (C-8); 118.9 (C-3´); 120.4 (CN); 123.7 (C-4a); 134.9 (C-8a); 146.8 (C-5´); 150.8 (C-2´); 152.5 (C-6); 186.5 (CO). **IR** (NaCl) *v*: 3370.3 (N-H), 2932.8 (C-H), 2232.4 (C≡N), 1676.1 (C=O) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{17}H_{16}N_2O_3$ (M = 296.32): C, 68.91; H, 5.44; N, 9.45. Found: C, 68.65; H, 5.45; N, 9.39.

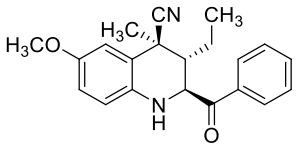
(±)-(2'S*,3'R*,4'S*)-2-Benzoyl-3-ethyl-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (6ma)



6ma

Reaction time: 4 h. Yellow oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 0.64 (t, *J* = 7.6 Hz, 3H, CH_2CH_3); 0.81-0.89 (m, 2H, CH_2CH_3); 1.92 (s, 3H, CH_3); 2.24-2.29 (m, 1H, H-3); 3.78 (s, 3H, OCH_3); 4.84 (bs, 1H, NH); 5.07-5.10 (m, 1H, H-2); 6.70 (d, *J* = 8.8 Hz, 1H, H-8); 6.79 (dd, J = 8.8, 2.7 Hz, 1H, H-7); 7.00 (d, *J* = 2.7 Hz, 1H, H-5); 7.51-7-57 (m, 2H, H-3' and H-5'); 7.63-7.66 (m, 1H, H-4'); 7.89-7.90 (m, 2H, H-2' and H-6') **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 14.1 (CH_2CH_3); 20.9 (CH_2CH_3); 30.7 (CH_3); 42.8 (C-4); 44.4 (C-3); 55.8 (C-2); 56.0 (OCH_3); 112.8 (C-7*); 116.2 (C-5*); 116.9 (C-8*); 119.2 (CN); 123.4 (C-4a); 128.1 (C-3' and C-5'); 129.3 (C-2' and C-6'); 134.1 (C-4'); 135.0 (C-1'); 152.4 (C-8a); 198.4 (C=O). **Elemental analysis (%)**: Calcd. for $C_{21}H_{22}N_2O_2$ (M = 334.41): C, 75.42; H, 6.63; N, 8.38. Found: C, 75.03; H, 6.38; N, 8.02

(±)-(2'S*,3'S*,4'S*)-2-Benzoyl-3-ethyl-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (6mb)

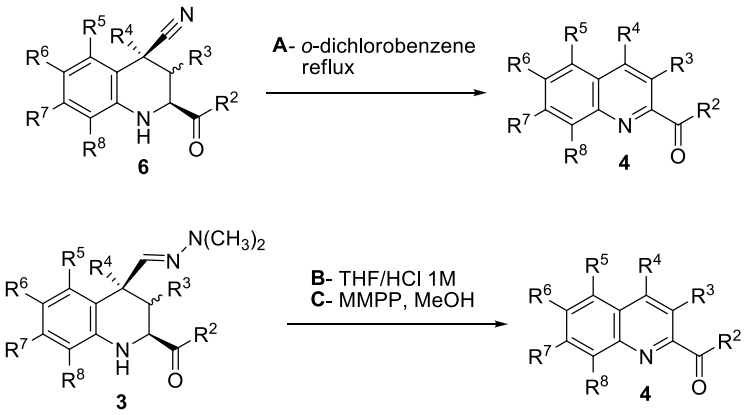


6mb

Reaction time: 4 h. Yellow oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 0.91 (t, *J* = 7.6 Hz, 3H, CH_2CH_3); 1.07-1.14 (m, 2H, CH_2CH_3); 1.66 (s, 3H, CH_3); 2.56 (td, *J* = 8.6, 3.9 Hz, 1H, H-3); 3.78 (s, 3H, OCH_3); 4.64 (d, *J* = 9.0 Hz, 1H, H-2); 6.54 (d, *J* = 8.7 Hz, 1H, H-8); 6.74 (dd, *J* = 8.7, 2.8 Hz, 1H, H-7); 7.01 (d, *J* = 2.8 Hz, 1H, H-5); 7.52 (t, *J* = 7.4 Hz, 2H, H-3' and H-5'); 7.64 (t, *J* = 7.3 Hz, 1H, H-4'); 8.02-8.05 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 13.4 (CH_2CH_3); 22.5 (CH_3); 22.9 (CH_2CH_3); 40.0 (C-4); 43.6 (C-3); 56.0 (OCH_3); 58.3 (C-2); 112.0 (C-7*); 115.9 (C-5*); 117.0 (C-8*); 123.0 (CN); 123.4 (C-4a); 129.1 (C-3' and C-5'); 129.2 (C-2' and C-6'); 134.0 (C-4'); 134.6 (C-1'*); 135.6 (C-8a*); 153.1 (C-6); 198.5 (C=O). **Elemental analysis (%)**: Calcd. for $C_{21}H_{22}N_2O_2$ (M = 334.41): C, 75.42; H, 6.63; N, 8.38. Found: C, 75.11; H, 6.41; N, 8.11.

5. Synthesis of 2-acylquinolines

5.1 Synthesis of 2-acylquinolines 4a-j and 4m



Cmpd.	R^2	R^3	R^4	R^5	R^6	R^7	R^8
4a	C_6H_5	H	CH_3	H	6-OCH_3	H	H
4b	4-FC_6H_4	H	CH_3	H	6-OCH_3	H	H
4c	4-$OCH_3C_6H_4$	H	CH_3	H	6-OCH_3	H	H
4d	C_6H_5	H	CH_2CH_3	H	6-OCH_3	H	H
4e	C_6H_5	H	CH_3	H	CH_3	H	CH_3
4f	4-FC_6H_4	H	CH_3	CH_3	H	CH_3	H
4g	OEt	H	CH_3	H	6-OCH_3	H	H
4h	OEt	H	CH_3	H	CH_3	H	CH_3
4i	OEt	H	CH_2CH_3	H	6-OCH_3	H	H
4j	2-furyl	H	CH_3	H	6-OCH_3	H	H
4m	C_6H_5	CH_2CH_3	CH_3	H	6-OCH_3	H	H

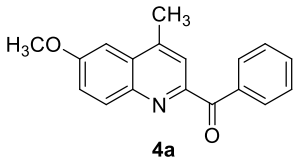
A. Synthesis of 2-acylquinolines 4 from nitriles 6. A solution of the suitable compound **6** (0.4 mmol) in *o*-dichlorobenzene (5 mL) was refluxed for 24 h. The reaction mixture was allowed to reach room temperature and then it was concentrated under reduced pressure. The oily residue was purified by flash column chromatography, eluting with mixtures of petroleum ether and ethyl acetate, to give compounds **4**.

B. Direct synthesis of 2-acylquinolines 4 from Povarov products 3 in acidic conditions. To a solution of the suitable starting hydrazone **3** (1 mmol) in THF (5 mL) was added dropwise 1M HCl (5 mL) with stirring, and the resulting solution was vigorously stirred at room temperature for the times specified in Table 2. Then, the reaction mixture was quenched with 3M aqueous NH_4OH, and the basic solution was extracted with ethyl acetate (10 mL). The aqueous layer was then extracted with CH_2Cl_2 (2 x 10 mL), and the combined organic layers were washed with water (1 x 20 mL) and brine (1 x 20 mL), and dried over anhydrous Na_2SO_4. Removal of the solvent and flash column chromatography on silica gel eluting with a mixture of petroleum ether:ethyl acetate (9:1, v/v) gave quinolines **4a**-**d** and **4g**.

C. Direct synthesis of 2-acylquinolines 4 from Povarov products 3 in oxidative conditions. To a solution of the suitable compound **3** (0.5 mmol) in methanol (5 mL) was added magnesium monoperoxyphthalate hexahydrate, MMPP (247 mg, 0.5 mmol). The solution was refluxed for 1 h, an additional amount of MMPP (247 mg, 0.5 mmol) was added and the reflux

was maintained until completion of the reaction, as judged by TLC. Water (10 mL) was added to the cooled reaction mixture, and the resulting suspension was extracted with CH_2Cl_2 (3 x 15 mL). The combined extracts were dried over anhydrous Na_2SO_4 and evaporated. The residue was purified with flash column chromatography on silica gel eluting with a mixture of petroleum ether:ethyl acetate (9:1, v/v).

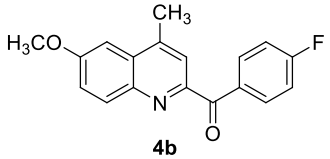
2-Benzoyl-6-methoxy-4-methylquinoline (4a)



4a

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Yellow solid, mp: 117-119 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.75 (s, 3H, CH_3); 4.00 (s, 3H, OCH_3); 7.24 (d, *J* = 2.7 Hz, 1H, H-5); 7.42 (dd, *J* = 9.2, 2.4 Hz, 1H, H-7); 7.50 (t, *J* = 7.4 Hz, 2H, H-3' and H-5'); 7.61 (t, *J* = 7.3 Hz, 1H, H-4'); 7.96 (s, 1H, H-3); 8.11 (d, *J* = 9.2 Hz, 1H, H-8); 8.22 (d, *J* = 7.3 Hz, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 19.3 (CH_3); 55.8 (OCH_3); 101.8 (C-5); 121.9 (C-3); 122.5 (C-7); 128.2 (C-3' and C-5'); 130.4 (C-4a); 131.6 (C-2' and C-6'); 132.8 (C-8); 133.0 (C-4'); 136.6 (C-1'); 142.5 (C-4); 144.0 (C-8a); 152.0 (C-2); 159.4 (C-6); 194.1 (C=O). **IR** (NaCl) *v*: 2924.3 (C-H), 1657.9 (C=O), 1619.8 cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{18}H_{15}NO_2$ (M = 277.32): C, 77.96; H, 5.45; N, 5.05. Found: C, 77.69; H, 5.41; N, 4.95.

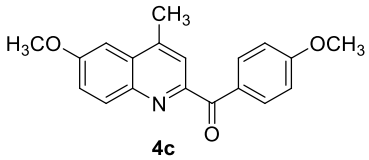
4-Fluorobenzoyl-6-methoxy-4-methylquinoline (4b)



4b

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Pale yellow solid, mp: 143-144 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.75 (s, 3H, CH_3); 4.00 (s, 3H, OCH_3); 7.14-7.21 (m, 2H, H-3' and H-5'); 7.24 (d, *J* = 2.7 Hz, 1H, H-5); 7.42 (dd, *J* = 9.2, 2.7 Hz, 1H, H-7); 7.97 (s, 1H, H-3); 8.08 (d, *J* = 9.2 Hz, 1H, H-8); 8.29-8.35 (m, 2H, H2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 19.3 (CH_3); 55.8 (OCH_3); 101.8 (C-5); 115.3 (d, *J* = 21.7 Hz, C-3' and C-5'); 121.9 (C-3*); 122.6 (C-7*); 130.5 (C-4a); 132.8 (C-8); 132.9 (d, *J* = 2.9 Hz, C-1'); 134.3 (d, *J* = 9.2 Hz, C-2' and C-6'); 142.5 (C-4*); 144.1 (C-8a*); 151.9 (C-2); 159.5 (C-6); 165.8 (d, *J* = 254.8 Hz, C-4'); 192.4 (C=O). **IR** (NaCl) *v*: 2921.4 (C-H), 1657.1 (C=O), 1620.8 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{18}H_{14}FNO_2$ (M = 295.31): C, 73.21; H, 4.78; N, 4.74. Found: C, 73.13; H, 5.00; N, 4.49.

6-Methoxy-4-methoxybenzoyl-4-methylquinoline (4c)

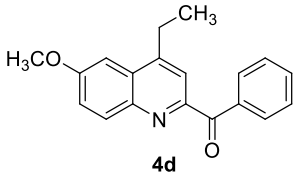


4c

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). White solid, mp: 142-144 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.75 (s, 3H, CH_3); 3.90 (s, 3H, OCH_3); 4.00 (s, 3H, OCH_3); 6.99 (d, *J* = 8.7 Hz, 2H, H-3' and H-5'); 7.24 (d, *J* = 2.2 Hz, 1H, H-5); 7.42 (dd, *J* = 9.2, 2.2 Hz, 1H, H-7); 7.91 (s, 1H, H-3); 8.11 (d, *J* = 9.2 Hz, 1H, H-8); 8.28 (d, *J* = 8.7 Hz, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 19.3 (CH_3); 55.6 (OCH_3); 55.8 (OCH_3); 101.8 (C-5); 113.6 (C-3' and C-5'); 122.0 (C-3*); 122.4 (C-7*); 129.4 (C-4a*); 130.3 (C-1'*); 132.7 (C-8); 134.0 (C-2' and C-6'); 142.5 (C-4*); 143.9 (C-8a*); 152.8 (C-2);

159.2 (C-6); 163.7 (C-4'); 192.6 (C=O). **IR** (NaCl) *v*: 2922.1 (C-H), 1646.5 (C=O), 1620.4 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{19}H_{17}NO_3$ (M = 307.34): C, 74.25; H, 5.58; N, 4.56. Found: C, 74.08; H, 5.84; N, 4.31.

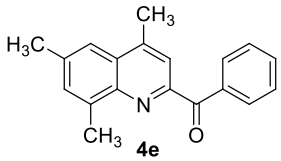
2-Benzoyl-4-ethyl-6-methoxyquinoline (4d)



4d

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Yellow solid, mp: 116-118 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.47 (t, *J* = 7.5 Hz, 3H, CH_2CH_3); 3.15 (q, *J* = 7.6 Hz, 2H, CH_2CH_3); 3.99 (s, 3H, OCH_3); 7.30 (d, *J* = 2.7 Hz, 1H, H-5); 7.41 (dd, *J* = 9.2, 2.8 Hz, 1H, H-7); 7.44-7.53 (m, 2H, H-3' and H-5'); 7.61 (m, 1H, H-4'); 7.98 (s, 1H, H-3); 8.11 (d, *J* = 9.2 Hz, 1H, H-8); 8.20-8.24 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 13.6 (CH_3); 25.5 (CH_2); 55.8 (OCH_3); 101.5 (C-5); 119.8 (C-3*); 122.2 (C-7*); 128.2 (C-3' and C-5'); 129.6 (C-4a); 131.6 (C-2' and C-6'); 132.9 (C-8); 133.0 (C-4'); 136.7 (C-1'); 142.9 (C-8a); 149.3 (C-4); 152.3 (C-2); 159.4 (C-6); 194.3 (C=O). **IR** (NaCl) *v*: 2868.5 (C-H), 1647.8 (C=O), 1619.7 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{19}H_{17}NO_2$ (M = 291.34): C, 78.33; H, 5.88; N, 4.81. Found: C, 78.01; H, 6.04; N, 4.59.

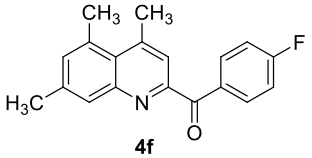
2-Benzoyl-4,6,8-trimethylquinoline (4e)



4e

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Orange solid, mp: 119-120 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.55 (s, 3H, CH_3); 2.73 (s, 3H, CH_3); 2.75 (s, 3H, CH_3); 7.47-7.53 (m, 3H, H-5, H-3' and H-5'); 7.62 (m, 1H, H-4'); 7.66 (s, 1H, H-7); 8.00 (s, 1H, H-3); 8.33-8.37 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 18.4 (CH_3); 19.4 (CH_3); 22.3 (CH_3); 120.7 (C-3*); 121.2 (C-5*); 127.9 (C-3' and C-5'); 129.2 (C-4a); 131.9 (C-2' and C-6'); 132.2 (C-4'*); 132.7 (C-7*); 136.9 (C-1'*); 138.3 (C-6*); 139.1 (C-8*); 144.4 (C-4); 144.8 (C-8a); 151.9 (C-2); 194.0 (C=O). **IR** (NaCl) *v*: 2920.5 (C-H), 1657.5 (C=O), 1619.8 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{19}H_{17}NO$ (M = 275.34): C, 82.88; H, 6.22; N, 5.09. Found: C, 82.56; H, 6.28; N, 5.00.

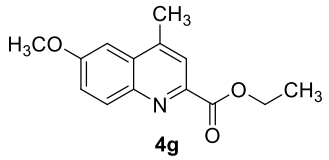
4-Fluorobenzoyl-4,5,7-trimethylquinoline (4f)



4f

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Orange solid, mp: 128-131 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.49 (s, 3H, CH_3); 2.92 (s, 3H, CH_3); 2.99 (s, 3H, CH_3); 7.17 (t, *J* = 8.7 Hz, 2H, H-3' and H-5'); 7.26 (s, 1H, H-3); 7.79 (s, 1H, H-8); 7.82 (s, 1H, H-6); 8.29-8.35 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 21.3 (CH_3); 25.5 (2 x CH_3); 115.3 (d, *J* = 21.7 Hz, C-3' and C-5'); 122.8 (C-3); 127.5 (C-4a); 129.1 (C-8); 132.7 (d, *J* = 3.1 Hz, C-1'); 133.9 (C-6); 134.3 (d, *J* = 9.2 Hz, C-2' and C-6'); 135.3 (C-5*); 139.3 (C-7*); 146.9 (C-4); 149.0 (C-8a); 153.4 (C-2); 165.9 (d, *J* = 255.2 Hz, C-4'); 192.4 (C=O). **IR** (NaCl) *v*: 2925.0 (C-H), 1660.4 (C=O), 1623.8 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{19}H_{16}FNO$ (M = 293.33): C, 77.80; H, 5.50; N, 4.77. Found: C, 77.96; H, 5.33; N, 4.59.

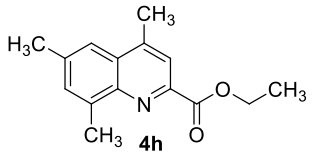
Ethyl 6-methoxy-4-methylquinoline-2-carboxylate (4g)



4g

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Yellow solid, mp: 131-133 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.48 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); 2.72 (s, 3H, CH_3); 3.98 (s, 3H, OCH_3); 4.53 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3); 7.19 (d, *J* = 2.7 Hz, 1H, H-5); 7.42 (dd, *J* = 9.3, 2.8 Hz, 1H, H-7); 8.02 (s, 1H, H-3); 8.21 (d, *J* = 9.3 Hz, 1H, H-8). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 14.5 (OCH_2CH_3); 19.2 (CH_3); 55.8 (OCH_3); 62.2 (OCH_2CH_3); 101.6 (C-5); 122.2 (C-3*); 122.7 (C-7*); 130.8 (C-4a); 133.1 (C-8); 143.5 (C-8a*); 144.0 (C-4*); 145.5 (C-2); 159.4 (C-6); 166.0 (C=O). **IR** (NaCl) *v*: 2920.6 (C-H), 1731.8 (C=O), 1107.6 (C-O) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{14}H_{15}NO_3$ (M = 245.27): C, 68.56; H, 6.16; N, 5.71. Found: C, 68.24; H, 5.98; N, 5.62.

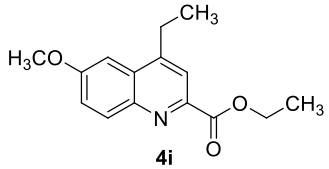
Ethyl 4,6,8-trimethylquinoline-2-carboxylate (4h)



4h

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Yellow solid, mp: 125-127 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.48 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); 2.53 (s, 3H, CH_3); 2.71 (s, 3H, CH_3); 2.85 (s, 3H, CH_3); 4.50 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3); 7.45 (s, 1H, H-5); 7.61 (s, 1H, H-7); 7.96 (s, 1H, H-3). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 14.5 (OCH_2CH_3); 18.2 (CH_3); 19.3 (CH_3); 22.2 (CH_3); 61.9 (OCH_2CH_3); 120.6 (C-3*); 121.6 (C-5*); 129.5 (C-4a); 132.4 (C-7); 138.2 (C-6*); 139.0 (C-8*); 144.8 (C-4); 145.3 (C-8a); 145.8 (C-2); 166.2 (C=O). **IR** (NaCl) *v*: 2929.7 (C-H), 1704.5 (C=O), 1118.0 (C-O) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{15}H_{17}NO_2$ (M = 243.30): C, 74.05; H, 7.04; N, 5.76. Found: C, 73.72; H 6.83; N, 6.06.

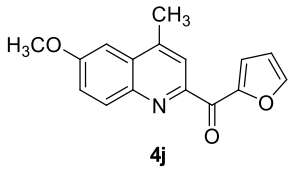
Ethyl 4-ethyl-6-methoxyquinoline-2-carboxylate (4i)



4i

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Orange oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.43 (t, *J* = 7.5 Hz, 3H, CH_2CH_3); 1.48 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); 3.12 (q, *J* = 7.6 Hz, 2H, CH_2CH_3); 3.98 (s, 3H, OCH_3); 4.54 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3); 7.25 (m, 1H, H-5); 7.41 (dd, *J* = 9.3, 2.8 Hz, 1H, H-7); 8.03 (s, 1H, H-3); 8.21 (d, *J* = 9.3 Hz, 1H, H-8). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 13.6 (OCH_2CH_3); 14.5 (CH_2CH_3); 25.4 (CH_2CH_3); 55.7 (OCH_3); 62.2 (OCH_2CH_3); 101.3 (C-5); 120.1 (C-3); 122.4 (C-7); 130.0 (C-4a); 133.2 (C-8); 143.8 (C-8a); 145.7 (C-4); 149.5 (C-2); 159.4 (C-6); 166.1 (C=O). **IR** (NaCl) *v*: 2927.4 (C-H), 1715.7 (C=O), 1111.1 (C-O) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{15}H_{17}NO_3$ (M = 259.30): C, 69.48; H, 6.61; N, 5.40. Found: C, 69.23; H, 6.42; N, 5.21.

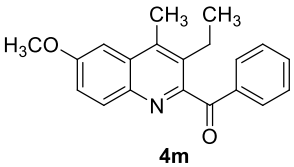
2-Furylcarbonyl-6-methoxy-4-methylquinoline (4j)



4j

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Yellow solid, mp: 150-152 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.75 (s, 3H, CH_3); 4.01 (s, 3H, OCH_3); 6.67 (dd, *J* = 3.5, 1.7 Hz, 1H, H-4´); 7.23 (d, *J* = 2.7 Hz, 1H, H-5); 7.45 (dd, *J* = 9.2, 2.7 Hz, 1H, H-7); 7.79 (dd, *J* = 1.6, 0.7 Hz, 1H, H-5´); 8.09 (s, 1H, H-3); 8.13 (d, *J* = 9.2 Hz, 1H, H-8); 8.29 (dd, *J* = 3.5, 0.7 Hz, 1H, H-3´). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 19.0 (CH_3); 55.6 (OCH_3); 101.6 (C-5); 112.4 (C-4´); 120.8 (C-3); 122.3 (C-7); 124.4 (C-3´); 130.6 (C-4a); 132.5 (C-8); 142.7 (C-4); 143.6 (C-8a); 147.5 (C-5´); 150.8 (C-2); 151.2 (C-2´); 159.3 (C-6); 179.6 (CO). **IR** (NaCl) *v*: 2939.4 (C-H), 1620.4 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. For $C_{16}H_{13}NO_3$ (M = 267.28): C, 71.90; H, 4.90; N, 5.24. Found: C, 71.76; H, 4.87; N, 5.14.

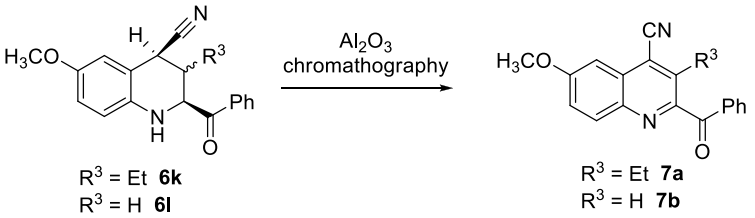
2-Benzoyl-3-ethyl-6-methoxy-4-methylquinoline (4m)



4m

Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). White solid, mp: 125-128 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.19 (t, *J* = 7.5 Hz, 3H, CH_2CH_3); 2.69 (s, 3H, CH_3); 2.82 (q, *J* = 7.5 Hz, 2H, CH_2CH_3); 3.99 (s, 3H, OCH_3); 7.25 (d, *J* = 2.6 Hz, 1H, H-5); 7.34 (dd, *J* = 9.2, 2.7 Hz, 1H, H-7); 7.44 (t, *J* = 7.5 Hz, 2H, H-3' and H-5'); 7.58 (m, 1H, H-4'); 7.90 (d, *J* = 7.0 Hz, 2H, H-2' and H-6'); 7.96 (d, *J* = 9.2 Hz, 1H, H-8). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 14.2 (CH_3); 15.3 (CH_3); 23.0 (CH_2); 55.7 (OCH_3); 101.9 (C-5); 121.3 (C-7); 128.6 (C-3' and C-5'); 129.6 (C-4a); 130.8 (C-2' and C-6'); 131.8 (C-8); 132.8 (C-3); 133.8 (C-4'); 136.5 (C-1'*); 141.1 (C-4* and C-8a*); 154.8 (C-2); 158.6 (C-6); 196.3 (CO). **IR** (NaCl) *v*: 2921.9 (C-H), 1674.0 (C=O); 1616.6 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{20}H_{19}NO_2$ (M = 305.37): C, 78.66; H, 6.27; N, 4.59. Found: C, 78.32; H, 6.01; N, 4.27.

5.2 Synthesis of 2-acylquinoline-4-carbonitriles 7a,b

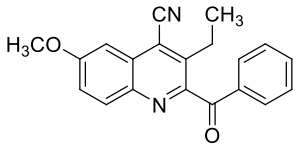


R^3 = Et **6k**
R^3 = H **6l**

R^3 = Et **7a**
R^3 = H **7b**

The crude nitriles **6k**,**l** obtained by the general method described above, were dissolved in CH_2Cl_2 (5 mL), to which alumina (100 mg) was added. The solvent was evaporated and the resulting solid was loaded onto a cartridge that was attached to the flash chromatography system. Chromatography on alumina furnished quinolines **7a** and **7b**, respectively.

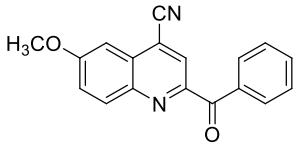
2-Benzoyl-3-ethyl-6-methoxyquinolin-4-carbonitrile (7a)



7a

Reaction time: 4h. Purification: flash chromatography on alumina with petroleum ether:ethyl acetate (9:1, v/v). White solid, mp: 138-141 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.34 (t, *J* = 7.5 Hz, 3H, CH_2CH_3); 3.10 (q, *J* = 7.5 Hz, 2H, CH_2CH_3); 4.03 (s, 3H, OCH_3); 7.37-7.53 (m, 4H, H-3', H-5', H-5 and H-7); 7.63 (m, 1H, H-4'); 7.91 (d, *J* = 7.1 Hz, 2H, H-2' and H-6'); 8.02 (d, *J* = Hz, 9.1, H-8). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 15.9 (CH_3); 25.2 (CH_2); 56.2 (OCH_3); 102.1 (C-5); 115.1 (C-4); 117.6 (CN); 124.2 (C-7); 128.5 (C-4a); 128.7 (C-3' and C-5'); 130.9 (C-2' and C-6'); 132.1 (C-8*); 134.2 (C-4'); 135.9 (C-3*); 140.8 (C-1'*); 141.3 (C-8a*); 153.2 (C-2); 161.1 (C-6); 193.8 (CO). **IR** (NaCl) *v*: 2927.5 (C-H), 2225.1 (CN), 1664.8 (C=O) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{20}H_{16}N_2O_2$ (M = 316.35): C, 75.93; H, 5.10; N, 8.86. Found: C, 75.65; H, 5.31; N, 8.52.

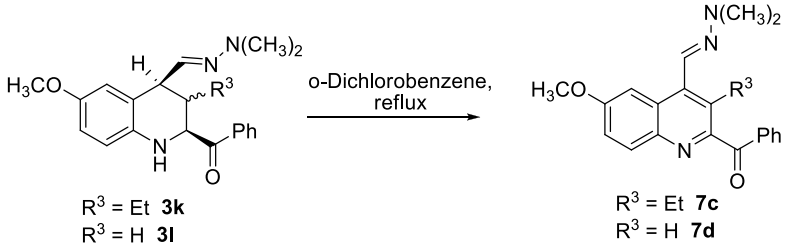
2-Benzoyl-6-methoxyquinolin-4-carbonitrile (7b)



7b

Reaction time: 2 h. Purification: flash chromatography on alumina with petroleum ether:ethyl acetate (9:1, v/v). Yellow solid, mp: 140-142 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 4.06 (s, 3H, OCH_3); 7.45 (d, *J* = 2.7 Hz, 1H, H-5); 7.50-7.57 (m, 3H, H-3', H-5' and H-7); 7.64 (m, 1H, H-4'); 8.17 (d, *J* = 9.3 Hz, 1H, H-8); 8.20-8.27 (m, 2H, H-2' and H-6'); 8.48 (s, 1H, H-3). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 56.3 (OCH_3); 102.3 (C-5); 115.8 (C-4); 118.0 (CN); 125.3 (C-7*); 125.6 (C-3*); 128.4 (C-3' and C-5'); 128.6 (C-4a); 131.5 (C-2' and C-6'); 133.2 (C-8*); 133.5 (C-4'*); 135.7 (C-1'); 142.9 (C-8a); 151.3 (C-2); 161.8 (C-6); 191.8 (CO). **IR** (NaCl) *v*: 2920.4 (C-H), 2229.9 (CN), 1664.4 (C=O) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{18}H_{12}N_2O_2$ (M = 288.30): C, 74.99; H, 4.20; N, 9.72. Found: C, 74.77; H, 4.32; N, 9.64.

5.3 Synthesis of 2-acyl-4-(dimethylhydrazonomethyl)quinolines 7c,d

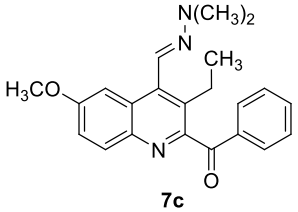


R^3 = Et **3k**
R^3 = H **3l**

R^3 = Et **7c**
R^3 = H **7d**

A solution of the suitable hydrazones **3k** or **3l** in *o*-dichlorobenzene (5 mL) was refluxed until no starting material was detected by TLC. The reaction mixture was allowed to reach room temperature and the solvent was evaporated under reduced pressure. The oily residue was purified by flash column chromatography, eluting with a 9:1 (v/v) mixture of petroleum ether and ethyl acetate, to give compounds **7c**,**d**.

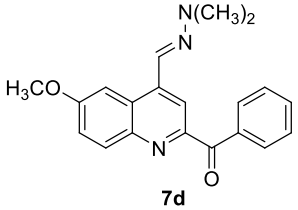
2-Benzoyl-4-[(2,2-dimethylhydrazono)methyl]-3-ethyl-6-methoxyquinoline (7c)



7c

Reaction time: 6 h. Yellow solid, mp: 109-111 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.23 (t, *J* = 7.5 Hz, 3H, CH_2CH_3); 2.87 (q, *J* = 7.5 Hz, 2H, CH_2CH_3); 3.17 (s, 6H, $N(CH_3)_2$); 3.95 (s, 3H, OCH_3); 7.32 (dd, *J* = 9.2, 2.8 Hz, 1H, H-7); 7.43 (d, *J* = 7.3 Hz, 2H, H-3' and H-5'); 7.56 (m, 1H, H-4'); 7.64 (s, 1H, CH=N); 7.88-7.95 (m, 3H, H-2', H-6' and H-8); 8.28 (d, *J* = 2.8 Hz, 1H, H-5). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 15.5 (CH_3); 22.7 (CH_2); 42.7 ($N(CH_3)_2$); 55.5 (OCH_3); 104.5 (C-5); 121.5 (C-7); 127.1 (C-4a); 127.4 (CH=N); 128.6 (C-3' and C-5'); 130.8 (C-2' and C-5'); 131.4 (C-8); 131.9 (C-3*); 133.8 (C-4'); 136.5 (C-4*); 137.4 (C-1'*); 142.4 (C-8a); 154.9 (C-2); 158.9 (C-6); 196.2 (CO). **IR** (NaCl) *v*: 2920.9 (C-H), 1669.6 (C=O); 1616.3 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{22}H_{23}N_3O_2$ (M = 361.44): C, 73.11; H, 6.41; N, 11.63. Found: C, 73.27; H, 6.61; N, 11.34.

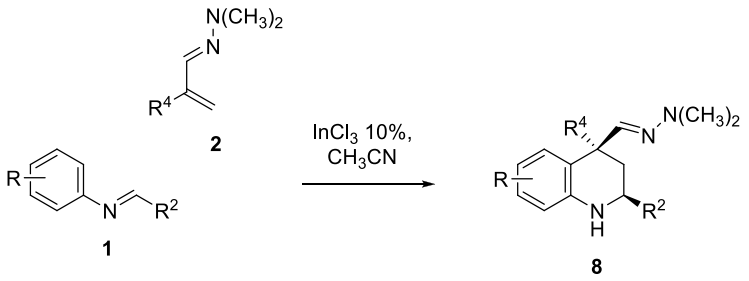
2-Benzoyl-4-((2,2-dimethylhydrazono)methyl)-6-methoxyquinoline (7d)



7d

Reaction time: 3 h. Yellow oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 3.19 (s, 6H, $N(CH_3)_2$); 3.99 (s, 3H, OCH_3); 7.40 (dd, *J* = 9.3, 2.8 Hz, 1H, H-7); 7.50 (t, *J* = 7.3 Hz, 2H, H-3' and H-5'); 7.58-7.61 (m, 2H, H-4' and CH=N); 8.08 (d, *J* = 9.2 Hz, 1H, H-8); 8.20-8.24 (m, 3H, H-2', H-6' and H-3); 8.27 (d, *J* = 2.8 Hz, 1H, H-5). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 42.7 ($N(CH_3)_2$); 55.6 (OCH_3); 103.5 (C-5); 118.8 (C-3); 122.1 (C-7); 127.0 (C-4a); 127.5 (CH=N); 128.2 (C-3' and C-5'); 131.6 (C-2' and C-6'); 132.6 (C-8); 132.9 (C-4'); 136.7 (C-4*); 139.9 (C-1'*); 144.0 (C-8a); 152.3 (C-2); 159.6 (C-6); 194.4 (CO). **IR** (NaCl) *v*: 2922.8 (C-H), 1653.9 (C=O); 1616.3 (C=N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{20}H_{19}N_3O_2$ (M = 333.38): C, 72.05; H, 5.74; N, 12.60. Found: C, 72.10; H, 5.86; N, 12.83.

6. Synthesis of 2-aryl-1,2,3,4-tetrahydroquinoline derivatives 8

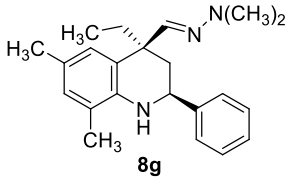


Cmpd.	R	R^2	R^4	Yield (%)
8a[a]	6-OCH_3	C_6H_5	CH_3	90
8b[a]	6-OCH_3	4-ClC_6H_4	CH_3	87
8c[a]	6-OCH_3	4-$OCH_3C_6H_4$	CH_3	80
8d[a]	6-OCH_3	4-$CH_3C_6H_4$	CH_3	93
8e[a]	6,8-$(CH_3)_2$	C_6H_5	CH_3	80
8f[a]	6-CH_3	4-$OCH_3C_6H_4$	CH_3	72
8g	6,8-$(CH_3)_2$	C_6H_5	CH_2CH_3	61
8h[a]	5,7-$(OCH_3)_2$	4-$CH_3C_6H_4$	CH_3	72

a: Povarov products known in literature.[7,8]

The reaction conditions were the same described in section 3.1. above

(±)-(2*S,4*S**)-4-[(2,2-Dimethylhydrazono)methyl]-4-ethyl-6,8-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline (8g)**

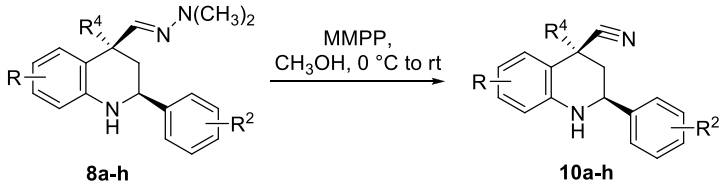


8g

Reaction time: 3 h. Purification: flash chromatography with petroleum ether:ethyl acetate (9:1, v/v). Yellow solid, mp: 121-123 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 0.97 (t, *J* = 7.3 Hz, 3H, CH_2CH_3); 1.99-2.11 (m, 7H, CH_3, H-3eq, H-3ax and CH_2); 2.23 (s, 3H, CH_3); 2.75 (s, 6H, $N(CH_3)_2$); 3.84 (bs, 1H, NH); 4.57 (dd, *J* = 11.1, 2.7 Hz, 1H, H-2); 6.63 (s, 1H, H-7); 6.80 (s, 2H, H-5 and CH=N); 7.32-7.51 (m, 5H, H-2', H-3', H-4', H-5' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 8.8 (CH_2CH_3); 17.7 ($ArCH_3$); 20.7 ($ArCH_3$); 32.2 (CH_2CH_3); 40.2 (C-3); 43.6 ($N(CH_3)_2$); 43.7 (C-4); 53.0 (C-2); 121.4 (C-4a); 125.4 (C-8); 125.8 (C-6); 126.8 (C-2' and C-6'); 127.0 (C-5); 127.7 (C-4'); 128.8 (C-3' and C-5'); 129.5 (C-7); 139.7 (C-8a); 143.6 (CH=N); 145.2 (C-1'). **IR** (NaCl) *v*: 3401.2 (N-H), 2958.6 (C-H), 1604.1 (C=C), 1251.2 (C-N) cm^{-1}. **Elemental analysis (%):** Calc. for $C_{22}H_{29}N_3$ (M = 335.49): C, 78.76; H, 8.71; N, 12.53. Found: C, 78.35; H, 8.68; N, 12.56.

[8] V. Sridharan, P. T. Perumal, C. Avendaño and J. C. Menéndez, *Org. Biomol. Chem*., 2007, **5**, 1351.

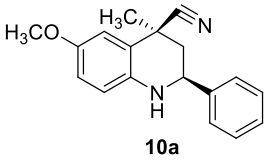
7. Isolation of 2-aryl-1,2,3,4-tetrahydroquinoline-4-carbonitrile derivatives 10a-h



For the synthesis of nitriles **10a-h** the synthetic conditions described in the Section 4 were applied**.**

Cmpd.	R	R^2	R^3	R^4	Yield (%)
10a	6-OCH_3	H	CH_3	H	70
10b	6-OCH_3	4-Cl	CH_3	H	97
10c	6-OCH_3	4-OCH_3	CH_3	H	93
10d	6-OCH_3	4-CH_3	CH_3	H	86
10e	6,8-CH_3	H	CH_3	H	84
10f	6-CH_3	4-OCH_3	CH_3	H	98
10g	6,8-CH_3	H	CH_2CH_3	H	77
10h	5,7-OCH_3	4-CH_3	CH_3	H	62

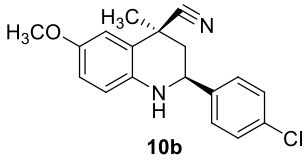
(±)-(2*S,4*S**)-6-Methoxy-4-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (10a)**



10a

Reaction time: 0.4 h. Yellow solid, mp: 115-117 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.82 (s, 3H, CH_3); 2.22 (dd, *J* = 13.1, 2.8 Hz, 1H, H-3eq); 2.45 (t, *J* = 12.9 Hz, 1H, H-3ax); 3.79 (s, 3H, OCH_3); 3.95 (bs, 1H, NH); 4.40 (dd, *J* = 11.8, 2.8 Hz, 1H, H-2); 6.54 (d, *J* = 8.7 Hz, 1H, H-8); 6.75 (dd, *J* = 8.8, 2.8 Hz, 1H, H-7); 6.97 (d, *J* = 2.8 Hz, 1H, H-5); 7.34-7.44 (m, 5H, H-2', H-3', H-4', H-5' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 30.7 (CH_3); 35.4 (C-4); 42.1 (C-3); 52.2 (C-2); 56.0 (OCH_3); 112.9 (C-7); 116.2 (C-5*); 116.4 (C-8*); 120.6 (CN); 124.6 (C-4a); 126.9 (C-2' and C-6'); 128.4 (C-4'); 129.0 (C-3' and C-5'); 137.2 (C-8a); 142.2 (C-1'); 152.5 (C-6). **IR** (Nujol) *v*: 3380 (N-H), 2665 (C-H), 1715 (CN) cm^{-1}.

(±)-(2S*,4S*)-2-(4-Chlorophenyl)-6-methoxy-4-methyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (10b)

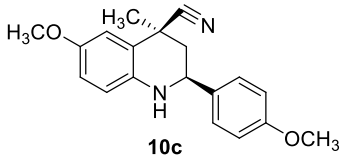


10b

Reaction time: 1 h. Yellow solid, mp: 158-159 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.81 (s, 3H, CH_3); 2.18 (dd, *J* = 13.2, 2.8 Hz, 1H, H-3eq); 2.39 (t, *J* = 12.4 Hz, 1H, H-3ax); 3.78 (s, 3H, OCH_3); 4.38 (dd, *J* = 11.7, 2.8 Hz, 1H, H-2); 6.56 (d, *J* = 8.8 Hz, 1H, H-8); 6.75 (dd, *J* = 8.8, 2.8 Hz, 1H, H-7); 6.96 (d, *J* = 2.8 Hz, 1H, H-5); 7.36 (s, 4H, H-2', H-3', H-5' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 30.7 (CH_3); 35.4 (C-4); 42.1 (C-3); 51.6 (C-2); 56.0 (OCH_3); 112.9 (C-7); 116.2 (C-5*); 116.5 (C-8*); 120.6 (CN); 124.4

(C-4a); 128.3 (C-2' and C-6'); 129.1 (C-3' and C-5'); 134.0 (C-4'); 136.9 (C-8a); 140.8 (C-1'); 152.6 (C-6). **IR** (Nujol) *v*: 3260 (N-H), 2660 (C-H), 2000 (CN) cm^{-1}.

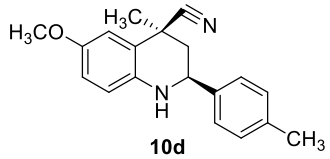
(±)-(2S*,4S*)-6-Methoxy-2-(4-methoxyphenyl)-4-methyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (10c)



10c

Reaction time: 1 h. Yellow solid, mp: 144-145 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.81 (s, 3H, CH_3); 2.18 (dd, *J* = 13.1, 2.8 Hz, 1H, H-3eq); 2.43 (t, *J* = 12.8 Hz, 1H, H-3ax); 3.79 (s, 3H, OCH_3); 3.82 (s, 3H, OCH_3); 3.90 (bs, 1H, NH); 4.34 (dd, *J* = 11.8, 2.7 Hz, 1H, H-2); 6.52 (d, *J* = 8.7 Hz, 1H, H-8); 6.74 (dd, *J* = 8.8, 2.8 Hz, 1H, H-7); 6.93 (m, 2H, H-2' and H-6'); 6.96 (d, *J* = 2.8 Hz, 1H, H-5); 7.34 (m, 2H, H-3' and H-5'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 30.7 (CH_3); 35.5 (C-4); 42.1 (C-3); 51.6 (C-2); 55.5 (OCH_3); 56.1 (OCH_3); 112.9 (C-7); 114.3 (C-2' and C-6'); 116.2 (C-5*); 116.3 (C-8*); 120.6 (CN); 124.7 (C-4a); 128.0 (C-3' and C-5'); 134.3 (C-4'); 137.3 (C-8a); 152.4 (C-1'); 159.6 (C-6). **IR** (NaCl) *v*: 3368.2 (N-H), 2927.4 (C-H), 2232.5 (CN) cm^{-1}.

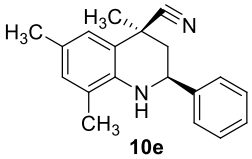
(±)-(2S*,4S*)-6-Methoxy-2-(4-methylphenyl)-4-methyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (10d)



10d

Reaction time: 1 h. Yellow solid, mp: 147-149 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.82 (s, 3H, CH_3); 2.19 (dd, *J* = 13.1, 2.8 Hz, 1H, H-3eq); 2.38 (s, 3H, CH_3); 2.44 (t, *J* = 12.9 Hz, 1H, H-3ax); 3.79 (s, 3H, OCH_3); 3.94 (bs, 1H, NH); 4.37 (dd, *J* = 11.8, 2.7 Hz, 1H, H-2); 6.53 (d, *J* = 8.7 Hz, 1H, H-8); 6.75 (dd, *J* = 8.7, 2.8 Hz, 1H, H-7); 6.98 (d, *J* = 2.8 Hz, 1H, H-5); 7.20 (d, *J* = 8.1 Hz, 2H, H2' and H-6'); 7.31 (d, *J* = 8.1 Hz, 2H, H-3' and H-5'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 21.2 (CH_3); 30.6 ($ArCH_3$); 35.4 (C-4); 42.0 (C-3); 51.8 (C-2); 56.0 (OCH_3); 112.9 (C-7); 116.1 (C-5*); 116.3 (C-8*); 120.5 (CN); 124.6 (C-4a); 126.7 (C-2' and C-6'); 129.6 (C-3' and C-5'); 137.2 (C-4'); 138.1 (C-8a); 139.2 (C-1'); 152.3 (C-6). **IR** (NaCl) *v*: 3393.7 (N-H), 2918.2 (C-H), 2229.6 (CN) cm^{-1}.

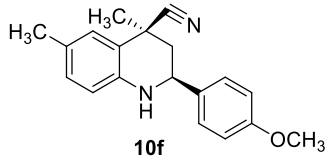
(±)-(2S*,4S*)-4,6,8-Trimethyl-2-(4-methylphenyl)-1,2,3,4-tetrahydroquinoline-4-carbonitrile (10e)



10e

Reaction time: 2 h. Yellow solid, mp: 142-143 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.83 (s, 3H, CH_3); 2.10 (s, 3H, Ar-CH_3); 2.23 (m, 1H, H-3eq); 2.29 (s, 3H, $ArCH_3$); 2.46 (t, *J* = 12.5 Hz, 1H, H-3ax); 3.90 (s, 1H, NH); 4.47 (dd, *J* = 11.9, 2.8 Hz, 1H, H-2); 6.89 (s, 1H, H-7); 7.16 (s, 1H, H-5); 7.38-51 (m, 5H, H-2',H-3', H-4', H-5' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 17.4 (CH_3); 20.5 (CH_3); 30.6 (CH_3); 35.4 (C-4); 42.0 (C-3); 52.2 (C-2); 119.3 (CN); 122.2 (C-4a); 124.9 (C-8); 126.3 (C-4'); 126.9 (C-2', C-6' and C-6); 128.5 (C-5); 129.1 (C-3' and C-5'); 131.1 (C-7); 138.7 (C-8a); 142.6 (C-1'). **IR** (NaCl) *v*: 3391.5 (N-H), 2960.0 (C-H), 2232.8 (CN) cm^{-1}.

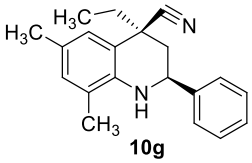
(±)-(2*S,4*S**)-2-(4-Methoxyphenyl)-4,6-dimethyl-1,2,3,4-tetrahydroquinoline-4-carbonitrile (10f)**



10f

Reaction time: 2 h. Yellow solid, mp: 136-137 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.79 (s, 3H, CH_3); 2.18 (dd, *J* = 13.1, 2.9 Hz, 1H, H-3eq); 2.28 (s, 3H, CH_3); 2.42 (t, *J* = 12.8 Hz, 1H, H-3ax); 3.83 (s, 3H, OCH_3); 4.01 (bs, 1H, NH); 4.37 (dd, *J* = 11.8, 2.8 Hz, 1H, H-2); 6.48 (d, *J* = 8.1 Hz, 1H, H-8); 6.91-6.94 (m, 3H, H-7, H-3' and H-5'); 7.23 (s, 1H, H-5); 7.32-7.36 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 20.5 (CH_3); 30.6 ($ArCH_3$); 35.2 (C-4); 42.1 (C-3); 51.4 (C-2); 55.5 (OCH_3); 114.3 (C-3' and C-5'); 115.1 (C-8); 119.7 (CN); 124.8 (C-4a); 127.6 (C-6); 128.0 (C-2' and C-6'); 128.5 (C-7); 129.9 (C-5); 134.2 (C-1'); 140.7 (C-8a); 159.6 (C-4'). **IR** (NaCl) *v*: 3368.8 (N-H), 2926.6 (C-H), 2232.8 (CN) cm^{-1}.

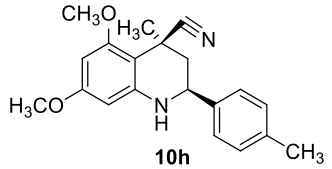
(±)-(2S*,4*S)-4,6,8-Trimethyl-2-(4-methylphenyl)-1,2,3,4-tetrahydroquinoline-4-carbonitrile (10g)**



10g

Reaction time: 2 h. Yellow solid, mp: 145-147 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.23 (t, *J* = 7.4 Hz, 3H, $CH_2\mathit{C}H_3$); 2.06 (dd, *J* = 7.4, 2.9 Hz, 1H, H-3eq); 2.11 (s, 3H, $ArCH_3$); 2.26-2.43 (m, 6H, $ArC\mathit{H}_3$, H-3ax and $C\mathit{H}_2CH_3$); 3.89 (bs, 1H, NH); 4.49 (dd, *J* = 11.4, 3.9 Hz, 1H, H-2); 6.90 (s, 1H, H-5); 7.13 (s, 1H, H-7); 7.38-7.51 (m, 5H, H2', H-3', H-4', H-5' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 9.2 ($CH_2\mathit{C}H_3$); 17.5 ($ArCH_3$); 20.5 ($ArCH_3$); 34.2 ($\mathit{C}H_2CH_3$); 38.4 (C-3); 40.8 (C-4); 52.0 (C-2); 118.5 (CN); 121.8 (C-4a); 123.5 (C-8); 126.3 (C-6); 126.6 (C-4'); 126.8 (C-2' and C-6'); 128.4 (C-5); 129.1 (C-3' and C-5'); 131.1 (C-7); 138.3 (C-8a); 143.0 (C-1'). **IR** (NaCl) *v*: 3360 (N-H), 2930 (C-H), 2250 (CN) cm^{-1}.

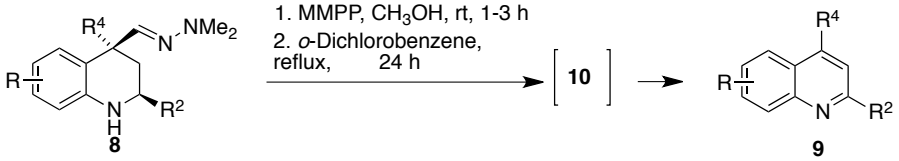
(±)-(2S*,4S*)-5,7-Dimethoxy-4-methyl-2-(4-methylphenyl)-1,2,3,4-tetrahydroquinoline-4-carbonitrile (10h)



10h

Reaction time: 2 h. Yellow solid, mp: 147-150 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.76 (s, 3H, CH_3); 2.19 (dd, *J* = 13.1, 2.3 Hz, 1H, H-3eq); 2.37-2.49 (m, 4H, H-3ax and $ArCH_3$); 3.74 (s, 3H, OCH_3); 3.90 (s, 3H, OCH_3); 4.13 (bs, 1H, NH); 4.26 (dd, *J* = 11.8, 2.1 Hz, 1H, H-2); 5.75 (d, *J* = 2.3 Hz, 1H, H-8); 5.96 (d, *J* = 2.3 Hz, 1H, H-6); 7.20 (d, *J* = 7.9 Hz, 2H, H-2' and H-6'); 7.30 (d, *J* = 8.0 Hz, 2H, H-3' and H-5'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 21.3 (CH_3); 27.6 ($ArCH_3$); 31.7 (C-4); 44.5 (C-3); 51.8 (C-2); 55.3 (OCH_3); 55.7 (OCH_3); 90.0 (C-6*); 90.2 (C-8*); 101.3 (C-4a); 124.9 (CN); 126.8 (C-2' and C-6'); 129.7 (C-3' and C-5'); 138.2 (C-4'*); 138.9 (C-1'*); 145.6 (C-8a); 159.5 (C-7*); 161.0 (C-5*). **IR** (NaCl) *v*: 3368.8 (N-H), 2931.1 (C-H), 12231.9 (CN) cm^{-1}.

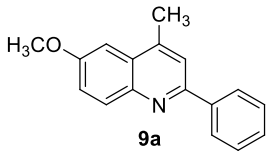
8. Synthesis of 2-arylquinolines 9a-h



The synthetic conditions described in the Section 4 were applied to hydrazones **8** and the crude nitriles **10** thus obtained were treated as described in Section 5.1.A. Compounds **9** were purified by flash chromatography, eluting with a mixture of petroleum ether:ethyl acetate (9:1, v/v).

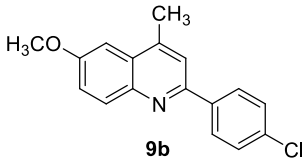
Cmpd.	R	R^2	R^4	Yield (%)
9a	6-OCH_3	C_6H_5	CH_3	92
9b	6-OCH_3	4-ClC_6H_4	CH_3	86
9c	6-OCH_3	4-$OCH_3C_6H_4$	CH_3	87
9d	6-OCH_3	4-$CH_3C_6H_4$	CH_3	86
9e	6,8-CH_3	C_6H_5	CH_3	95
9f	6-CH_3	4-$OCH_3C_6H_4$	CH_3	92
9g	6,8-CH_3	C_6H_5	CH_2CH_3	89
9h	5,7-OCH_3	4-$CH_3C_6H_4$	CH_3	95

6-Methoxy-4-methyl-2-phenylquinoline (9a)[9,10]



Reaction time: 24 h. White solid, mp: 128-129 °C. Spectral data were identical to those found in the literature [1]**H-NMR** ($CDCl_3$, 250 MHz) δ: 2.72 (s, 3H, CH_3); 3.96 (s, 3H, OCH_3); 7.19 (d, *J* = 2.7 Hz, 1H, H-5); 7.38 (dd, *J* = 9.2, 2.7 Hz, 1H, H-7); 7.43-7.54 (m, 3H, H-3', H-5'and H-4'); 7.68 (s, 1H, H-3); 8.10-8.13 (m, 3H, H-8, H-2' and H-6').

2-(4-Chlorophenyl)-6-methoxy-4-methylquinoline (9b)



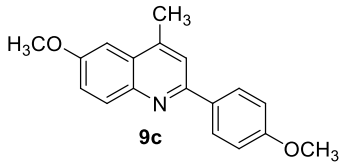
Reaction time: 24 h. White solid, mp: 119-122 °C. [1]**H-NMR** ($CDCl_3$, 250 MHz) δ: 2.72 (s, 3H, CH_3); 3.97 (s, 3H, OCH_3); 7.20 (d, *J* = 2.8 Hz, 1H, H-5); 7.38 (dd, *J* = 9.2, 2.8 Hz, 1H, H-7); 7.45-7.49 (m, 2H, H-3' and H-5'); 7.65 (s, 1H, H-3); 8.04-8.09 (m, 3H, H-8, H-2' and H-6'). [13]**C-NMR** ($CDCl_3$, 63 MHz) δ: 19.4 (CH_3); 55.7 (OCH_3); 102.0 (C-5); 119.7 (C-3); 121.8 (C-7); 128.3 (C-4a);

[9] J. W. Cornforth, *J. Chem. Soc*., 1948, 93.

[10] F. Xiao, W. Chen, Y. Liao and G.-J. Deng, *Org. Biomol. Chem*., 2012, **10**, 8593.

128.6 (C-2' and C-6'); 129.0 (C-3' and C-5'); 131.9 (C-8); 135.1 (C-4'); 138.4 (C-1'); 143.6 (C-8a); 144.2 (C-4); 153.5 (C-2); 157.8 (C-6). **IR** (NaCl) *v*: 2918.0 (C-H), 1624.6 (C=N), 717.2 (C-Cl) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{17}H_{14}ClNO$ (M= 283.75): C, 71.96; H, 4.97; N, 4.94. Found: C, 72.08; H, 5.27; N, 5.00.

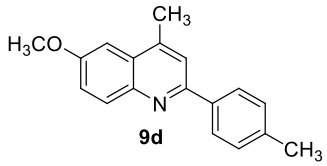
6-Methoxy-2-(4-methoxyphenyl)-4-methylquinoline (9c)[11]



9c

Reaction time: 24 h. White solid, mp: 109-111 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.70 (s, 3H, CH_3); 3.87 (s, 3H, OCH_3); 3.95 (s, 3H, OCH_3); 7.01-7.04 (m, 2H, H-3' and H-5'); 7.17 (d, *J* = 2.7 Hz, 1H, H-5); 7.36 (dd, *J* = 9.2, 2.8 Hz, 1H, H-7); 7.63 (s, 1H, H-3); 8.05-8.10 (m, 3H, H-8, H-2' and H-6').

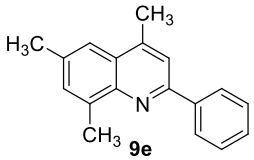
6-Methoxy-4-methyl-2-(4-methylphenyl)quinoline (9d)



9d

Reaction time: 24 h. White solid, mp: 124-127 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.43 (s, 3H, CH_3); 2.71 (s, 3H, CH_3); 3.96 (s, 3H, OCH_3); 7.19 (d, *J* = 2.7 Hz, 1H, H-5); 7.27-7.41 (m, 3H, H-7, H-3' and H-5'); 7.67 (s, 1H, H-3); 8.01-8.08 (m, 3H, H-8, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 19.4 (CH_3); 21.5 (CH_3); 55.7 (OCH_3); 102.0 (C-5); 120.0 (C-3*); 121.5 (C-7*); 127.2 (C-2' and C-6'); 128.1 (C-4a); 129.6 (C-3' and C-5'); 131.8 (C-8); 135.4 (C-4'*); 137.2 (C-1'*); 143.2 (C-8a*); 144.2 (C-4*); 154.9 (C-2); 157.5 (C-6). **IR** (NaCl) *v*: 3058.7 (C-H), 1603.8 (C=C), 1030.2 (C-N) cm^{-1}. IR (NaCl) *v*: 3058.7 (C-H), 1603.8 (C=C), 1030.2 (C-N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{18}H_{17}NO$ (M = 263.33): C, 82.10; H, 6.51; N, 5.32. Found: 81.90; H, 6.32; N, 5.12.

4,6,8-Trimethyl-2-phenylquinoline (9e)

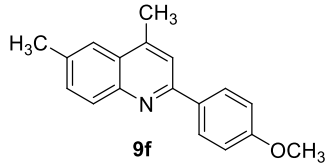


9e

Reaction time: 24 h. Yellow solid, mp: 121-123 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.54 (s, 3H, CH_3); 2.73 (s, 3H, CH_3); 2.90 (s, 3H, CH_3); 7.43 (s, 1H, H-5); 7.45-7.57 (m, 3H, H-3', H-4' and H-5'); 7.60 (s, 1H, H-7); 7.71 (s, 1H, H-3); 8.24-8.28 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 18.4 (CH_3); 19.5 (CH_3); 22.0 (CH_3); 119.1 (C-3); 120.6 (C-5); 127.2 (C-4a); 127.4 (C-2' and C-6'); 128.8 (C-3' and C-5'); 129.0 (C-4'); 131.8 (C-7); 135.4 (C-6); 137.8 (C-8); 140.2 (C-1'); 144.1 (C-4*); 145.7 (C-8a*); 154.3 (C-2). **IR** (NaCl) *v*: 3058.7 (C-H), 1603.8 (C=C), 1030.2 (C-N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{18}H_{17}N$ (M = 247.33): C, 87.41; H, 6.93; N, 5.66. Found: C, 87.45; H, 6.82; N, 5.94.

[11] R.E. Swenson, T.J. Sowin and H. Q. Zhang, *J. Org. Chem*. 2002, **67**, 9182.

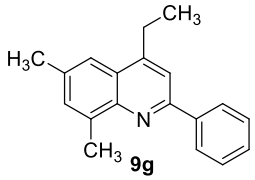
2-(4-Methoxyphenyl)-4,6-dimethylquinoline (9f)[11]



9f

Reaction time: 24 h. Yellow solid, mp: 127-129 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.57 (s, 3H, CH_3); 2.74 (s, 3H, CH_3); 3.88 (s, 3H, OCH_3); 7.04 (d, *J* = 8.9 Hz, 2H, H-3' and H-5'); 7.55 (d, *J* = 8.4 Hz, 1H, H-7); 7.65 (s, 1H, H-5); 7.74 (s, 1H, H-3); 8.10-8.14 (m, 3H, H-8, H-2' and H-6').

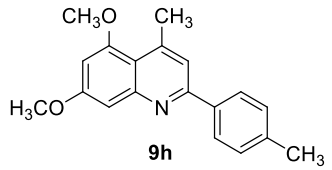
4-Ethyl-6,8-dimethyl-2-phenylquinoline (9g)



9g

Reaction time: 24 h. White solid, mp: 116-118 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 1.44 (t, *J* = 7.5 Hz, 3H, CH_2CH_3); 2.53 (s, 3H, CH_3); 2.87 (s, 3H, CH_3); 3.14 (q, *J* = 7.3 Hz, 2H, CH_2CH_3); 7.41 (s, 1H, H-5); 7.44-7.56 (m, 3H, H-3', H-4' and H-5'); 7.65 (s, 1H, H-7); 7.73 (s, 1H, H-3); 8.23-8.27 (m, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 14.5 (CH_3); 18.5 (CH_3); 22.1 (CH_3); 25.8 (CH_2CH_3); 117.2 (C-3); 120.2 (C-5); 126.4 (C-4a); 127.5 (C-2' and C-6'); 128.8 (C-3' and C-5'); 129.0 (C-4'); 131.7 (C-7); 135.4 (C-6); 138.0 (C-8); 140.4 (C-1'); 146.0 (C-4); 149.8 (C-8a); 154.5 (C-2). **IR** (NaCl) *v*: 2917.4 (C-H), 1596.8 (C-C), 1029.1 (C-N) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{19}H_{19}N$ (M = 261.36): C, 87.31; H, 7.33; N, 5.36. Found: C, 87.06; H, 7.35; N, 5.51.

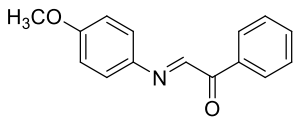
5,7-Dimethoxy-4-methyl-2-(4-methylphenyl)quinoline (9h)



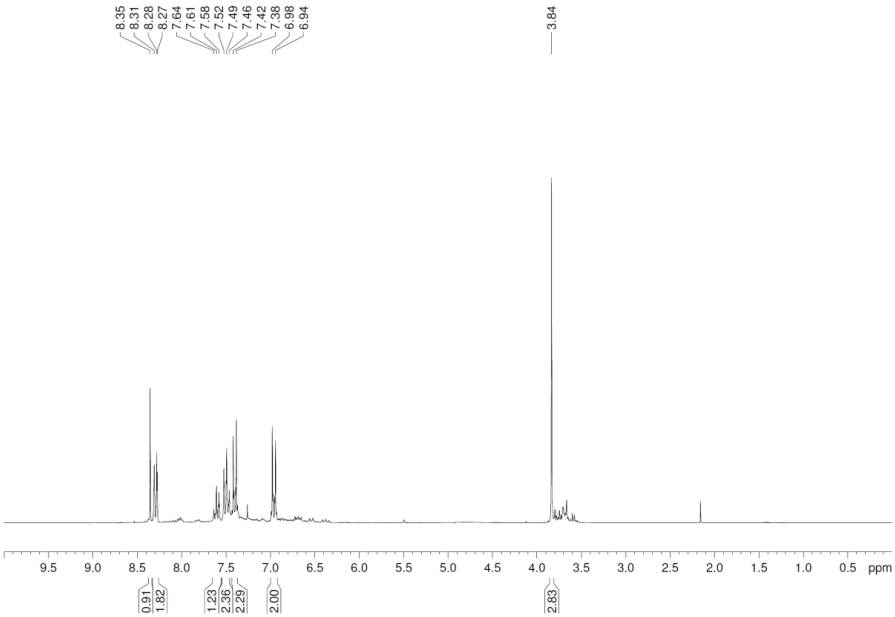
9h

Reaction time, 48 h. Yellow solid, mp: 130-133 °C. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 2.42 (s, 3H, CH_3); 2.87 (s, 3H, CH_3); 3.92 (s, 3H, OCH_3); 3.95 (s, 3H, OCH_3); 6.47 (d, *J* = 2.4 Hz, 1H, H-6); 7.11 (d, *J* = 2.4 Hz, 1H, H-8); 7.30 (d, *J* = 7.9 Hz, 2H, H-3' and H-5'); 7.41 (s, 1H, H-3); 8.01 (d, *J* = 8.2 Hz, 2H, H-2' and H-6'). **^{13}C-NMR** ($CDCl_3$, 63 MHz) δ: 21.5 (CH_3); 24.7 (CH_3); 55.6 (OCH_3); 55.7 (OCH_3); 98.3 (C-6*); 101.1 (C-8*); 115.6 (C-4a); 119.1 (C-3); 127.4 (C-3' and C-5'); 129.6 (C-2' and C-6'); 136.9 (C-4'); 139.2 (C-1'); 146.3 (C-4); 151.9 (C-8a); 157.3 (C-5*); 158.7 (C-7*); 160.6 (C-2). **IR** (NaCl) *v*: 2928.3 (C-H), 1620.1 (C-C), 1135.4 (C-O) cm^{-1}. **Elemental analysis (%)**: Calc. for $C_{19}H_{19}NO_2$ (M = 293.36): C, 77.79; H, 6.53; N, 4.77. Found: C, 77.78; H, 6.71; N, 4.87.

SPECTRA


H3CO
N
O

1a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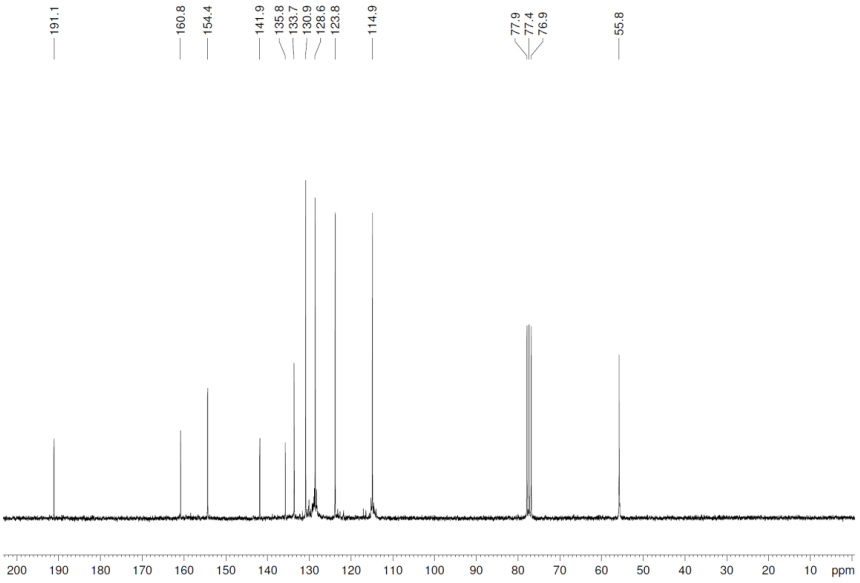
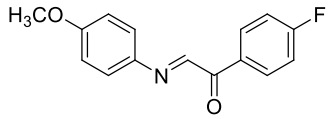
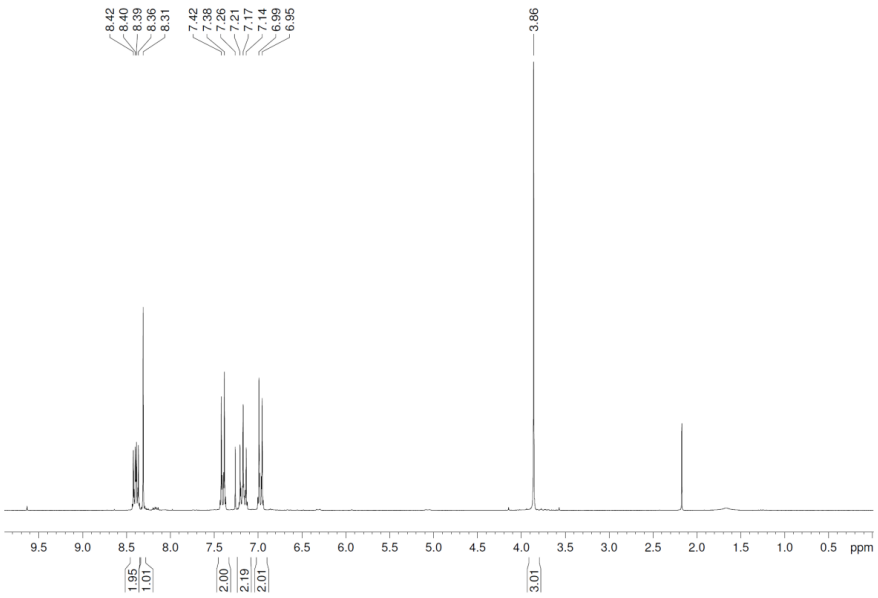
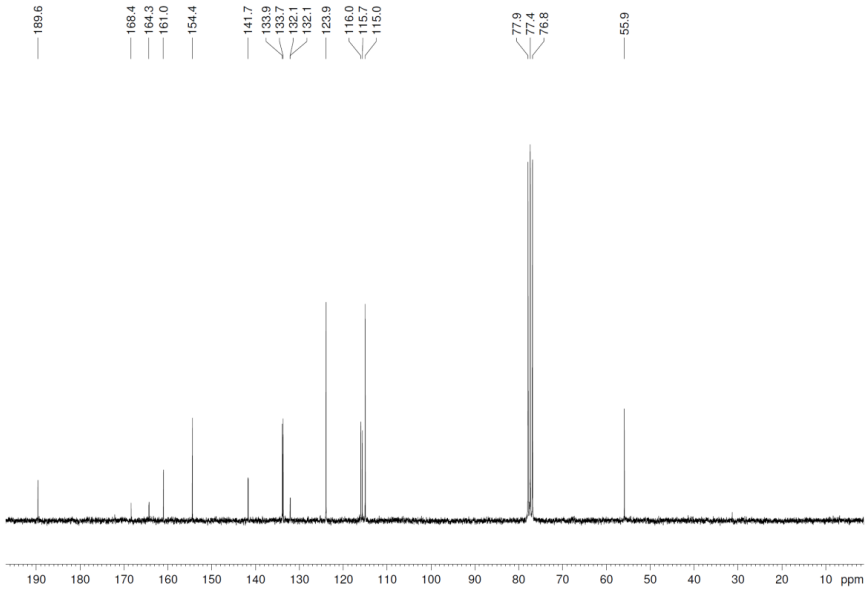
8.31
8.28
8.27
7.64
7.61
7.58
7.52
7.49
7.46
7.42
7.38
6.98
6.94
3.84
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.91
1.82
1.23
2.36
2.29
2.00
2.83

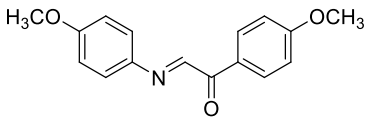

191.1
160.8
154.4
141.9
135.8
133.7
130.9
128.6
123.8
114.9
77.9
77.4
76.9
55.8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


H3CO
N
O
F

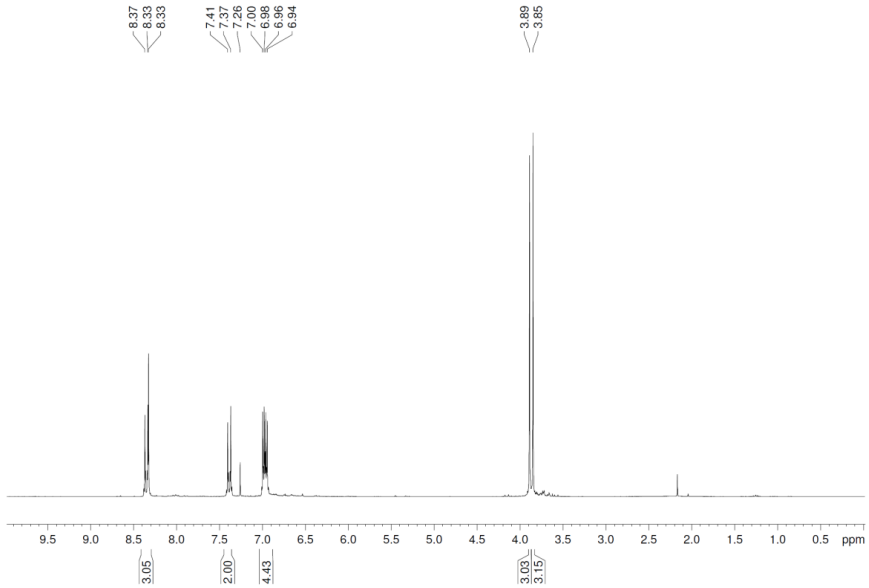
1b

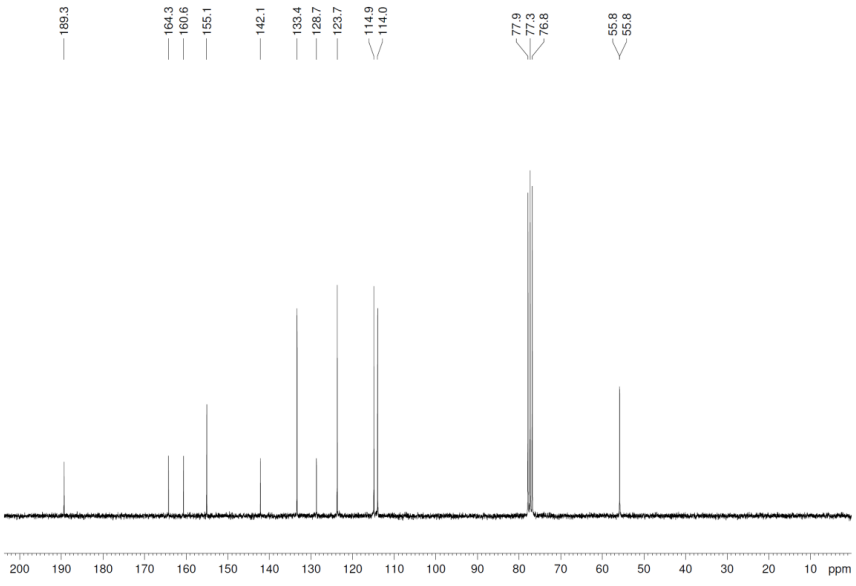

8.42
8.40
8.39
8.36
8.31
7.42
7.38
7.26
7.21
7.17
7.14
6.99
6.95
3.86
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.95
1.01
2.00
2.19
2.01
3.01

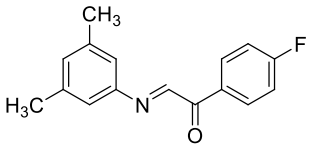

189.6
168.4
164.3
161.0
154.4
141.7
133.9
133.7
132.1
132.1
123.9
116.0
115.7
115.0
77.9
77.4
76.8
55.9
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


H3CO
OCH3
N
O

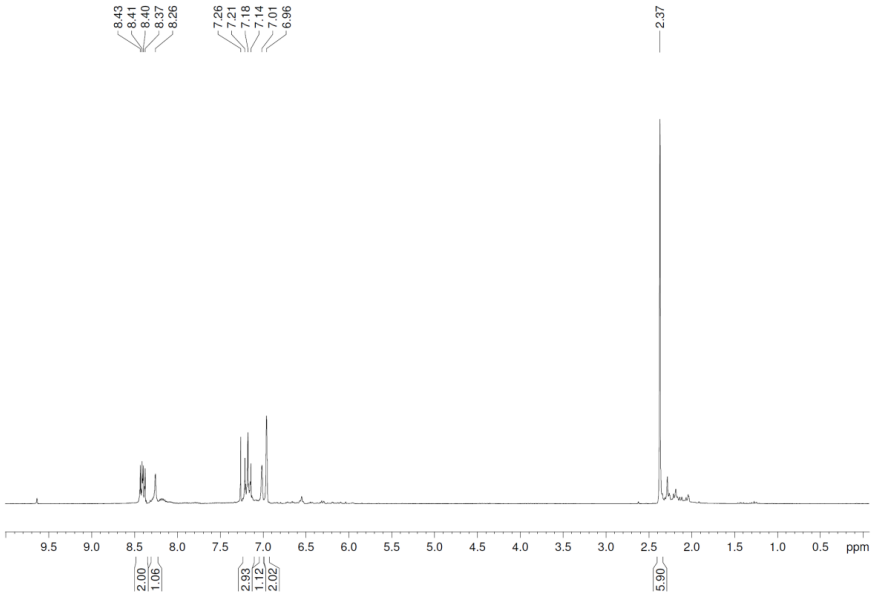
1c

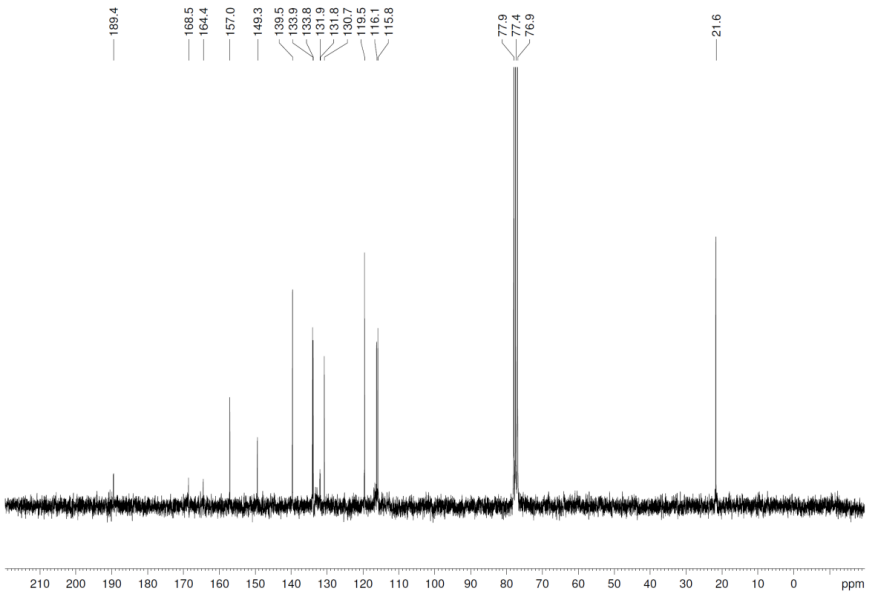

8.37
8.33
8.33
7.41
7.37
7.26
7.00
6.98
6.96
6.94
3.89
3.85
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.05
2.00
4.43
3.03
3.15

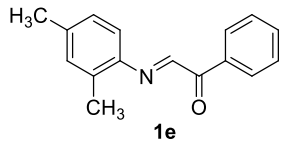

189.3
164.3
160.6
155.1
142.1
133.4
128.7
123.7
114.9
114.0
77.9
77.3
76.8
55.8
55.8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


CH3
H3C
N
O
F

1d

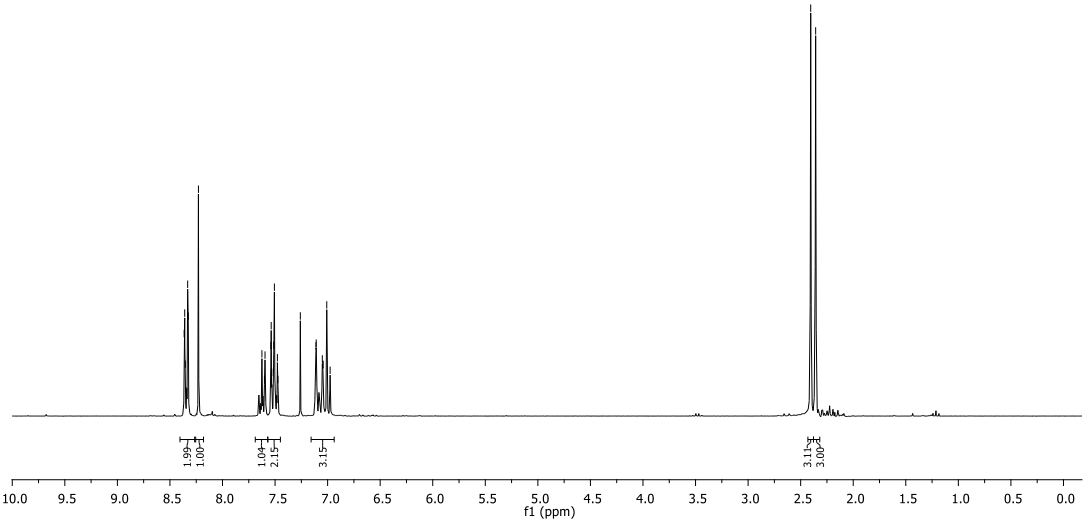

8.43
8.41
8.40
8.37
8.26
7.26
7.21
7.18
7.14
7.01
6.96
2.37
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.06
2.93
1.12
2.02
5.90

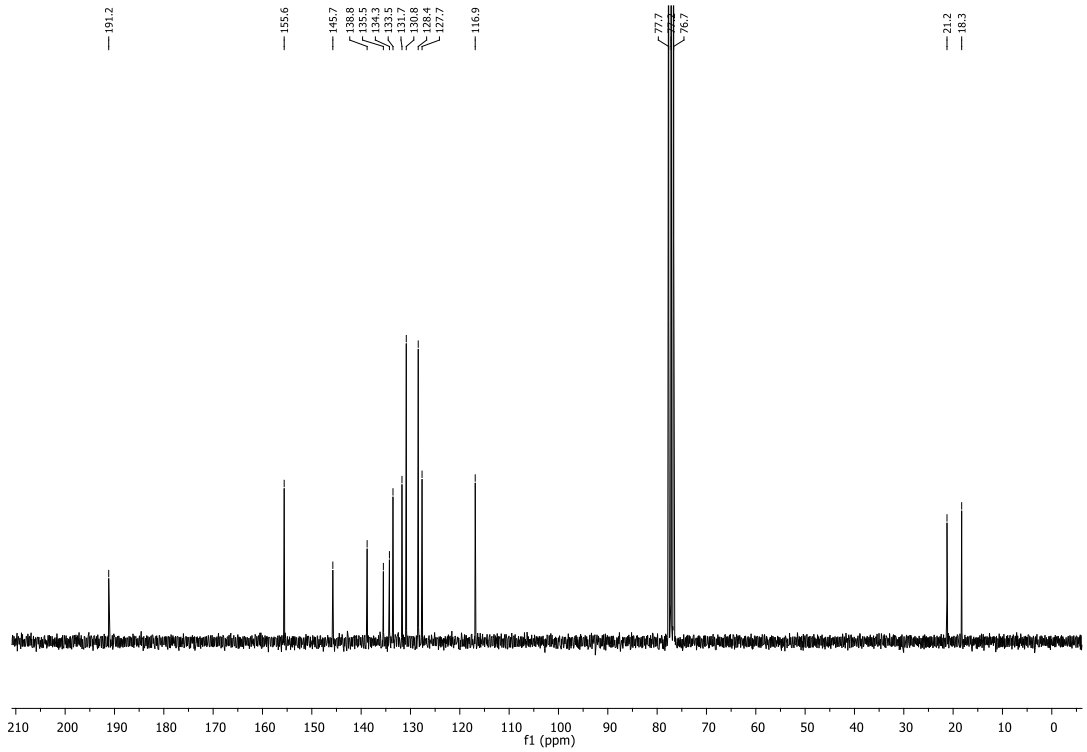

189.4
168.5
164.4
157.0
149.3
139.5
133.9
133.8
131.9
131.8
130.7
119.5
116.1
115.8
77.9
77.4
76.9
21.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

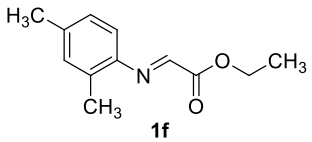

H3C
N
CH3
O

1e

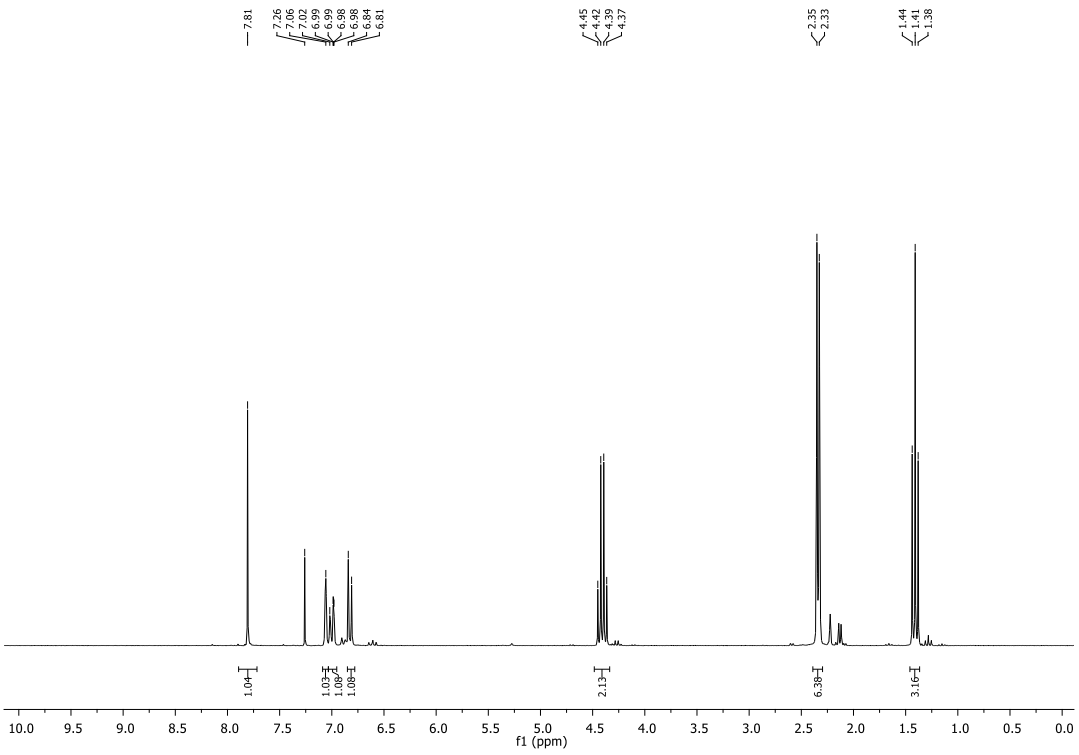

8.36
8.36
8.35
8.33
8.33
8.23
7.63
7.60
7.60
7.54
7.54
7.53
7.51
7.51
7.48
7.47
7.26
7.11
7.11
7.05
7.05
7.04
7.01
6.98
2.40
2.36

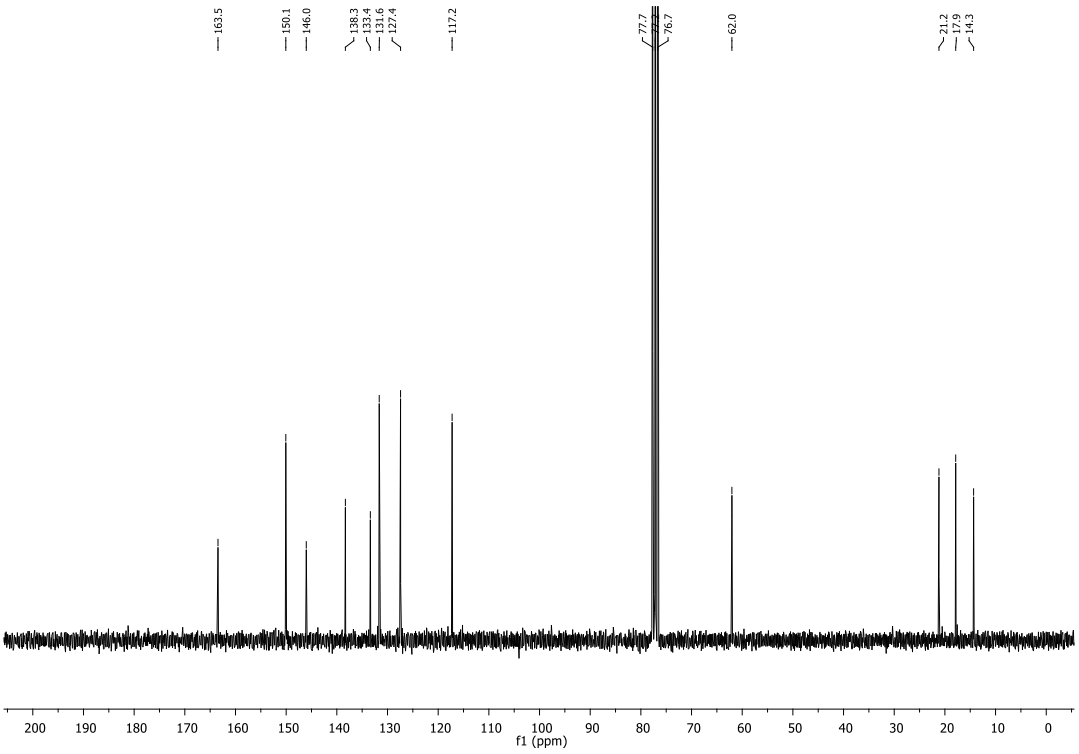

1.99
1.00
1.04
2.15
3.15
3.11
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

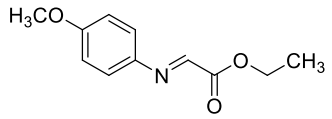

191.2
155.6
145.7
138.8
135.5
134.3
131.5
131.7
130.8
128.4
127.7
116.9
77.7
77.2
76.7
21.2
18.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


H3C
CH3
N
O
CH3
O

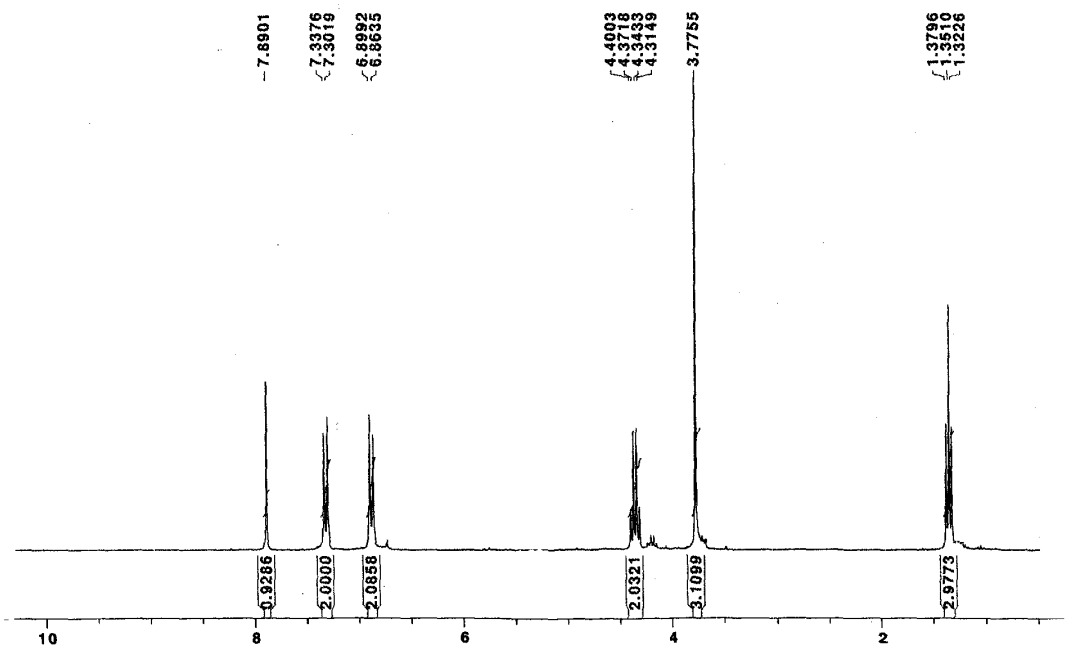
1f

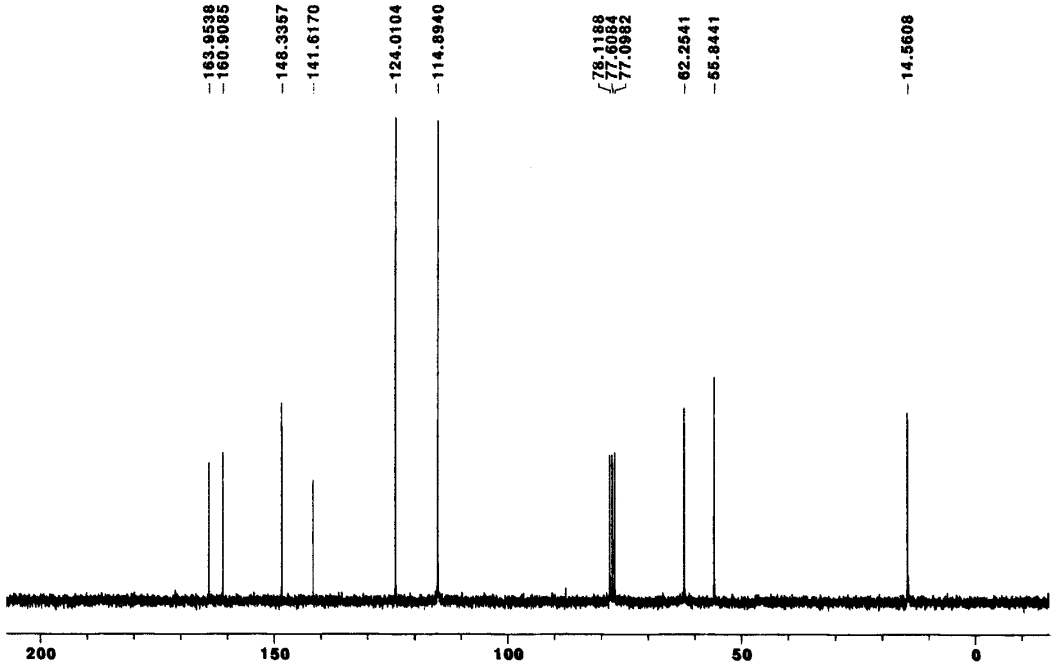

7.81
7.26
7.06
7.02
6.99
6.99
6.98
6.98
6.84
6.81
4.45
4.42
4.39
4.37
2.35
2.33
1.44
1.41
1.38
1.04
1.03
1.09
1.08
2.13
6.38
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

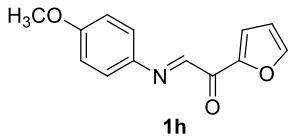

163.5
150.1
146.0
138.3
133.4
131.6
127.4
117.2
77.7
77.2
76.7
62.0
21.2
17.9
14.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


H3CO
N
O
O
CH3
O

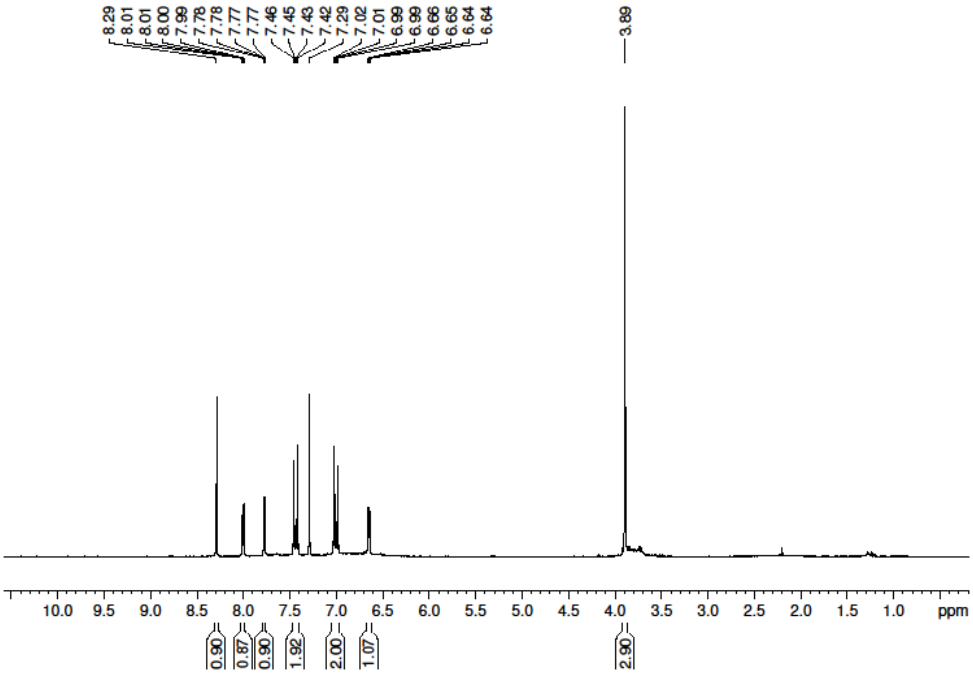
1g

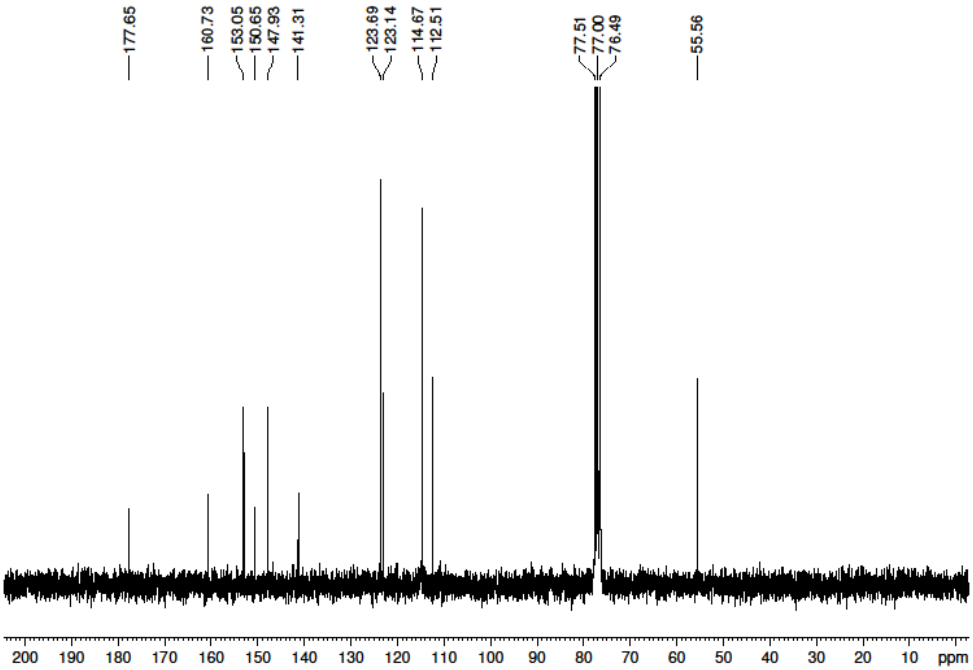

7.8901
7.3376
7.3019
6.8992
6.8635
4.4003
4.3718
4.3433
4.3149
3.7755
1.3796
1.3510
1.3226
0.9286
2.0000
2.0858
2.0321
3.1099
2.9773
10
8
6
4
2

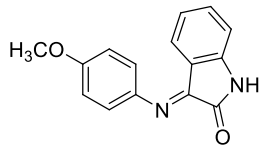

163.9538
160.9085
148.3357
141.6170
124.0104
114.8940
78.1188
77.6084
77.0982
62.2541
55.8441
14.5608
200
150
100
50
0


H3CO
N
O
O

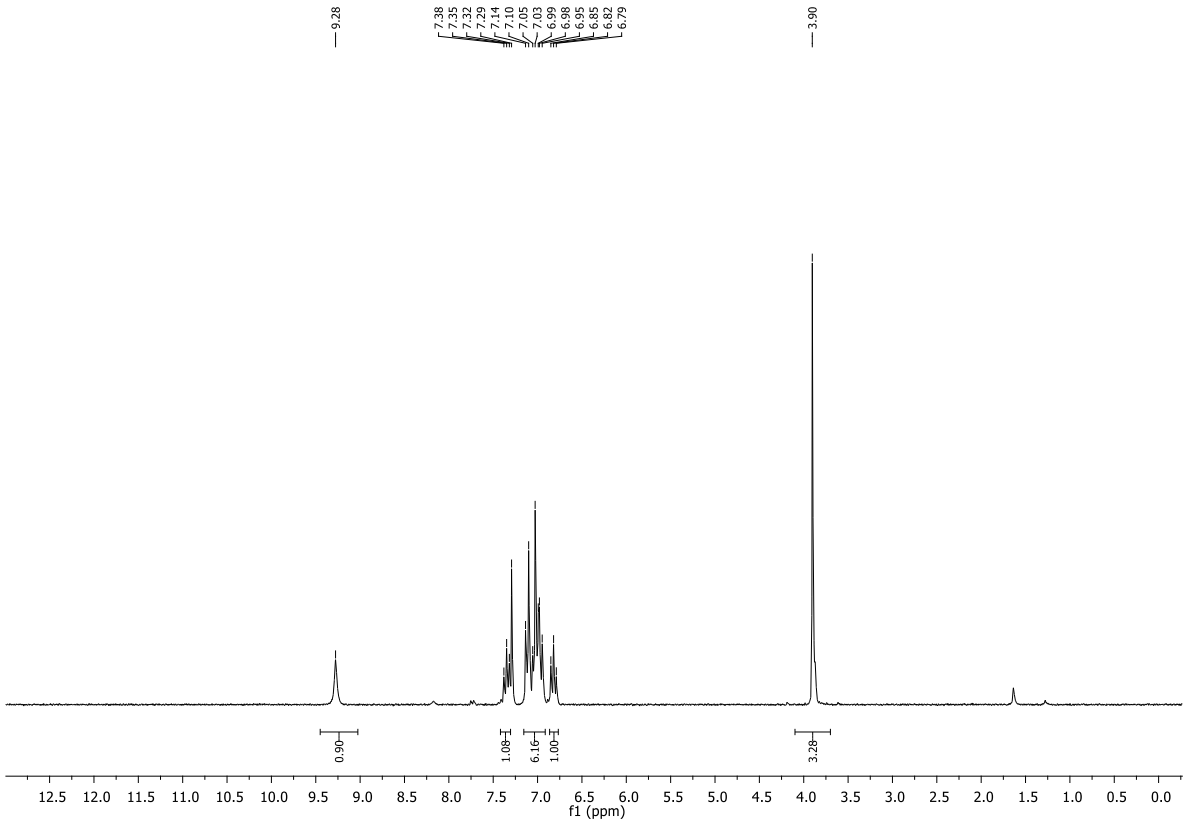
1h

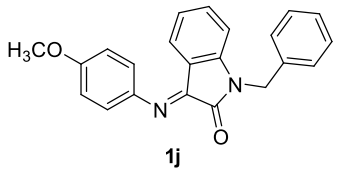

8.29
8.01
8.01
8.00
7.99
7.78
7.78
7.77
7.77
7.46
7.45
7.43
7.42
7.29
7.02
7.01
6.99
6.99
6.66
6.65
6.64
6.64
3.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.90
0.87
0.90
1.92
2.00
1.07
2.90


177.65
160.73
153.05
150.65
147.93
141.31
123.69
123.14
114.67
112.51
77.51
77.00
76.49
55.56
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


H3CO
NH
N
O

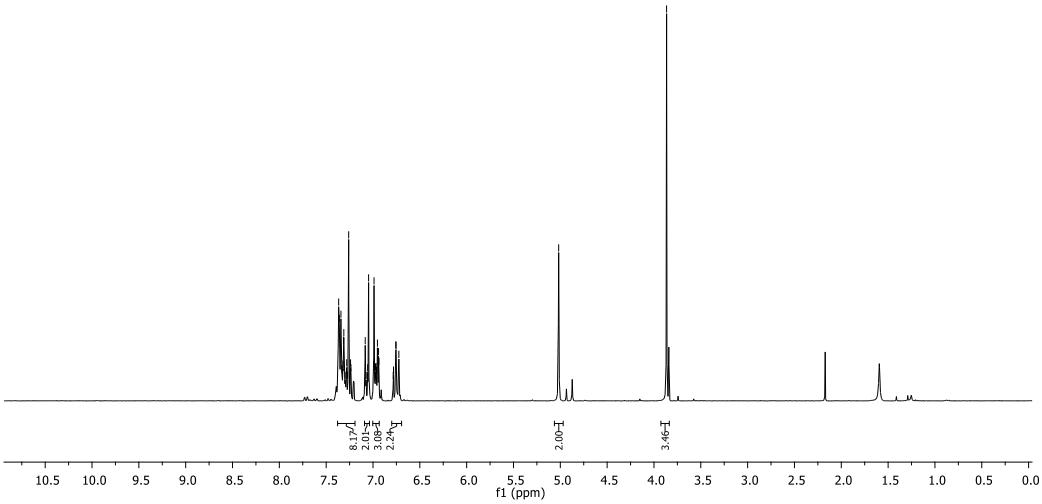
1i

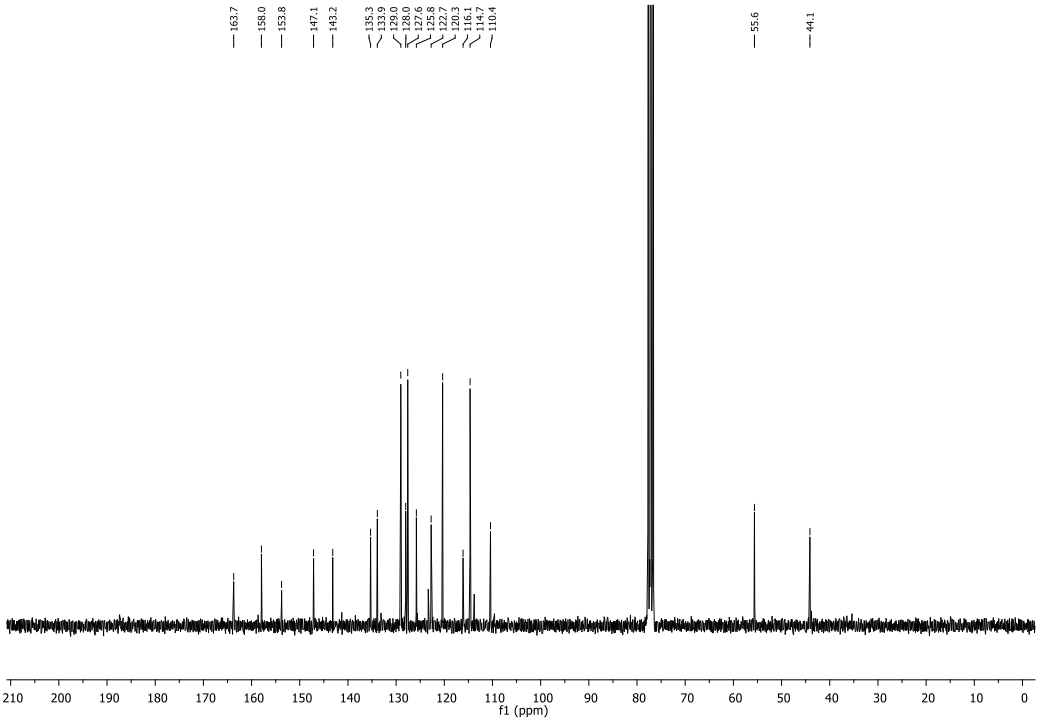

9.28
7.38
7.35
7.32
7.29
7.14
7.10
7.05
7.03
6.99
6.98
6.95
6.85
6.82
6.79
3.90
0.90
1.08
6.16
1.00
3.28
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

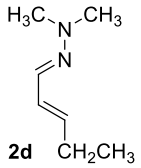

H3CO
N
N
O

1j

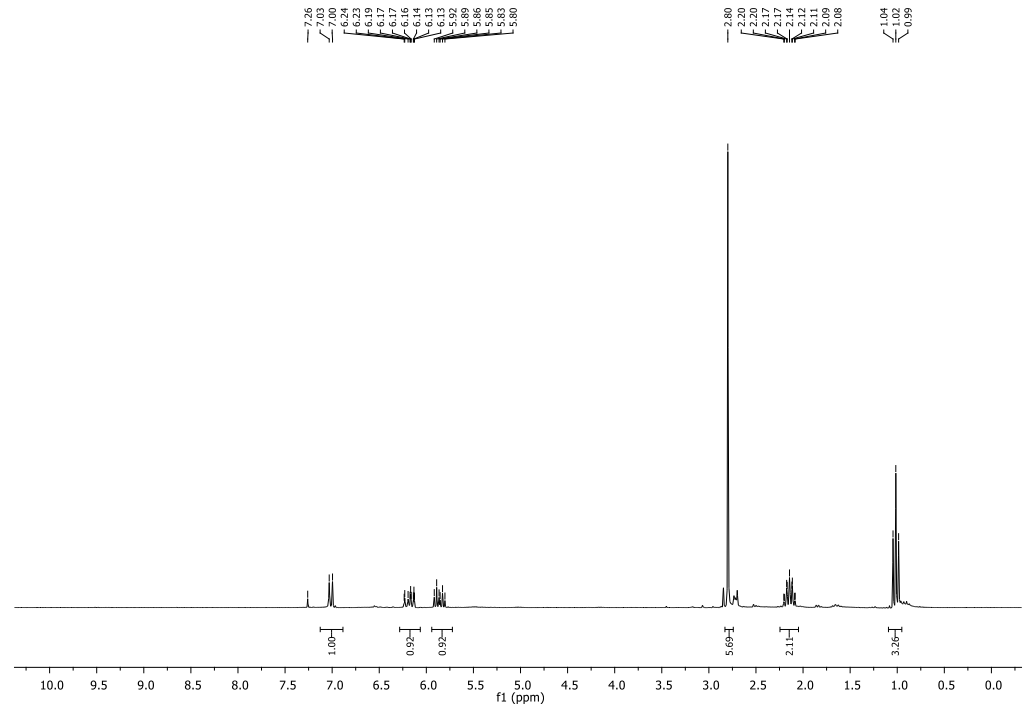

7.37
7.36
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.28
7.27
7.26
7.24
7.24
7.08
7.07
7.06
7.05
6.99
6.98
6.97
6.97
6.96
6.95
6.94
6.94
6.78
6.78
6.76
6.75
6.72
5.02
3.87

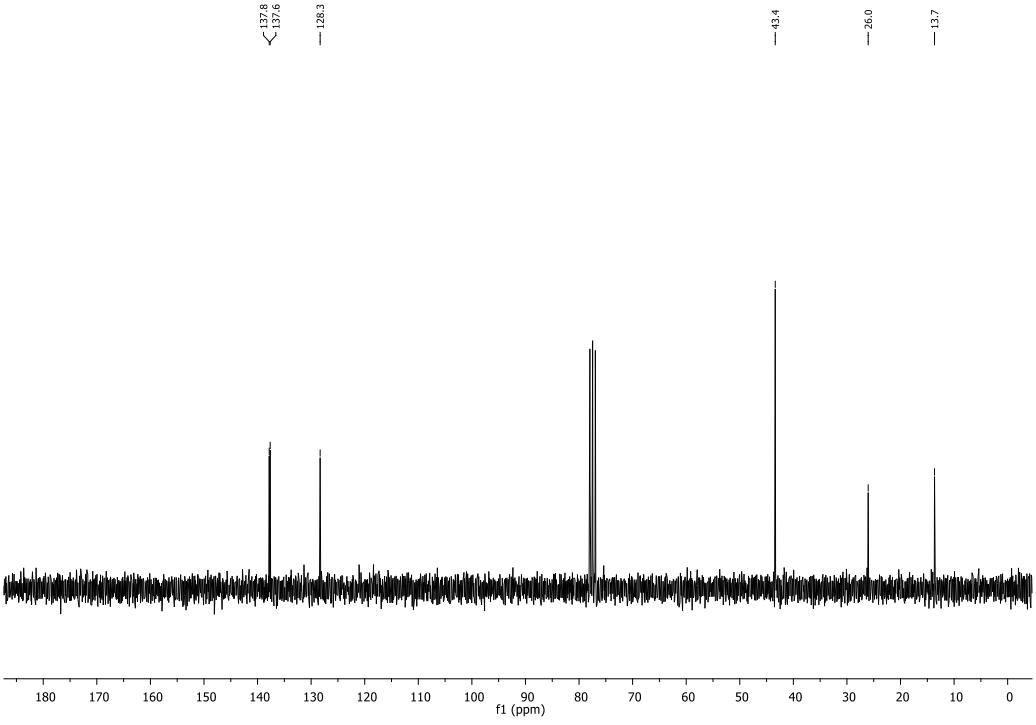

8.17
2.01
3.08
2.24
2.00
3.46
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

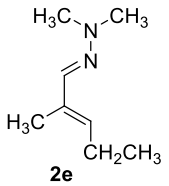

163.7
158.0
153.8
147.1
143.2
135.3
133.9
129.0
128.0
127.6
125.8
122.7
120.3
116.1
114.7
110.4
55.6
44.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


H3C
CH3
N
N
CH2CH3

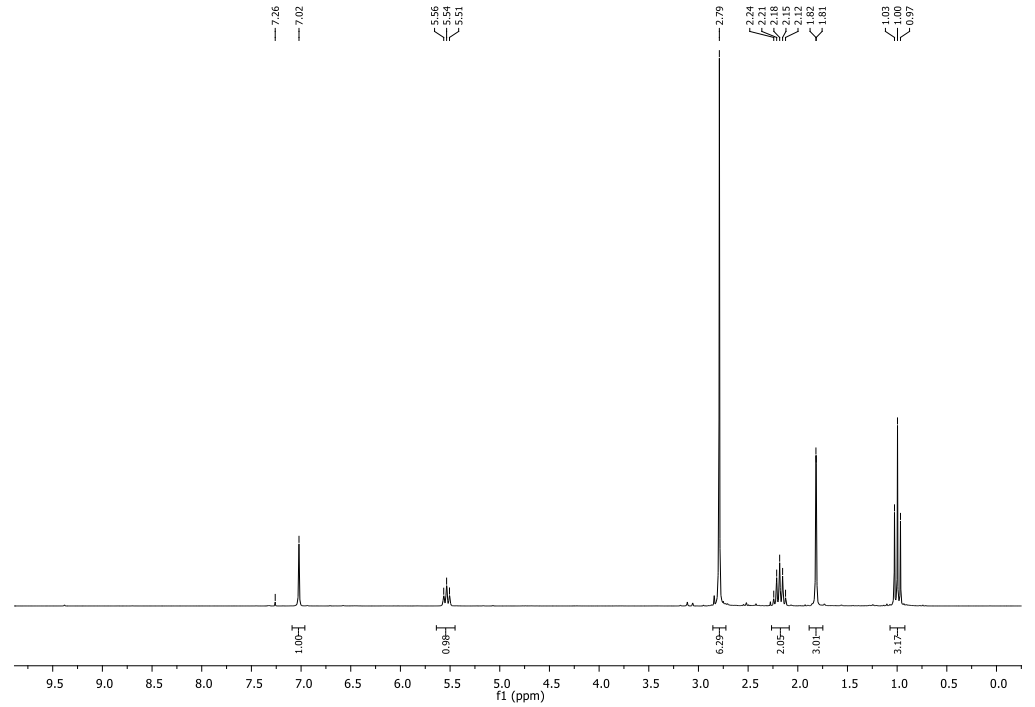
2d

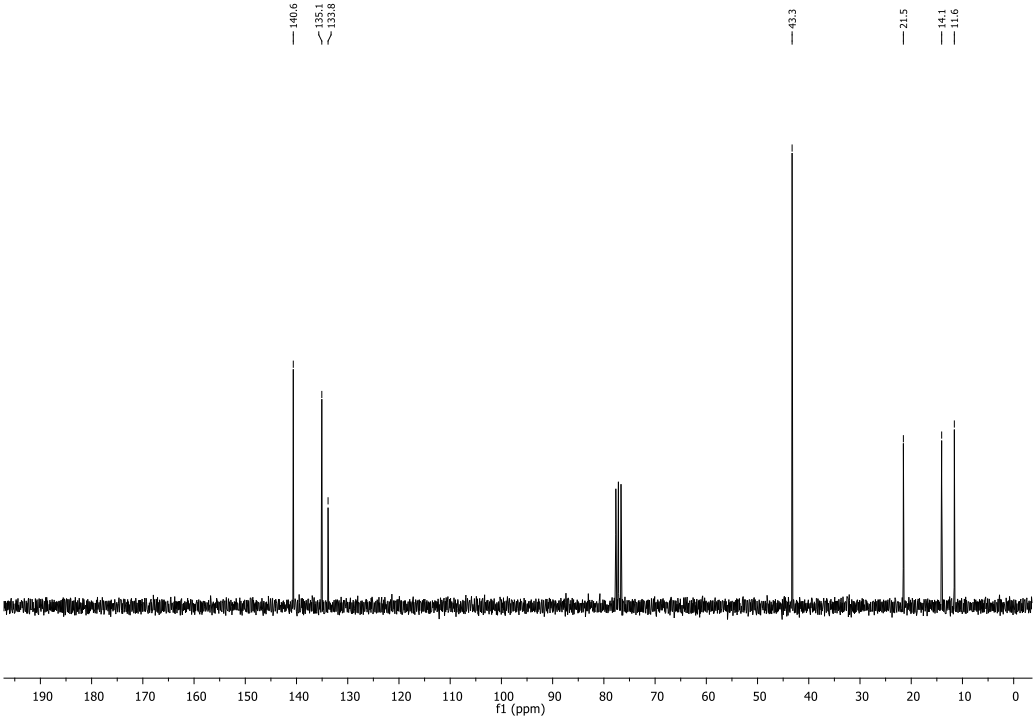

7.26
7.03
7.00
6.24
6.23
6.19
6.17
6.17
6.16
6.14
6.13
6.13
5.92
5.89
5.86
5.85
5.83
5.80
2.80
2.20
2.20
2.17
2.17
2.14
2.12
2.11
2.09
2.08
1.04
1.02
0.99
1.00
0.92
0.92
5.69
2.11
3.26
f1 (ppm)

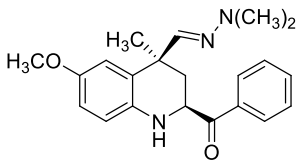

137.8
137.6
128.3
43.4
26.0
13.7
f1 (ppm)



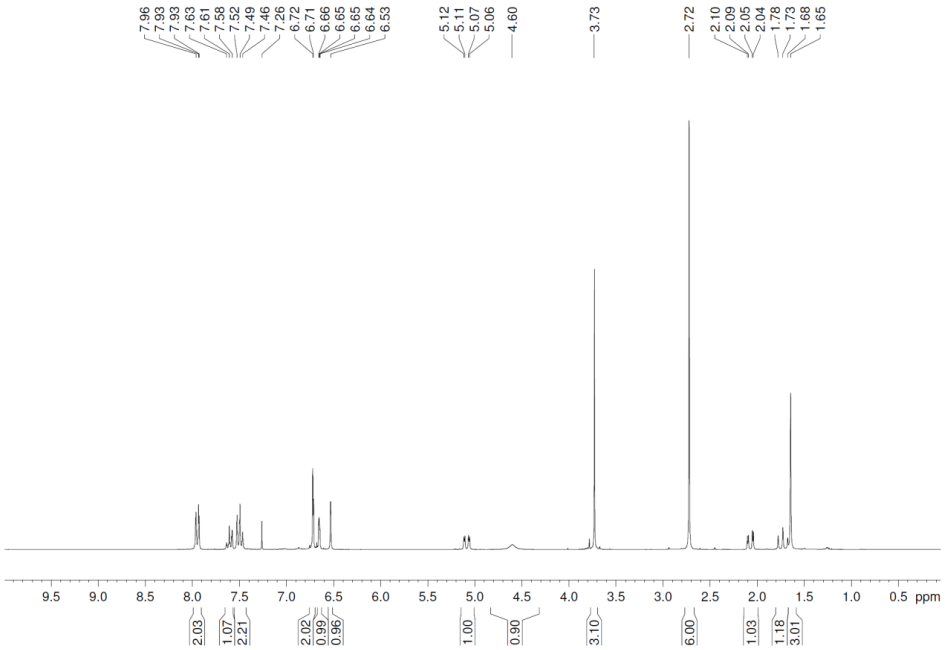
2e

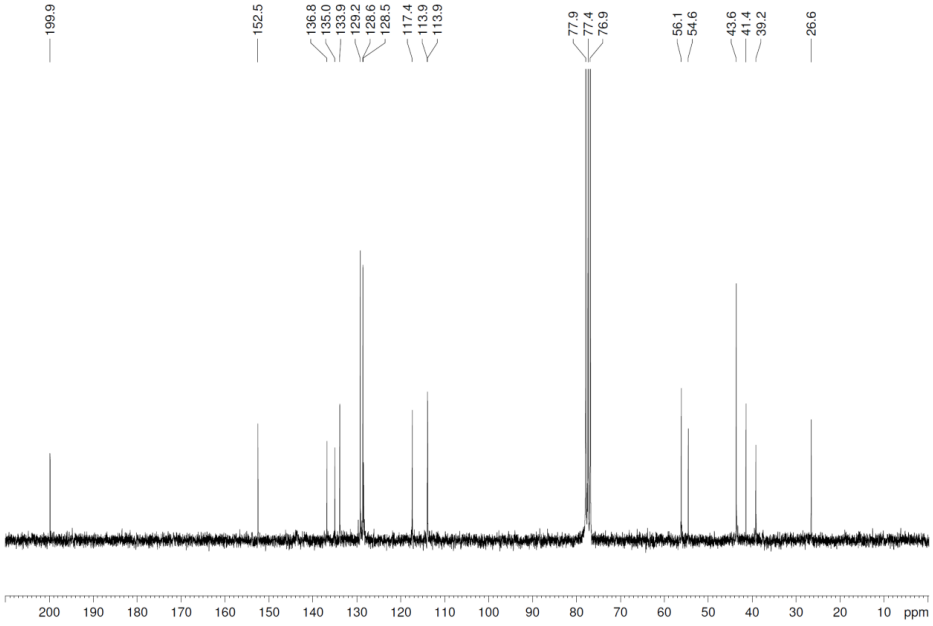

7.26
7.02
5.56
5.54
5.51
2.79
2.24
2.21
2.18
2.15
2.12
1.82
1.81
1.03
1.00
0.97
1.00
0.98
6.29
2.05
3.01
3.17
f1 (ppm)

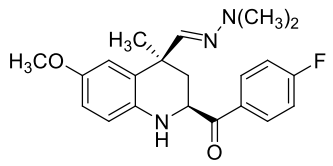

140.6
135.1
133.8
43.3
21.5
14.1
11.6
f1 (ppm)


N(CH3)2
H3C
N
H3CO
N
H
O

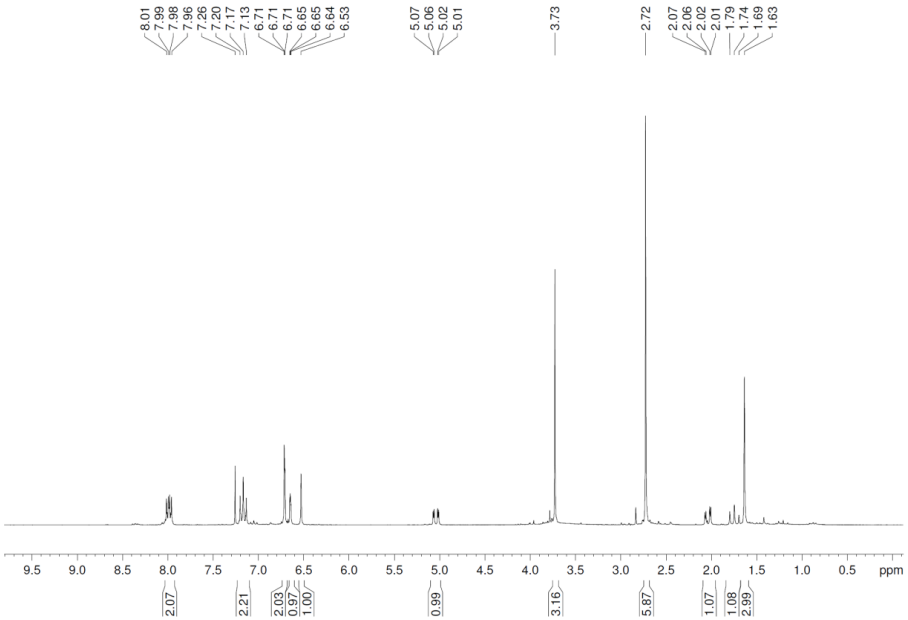
3a

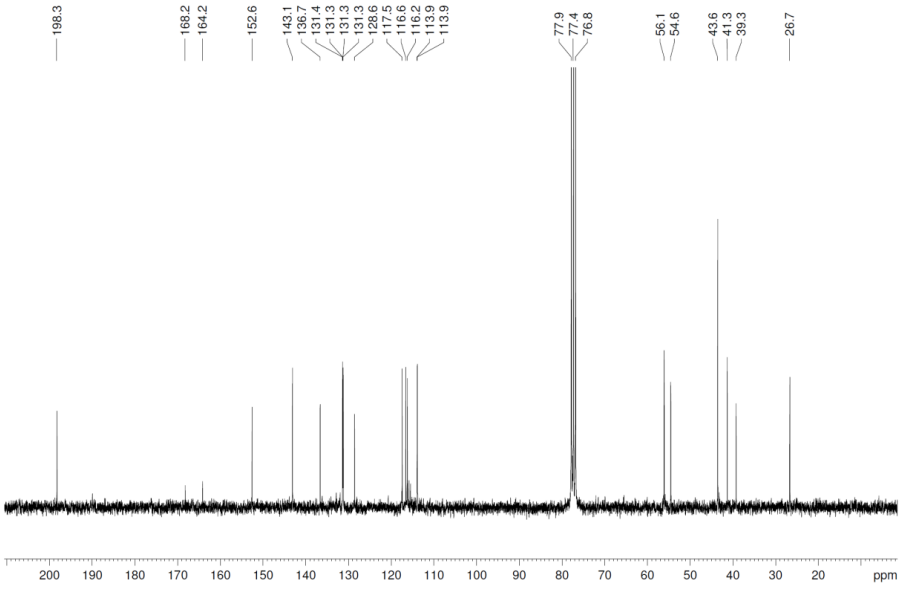

7.96
7.93
7.93
7.63
7.61
7.58
7.52
7.49
7.46
7.26
6.72
6.71
6.66
6.65
6.65
6.64
6.53
5.12
5.11
5.07
5.06
4.60
3.73
2.72
2.10
2.09
2.05
2.04
1.78
1.73
1.68
1.65
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.03
1.07
2.21
2.02
0.99
0.96
1.00
0.90
3.10
6.00
1.03
1.18
3.01

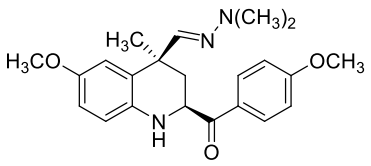

199.9
152.5
136.8
135.0
133.9
129.2
128.6
128.5
117.4
113.9
113.9
77.9
77.4
76.9
56.1
54.6
43.6
41.4
39.2
26.6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


N(CH3)2
H3C
N
H3CO
F
N
H
O

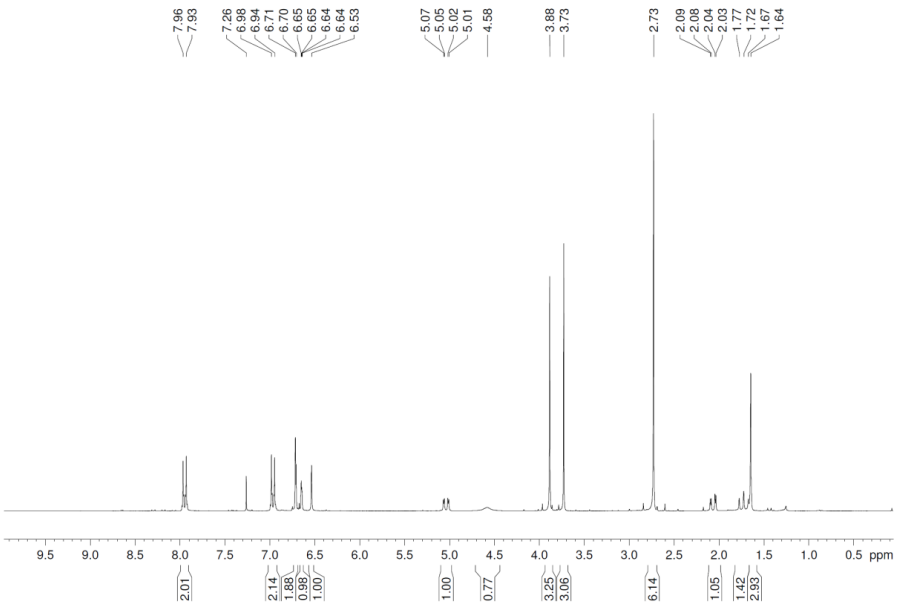
3b

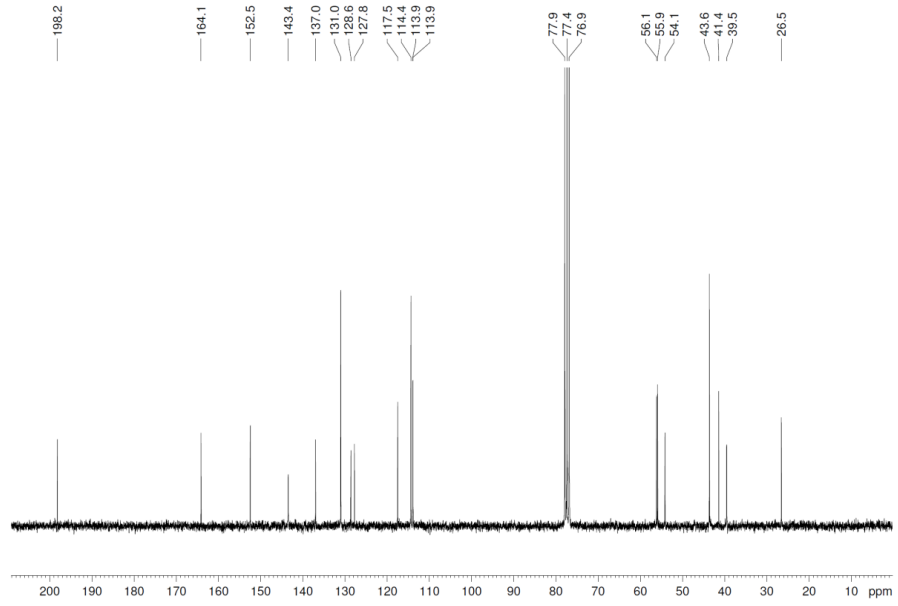

8.01
7.99
7.98
7.96
7.26
7.20
7.17
7.13
6.71
6.71
6.71
6.65
6.65
6.64
6.53
5.07
5.06
5.02
5.01
3.73
2.72
2.07
2.06
2.02
2.01
1.79
1.74
1.69
1.63
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.07
2.21
2.03
0.97
1.00
0.99
3.16
5.87
1.07
1.08
2.99

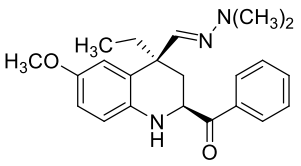

198.3
168.2
164.2
152.6
143.1
136.7
131.4
131.3
131.3
131.3
128.6
117.5
116.6
116.2
113.9
113.9
77.9
77.4
76.8
56.1
54.6
43.6
41.3
39.3
26.7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


N(CH3)2
H3C
N
H3CO
OCH3
N
H
O

3c

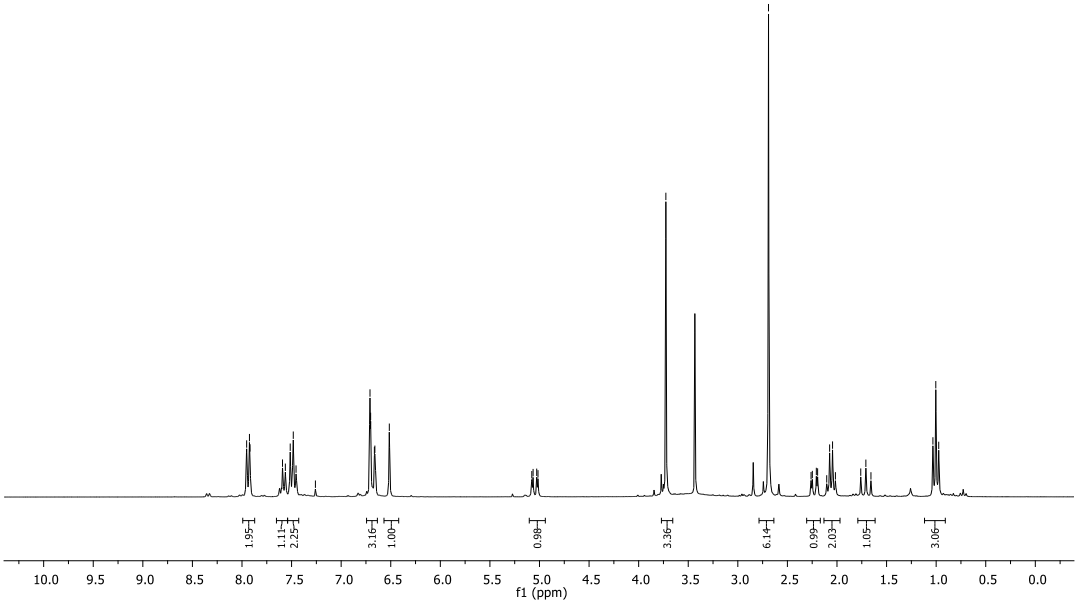

7.96
7.93
7.26
6.98
6.94
6.71
6.70
6.65
6.65
6.64
6.64
6.53
5.07
5.05
5.02
5.01
4.58
3.88
3.73
2.73
2.09
2.08
2.04
2.03
1.77
1.72
1.67
1.64
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.01
2.14
1.88
0.98
1.00
1.00
0.77
3.25
3.06
6.14
1.05
1.42
2.93


198.2
164.1
152.5
143.4
137.0
131.0
128.6
127.8
117.5
114.4
113.9
113.9
77.9
77.4
76.9
56.1
55.9
54.1
43.6
41.4
39.5
26.5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

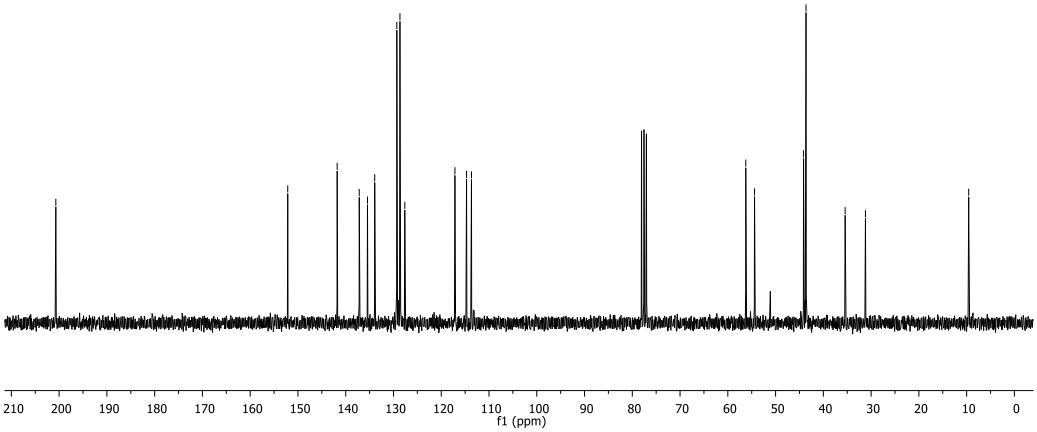

N(CH3)2
H3C
N
H3CO
N
H
O

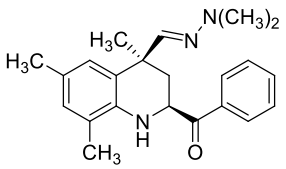
3d


7.95
7.92
7.92
7.59
7.56
7.51
7.48
7.45
7.26
6.71
6.70
6.67
6.66
6.51
5.08
5.06
5.03
5.02
3.73
2.69
2.26
2.25
2.21
2.20
2.10
2.07
2.04
2.02
1.76
1.71
1.66
1.03
1.00
0.97

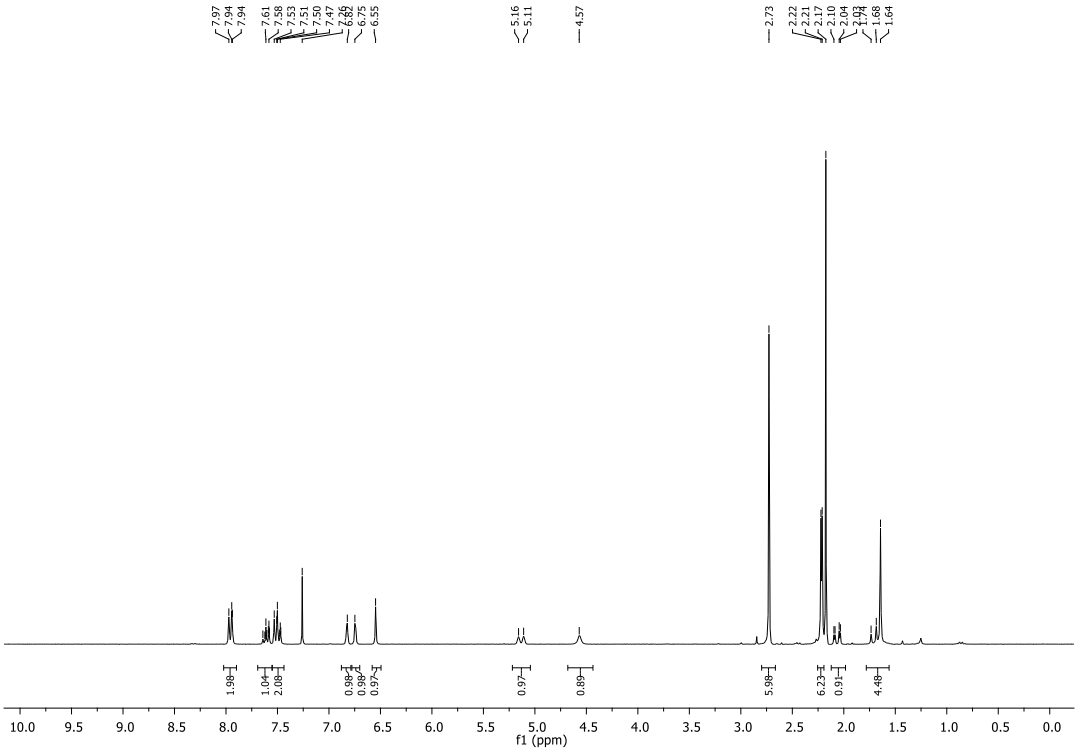

1.95
1.11
2.25
3.16
1.00
0.98
3.36
6.14
0.99
2.03
1.05
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

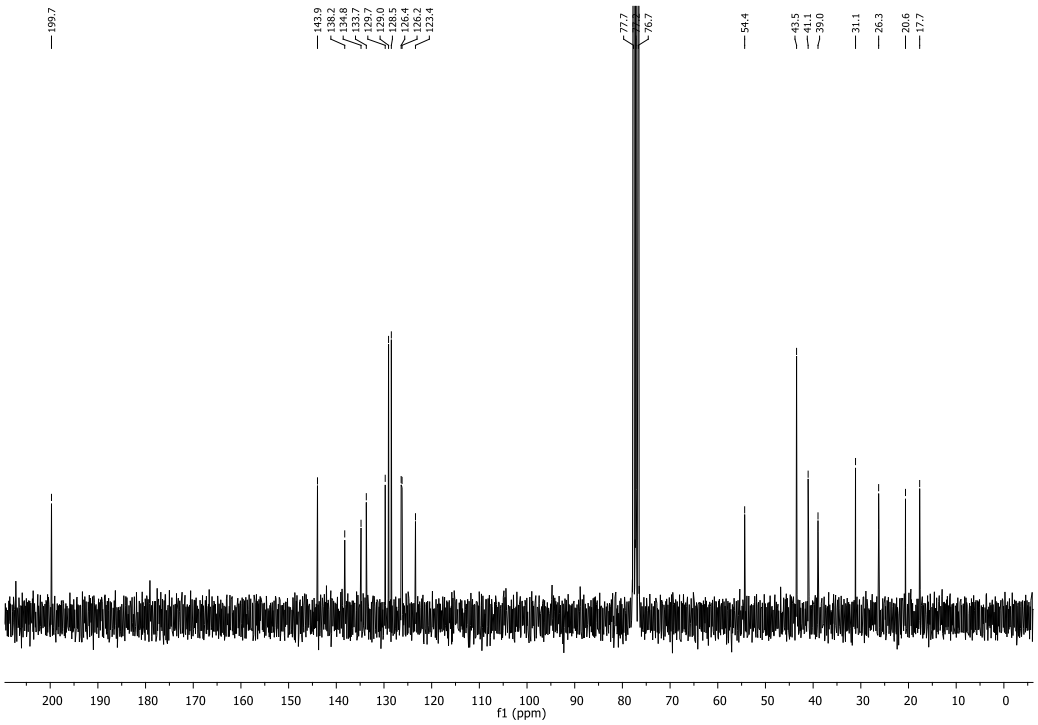

200.7
152.1
141.8
137.2
135.4
133.9
129.3
128.6
127.6
117.1
114.7
113.7
56.2
54.4
44.1
43.6
35.4
31.2
9.6

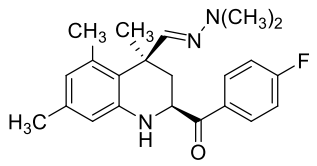

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N(CH3)2
H3C
N
H3C
N
H
CH3
O

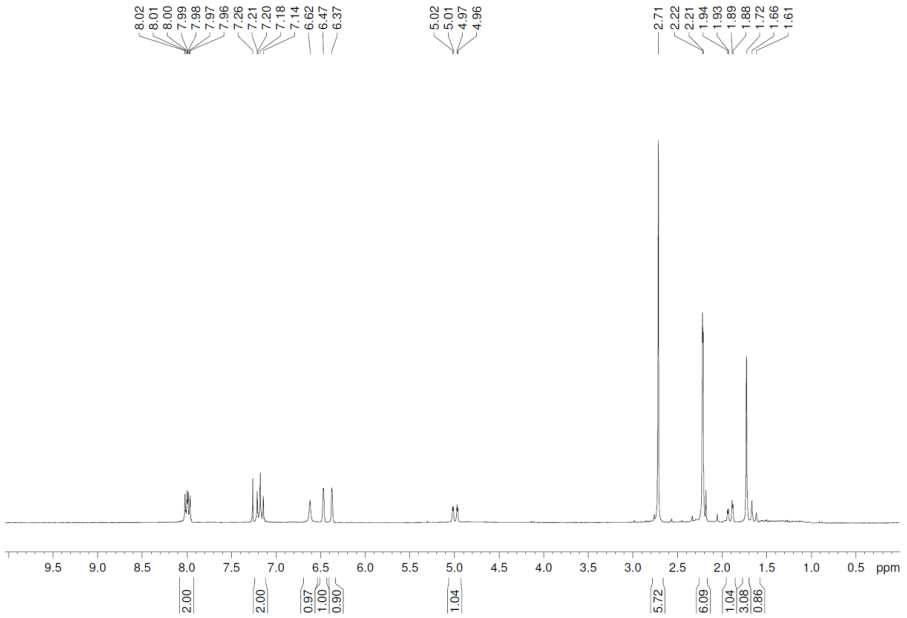
3e

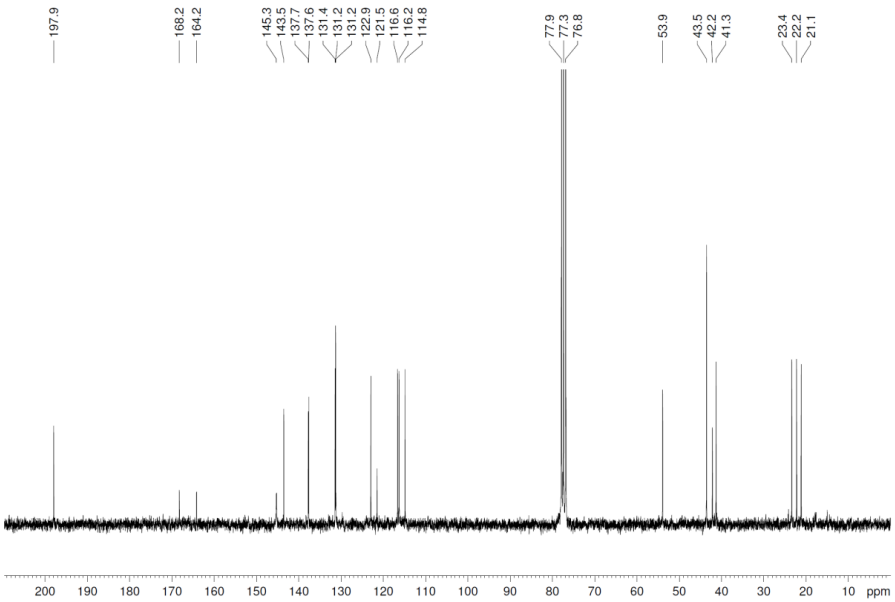

7.97
7.94
7.94
7.61
7.58
7.53
7.51
7.50
7.47
6.82
6.75
6.55
5.16
5.11
4.57
2.73
2.22
2.21
2.17
2.10
2.04
1.68
1.64
1.98
1.04
2.08
0.98
0.98
0.97
0.97
0.89
5.98
6.23
0.91
4.48
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

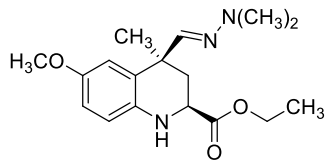

199.7
143.9
138.2
134.8
133.7
129.7
129.0
128.5
126.4
126.2
123.4
77.7
77.3
76.7
54.4
43.5
41.1
39.0
31.1
26.3
20.6
17.7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CH3
CH3
N
N(CH3)2
F
H3C
N
H
O

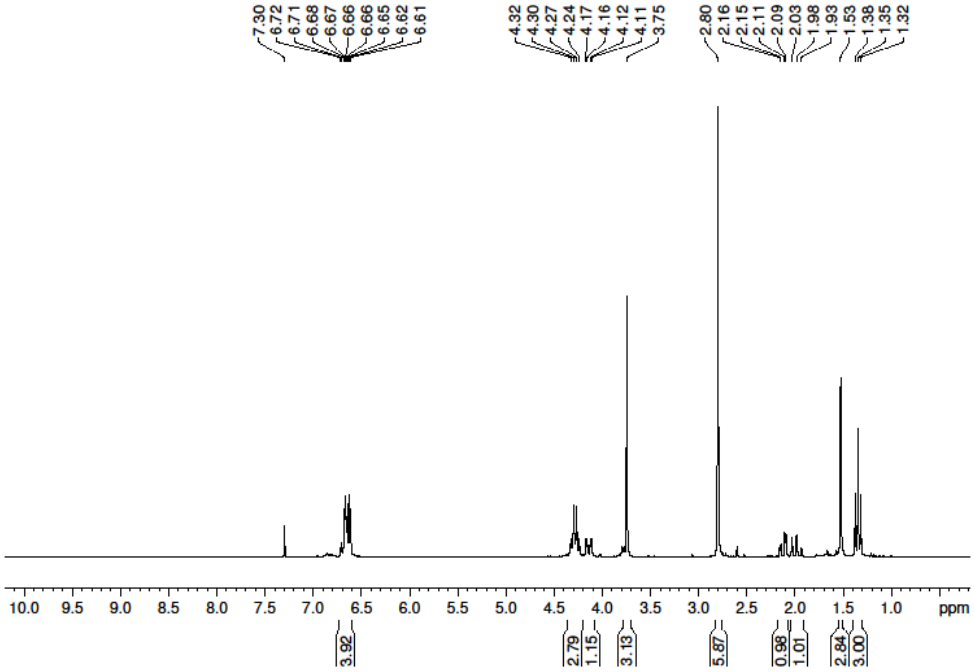
3f

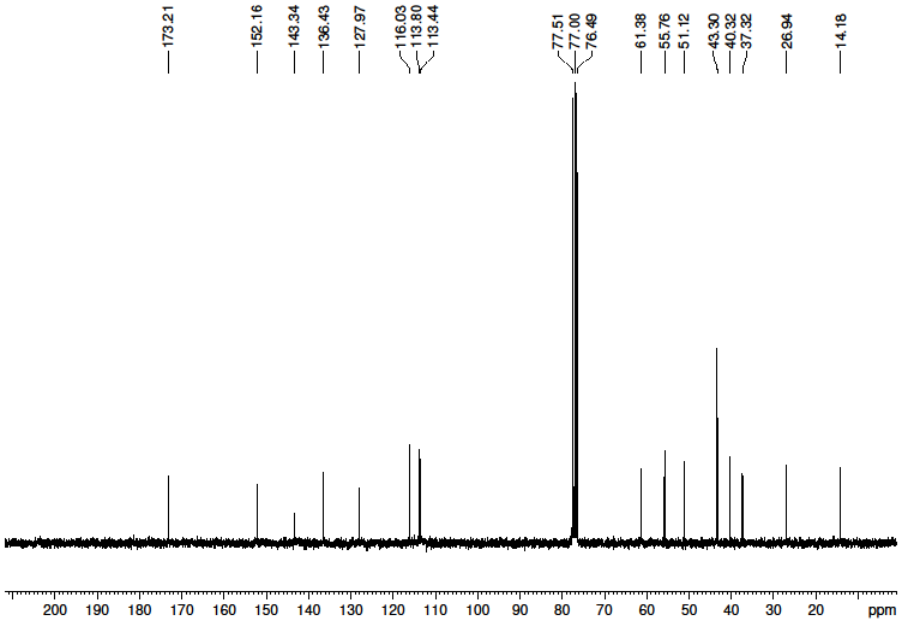

8.02
8.01
8.00
7.99
7.98
7.97
7.96
7.26
7.21
7.20
7.18
7.14
6.62
6.47
6.37
5.02
5.01
4.97
4.96
2.71
2.22
2.21
1.94
1.93
1.89
1.88
1.72
1.66
1.61
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.00
0.97
1.00
0.90
1.04
5.72
6.09
1.04
3.08
0.86

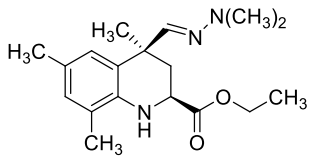

197.9
168.2
164.2
145.3
143.5
137.7
137.6
131.4
131.2
131.2
122.9
121.5
116.6
116.2
114.8
77.9
77.3
76.8
53.9
43.5
42.2
41.3
23.4
22.2
21.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


N(CH3)2
CH3
H3CO
N
H
O
O
CH3

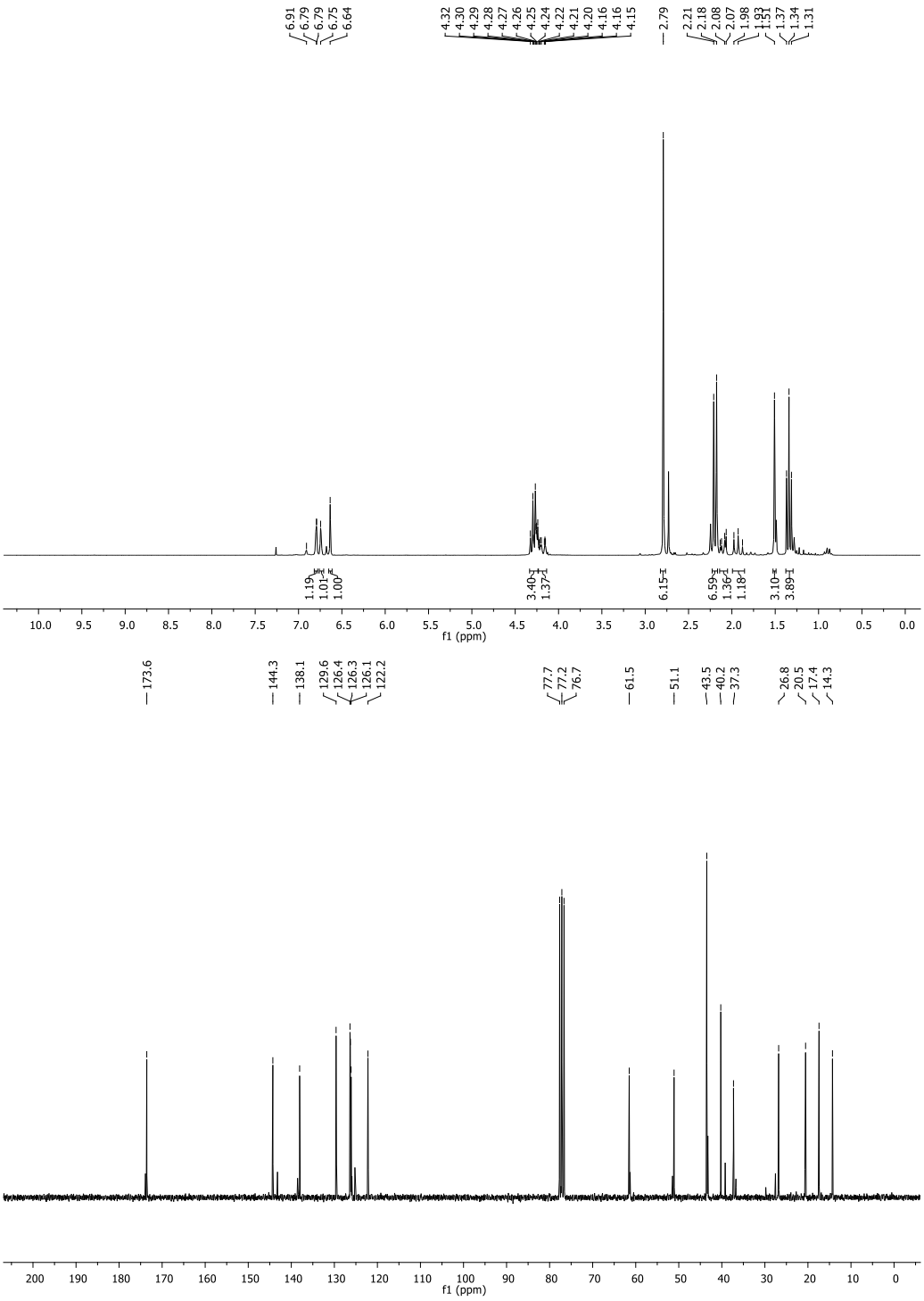
3g

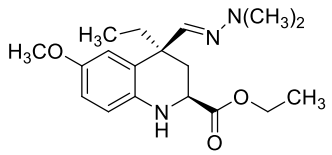

7.30
6.72
6.71
6.68
6.67
6.66
6.66
6.66
6.65
6.62
6.61
4.32
4.30
4.27
4.24
4.17
4.16
4.12
4.11
3.75
2.80
2.16
2.15
2.11
2.09
2.03
1.98
1.93
1.53
1.38
1.35
1.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.92
2.79
1.15
3.13
5.87
0.98
1.01
2.84
3.00


173.21
152.16
143.34
136.43
127.97
116.03
113.80
113.44
77.51
77.00
76.49
61.38
55.76
51.12
43.30
40.32
37.32
26.94
14.18
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

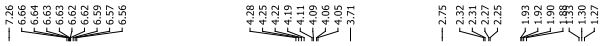

H3C
N(CH3)2
N
H3C
N
H
O
O
CH3
CH3

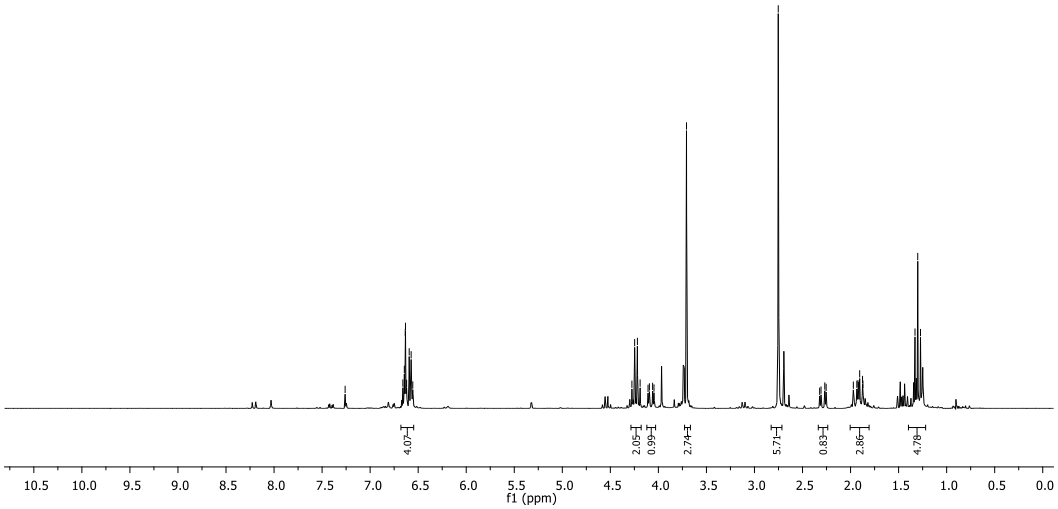
3h


6.91
6.79
6.79
6.75
6.64
4.32
4.30
4.29
4.28
4.27
4.26
4.25
4.24
4.22
4.21
4.20
4.16
4.16
4.15
2.79
2.21
2.18
2.08
2.07
1.98
1.93
1.51
1.37
1.34
1.31
1.19
1.01
1.00
3.40
1.37
6.15
6.59
1.36
1.18
3.10
3.89
f1 (ppm)
173.6
144.3
138.1
129.6
126.4
126.3
126.1
122.2
77.7
77.2
76.7
61.5
51.1
43.5
40.2
37.3
26.8
20.5
17.4
14.3
f1 (ppm)

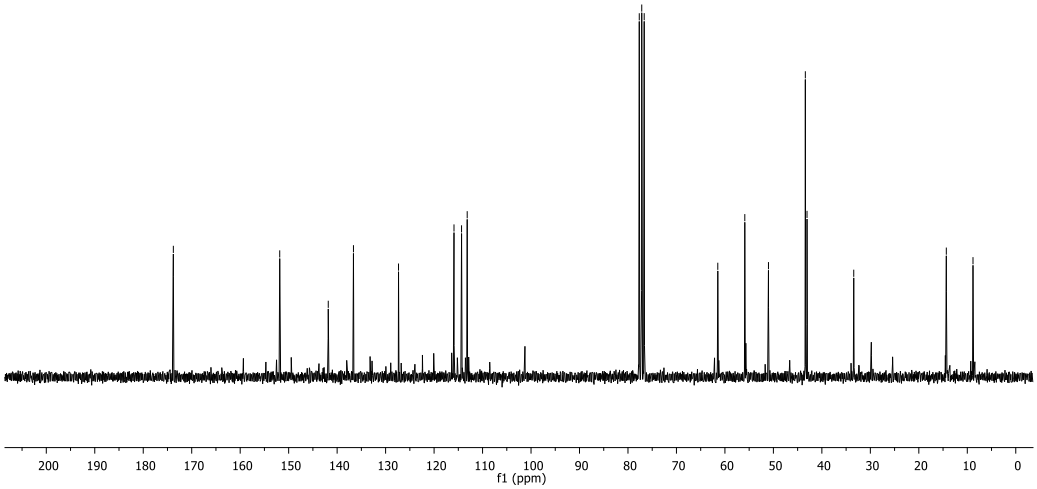

H3C
N(CH3)2
N
H3CO
N
H
O
O
CH3
O

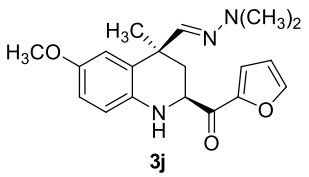
3i


7.26
6.66
6.64
6.63
6.62
6.62
6.59
6.57
6.56
4.28
4.25
4.22
4.19
4.11
4.09
4.06
4.05
3.71
2.75
2.32
2.31
2.27
2.25
1.93
1.92
1.90
1.88
1.33
1.30
1.27

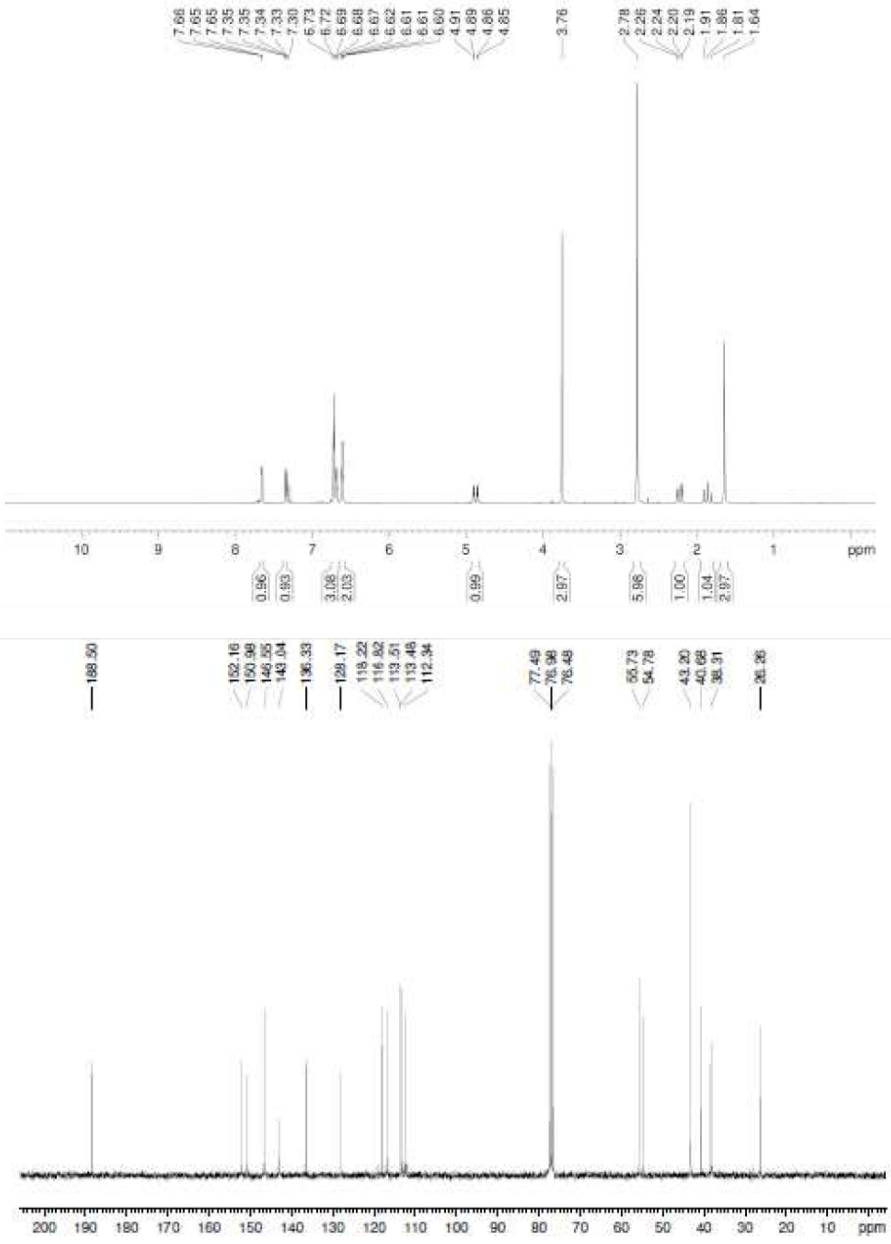

4.07
2.05
0.99
2.74
5.71
0.83
2.86
4.78
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

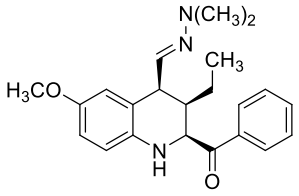

173.8
151.8
141.8
136.6
127.3
115.9
114.3
113.2
77.7
77.2
76.7
61.5
55.9
51.0
43.4
43.1
33.4
14.3
8.8


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


H3C
N(CH3)2
H3CO
N
H
O
O

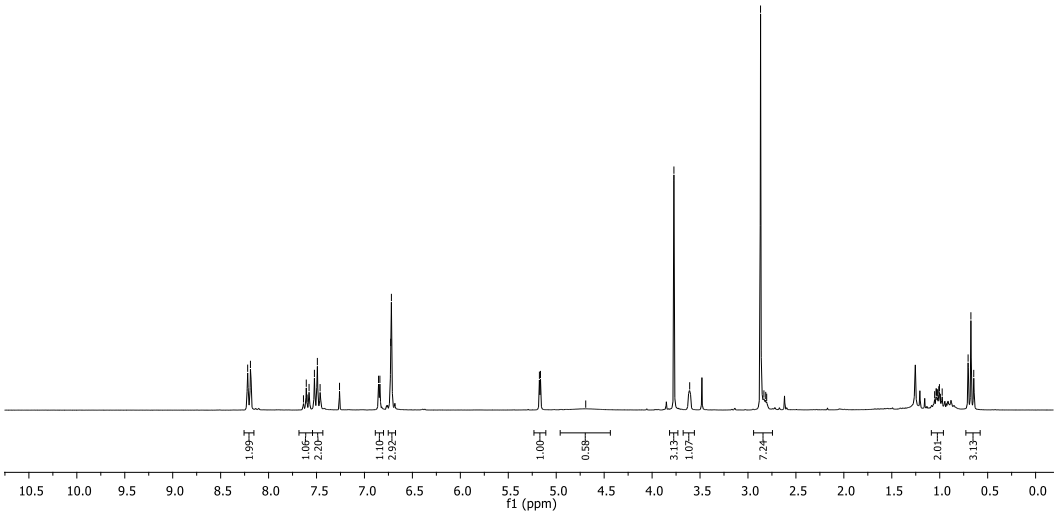
3j

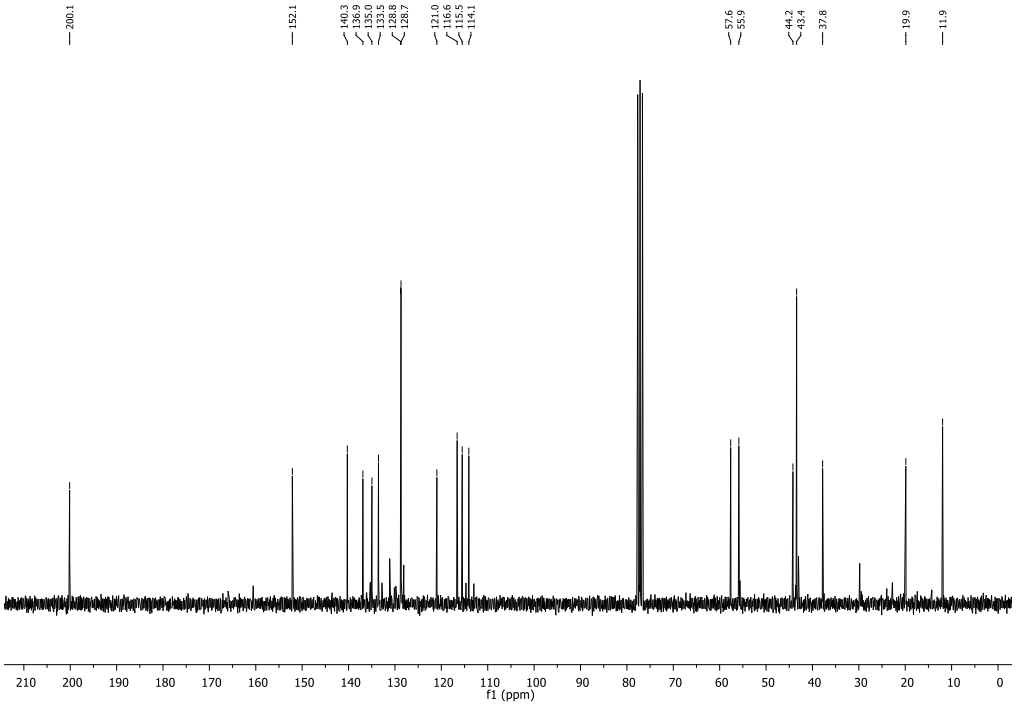

7.66
7.65
7.65
7.35
7.35
7.34
7.33
7.30
6.73
6.72
6.69
6.68
6.67
6.62
6.61
6.61
6.60
4.91
4.89
4.86
4.85
3.76
2.78
2.26
2.24
2.20
2.19
1.91
1.86
1.81
1.64
10
9
8
7
6
5
4
3
2
1
ppm
0.96
0.93
3.08
2.03
0.99
2.97
5.96
1.00
1.04
2.97
188.50
152.16
150.98
146.55
143.04
136.33
129.17
118.22
116.82
113.51
113.48
112.34
77.49
76.98
76.48
55.73
54.78
43.20
40.68
38.91
26.26
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

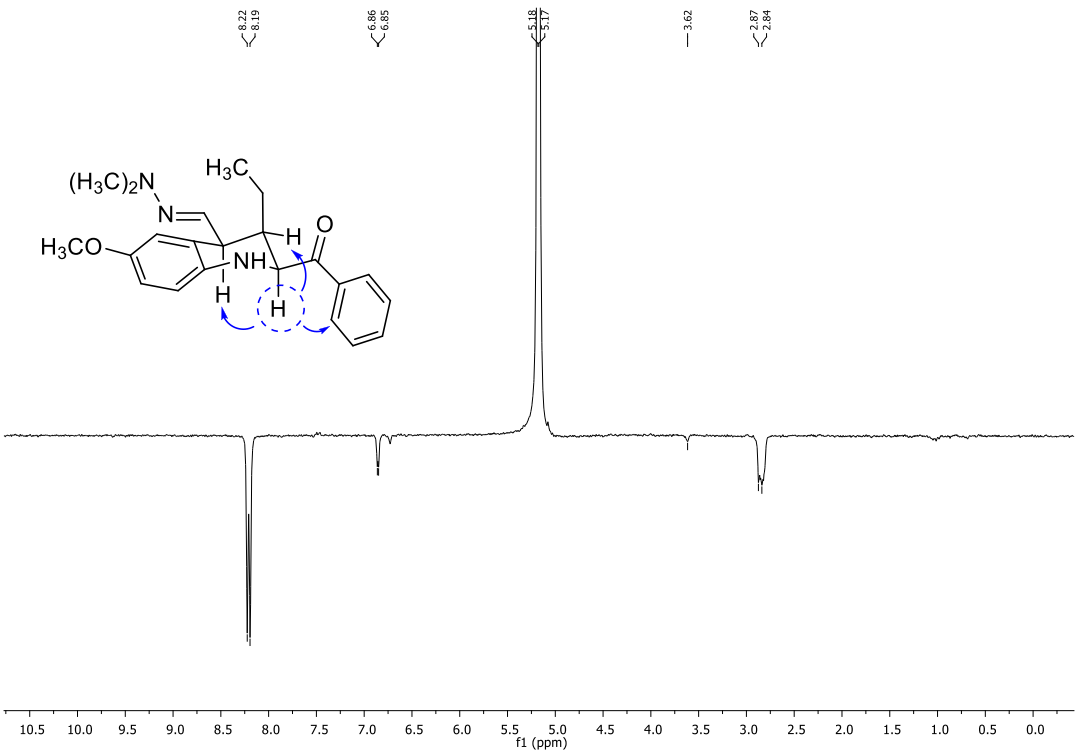

N(CH3)2
N
CH3
H3CO
N
H
O

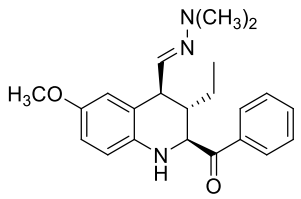
3ka


8.22
8.19
7.61
7.60
7.58
7.52
7.49
7.46
6.84
6.73
6.72
5.18
5.16
4.69
3.77
3.61
2.87
2.83
2.81
2.80
1.05
1.04
1.03
1.02
1.01
1.00
0.99
0.97
0.70
0.67
0.65

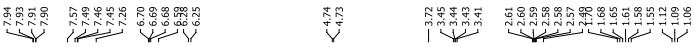

1.99
1.06
2.20
1.10
2.92
1.00
0.58
3.13
1.07
7.24
2.01
3.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

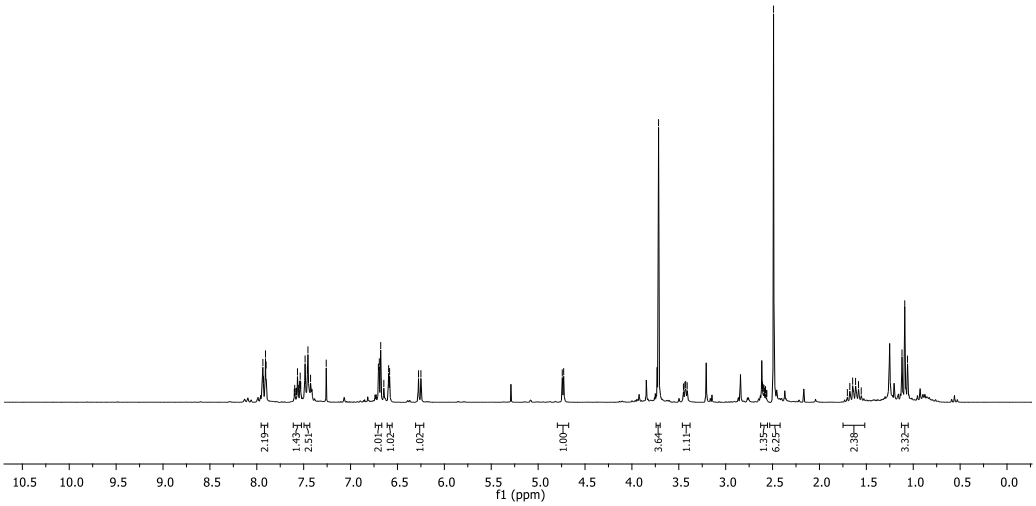

200.1
152.1
140.3
136.9
135.0
133.5
128.8
128.7
121.0
116.6
115.5
114.1
57.6
55.9
44.2
43.4
37.8
19.9
11.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

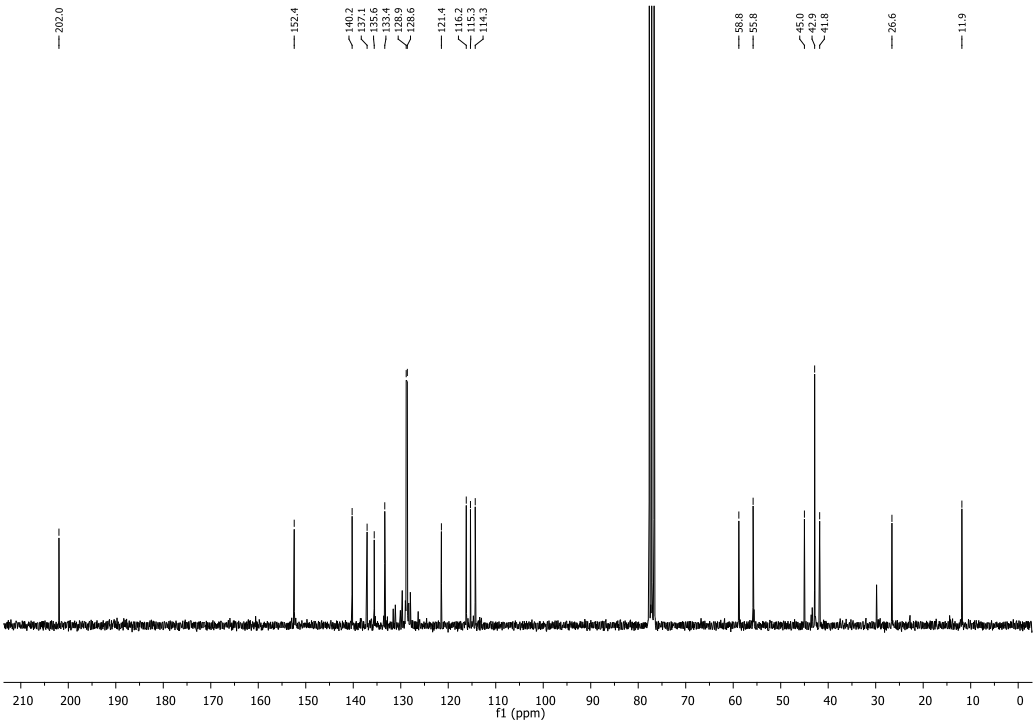

8.22
8.19
6.86
6.85
5.18
5.17
3.62
2.87
2.84
(H3C)2N
N
H3C
H3CO
NH
H
O
H
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

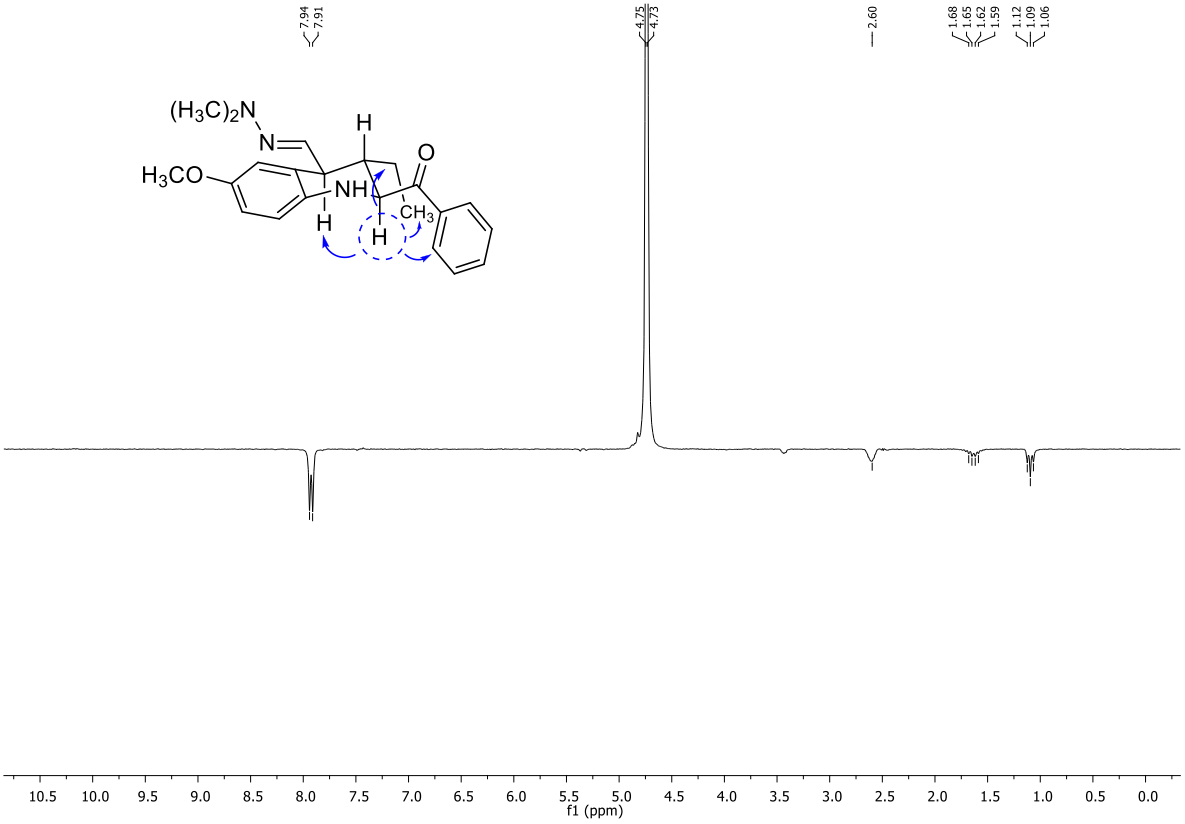

N(CH3)2
N
H3CO
N
H
O

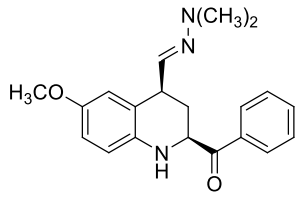
3kb


7.94
7.93
7.91
7.90
7.57
7.49
7.46
7.45
7.26
6.70
6.69
6.68
6.58
6.56
6.25
4.74
4.73
3.72
3.45
3.44
3.43
3.41
2.61
2.60
2.59
2.58
2.58
2.57
2.40
1.68
1.65
1.61
1.58
1.55
1.12
1.09
1.06

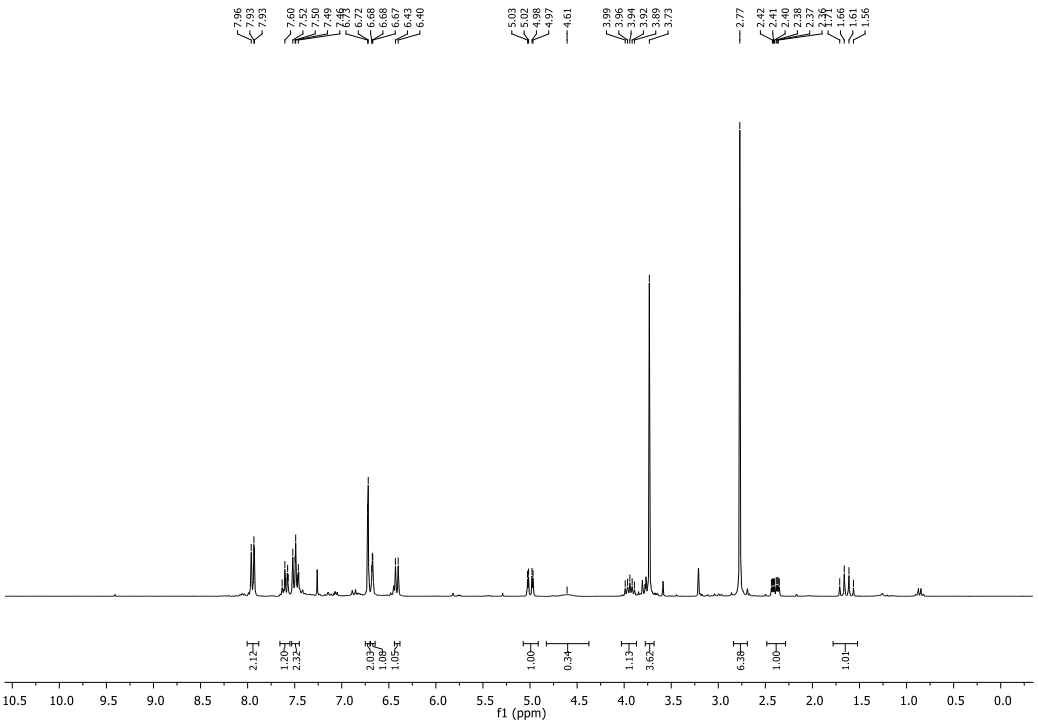

2.19
1.43
2.51
2.01
1.02
1.02
1.00
3.64
1.11
1.35
6.25
2.38
3.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

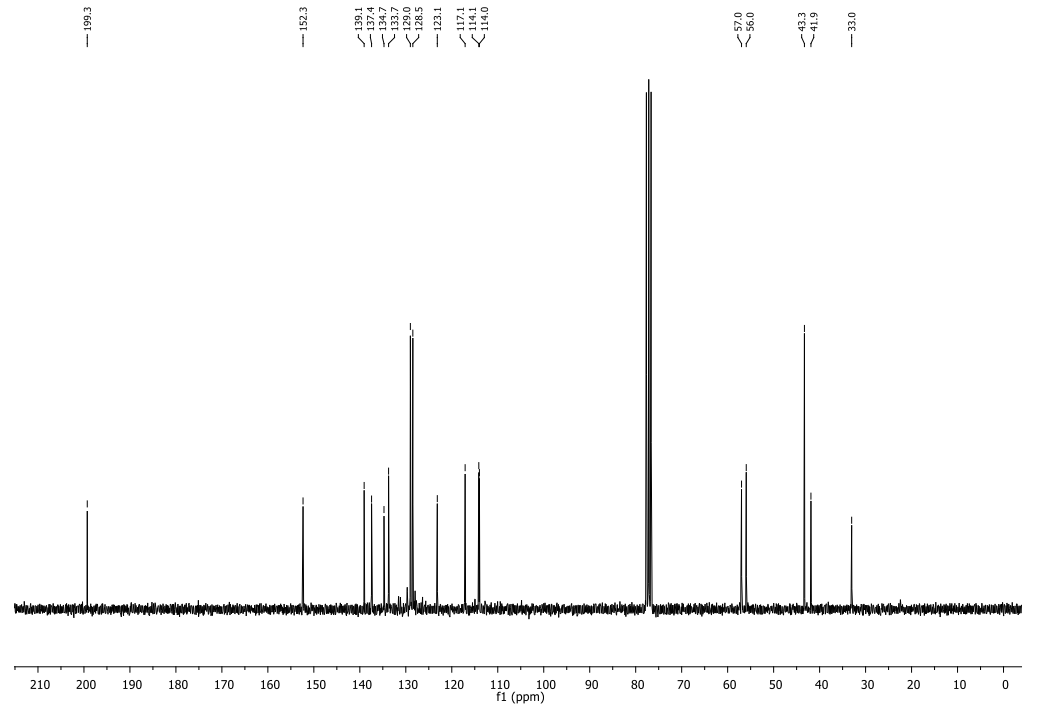

202.0
152.4
140.2
137.1
135.6
133.4
128.9
128.6
121.4
116.2
115.3
114.3
58.8
55.8
45.0
42.9
41.8
26.6
11.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

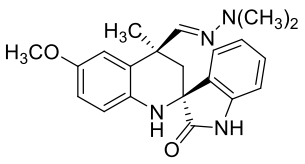

7.94
7.91
4.75
4.73
2.60
1.68
1.65
1.62
1.59
1.12
1.09
1.06
(H3C)2N
N
H
O
H3CO
NH
CH3
H
H
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


N(CH3)2
N
H3CO
N
H
O

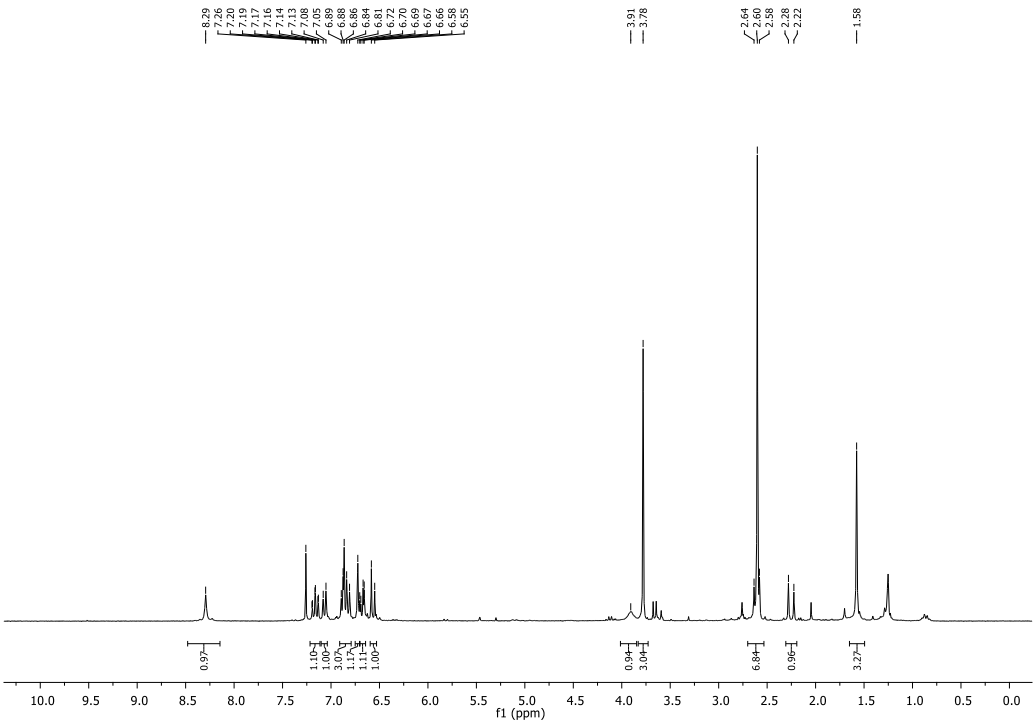
3l

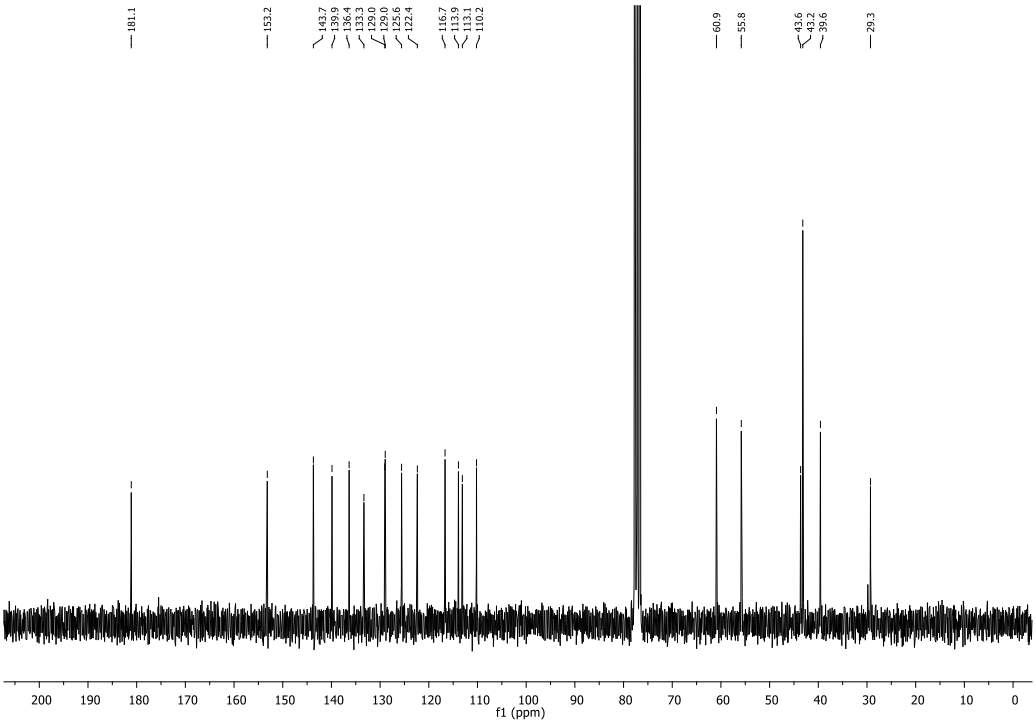

7.96
7.93
7.93
7.60
7.52
7.50
7.49
7.46
7.45
6.72
6.68
6.68
6.67
6.43
6.40
5.03
5.02
4.98
4.97
4.61
3.99
3.96
3.94
3.92
3.89
3.73
2.77
2.42
2.41
2.40
2.38
2.37
1.66
1.61
1.56
2.12
1.20
2.32
2.03
1.08
1.05
1.00
0.34
1.13
3.62
6.38
1.00
1.01
f1 (ppm)

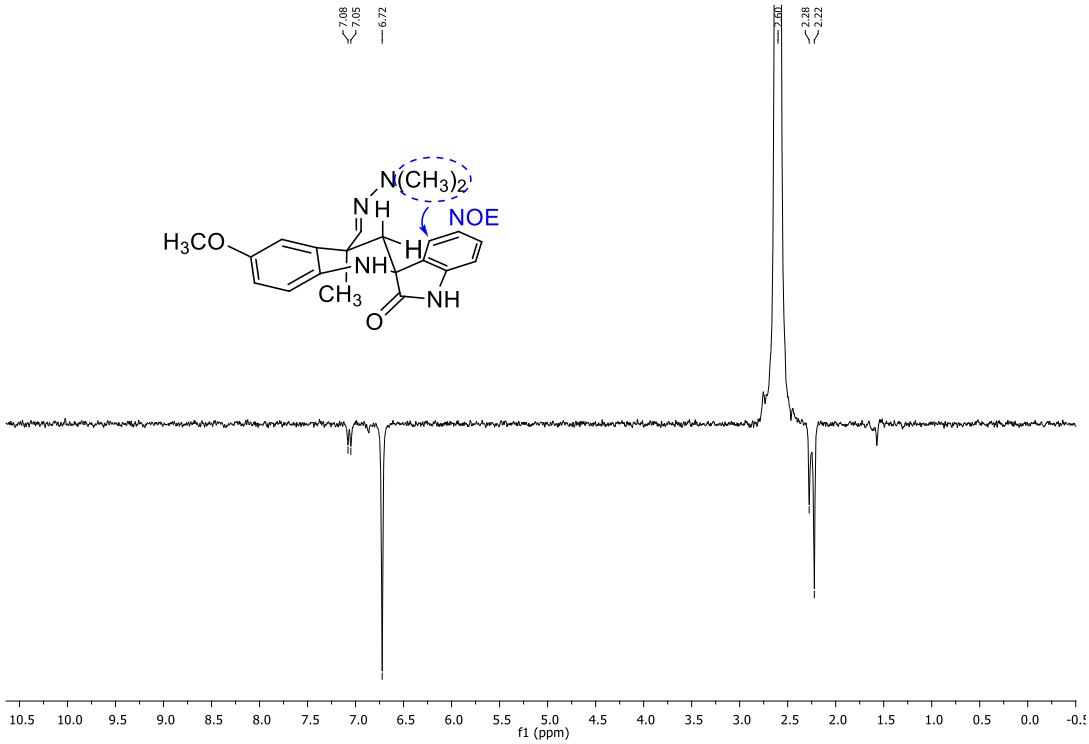

199.3
152.3
139.1
137.4
134.7
133.7
129.0
128.5
123.1
117.1
114.1
114.0
57.0
56.0
43.3
41.9
33.0
f1 (ppm)

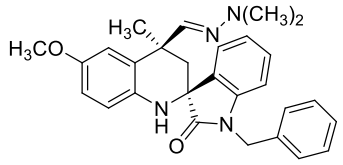

H3C
N(CH3)2
H3CO
N
H
NH
O

3n

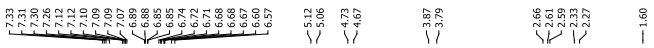

8.29
7.26
7.20
7.19
7.17
7.16
7.14
7.13
7.08
7.05
6.89
6.88
6.86
6.84
6.81
6.72
6.70
6.69
6.67
6.66
6.58
6.55
3.91
3.78
2.64
2.60
2.58
2.28
2.22
1.58
0.97
1.10
1.00
3.07
1.17
1.11
1.00
0.94
3.04
6.84
0.96
3.27
f1 (ppm)

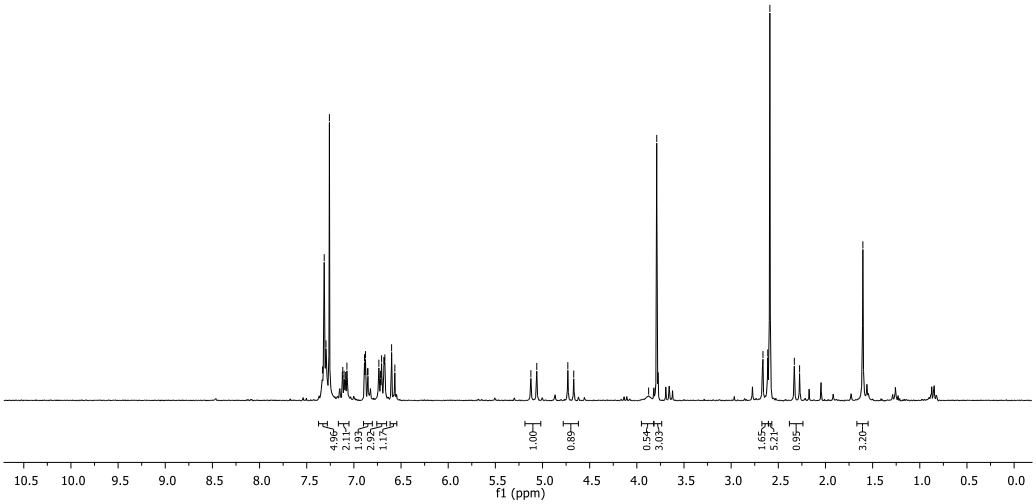

181.1
153.2
143.7
139.9
136.4
133.3
129.0
129.0
125.6
122.4
116.7
113.9
113.1
110.2
60.9
55.8
43.6
43.2
39.6
29.3
f1 (ppm)

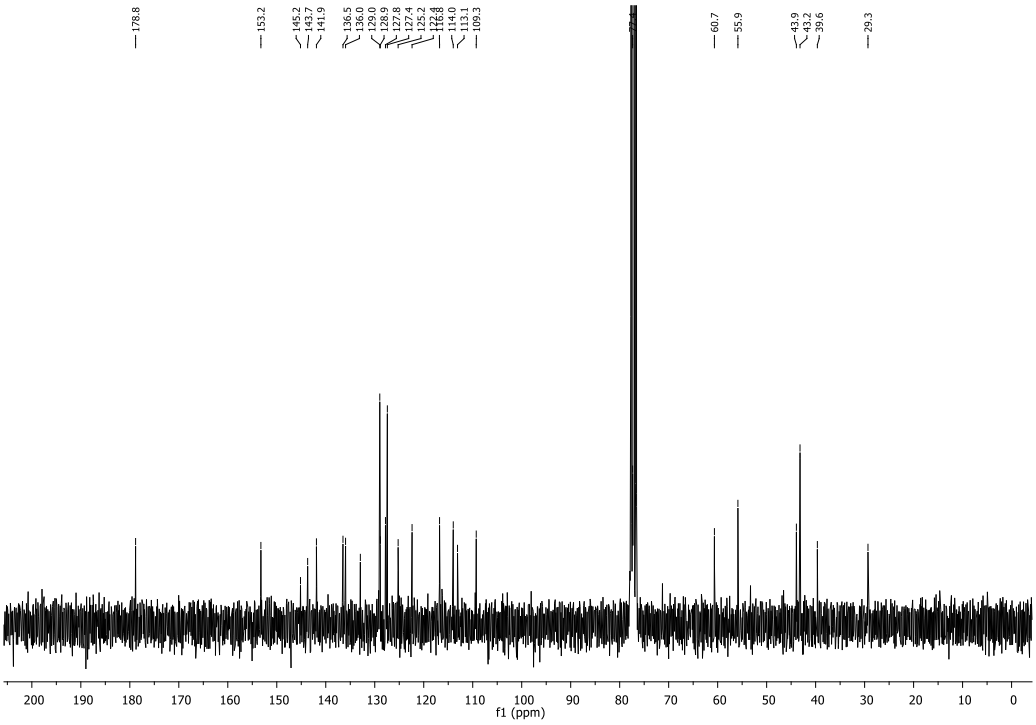

7.08
7.05
6.72
2.28
2.22
N(CH3)2
NH
NOE
H3CO
H
NH
CH3
NH
O
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

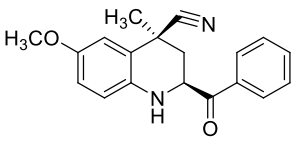

H3C
N(CH3)2
H3CO
N
H
O
N

3o


7.33
7.31
7.30
7.26
7.12
7.10
7.09
7.09
7.07
6.89
6.88
6.85
6.85
6.74
6.72
6.71
6.68
6.68
6.67
6.60
6.57
5.12
5.06
4.73
4.67
3.87
3.79
2.66
2.61
2.59
2.33
2.27
1.60

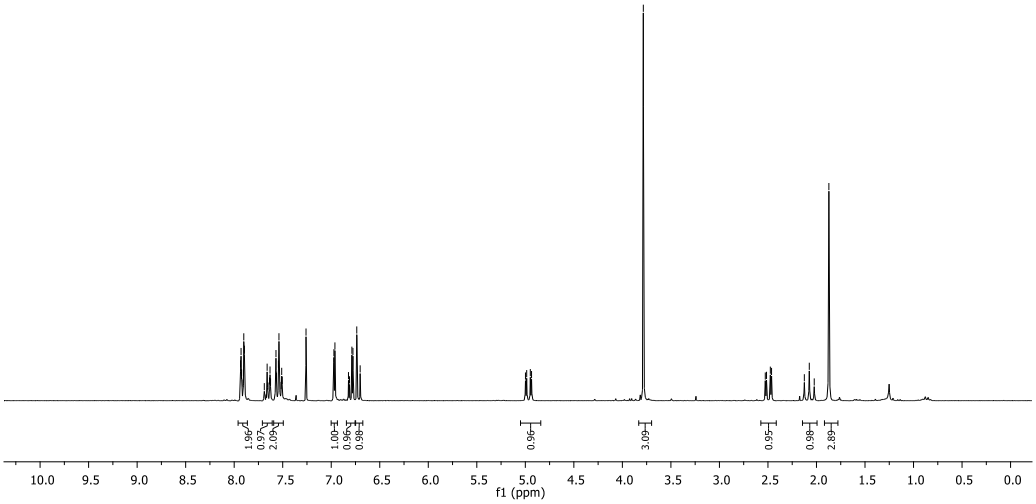

4.96
2.14
1.93
2.92
1.17
1.00
0.89
0.54
3.03
1.65
5.21
0.95
3.20
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

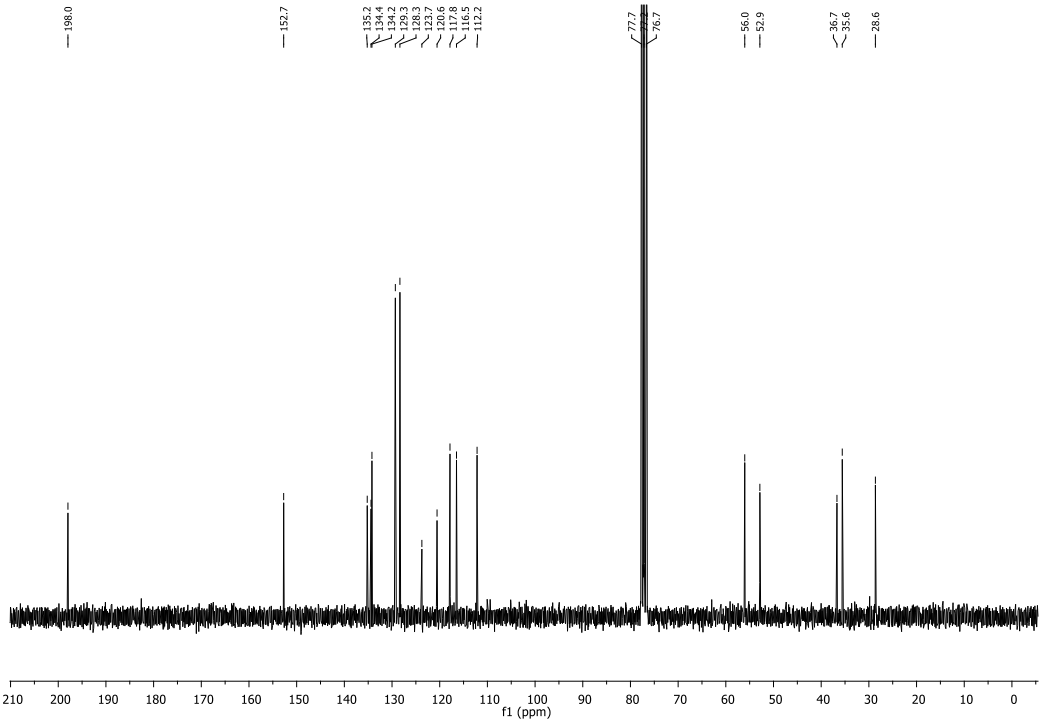

178.8
153.2
145.2
143.7
141.9
136.5
136.0
129.0
128.9
127.8
127.4
125.2
122.8
114.0
113.1
109.3
60.7
55.9
43.9
43.2
39.6
29.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

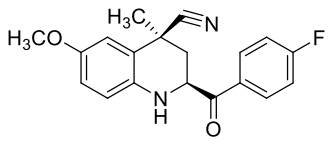

H3C
N
H3CO
N
H
O

6a

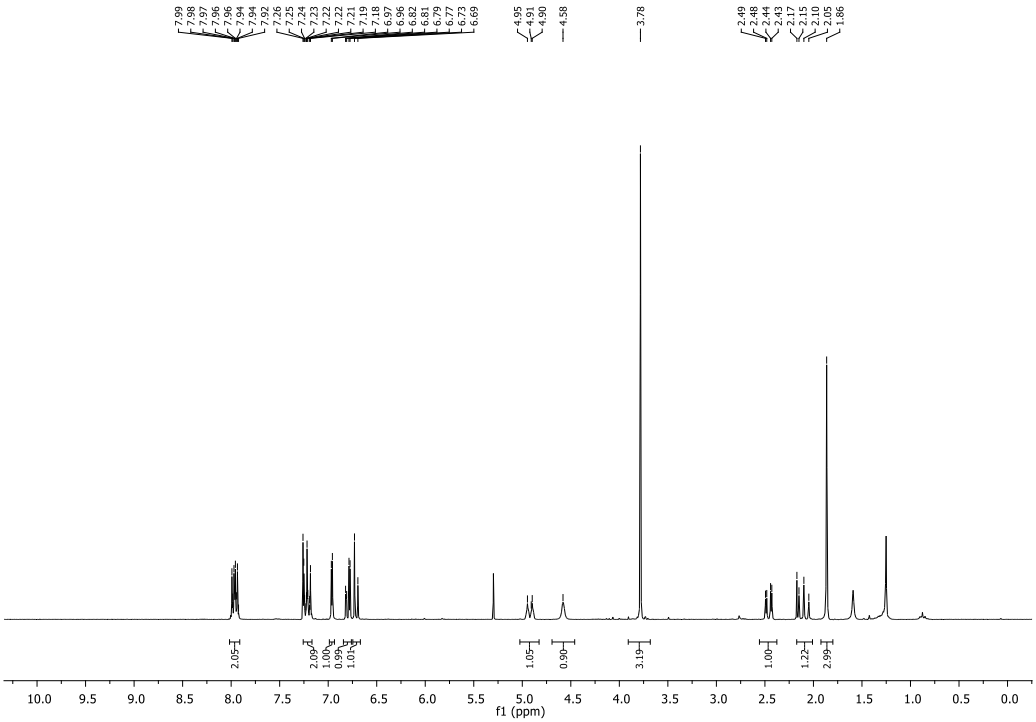

7.93
7.93
7.92
7.91
7.90
7.90
7.69
7.66
7.65
7.64
7.63
7.63
7.57
7.56
7.54
7.54
7.52
7.51
7.51
7.26
6.97
6.96
6.82
6.81
6.79
6.78
6.74
6.70
5.00
4.99
4.95
4.94
3.78
2.53
2.51
2.48
2.46
2.13
2.07
2.02
1.87

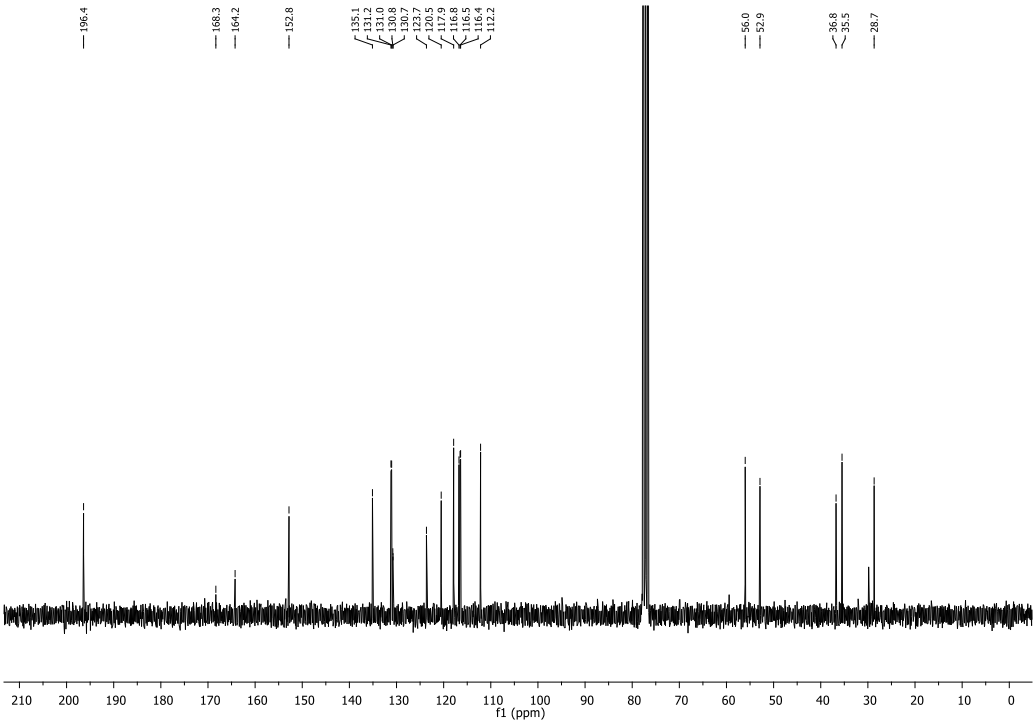

1.96
0.97
2.09
1.00
0.96
0.98
0.96
3.09
0.95
0.98
2.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

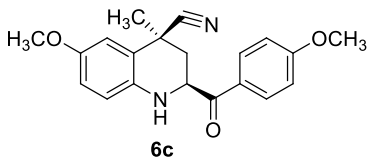

198.0
152.7
135.2
134.4
134.2
129.3
128.3
123.7
120.6
117.8
116.5
112.2
77.7
76.7
56.0
52.9
36.7
35.6
28.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



6b

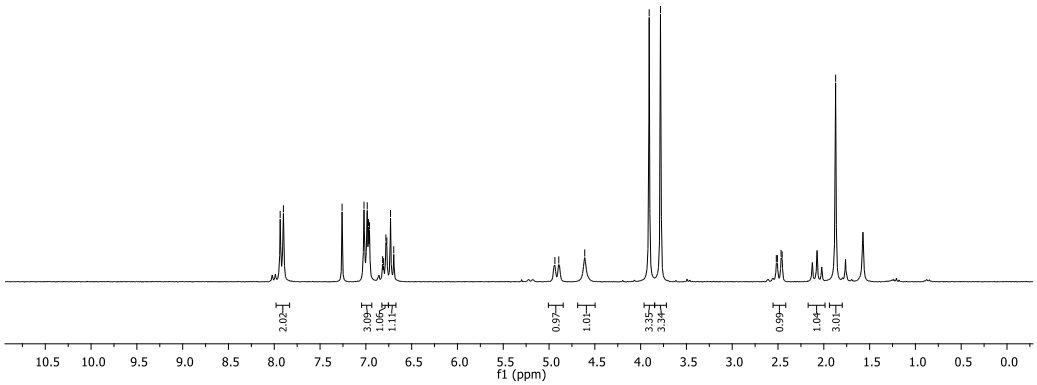


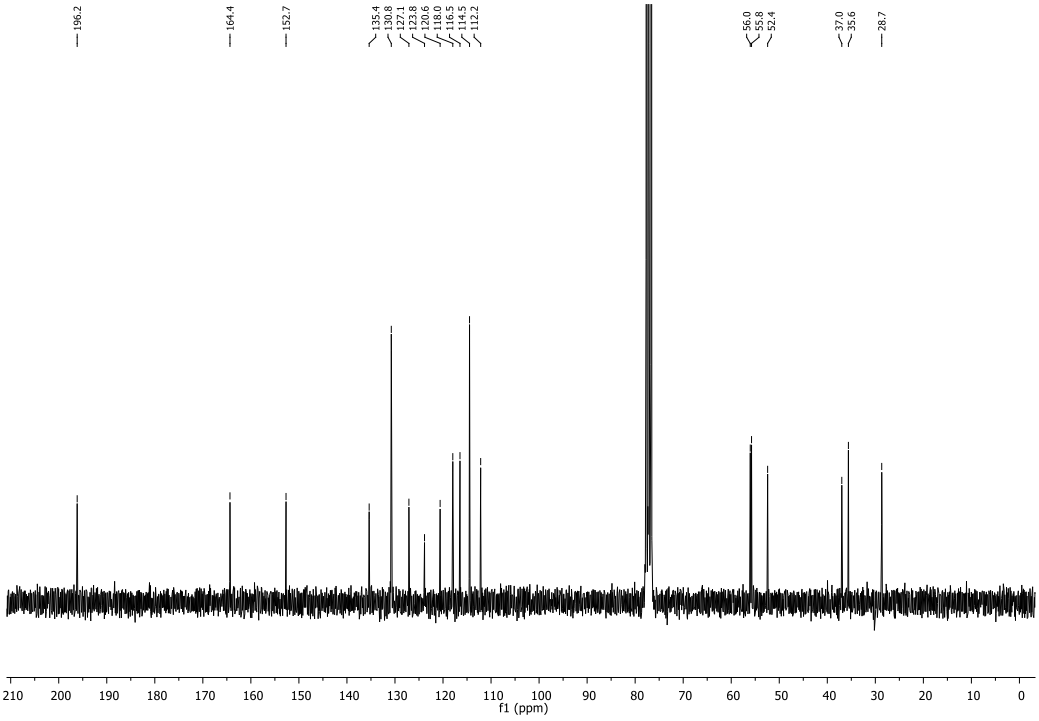


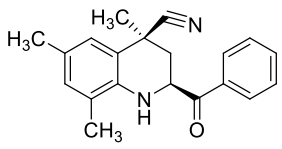

H3C
N
H3CO
OCH3
N
H
O

6c

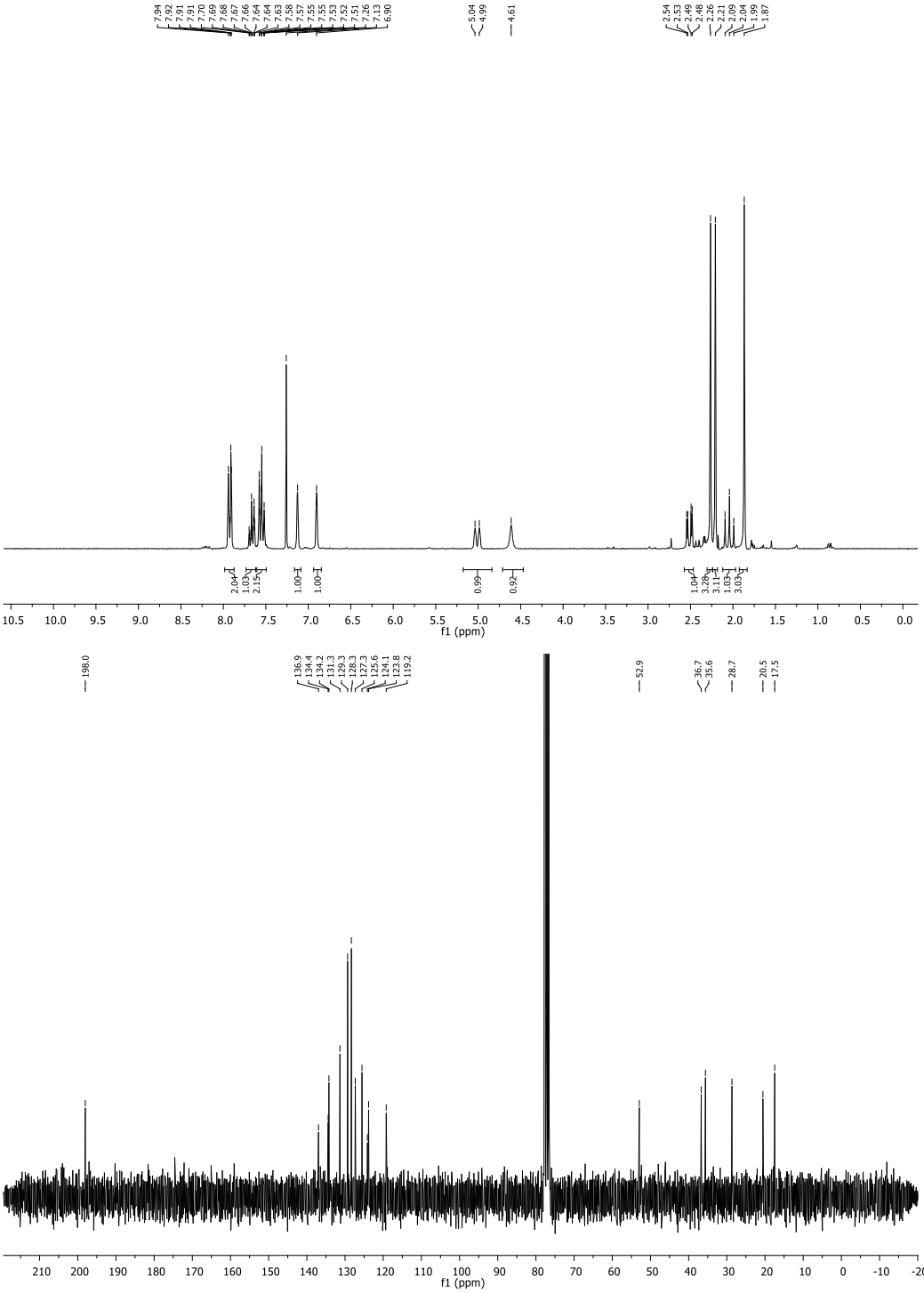

7.94
7.90
7.26
7.02
6.98
6.97
6.96
6.82
6.81
6.78
6.77
6.73
6.70
4.94
4.89
4.61
3.91
3.78
2.52
2.51
2.47
2.45
1.87

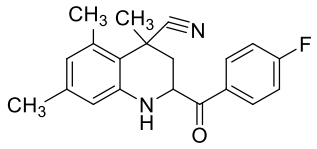

2.02
3.09
1.06
1.11
0.97
1.01
3.35
3.34
0.99
1.04
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.2
164.4
152.7
135.4
130.8
127.1
123.8
120.6
118.0
116.5
114.5
112.2
56.0
55.8
52.4
37.0
35.6
28.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

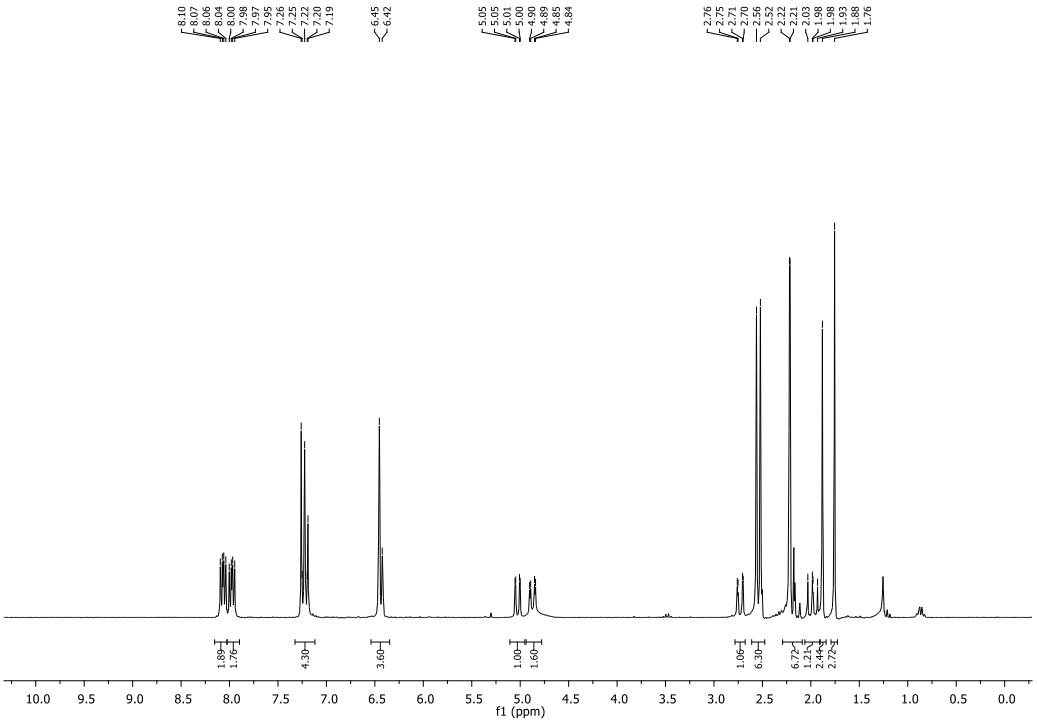


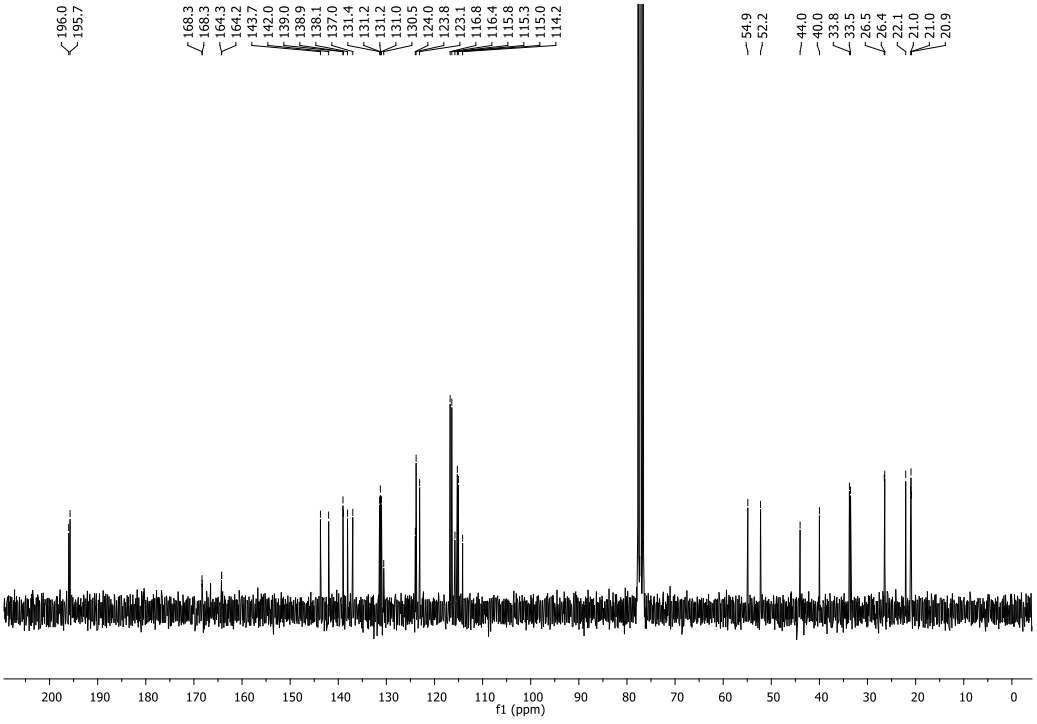
6e

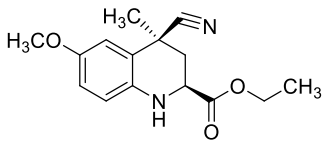

7.94
7.92
7.91
7.91
7.70
7.69
7.68
7.67
7.66
7.64
7.63
7.58
7.57
7.55
7.55
7.53
7.52
7.51
7.26
7.13
6.90
5.04
4.99
4.61
2.54
2.53
2.49
2.48
2.26
2.21
2.09
2.04
1.99
1.87
2.04
1.05
2.15
1.00
1.00
0.99
0.92
1.04
3.28
3.11
1.03
3.03
f1 (ppm)
198.0
136.9
134.4
134.2
131.1
129.3
128.3
127.3
125.6
124.1
123.8
119.2
52.9
36.7
35.6
28.7
20.5
17.5
f1 (ppm)


CH3
CH3
N
F
CH3
N
H
O

6f

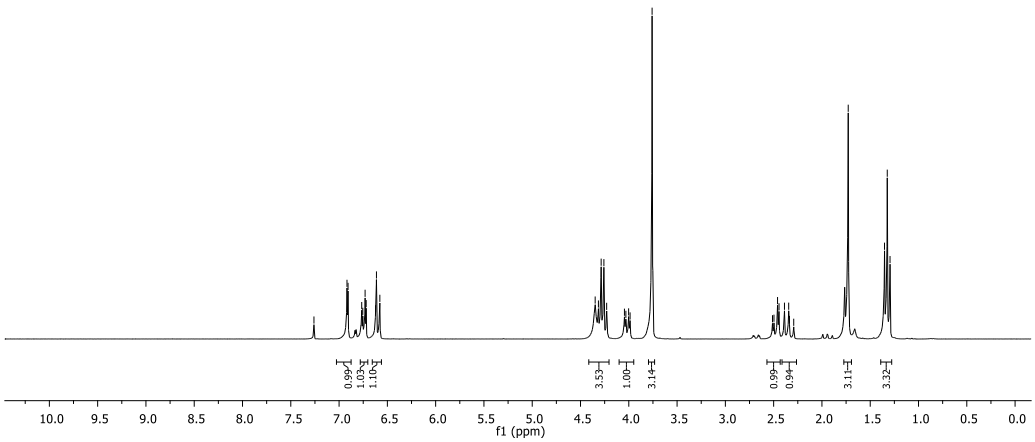

8.10
8.07
8.06
8.04
8.00
7.98
7.97
7.95
7.26
7.25
7.22
7.20
7.19
6.45
6.42
5.05
5.05
5.01
5.00
4.90
4.89
4.85
4.84
2.76
2.75
2.71
2.70
2.56
2.52
2.22
2.21
2.03
1.98
1.98
1.93
1.88
1.76
1.89
1.76
4.30
3.60
1.00
1.60
1.06
6.30
6.72
1.72
2.44
2.72
f1 (ppm)

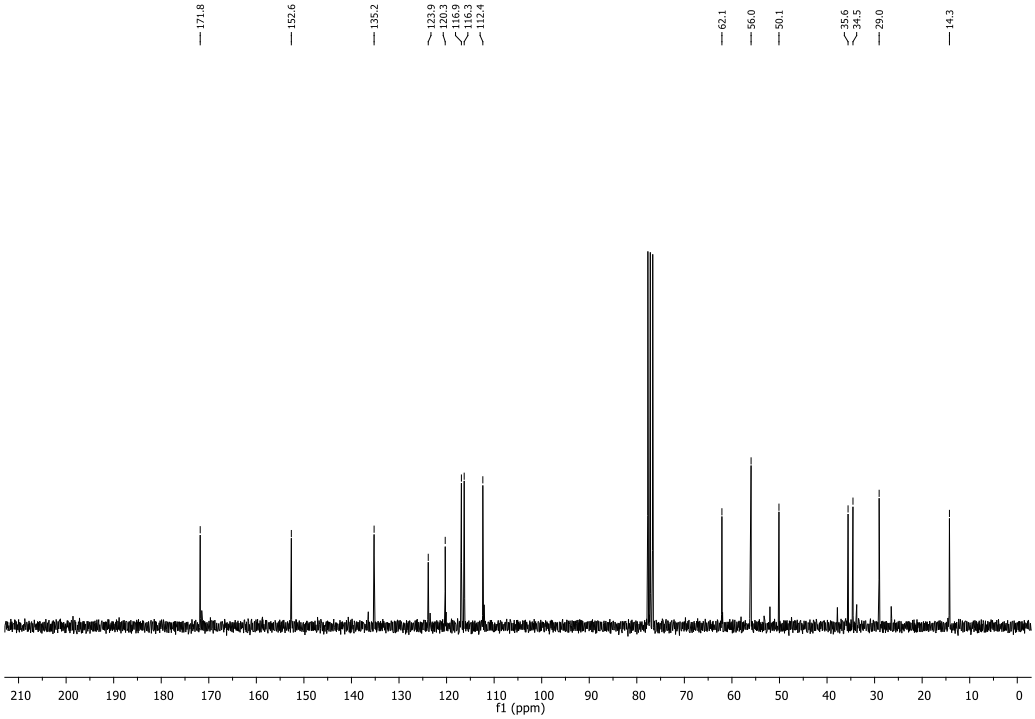

196.0
195.7
168.3
168.3
164.3
164.2
143.7
142.0
139.0
138.9
138.1
137.0
131.4
131.2
131.2
131.0
130.5
124.0
123.8
123.1
116.8
116.4
115.8
115.3
115.0
114.2
54.9
52.2
44.0
40.0
33.8
33.5
26.5
26.4
22.1
21.0
21.0
20.9
f1 (ppm)

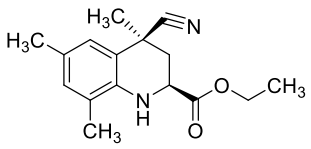

H3C
N
H3CO
O
CH3
N
H
O

6g

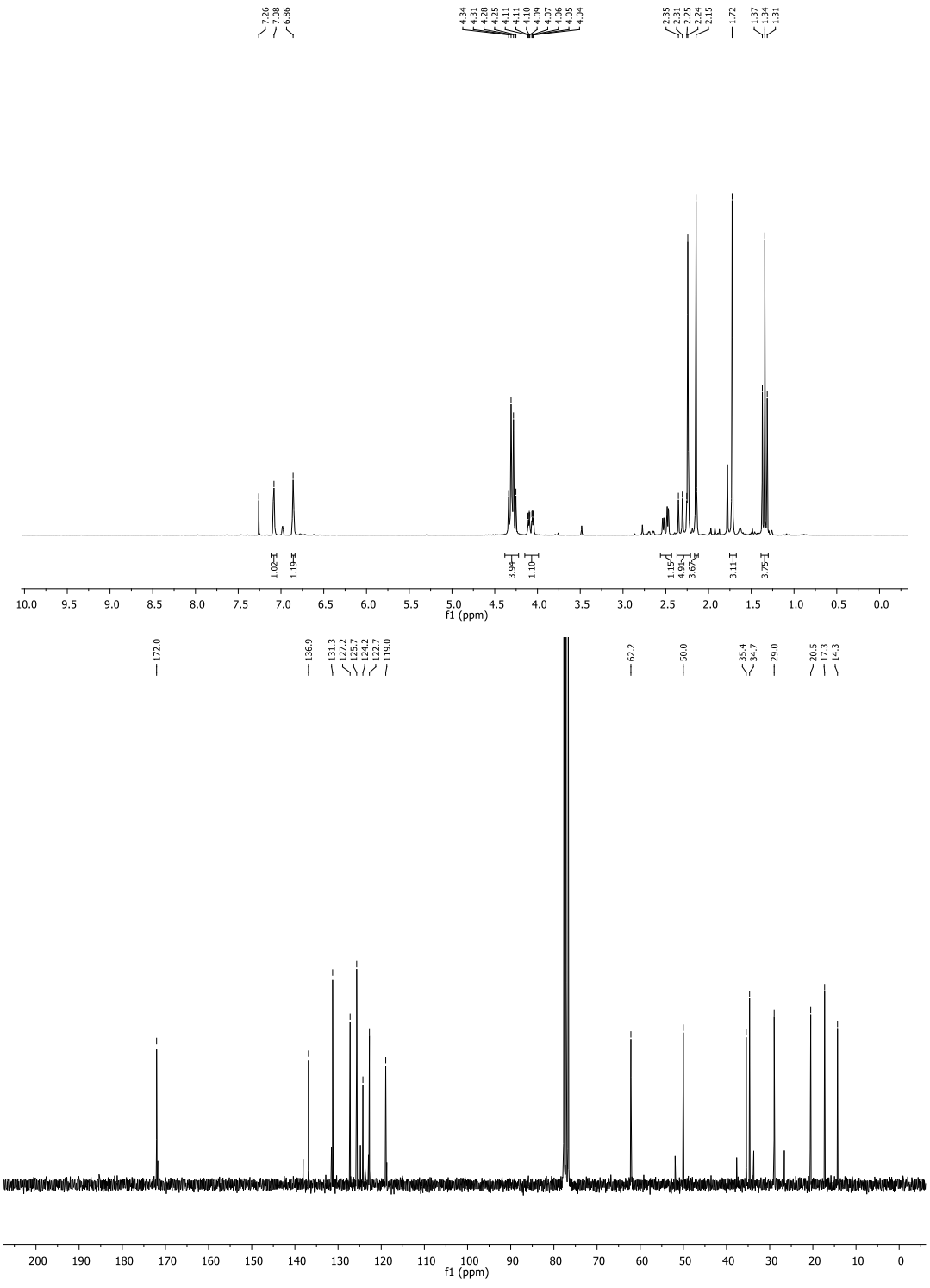

7.26
6.92
6.91
6.77
6.75
6.73
6.72
6.62
6.61
6.58
4.35
4.31
4.29
4.26
4.23
4.05
4.03
4.00
3.99
3.76
2.51
2.50
2.46
2.44
2.39
2.34
2.34
2.29
1.73
1.35
1.32
1.29

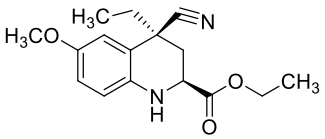

0.99
1.03
1.10
3.53
1.00
3.14
0.99
0.94
3.11
3.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.8
152.6
135.2
123.9
120.3
116.9
116.3
112.4
62.1
56.0
50.1
35.6
34.5
29.0
14.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

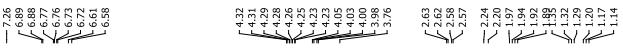


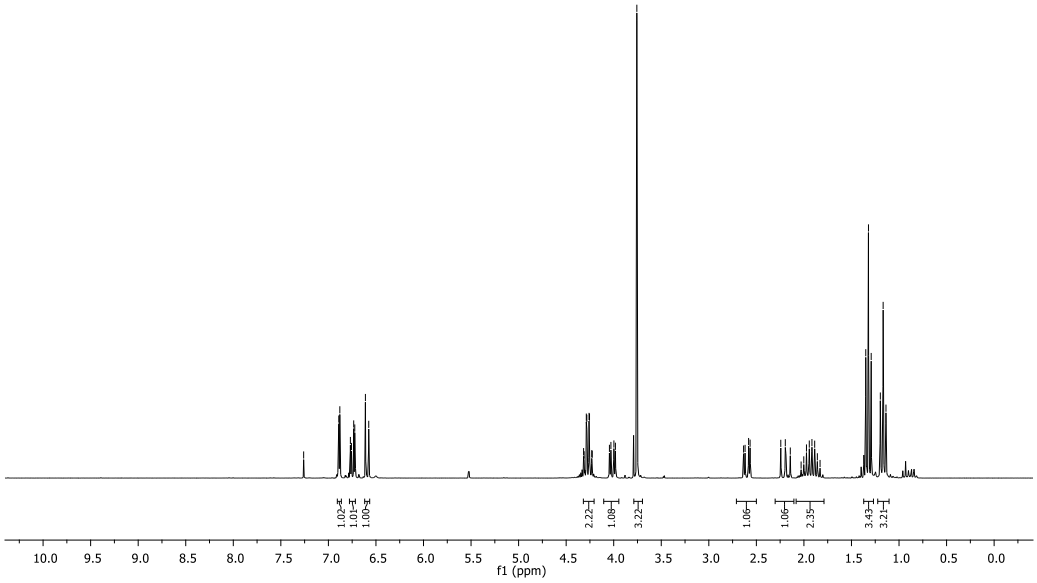
6h

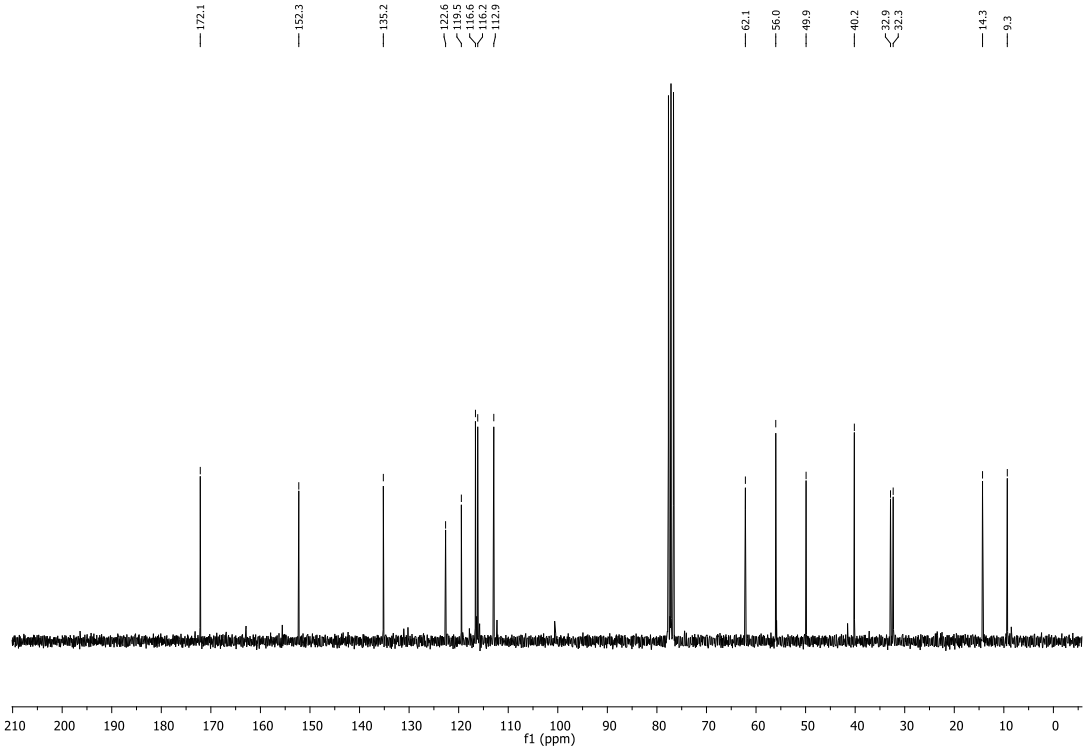


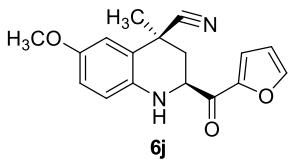


6i

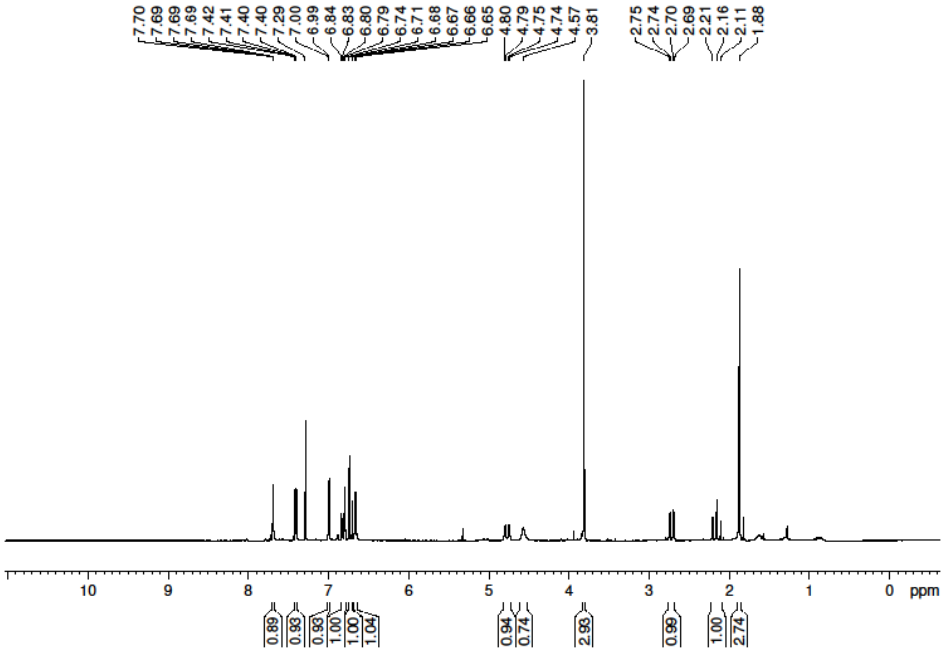


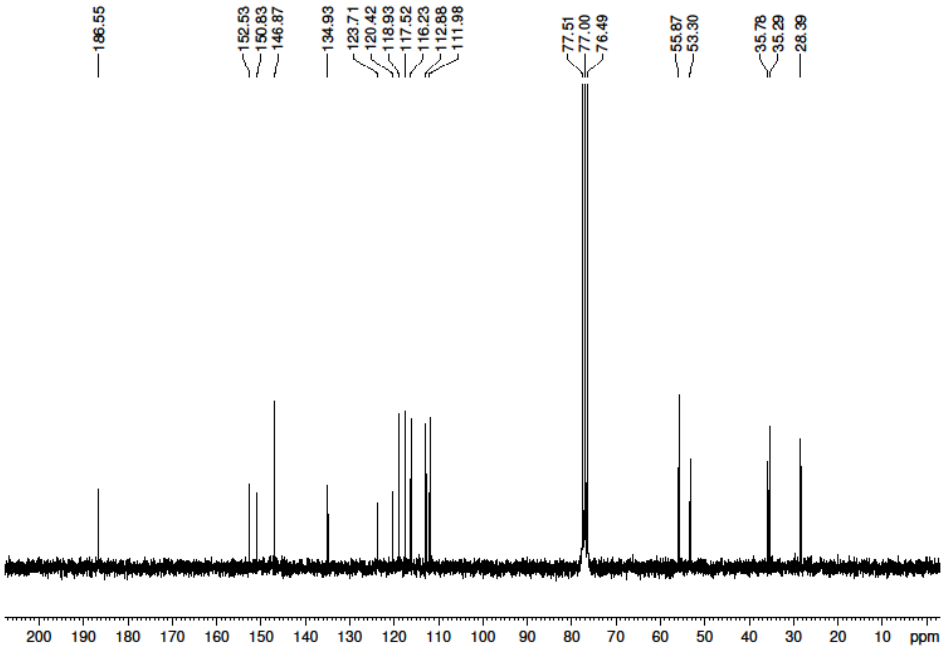





H3C
N
H3CO
N
H
O
O

6j


7.70
7.69
7.69
7.69
7.42
7.41
7.40
7.40
7.29
7.00
6.99
6.84
6.83
6.80
6.79
6.74
6.71
6.68
6.67
6.66
6.65
4.80
4.79
4.75
4.74
4.57
3.81
2.75
2.74
2.70
2.69
2.21
2.16
2.11
1.88
10 9 8 7 6 5 4 3 2 1 0 ppm
0.89
0.93
0.93
1.00
1.00
1.04
0.94
0.74
2.93
0.99
1.00
2.74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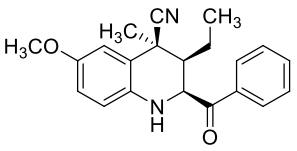
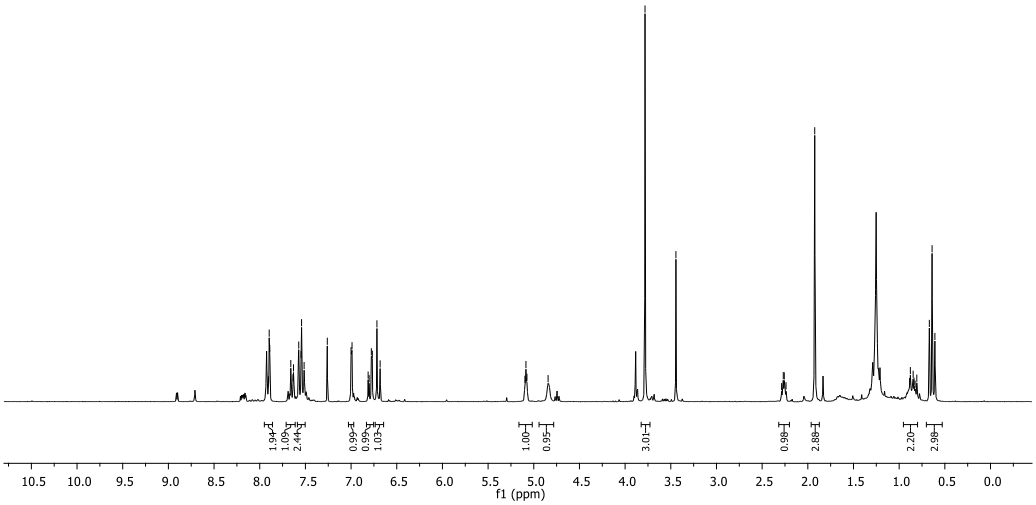
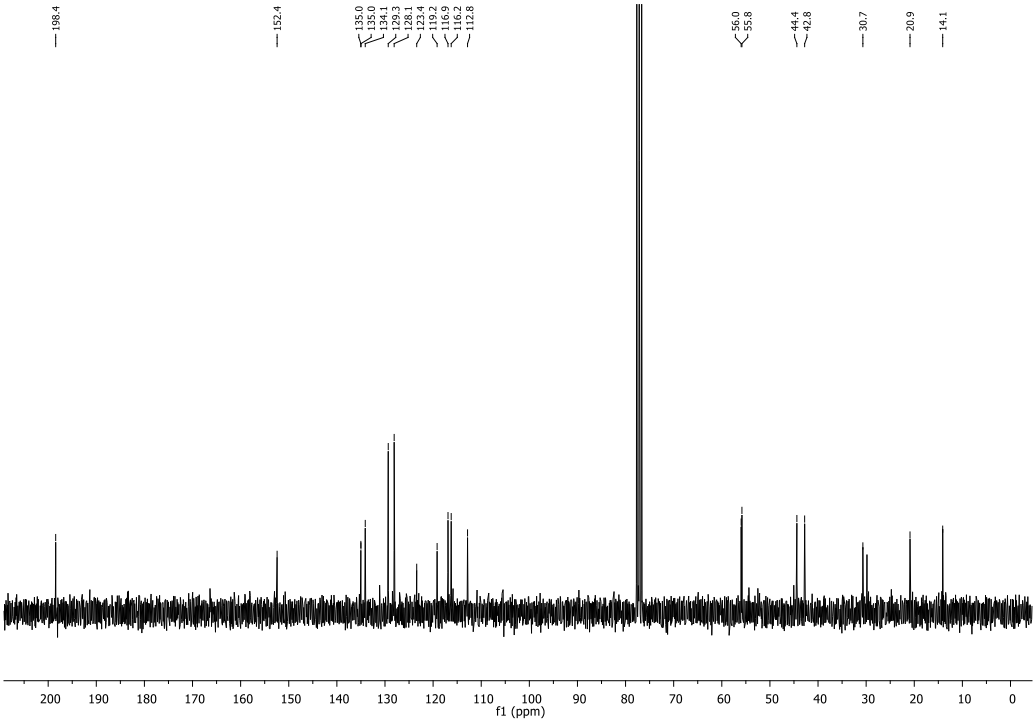
152.53
150.83
146.87
134.93
123.71
120.42
118.93
117.52
116.23
112.88
111.98
77.51
77.00
76.49
55.87
53.30
35.78
35.29
28.39
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

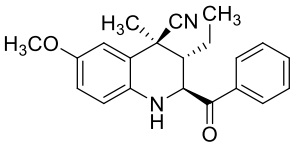

CN
CH3
H3C
H3CO
N
H
O

6ma


7.90
7.90
7.89
7.66
7.64
7.63
7.57
7.55
7.54
7.51
7.26
7.00
6.99
6.81
6.80
6.78
6.77
6.72
6.68
5.10
5.09
5.07
4.84
3.78
3.44
2.29
2.27
2.26
2.24
1.92
0.89
0.88
0.85
0.84
0.83
0.81
0.67
0.64
0.61

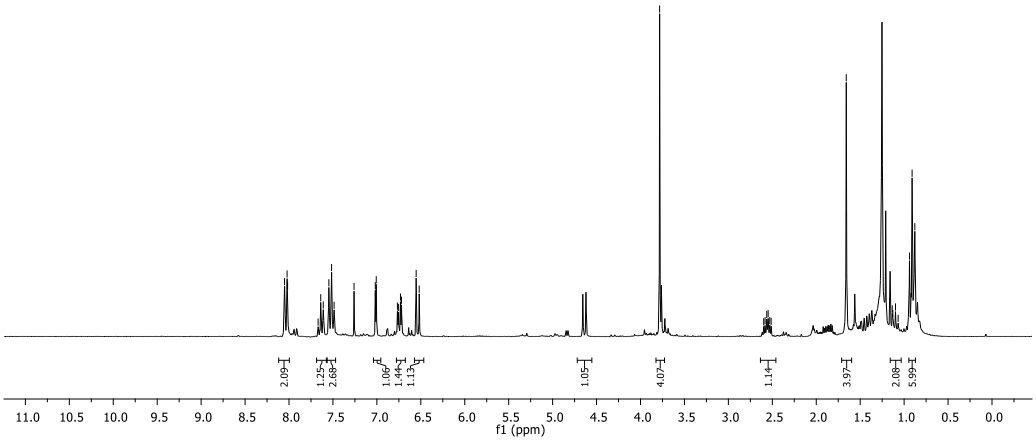

1.94
1.09
2.44
0.99
0.99
1.03
1.00
0.95
3.01
0.98
2.88
2.20
2.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

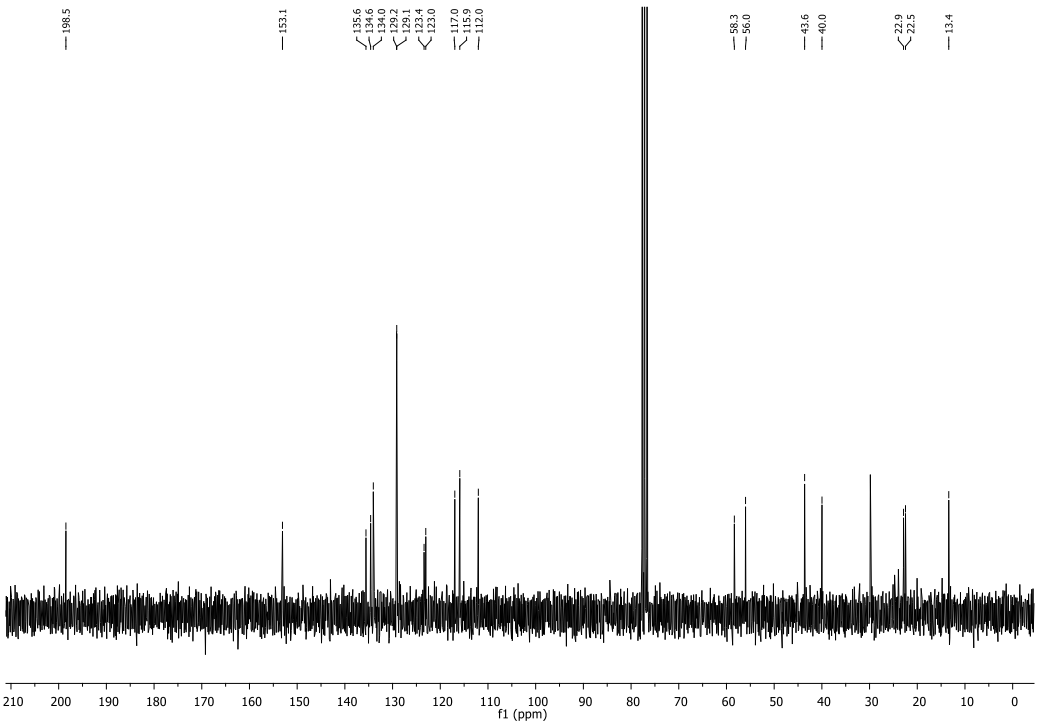

198.4
152.4
135.0
135.0
134.1
129.3
128.1
123.4
119.2
116.9
116.2
112.8
56.0
55.8
44.4
42.8
30.7
20.9
14.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

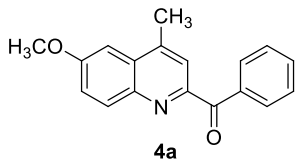

H3C
CN
CH3
H3CO
N
H
O

6mb

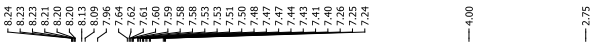

8.05
8.02
8.02
7.67
7.64
7.61
7.55
7.52
7.49
7.26
7.02
7.01
6.77
6.76
6.73
6.72
6.55
6.52
3.78
2.60
2.58
2.56
2.55
2.53
2.51
1.66
1.14
1.13
1.10
1.07
0.94
0.91
0.88

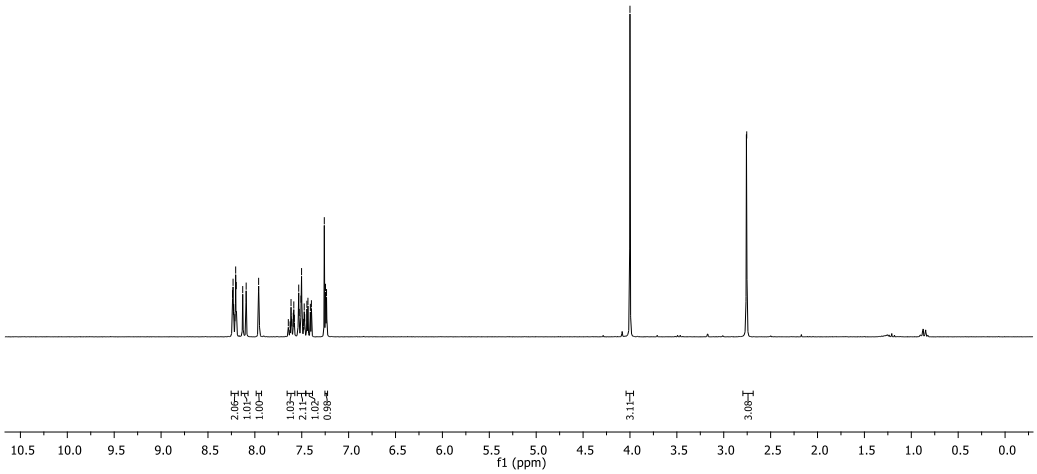

2.09
1.25
2.68
1.06
1.44
1.13
1.05
4.07
1.14
3.97
2.08
5.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

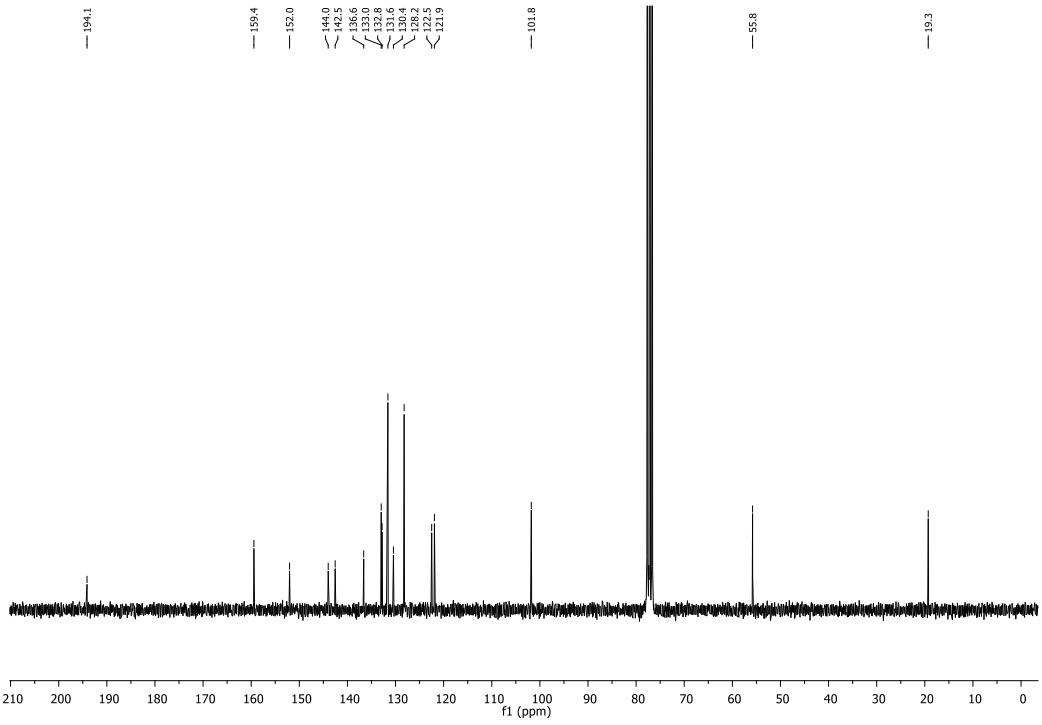

198.5
153.1
135.6
134.6
134.0
129.2
129.1
123.4
123.0
117.0
115.9
112.0
58.3
56.0
43.6
40.0
22.9
22.5
13.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

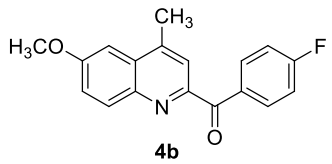

CH3
H3CO
N
O

4a

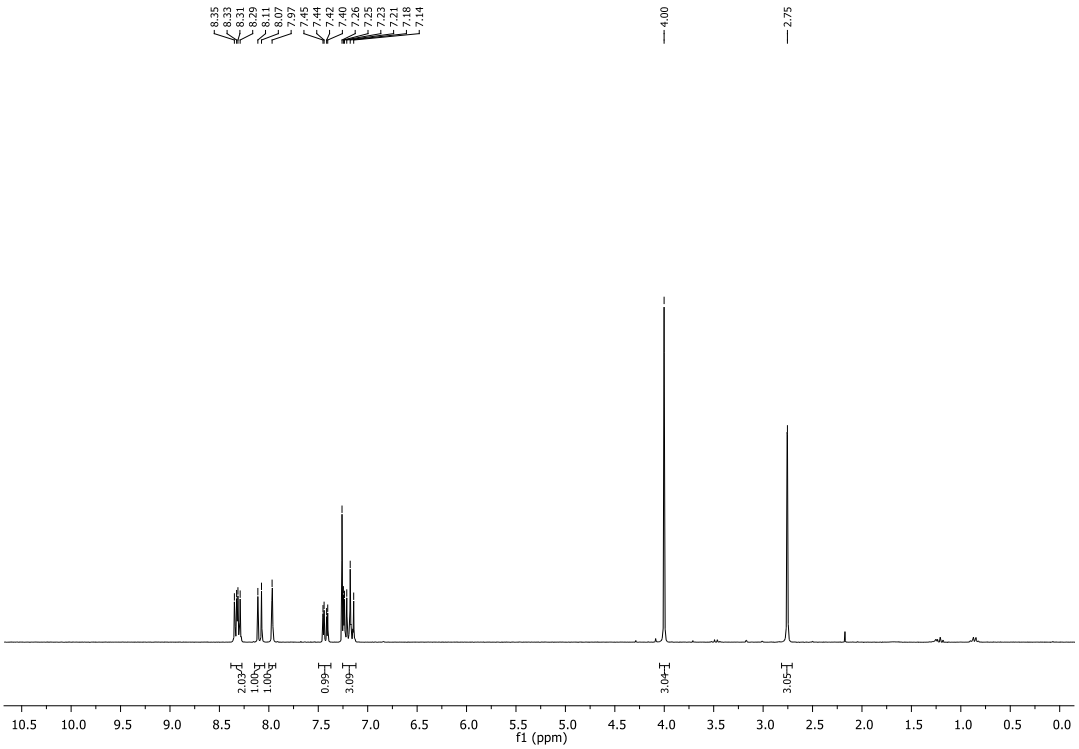

8.24
8.23
8.23
8.21
8.21
8.20
8.13
8.09
7.96
7.64
7.62
7.61
7.60
7.59
7.58
7.58
7.53
7.53
7.51
7.50
7.48
7.47
7.47
7.44
7.43
7.41
7.40
7.26
7.25
7.24
4.00
2.75

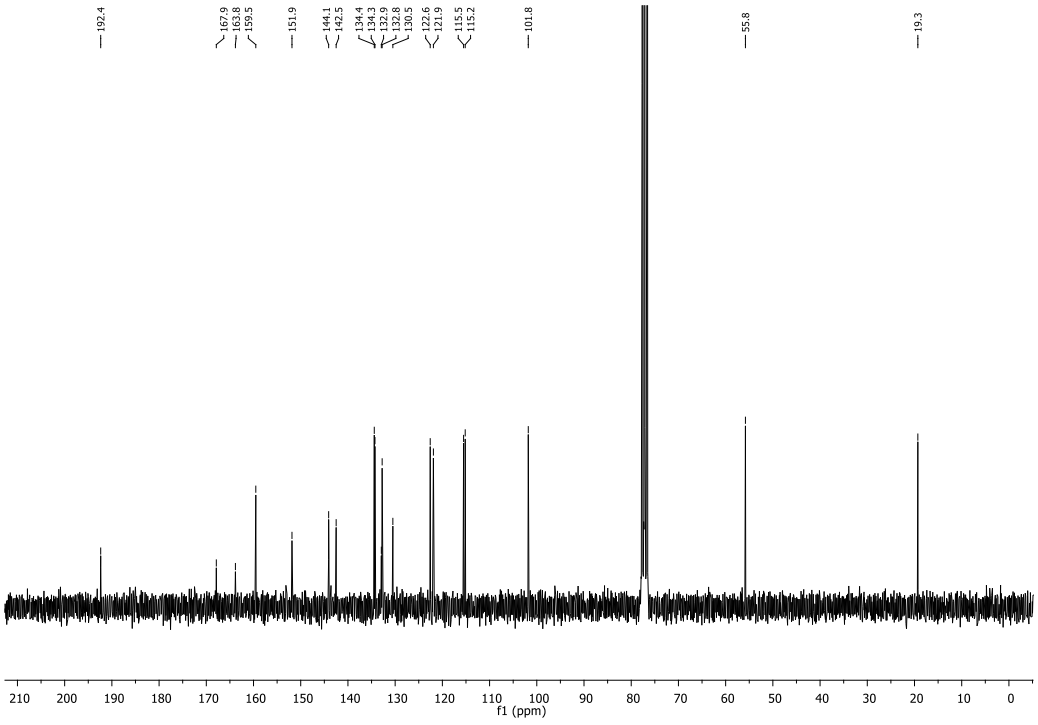

2.06
1.01
1.00
1.03
2.11
1.02
0.98
3.11
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

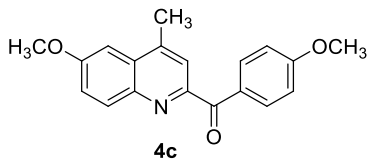

194.1
159.4
152.0
144.0
142.5
136.6
133.0
132.8
131.6
130.4
128.2
122.5
121.9
101.8
55.8
19.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CH3
H3CO
F
N
O

4b

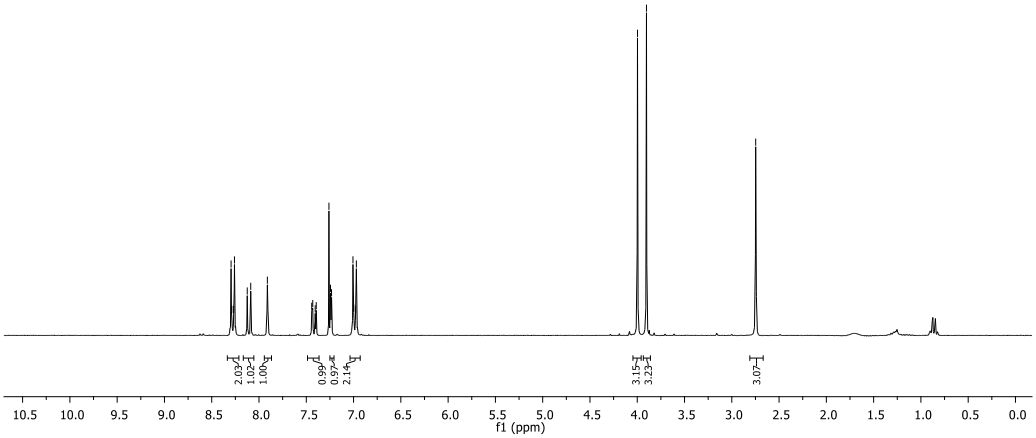

8.35
8.33
8.31
8.29
8.11
8.07
7.97
7.45
7.44
7.42
7.40
7.26
7.25
7.23
7.21
7.18
7.14
4.00
2.75
2.02
1.06
1.00
0.99
3.09
3.04
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

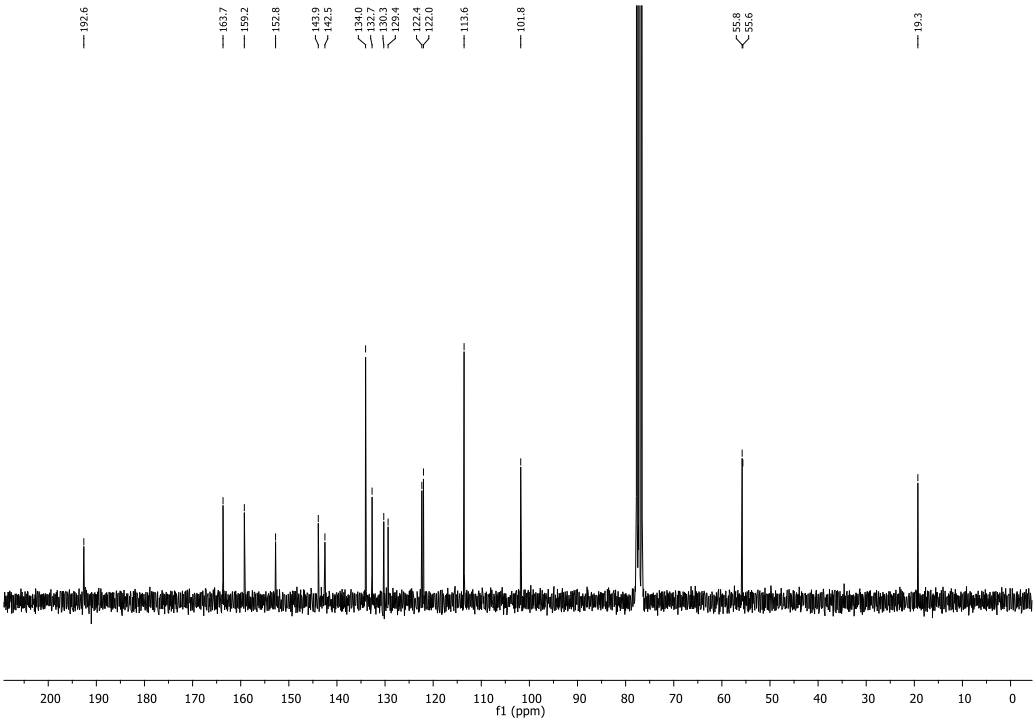

192.4
167.9
163.8
159.5
151.9
144.1
142.5
134.4
134.3
132.9
132.8
130.5
122.6
121.9
115.5
115.2
101.8
55.8
19.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

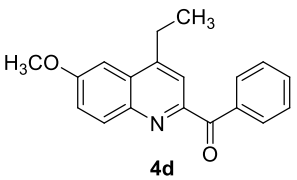

CH3
H3CO
OCH3
N
O

4c


8.30
8.29
8.27
8.26
8.12
8.09
7.91
7.44
7.43
7.41
7.39
7.36
7.24
7.23
7.01
7.00
6.98
6.97
4.00
3.90
2.75

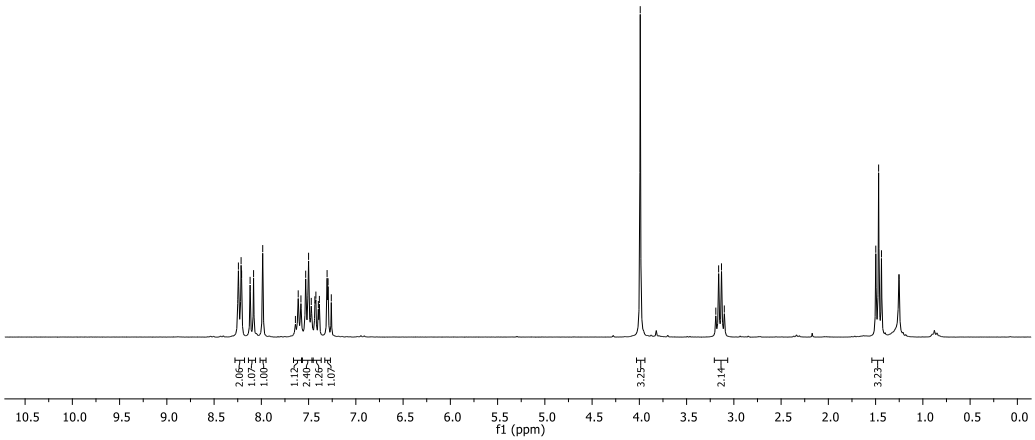

2.03
1.02
1.00
0.99
0.97
2.14
3.15
3.23
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

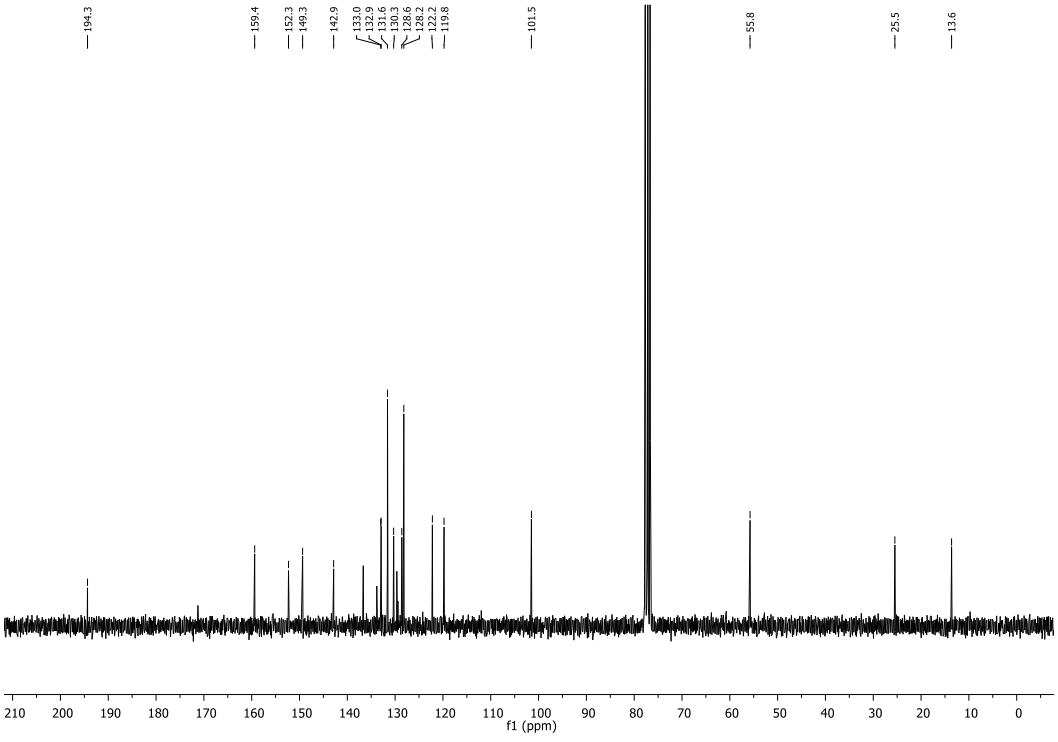

192.6
163.7
159.2
152.8
143.9
142.5
134.0
132.7
130.3
129.4
122.4
122.0
113.6
101.8
55.8
55.6
19.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

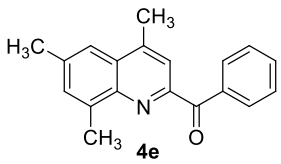

CH3
H3CO
N
O

4d

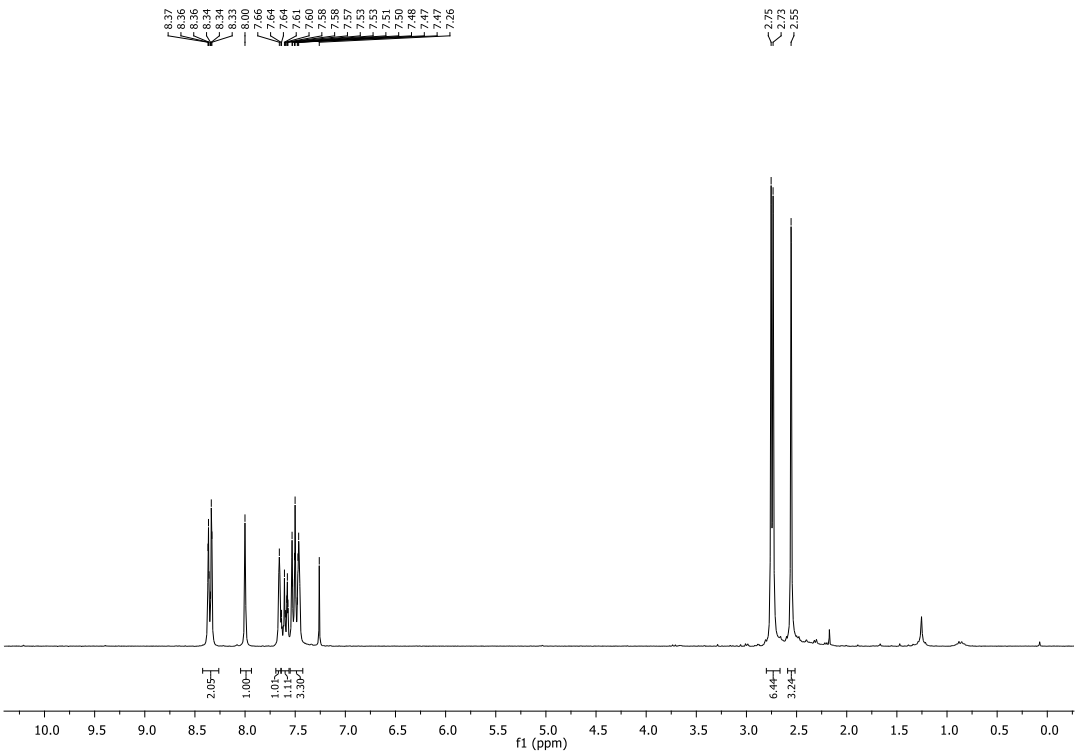

8.24
8.21
8.21
8.12
8.08
7.99
7.64
7.61
7.58
7.53
7.50
7.47
7.43
7.42
7.40
7.39
7.30
7.29
7.26
3.99
3.19
3.16
3.13
3.10
1.50
1.47
1.44

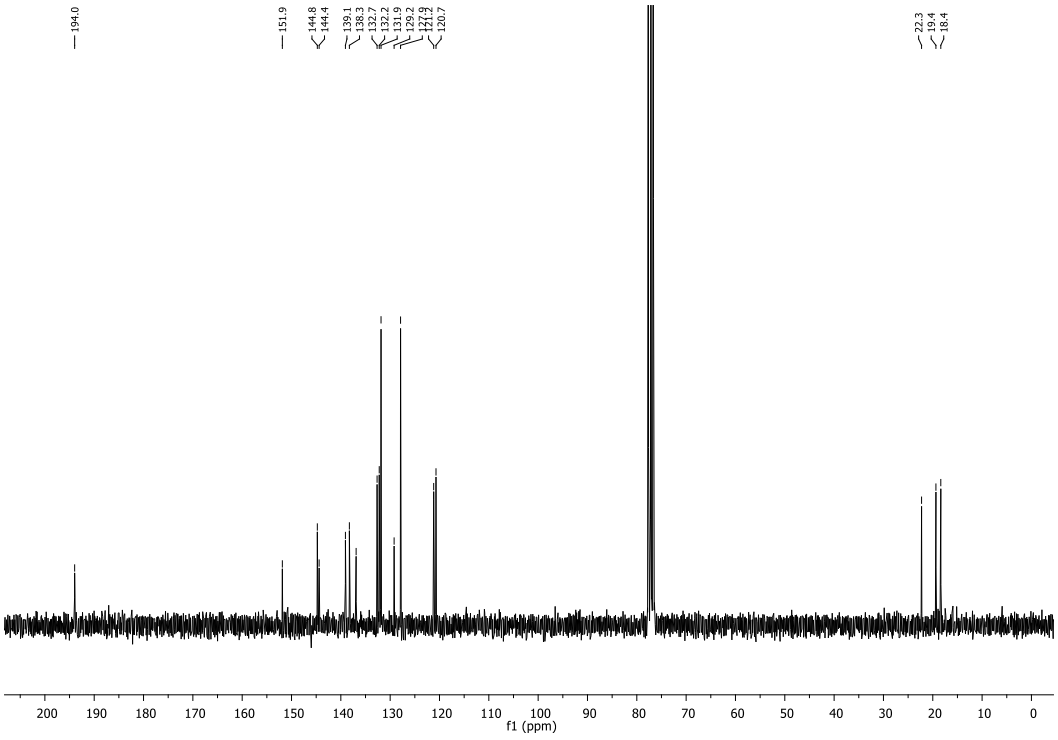

2.06
1.07
1.00
1.12
2.40
1.26
1.07
3.25
2.14
3.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


194.3
159.4
152.3
149.3
142.9
133.0
132.9
131.6
130.3
128.6
128.2
122.2
119.8
101.5
55.8
25.5
13.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CH3
H3C
N
CH3
O

4e


8.37
8.36
8.36
8.34
8.34
8.33
8.00
7.66
7.64
7.64
7.61
7.60
7.58
7.58
7.57
7.53
7.53
7.51
7.50
7.48
7.47
7.47
7.26
2.75
2.73
2.55
2.05
1.00
1.01
1.11
3.30
6.44
3.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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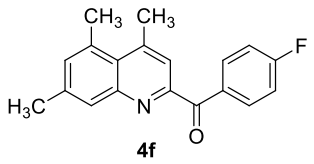
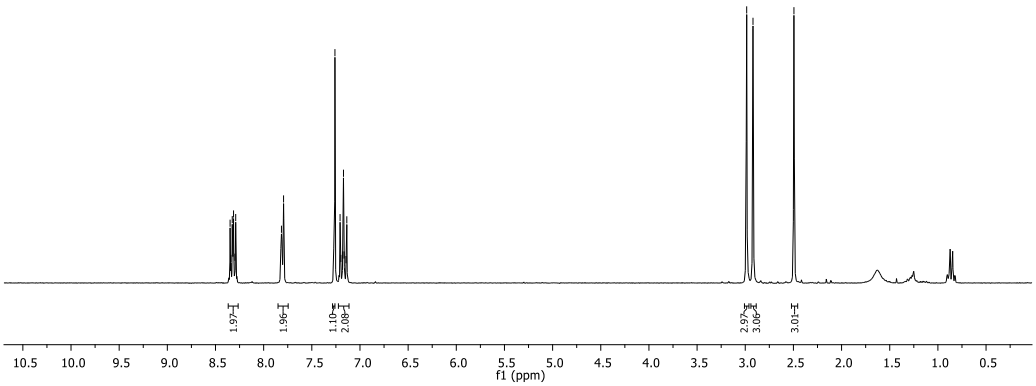
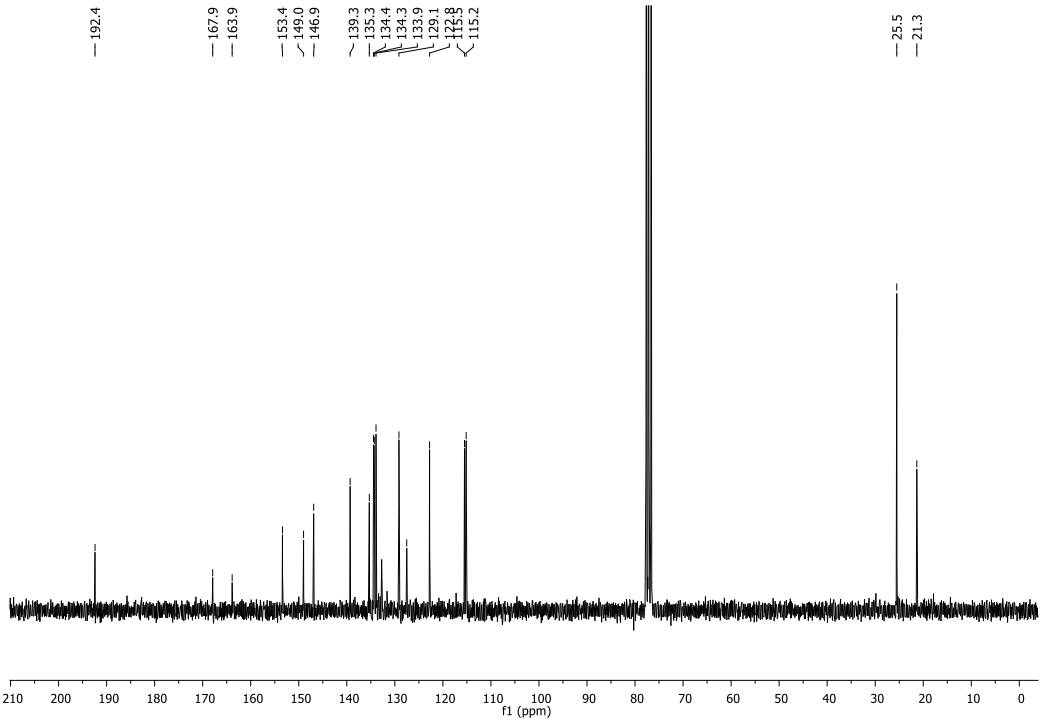
151.9
144.8
144.4
139.1
138.3
132.7
132.2
131.9
129.2
127.9
127.2
120.7
22.3
19.4
18.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

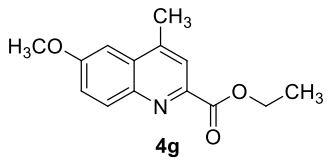

CH3
CH3
F
H3C
N
O

4f

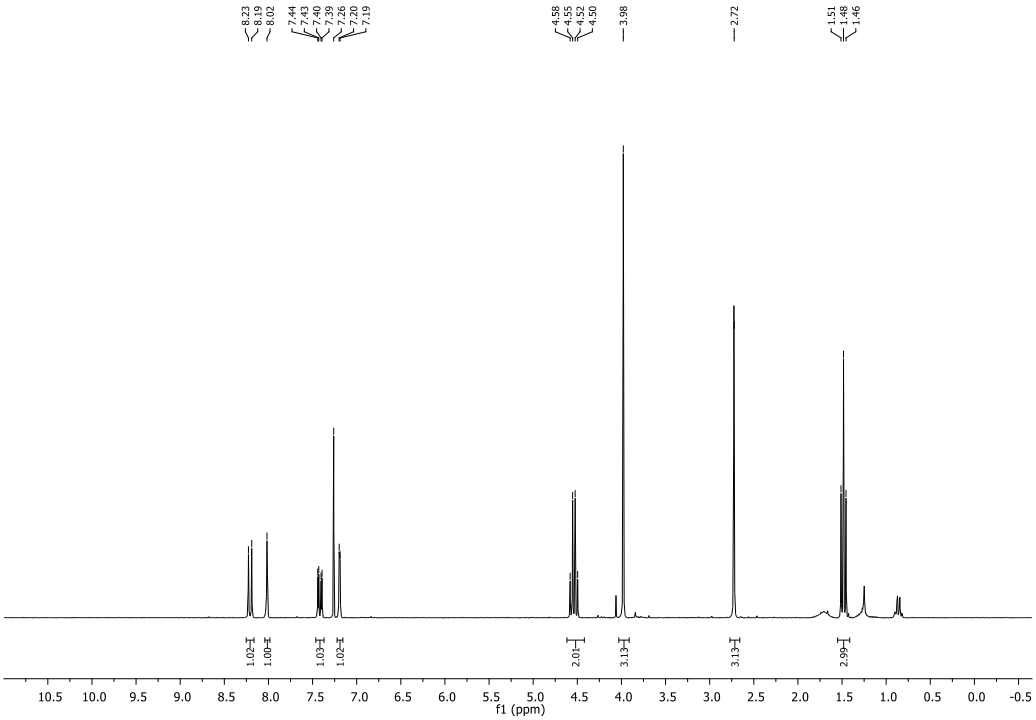

8.35
8.34
8.33
8.31
8.30
8.29
7.82
7.79
7.26
7.21
7.20
7.18
7.17
7.16
7.15
7.14
2.99
2.92
2.49

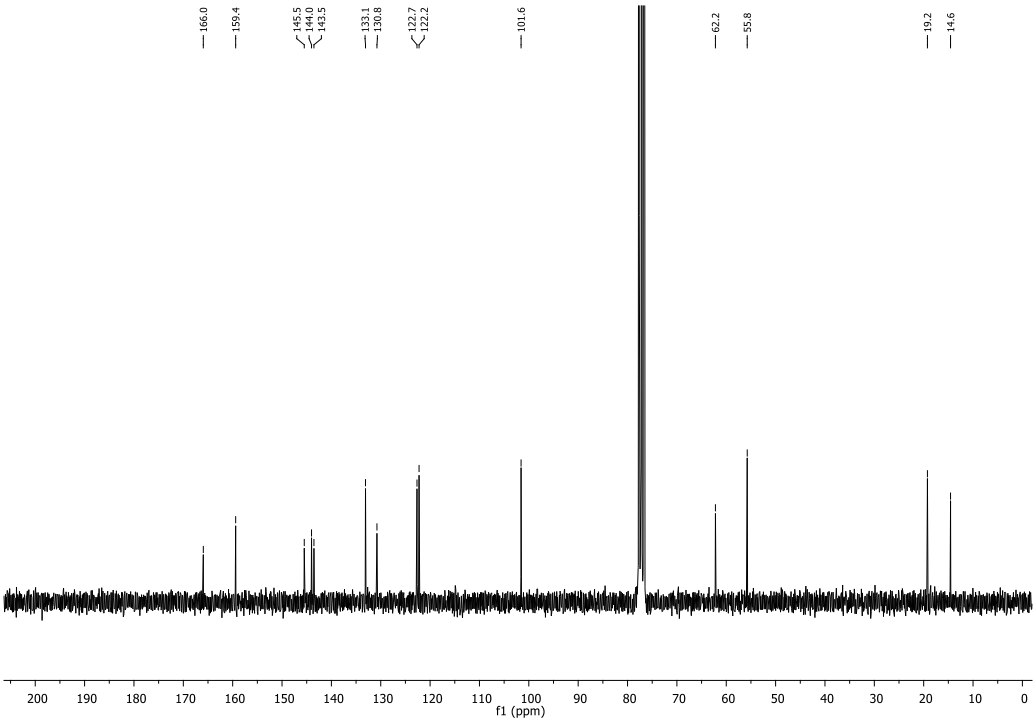

1.97
1.96
1.10
2.08
2.97
3.06
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

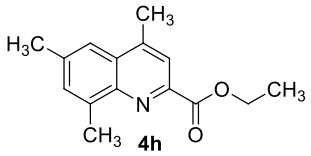

192.4
167.9
163.9
153.4
149.0
146.9
139.3
135.3
134.4
134.3
133.9
129.1
122.8
115.5
115.2
25.5
21.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CH3
H3CO
N
O
O
CH3
O

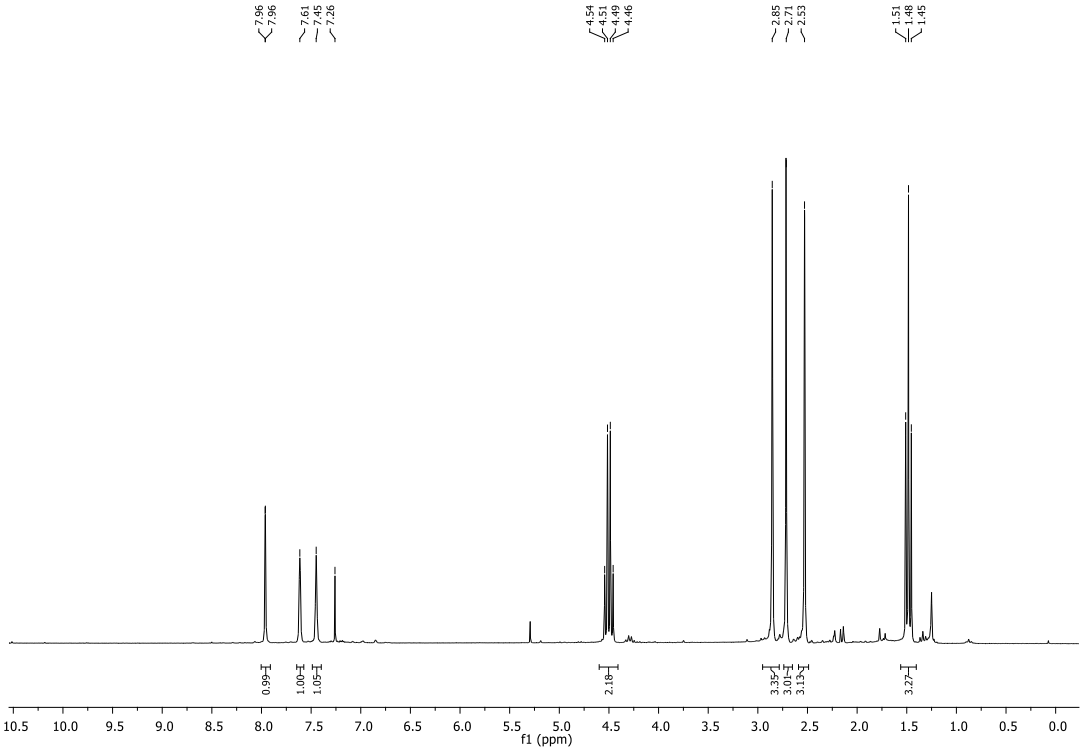
4g

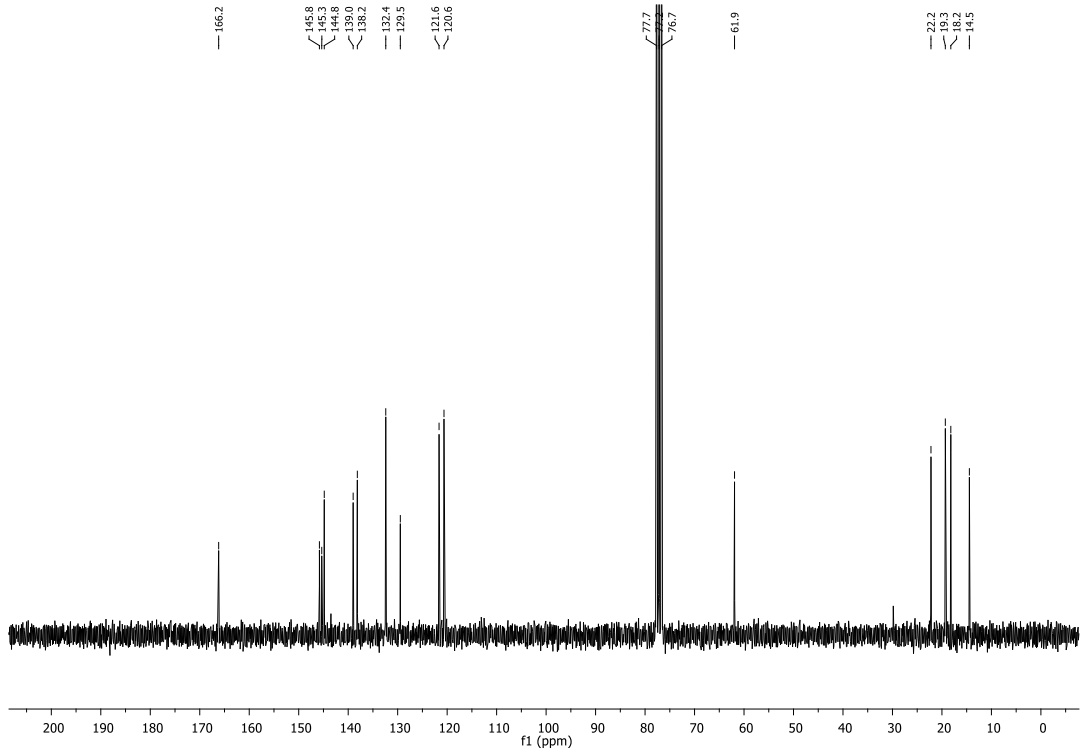

8.23
8.19
8.02
7.44
7.43
7.40
7.39
7.26
7.20
7.19
4.58
4.55
4.52
4.50
3.98
2.72
1.51
1.48
1.46
1.02
1.00
1.03
1.02
2.01
3.13
3.13
2.99
f1 (ppm)

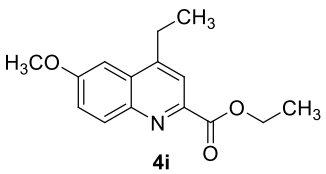

166.0
159.4
145.5
144.0
143.5
133.1
130.8
122.7
122.2
101.6
62.2
55.8
19.2
14.6
f1 (ppm)


CH3
H3C
N
O
O
CH3
CH3

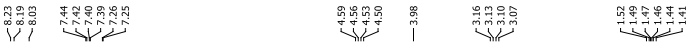
4h

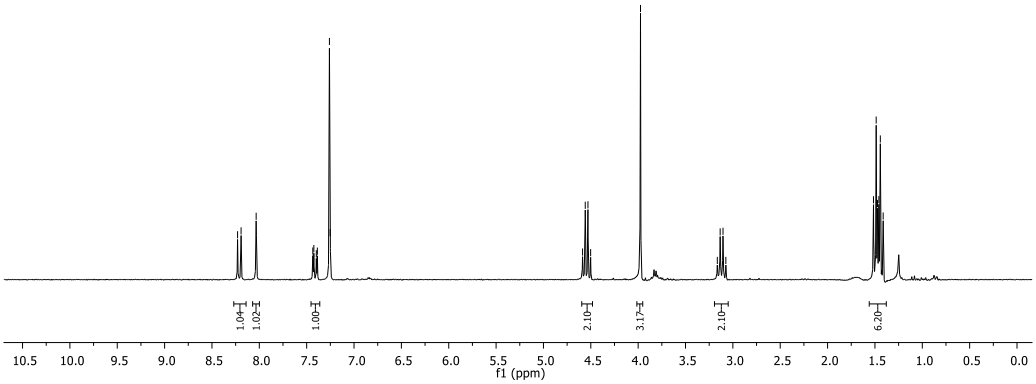

7.96
7.96
7.61
7.45
7.26
4.54
4.51
4.49
4.46
2.85
2.71
2.53
1.51
1.48
1.45
0.99
1.00
1.05
2.18
3.35
3.01
3.13
3.27
f1 (ppm)

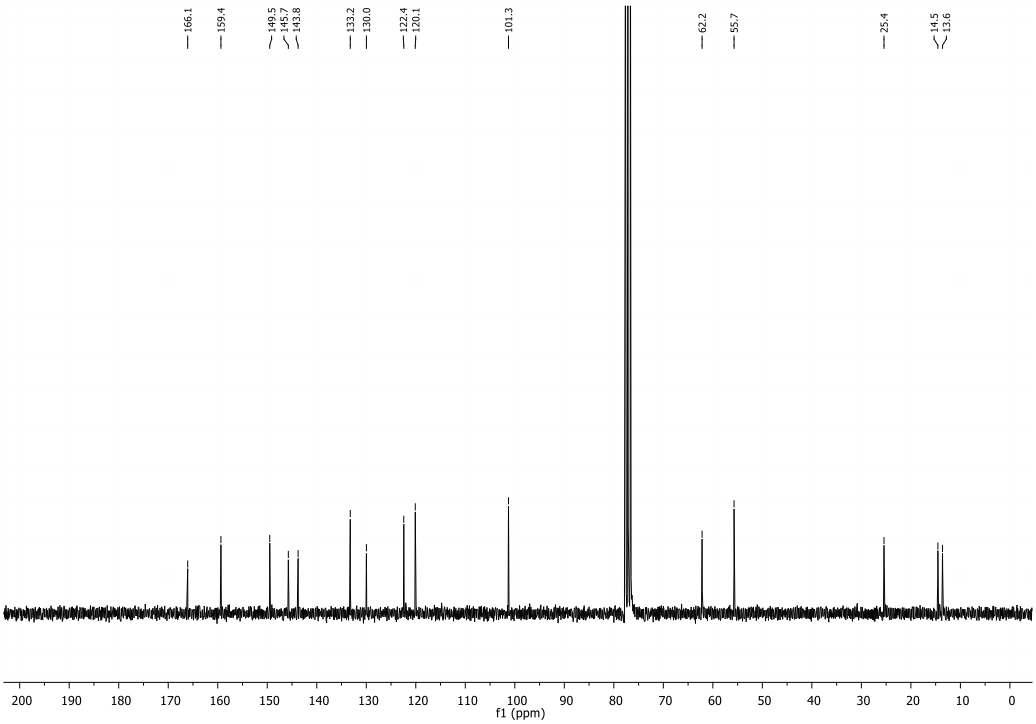

166.2
145.8
145.3
144.8
139.0
138.2
132.4
129.5
121.6
120.6
77.7
77.2
76.7
61.9
22.2
19.3
18.2
14.5
f1 (ppm)

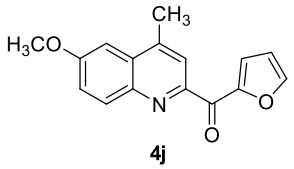

CH3
H3CO
N
O
CH3
O

4i

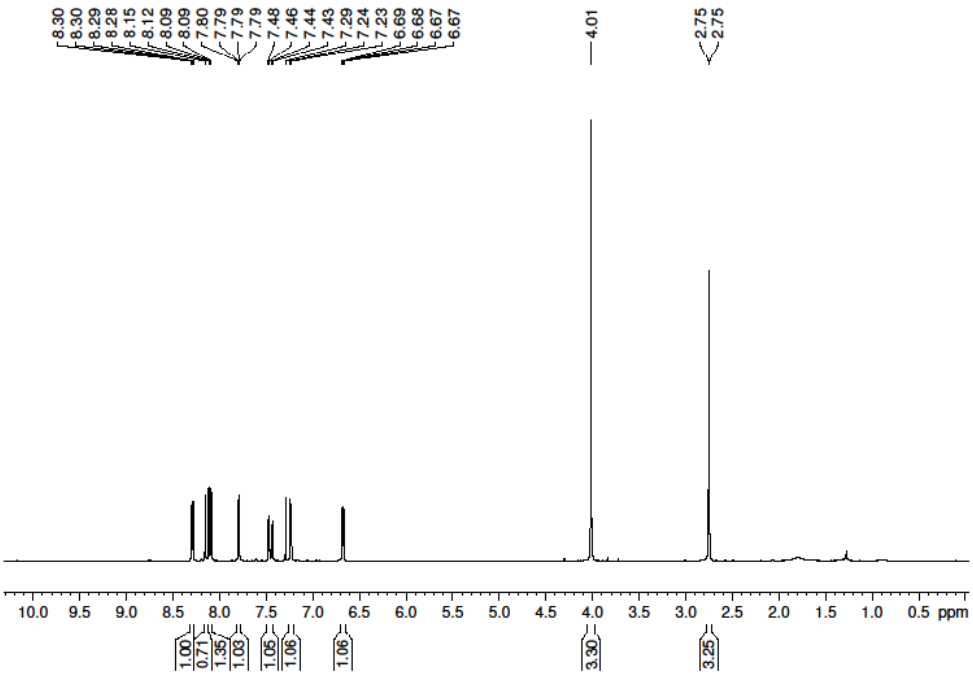

8.23
8.19
8.03
7.44
7.42
7.40
7.39
7.26
7.25
4.59
4.56
4.53
4.50
3.98
3.16
3.13
3.10
3.07
1.52
1.49
1.47
1.46
1.44
1.41

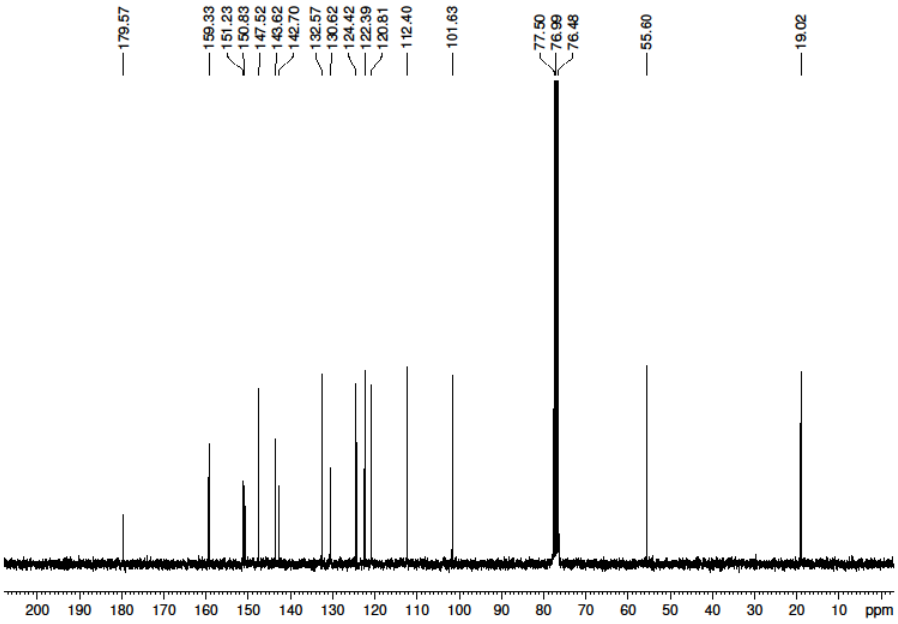

1.04
1.02
1.00
2.10
3.17
2.10
6.20
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

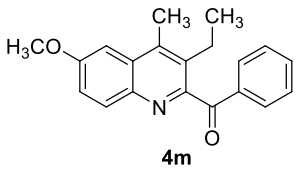

166.1
159.4
149.5
145.7
143.8
133.2
130.0
122.4
120.1
101.3
62.2
55.7
25.4
14.5
13.6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CH3
H3CO
N
O
O

4j

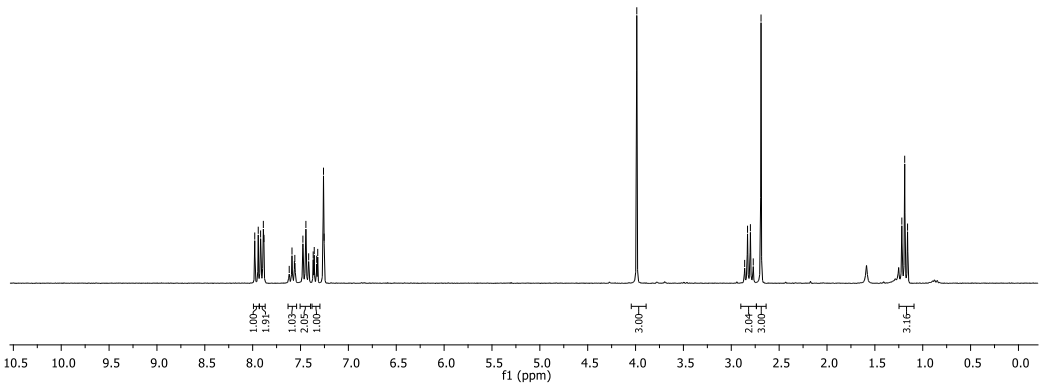

8.30
8.30
8.29
8.28
8.15
8.12
8.09
8.09
7.80
7.79
7.79
7.79
7.48
7.46
7.44
7.43
7.29
7.24
7.23
6.69
6.68
6.67
6.67
4.01
2.75
2.75
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.71
1.35
1.03
1.05
1.06
1.06
3.30
3.25

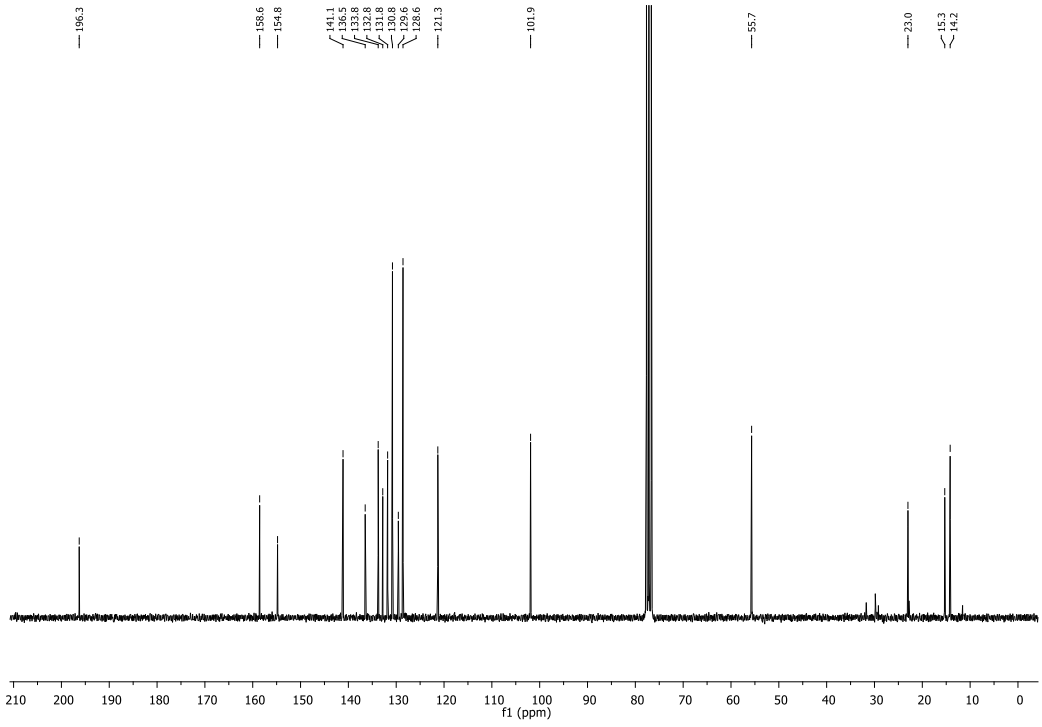

179.57
159.33
151.23
150.83
147.52
143.62
142.70
132.57
130.62
124.42
122.39
120.81
112.40
101.63
77.50
76.99
76.48
55.60
19.02
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

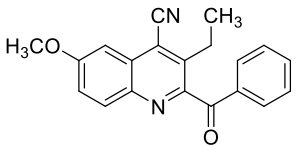

CH3
CH3
H3CO
N
O

4m


7.98
7.94
7.92
7.89
7.88
7.62
7.59
7.56
7.56
7.48
7.44
7.41
7.37
7.36
7.33
7.32
7.26
7.25
3.99
2.86
2.83
2.80
2.77
2.69
1.22
1.19
1.16

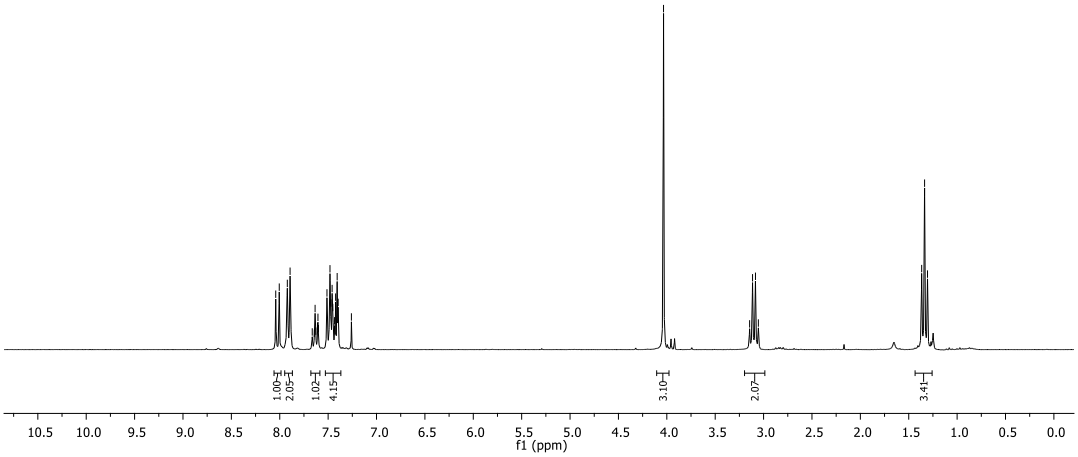

1.00
1.91
1.03
2.05
1.00
3.00
2.04
3.00
3.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

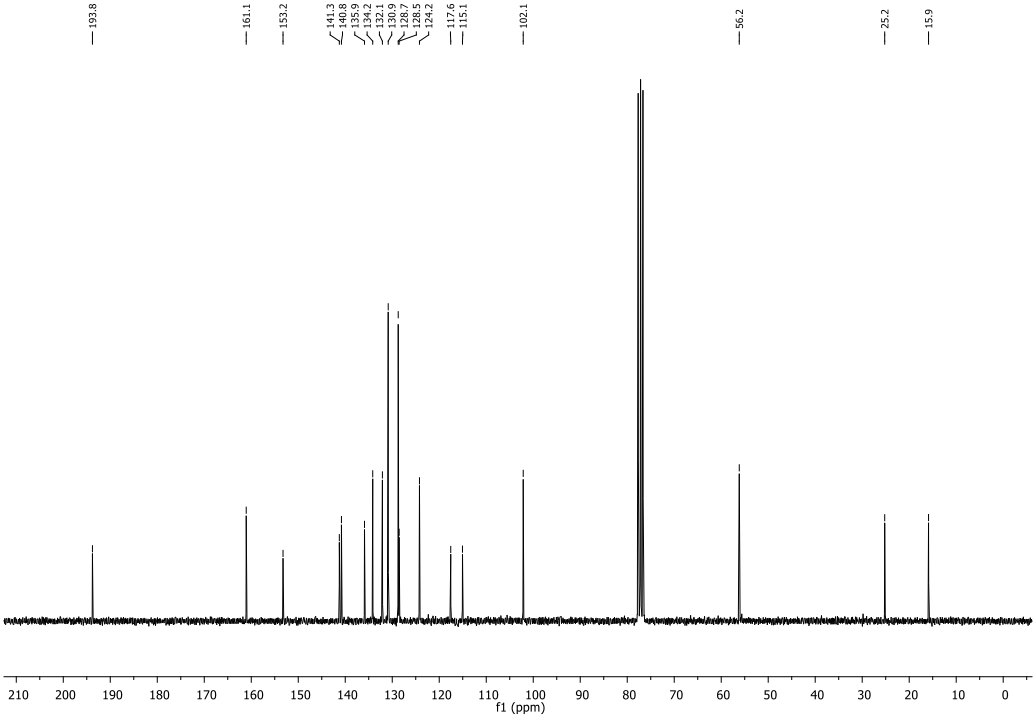

196.3
158.6
154.8
141.1
136.5
133.8
132.8
131.8
130.8
129.6
128.6
121.3
101.9
55.7
23.0
15.3
14.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

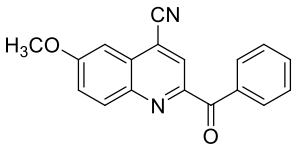

CN
CH3
H3CO
N
O

7a

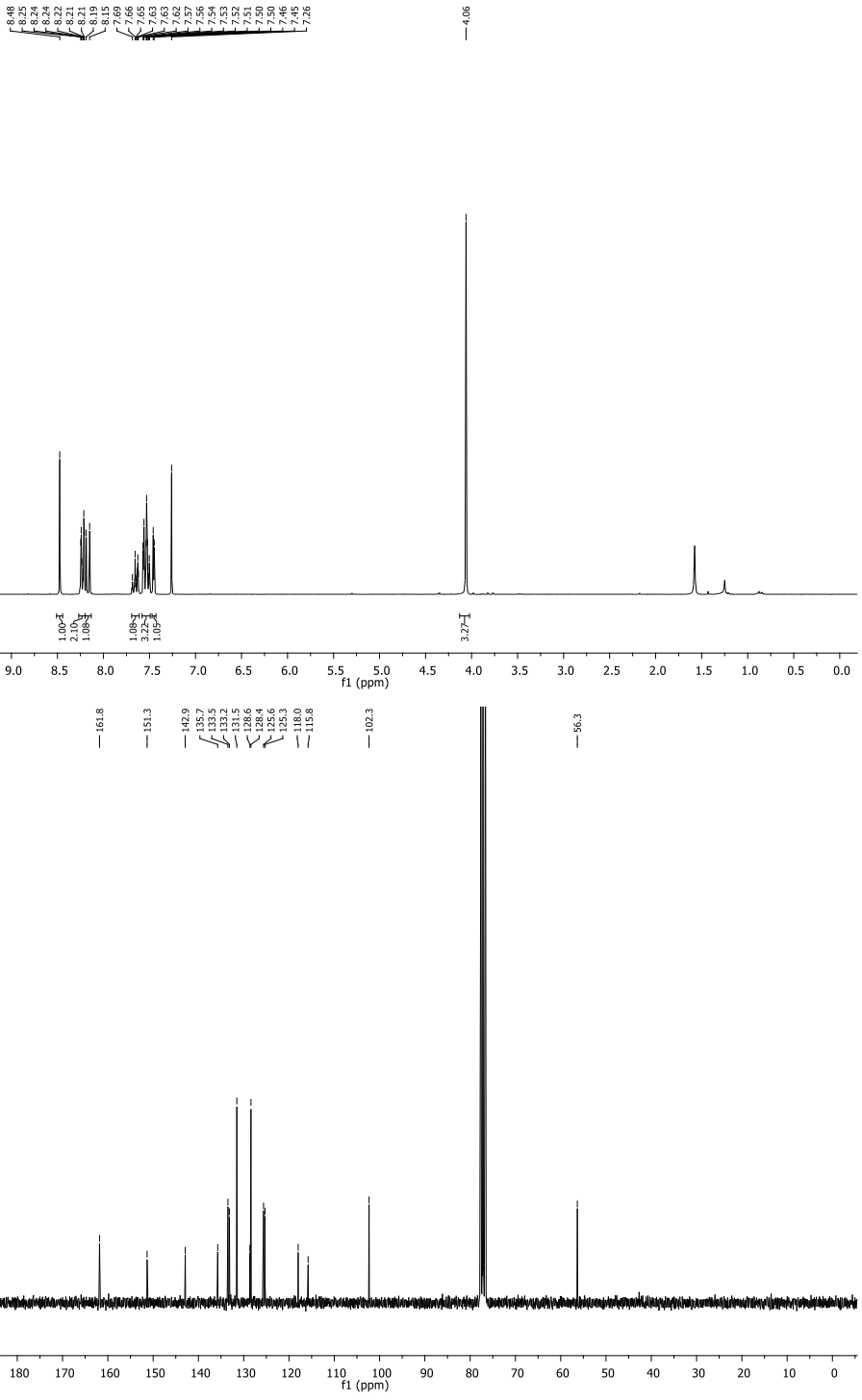

8.04
8.01
7.92
7.89
7.66
7.64
7.63
7.63
7.61
7.61
7.60
7.51
7.48
7.47
7.46
7.45
7.43
7.42
7.41
7.40
7.26
4.03
3.14
3.11
3.08
3.05
1.37
1.34
1.31

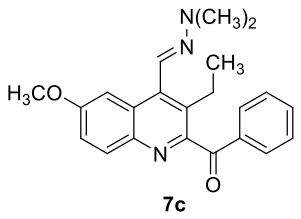

1.00
2.05
1.02
4.15
3.10
2.07
3.41
f1 (ppm)


193.8
161.1
153.2
141.3
140.8
135.9
134.2
132.1
130.9
128.7
128.5
124.2
117.6
115.1
102.1
56.2
25.2
15.9
f1 (ppm)

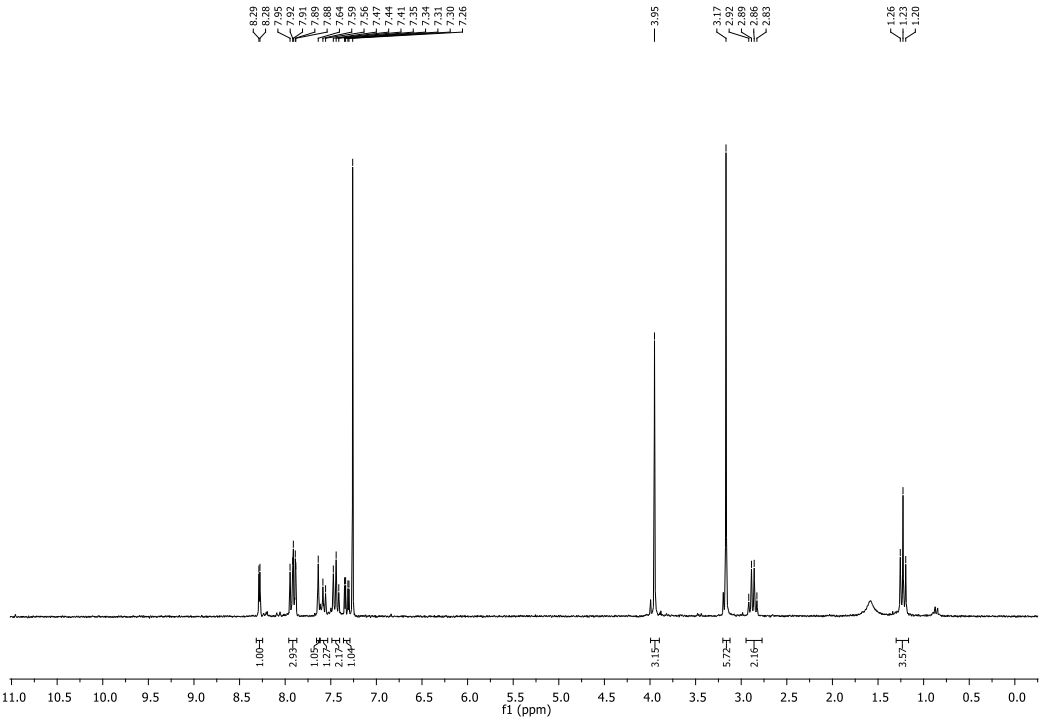

CN
H3CO
N
O

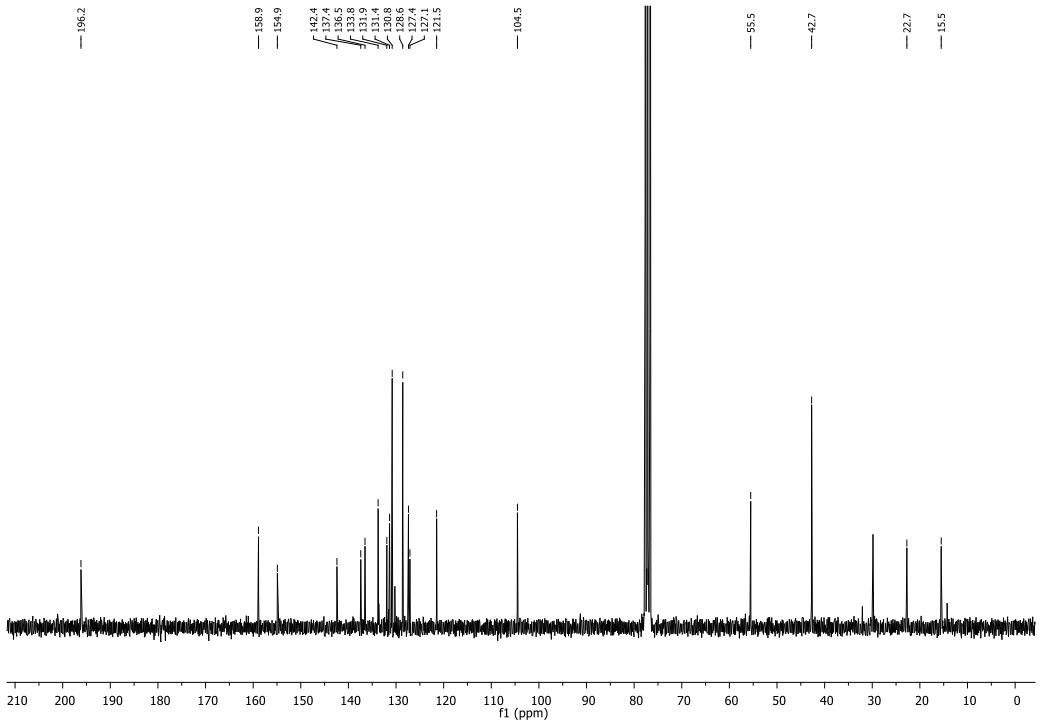
7b

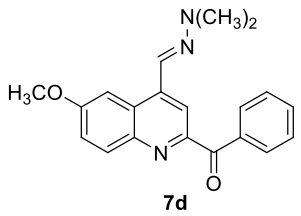

8.48
8.25
8.24
8.24
8.22
8.21
8.21
8.19
8.15
7.69
7.66
7.65
7.63
7.63
7.62
7.57
7.56
7.54
7.53
7.52
7.51
7.50
7.50
7.46
7.45
7.26
4.06
1.00
2.10
1.08
1.08
3.22
1.05
3.27
f1 (ppm)
191.8
161.8
151.3
142.9
135.7
133.5
133.2
131.5
128.6
128.4
125.6
125.3
118.0
115.8
102.3
56.3
f1 (ppm)


N(CH3)2
N
CH3
H3CO
N
O

7c

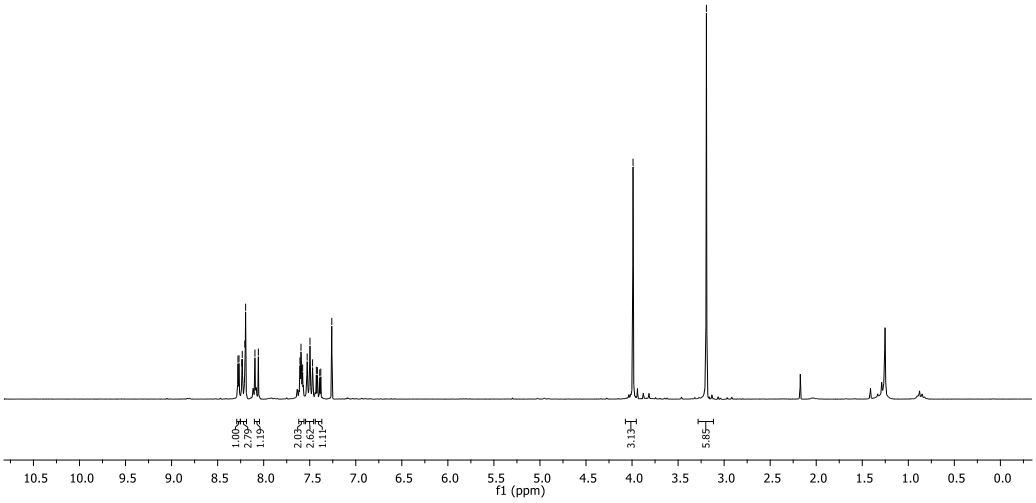

8.29
8.28
7.95
7.92
7.91
7.89
7.88
7.64
7.59
7.56
7.47
7.44
7.41
7.35
7.34
7.31
7.30
7.26
3.95
3.17
3.02
2.89
2.86
2.83
1.26
1.23
1.20
1.00
2.93
1.05
1.27
2.17
1.04
3.15
5.72
2.16
3.57
f1 (ppm)

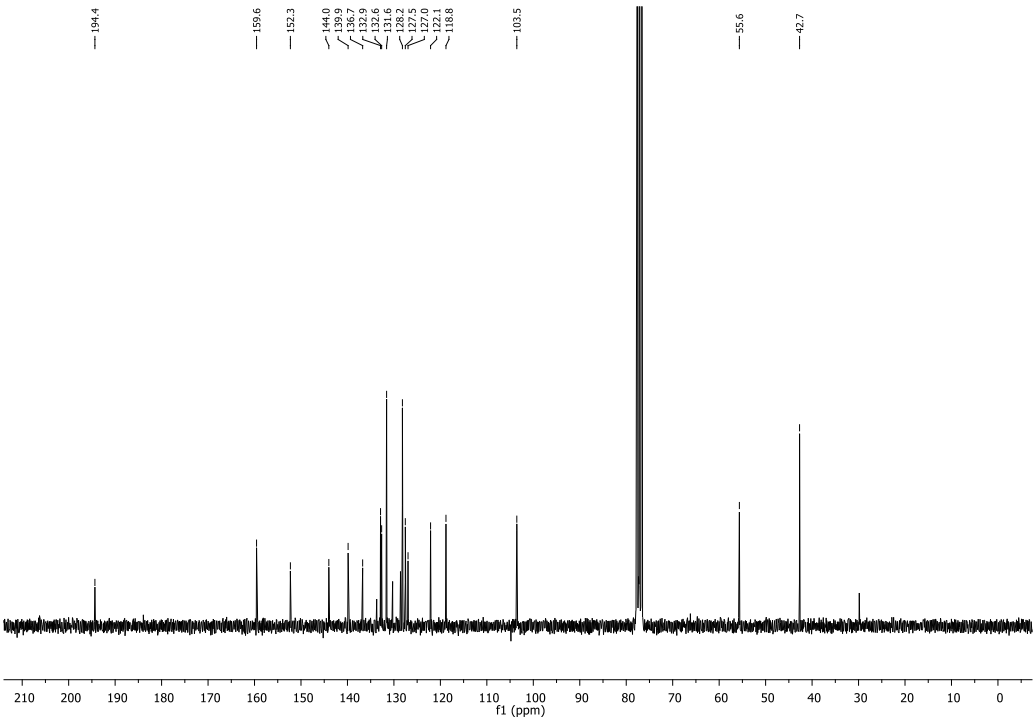

196.2
158.9
154.9
142.4
137.4
136.5
133.8
131.9
131.4
130.8
128.6
127.4
127.1
121.5
104.5
55.5
42.7
22.7
15.5
f1 (ppm)

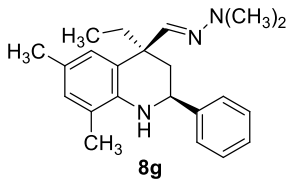

N(CH3)2
N
H3CO
N
O

7d

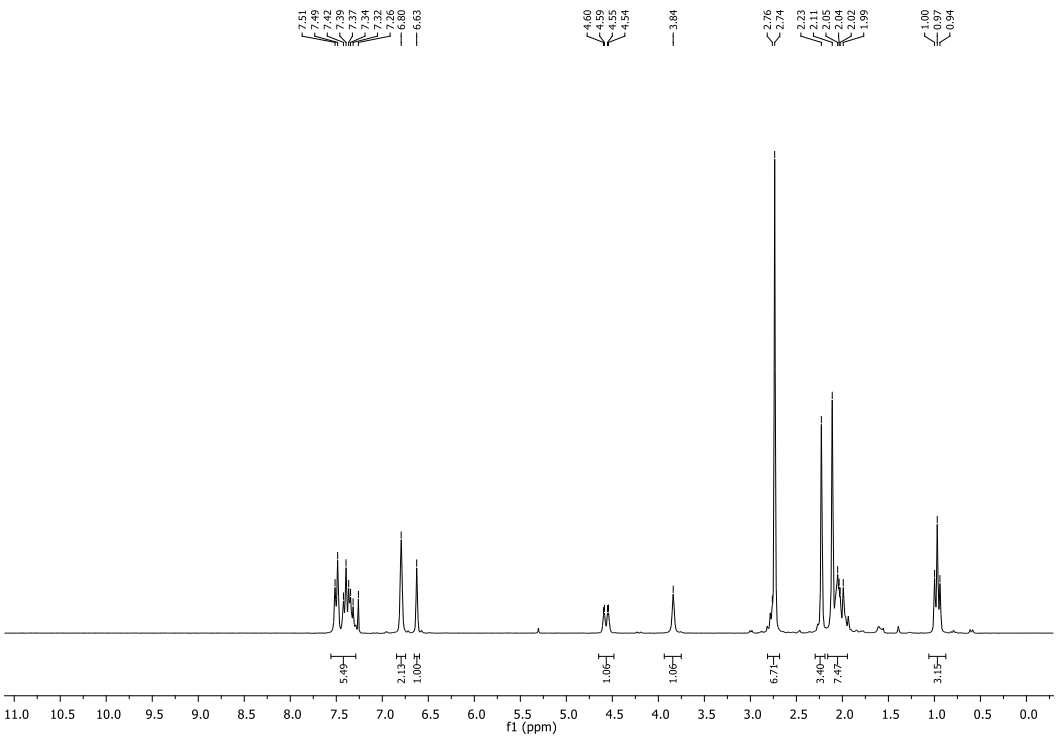

8.28
8.27
8.24
8.23
8.20
8.20
8.06
8.06
7.61
7.59
7.58
7.58
7.53
7.50
7.47
7.43
7.42
7.39
7.38
7.26
3.99
3.19

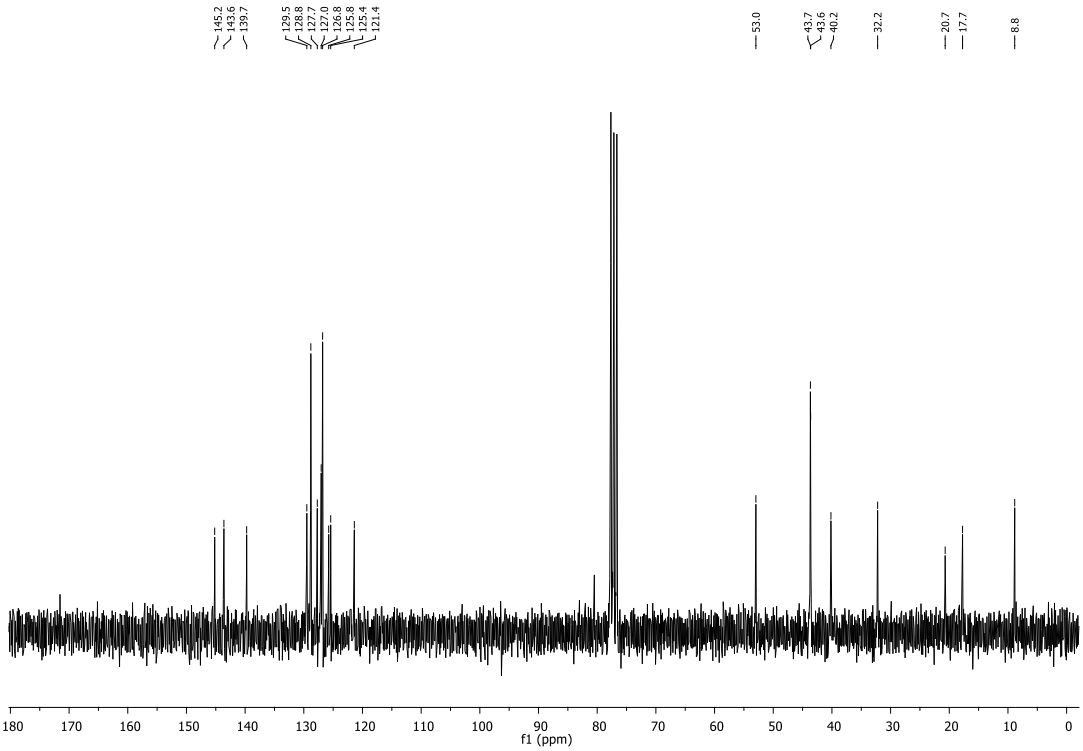

1.00
2.79
1.19
2.03
2.62
1.11
3.13
5.85
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

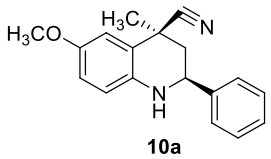

194.4
159.6
152.3
144.0
139.9
136.7
132.9
132.6
131.6
128.2
127.5
127.0
122.1
118.8
103.5
55.6
42.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


H3C
H3C
N(CH3)2
N
N
H
CH3

8g


7.51
7.49
7.42
7.39
7.37
7.34
7.32
7.26
6.80
6.63
4.60
4.59
4.55
4.54
3.84
2.76
2.74
2.23
2.11
2.05
2.04
2.02
1.99
1.00
0.97
0.94
5.49
2.13
1.00
1.06
1.06
6.71
3.40
7.47
3.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.2
143.6
139.7
129.5
128.8
127.7
127.0
126.8
125.8
125.4
121.4
53.0
43.7
43.6
40.2
32.2
20.7
17.7
8.8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


H3CO
H3C
N
N
H

10a


7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.26
6.89
6.97
6.78
6.77
6.74
6.73
6.55
6.52
4.43
4.42
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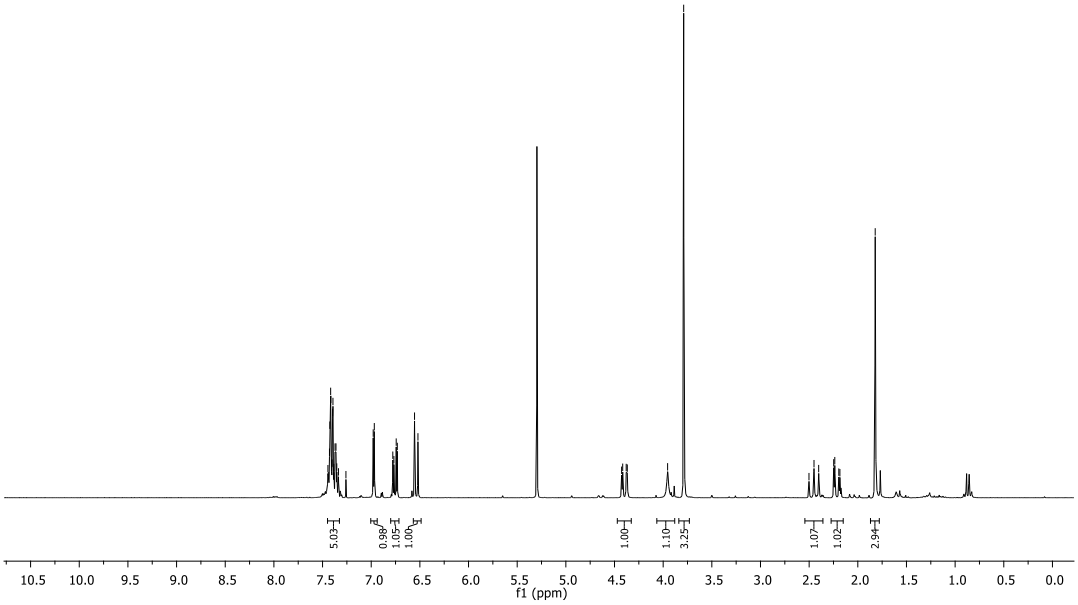
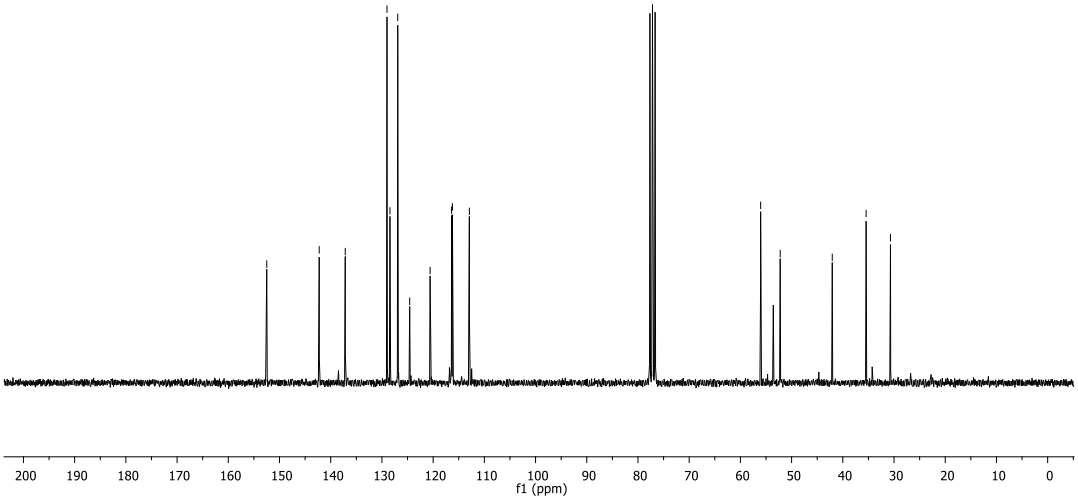
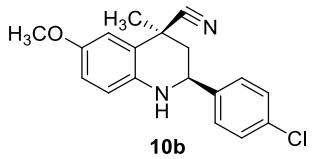
2.40
2.25
2.24
2.20
2.18
1.82

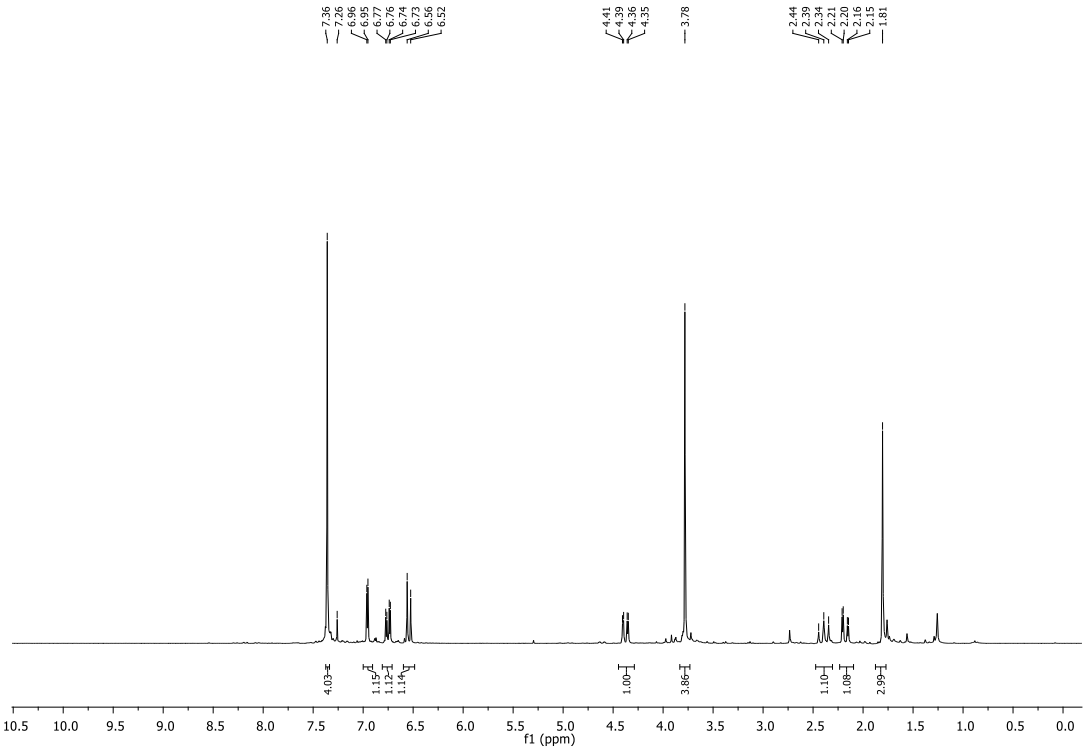

5.03
0.98
1.05
1.05
1.00
1.10
3.25
1.07
1.02
2.94
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

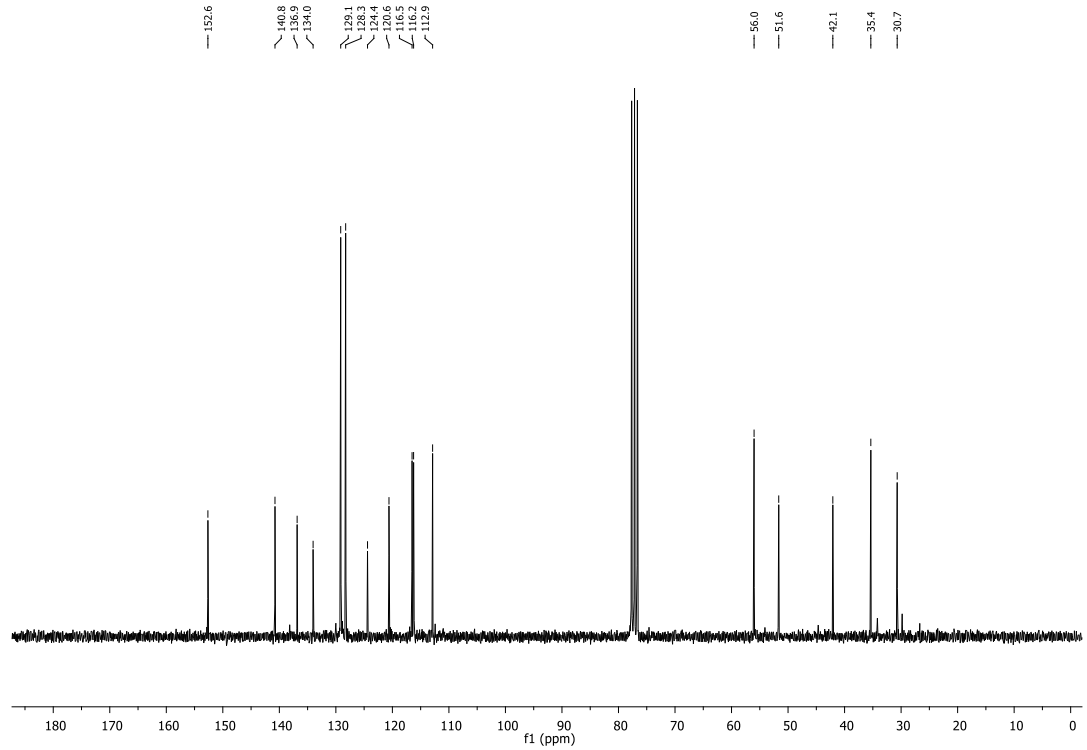

152.5
142.2
137.2
129.0
128.4
126.9
124.6
120.6
116.4
116.2
112.9
56.0
52.2
42.1
35.4
30.7

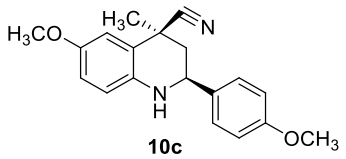

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


H3C
N
H3CO
N
H
Cl

10b

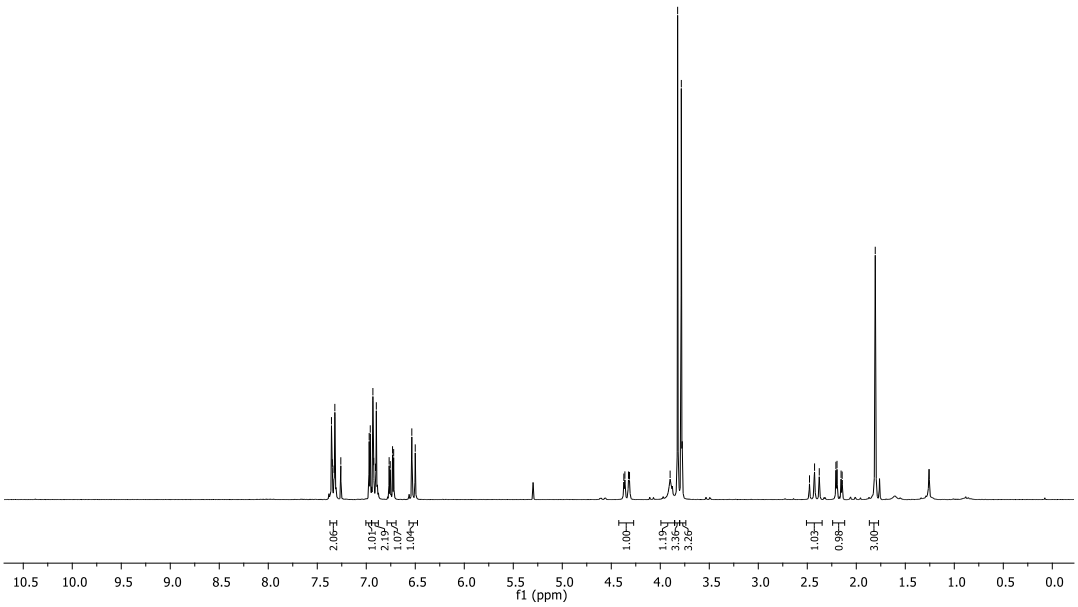

7.36
7.26
6.96
6.95
6.77
6.76
6.74
6.73
6.56
6.52
4.41
4.39
4.36
4.35
3.78
2.44
2.39
2.34
2.21
2.20
2.16
2.15
1.81
4.03
1.15
1.12
1.14
1.00
3.86
1.10
1.08
2.99
f1 (ppm)

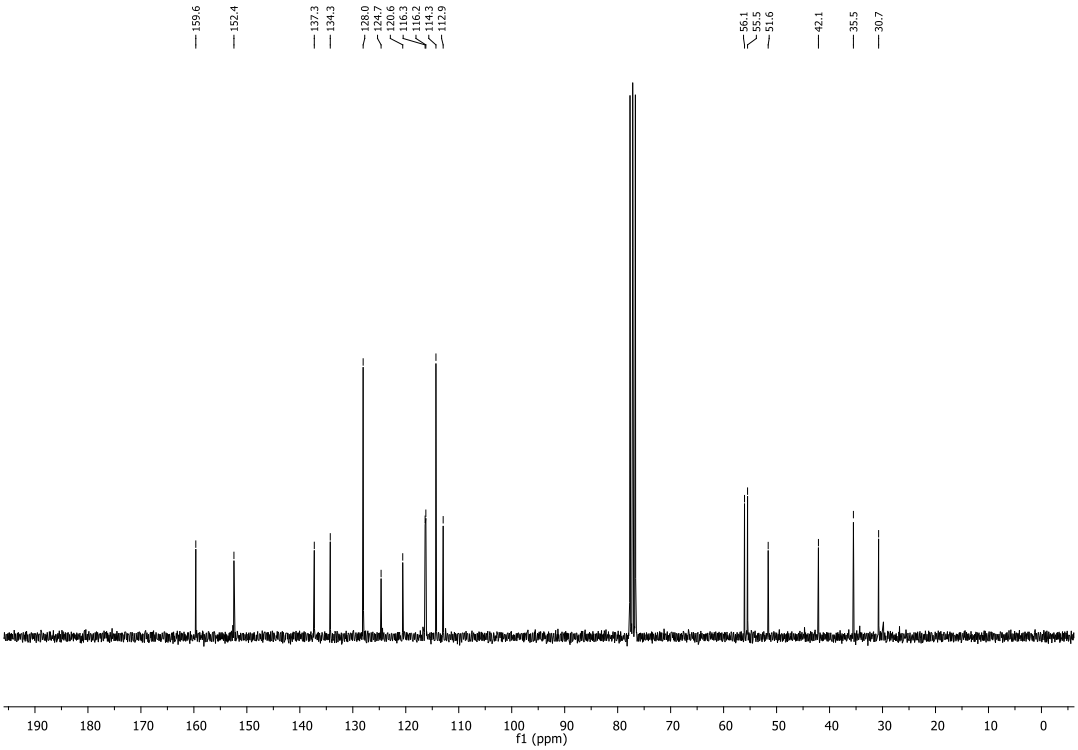

152.6
140.8
136.9
134.0
129.1
128.3
124.4
120.6
116.5
116.2
112.9
56.0
51.6
42.1
35.4
30.7
f1 (ppm)

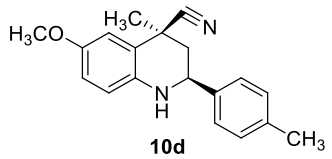

H3C
N
H3CO
N
H
OCH3

10c

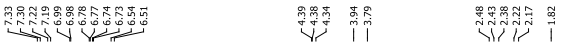

7.36
7.35
7.33
7.32
7.26
6.97
6.96
6.93
6.92
6.91
6.90
6.77
6.76
6.73
6.72
6.54
6.50
4.37
4.36
4.32
4.31
3.90
3.82
3.79
2.48
2.43
2.38
2.21
2.20
2.16
2.14
1.81

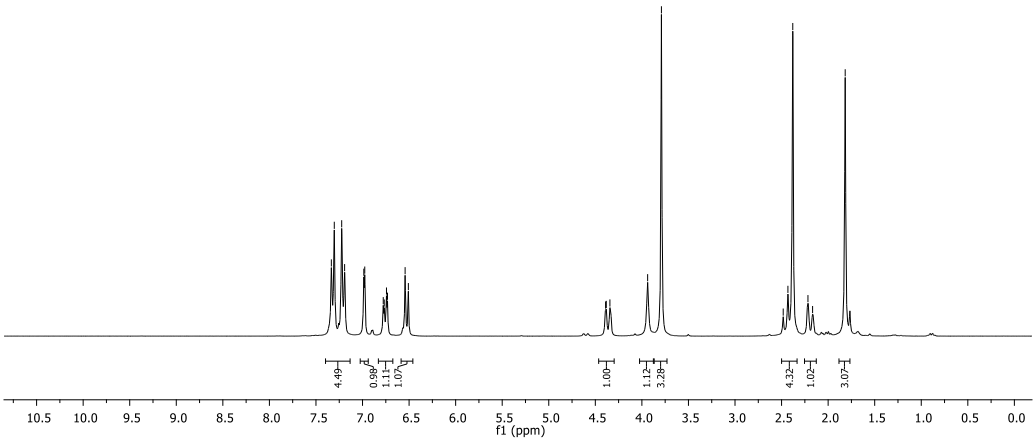

2.06
1.01
2.19
1.07
1.04
1.00
1.19
3.36
3.28
1.03
0.98
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.6
152.4
137.3
134.3
128.0
124.7
120.6
116.3
116.2
114.3
112.9
56.1
55.5
51.6
42.1
35.5
30.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

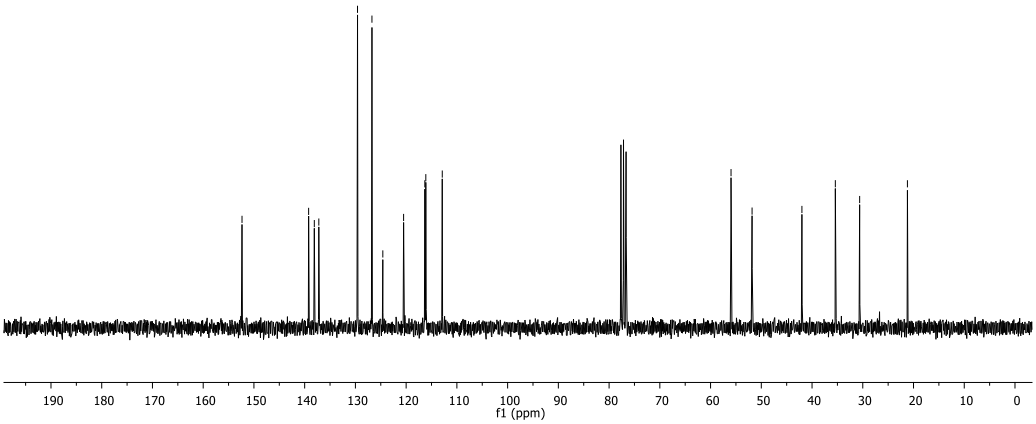

H3CO
H3C
N
N
H
CH3

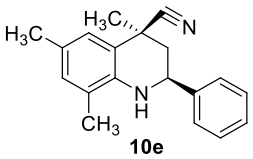
10d


7.33
7.30
7.22
7.19
6.99
6.98
6.78
6.77
6.74
6.73
6.54
6.51
4.39
4.38
4.34
3.94
3.79
2.48
2.43
2.38
2.22
2.17
1.82


4.49
0.98
1.11
1.07
1.00
1.12
3.28
4.32
1.02
3.07
f1 (ppm)

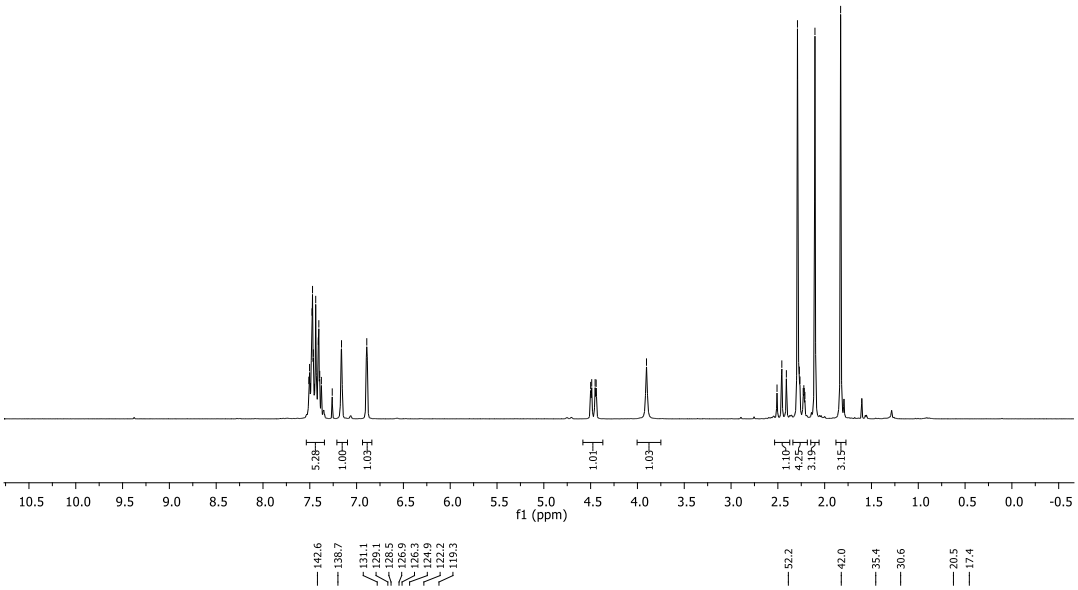

152.3
139.2
138.1
137.2
129.6
128.7
126.6
120.5
116.3
116.1
112.9
56.0
51.8
42.0
35.4
30.6
21.2

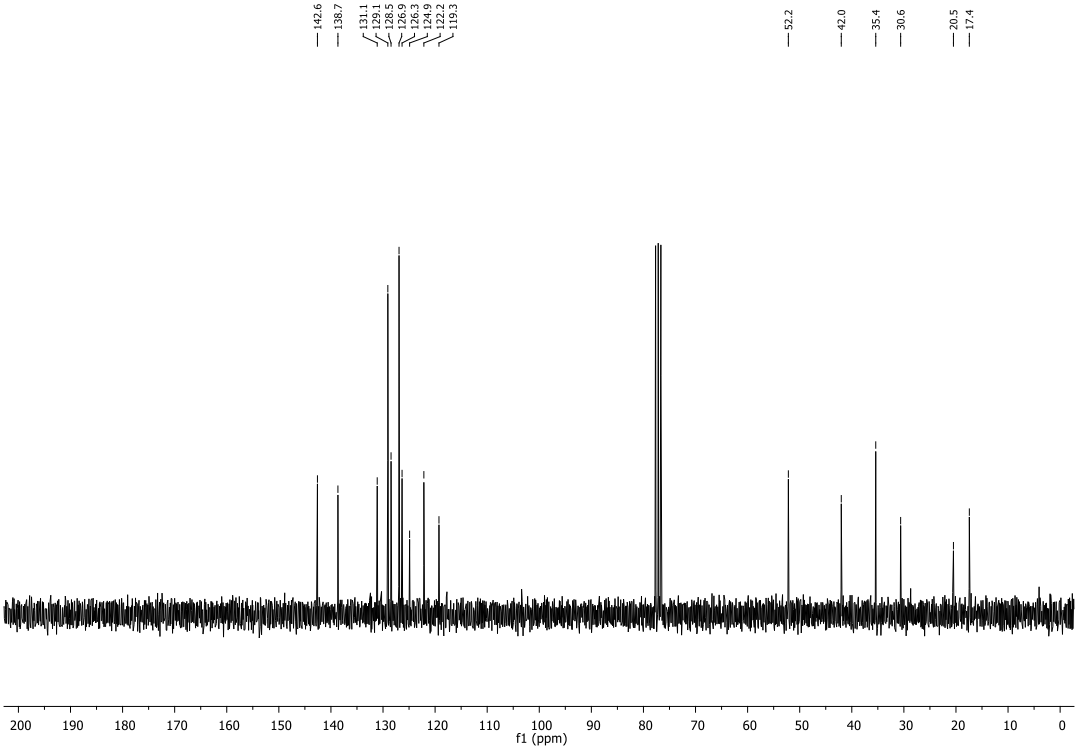

f1 (ppm)

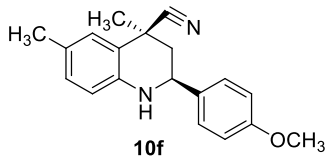

H3C
H3C
N
N
H
CH3

10e


7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.44
7.41
7.40
7.39
7.38
7.26
7.16
6.89
4.50
4.49
4.45
4.44
3.90
2.51
2.46
2.41
2.29
2.27
2.26
2.23
2.22
2.22
2.21
2.10
1.83

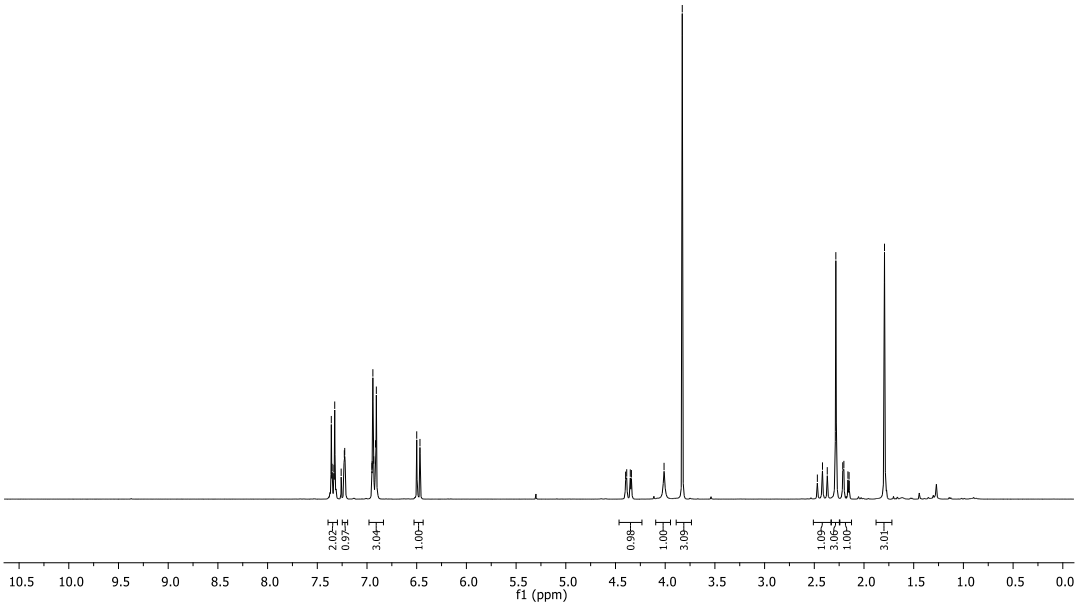

5.28
1.00
1.03
1.01
1.03
1.10
4.25
3.19
3.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


142.6
138.7
131.1
129.1
128.5
126.9
126.3
124.9
122.2
119.3
52.2
42.0
35.4
30.6
20.5
17.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

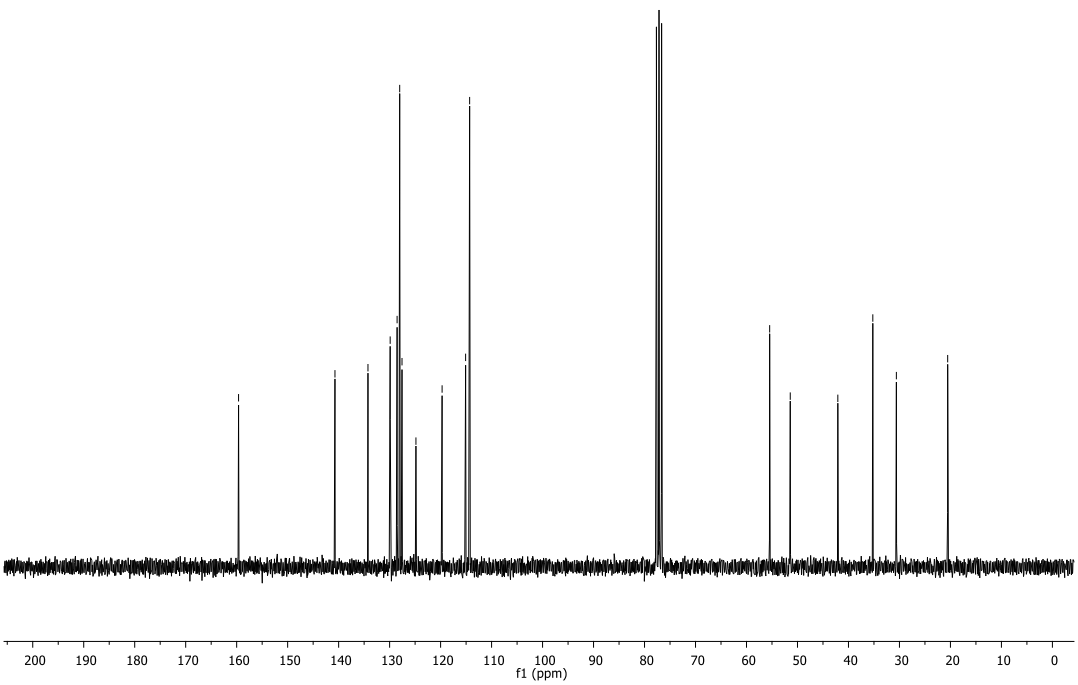

H3C
H3C
N
N
H
OCH3

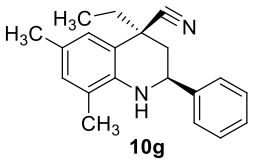
10f


7.36
7.35
7.33
7.32
7.26
7.23
7.22
6.94
6.91
6.81
6.50
6.47
4.40
4.39
4.35
4.34
4.01
3.83
2.47
2.42
2.37
2.28
2.21
2.20
2.16
2.15
1.79

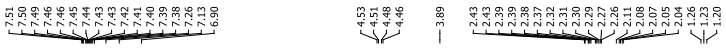

2.02
0.97
3.04
1.00
0.98
1.00
3.09
1.09
3.06
1.00
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

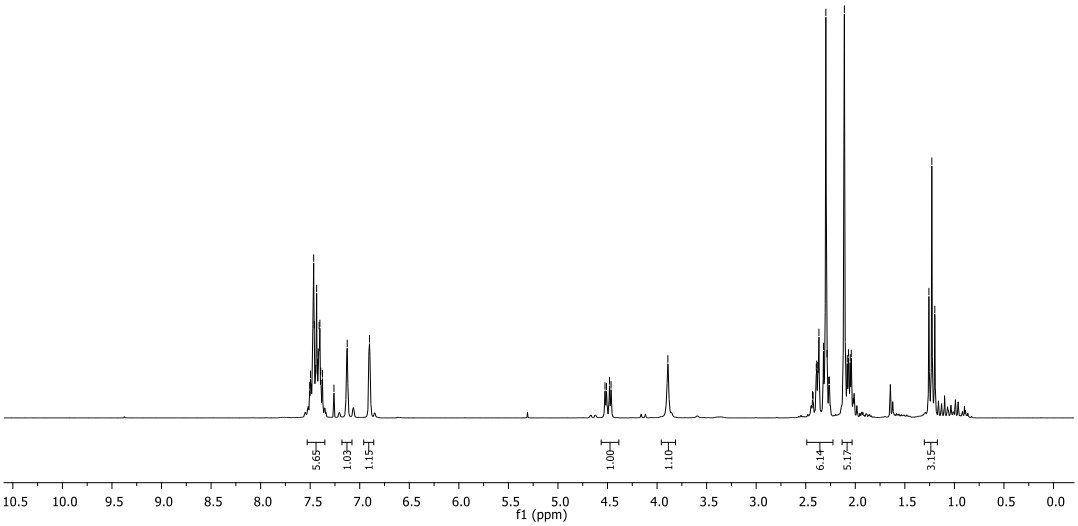

159.6
140.7
134.2
129.9
128.5
128.0
127.6
124.8
119.7
115.1
114.3
55.5
51.4
42.1
35.2
30.6
20.5


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

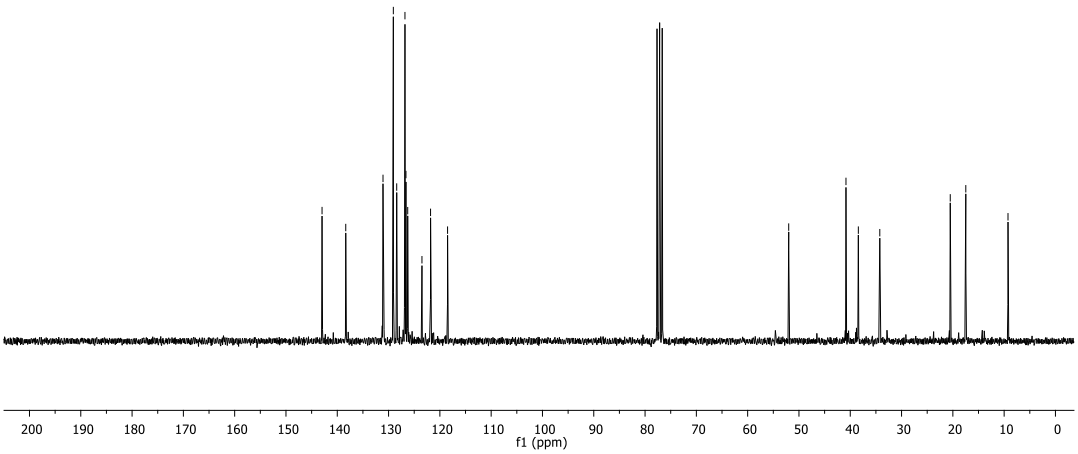


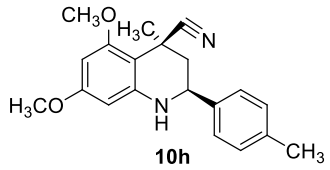
10g


7.51
7.50
7.49
7.46
7.46
7.45
7.44
7.43
7.43
7.42
7.41
7.40
7.39
7.38
7.26
7.13
6.90
4.53
4.51
4.48
4.46
3.89
2.43
2.43
2.39
2.39
2.38
2.37
2.32
2.31
2.30
2.29
2.27
2.26
2.11
2.08
2.07
2.05
2.04
1.26
1.23
1.20

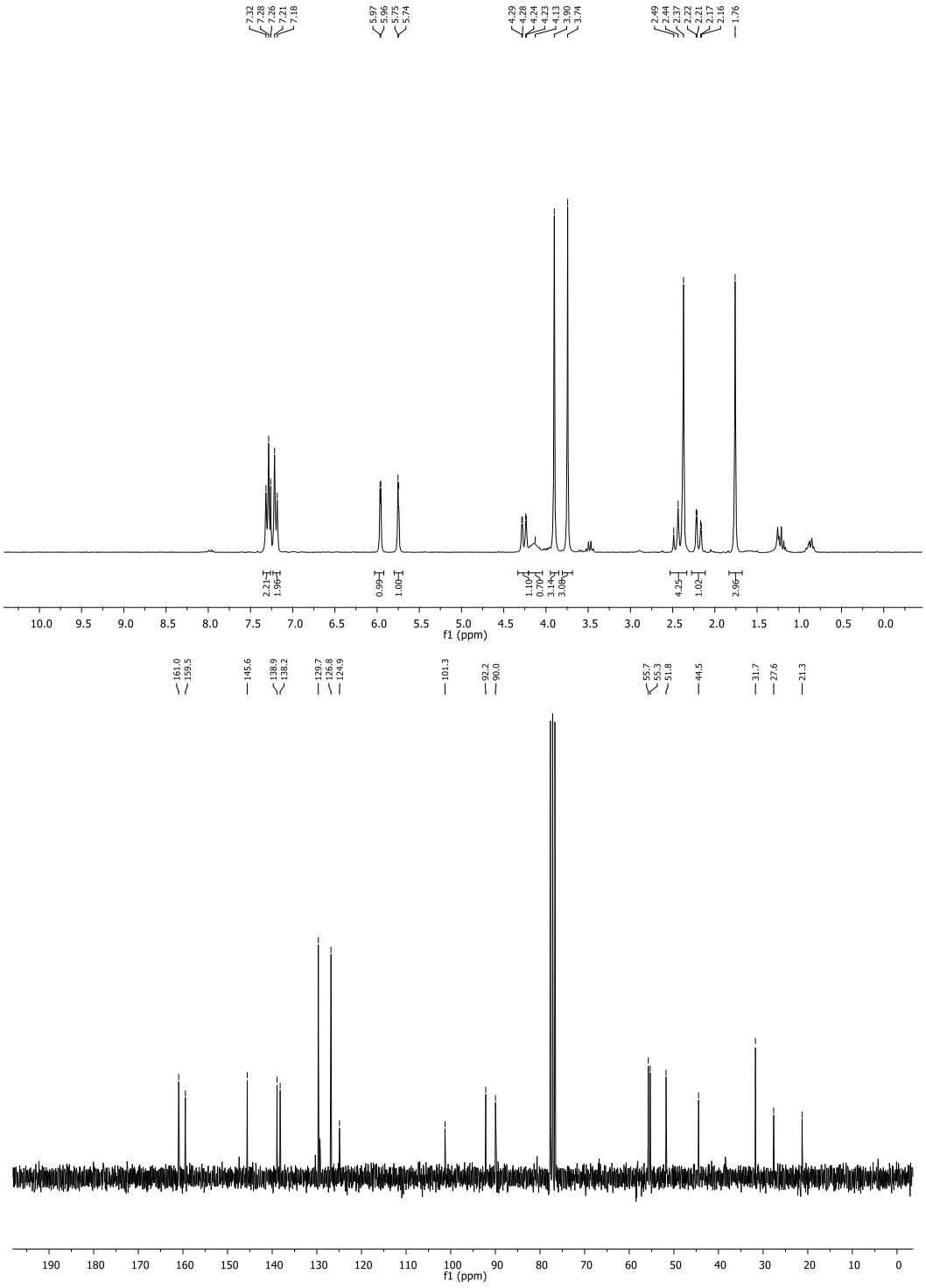

5.65
1.03
1.15
1.00
1.10
6.14
5.17
3.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

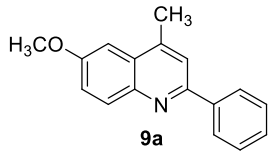

143.0
138.3
131.1
129.1
128.4
126.8
126.6
126.3
123.5
121.8
118.5
52.0
40.8
38.4
34.2
20.5
17.5
9.2


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

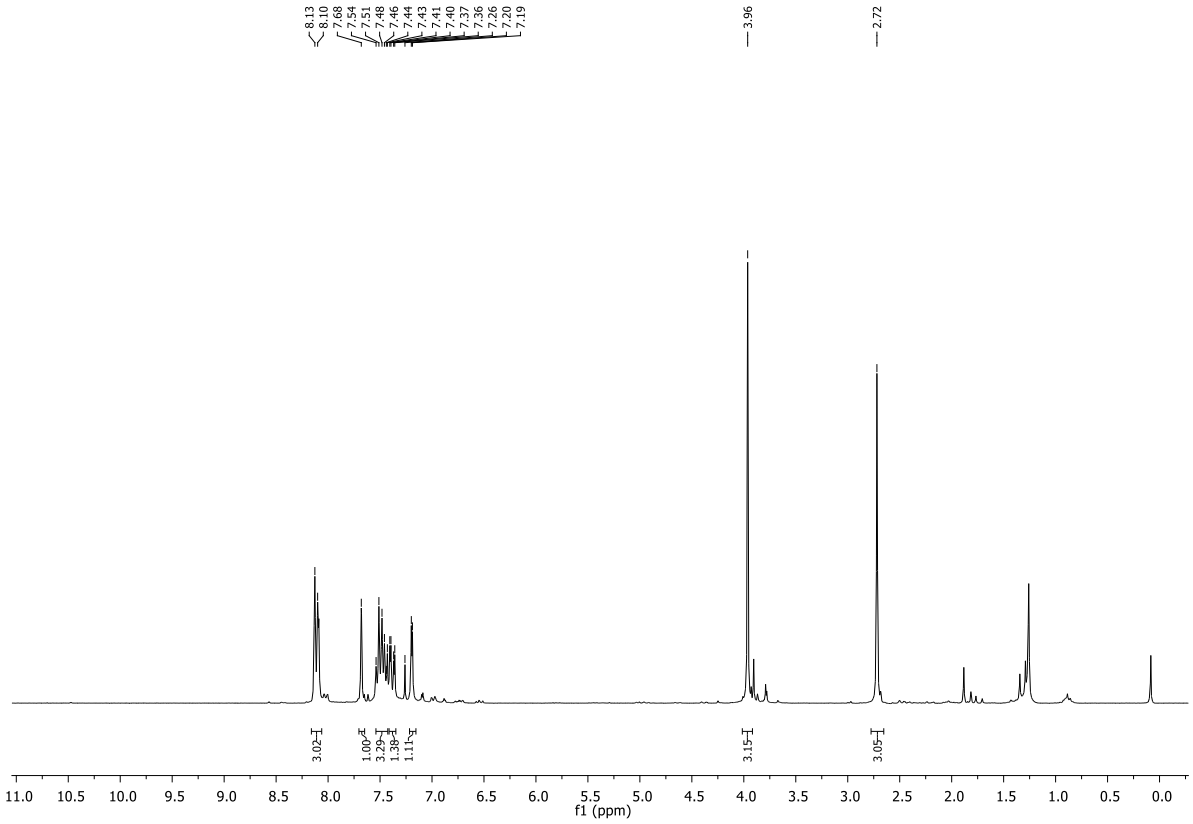

CH3O
H3C
N
H3CO
N
H
CH3

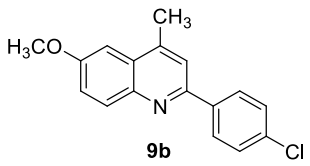
10h


7.32
7.28
7.26
7.21
7.18
5.97
5.96
5.75
5.74
4.29
4.28
4.24
4.23
4.13
3.90
3.74
2.49
2.44
2.37
2.22
2.21
2.17
2.16
1.76
2.21
1.96
0.99
1.00
1.10
0.70
3.14
3.08
4.25
1.02
2.96
f1 (ppm)
161.0
159.5
145.6
138.9
138.2
129.7
126.8
124.9
101.3
92.2
90.0
55.7
55.3
51.8
44.5
31.7
27.6
21.3
f1 (ppm)


CH3
H3CO
N

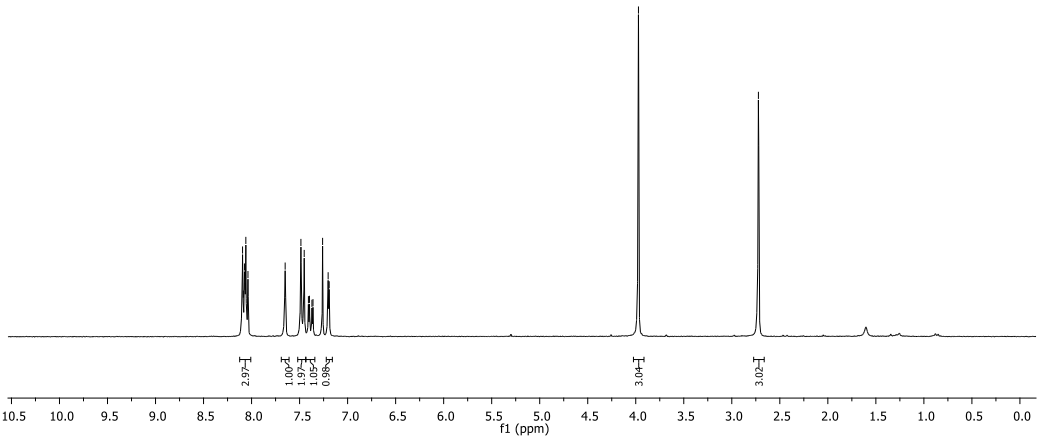
9a

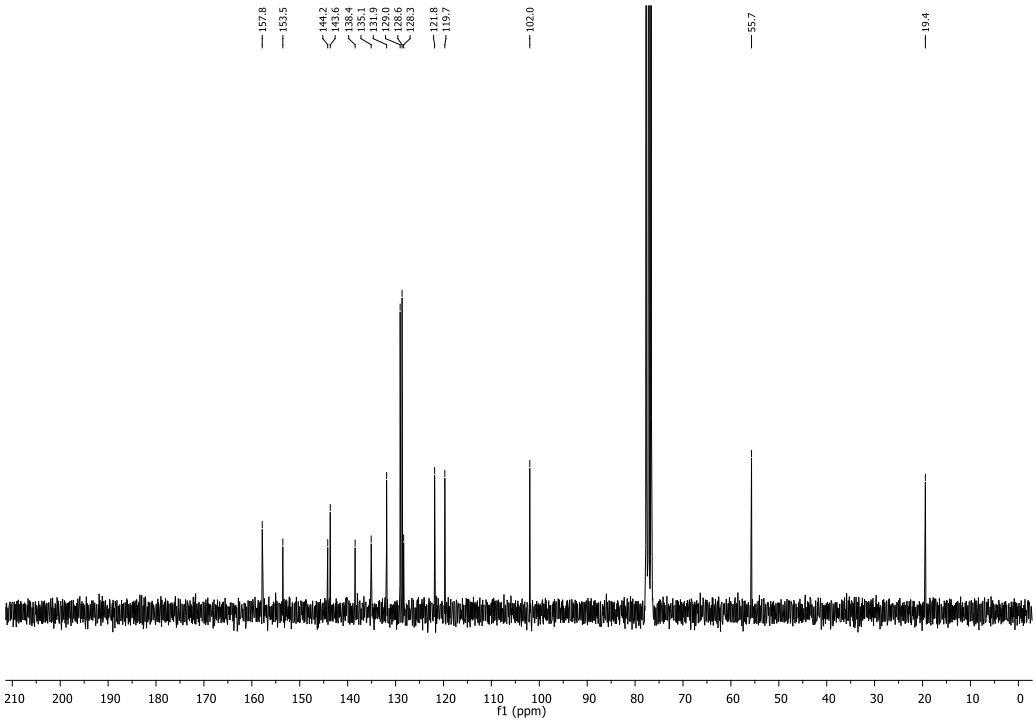

8.13
8.10
7.68
7.54
7.51
7.48
7.46
7.44
7.43
7.41
7.40
7.37
7.36
7.26
7.20
7.19
3.96
2.72
3.02
1.00
3.29
1.38
1.11
3.15
3.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

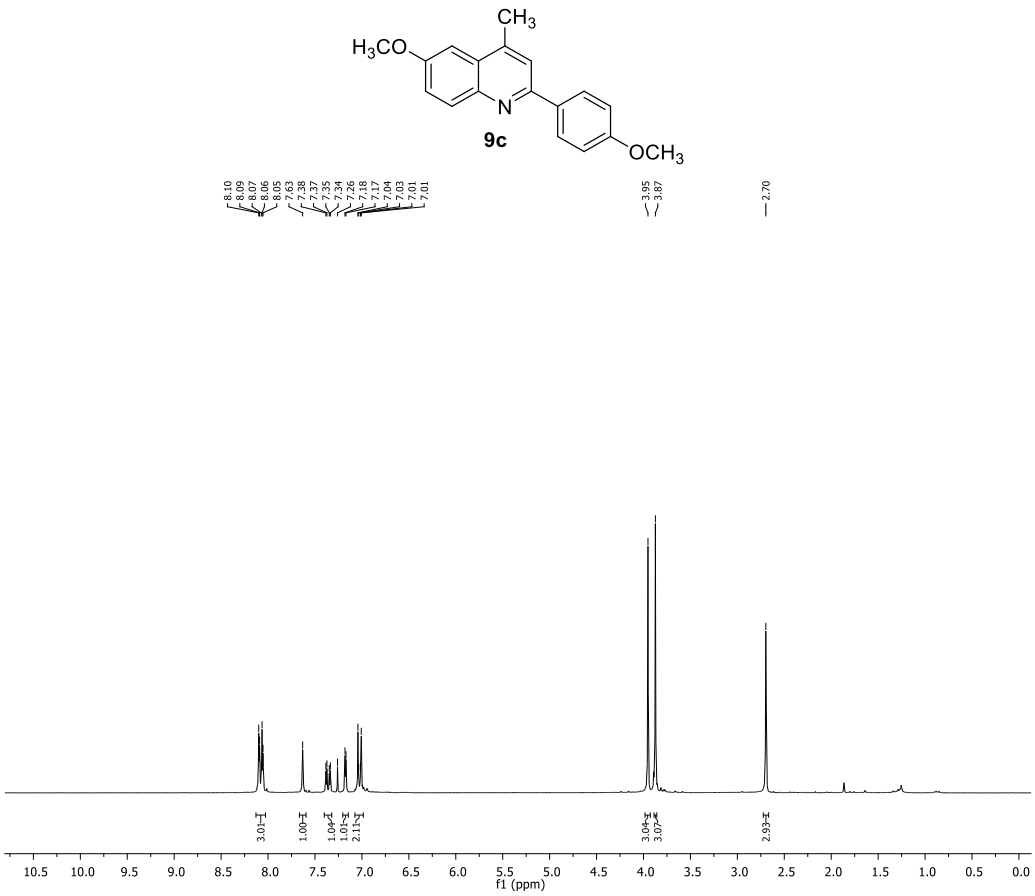

CH3
H3CO
N
Cl

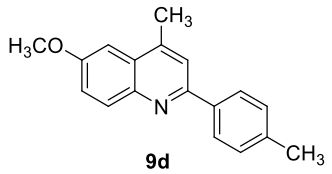
9b


8.09
8.09
8.07
8.07
8.06
8.04
7.65
7.49
7.45
7.41
7.40
7.37
7.36
7.26
7.20
7.19
3.97
2.72


2.97
1.00
1.97
1.05
0.98
3.04
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

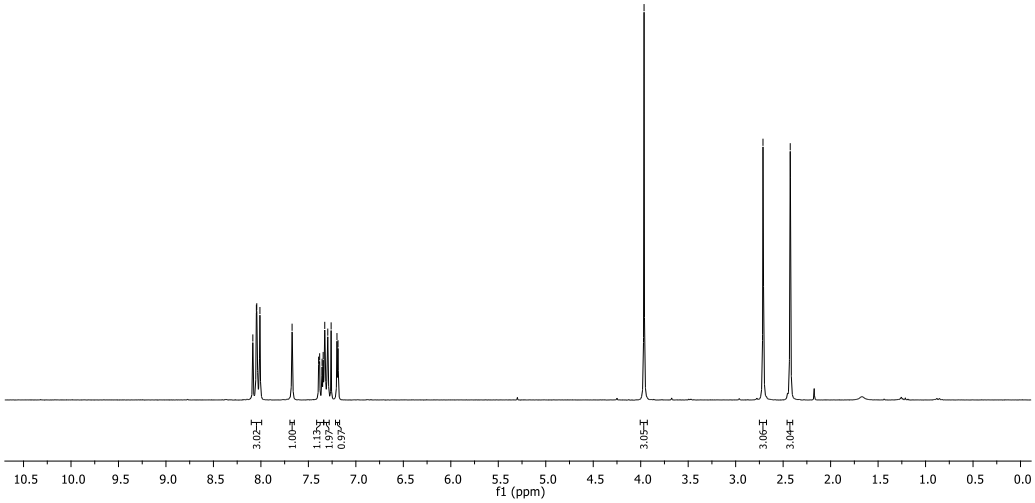

157.8
153.5
144.2
143.6
138.4
135.1
131.9
129.0
128.6
128.3
121.8
119.7
102.0
55.7
19.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

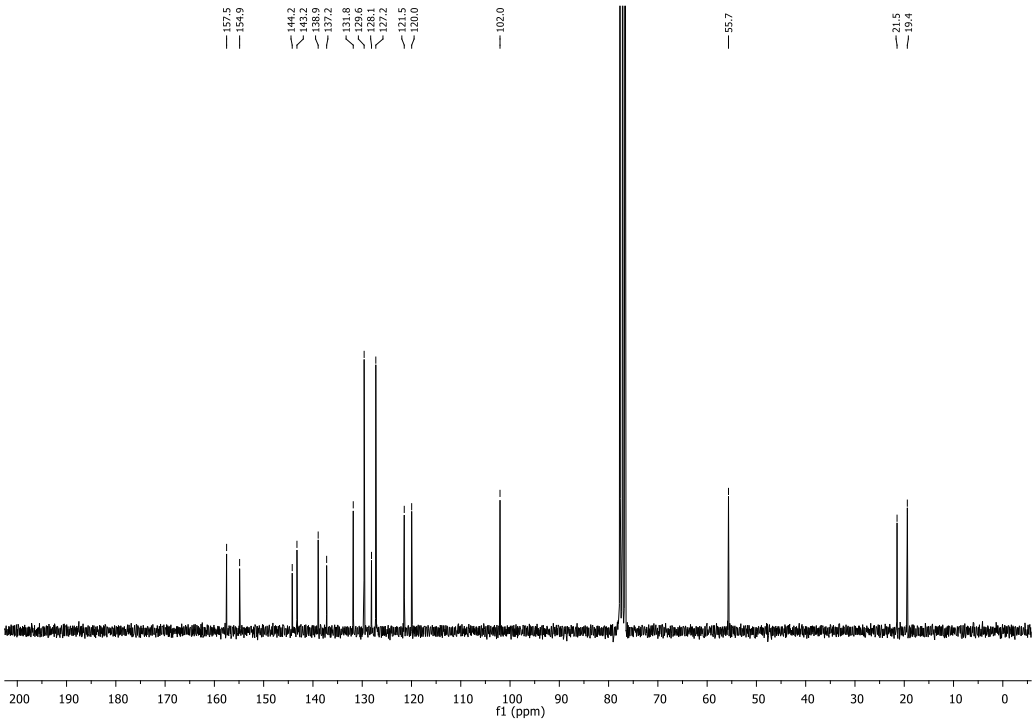

CH3
H3CO
N
OCH3
9c
8.10
8.09
8.07
8.06
8.05
7.63
7.38
7.37
7.35
7.34
7.26
7.18
7.17
7.04
7.03
7.01
7.01
3.95
3.87
2.70
3.01
1.00
1.04
1.01
2.11
3.04
3.07
2.93
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

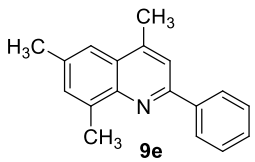

CH3
H3CO
N
CH3

9d


8.08
8.05
8.04
8.01
7.67
7.39
7.38
7.36
7.34
7.33
7.30
7.26
7.20
7.19
3.96
2.71
2.43

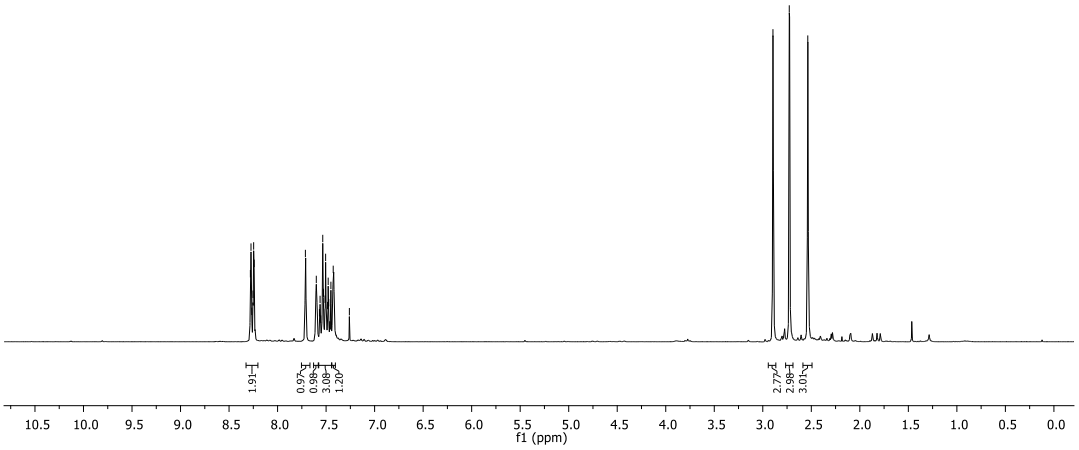

3.02
1.00
1.13
1.97
0.97
3.05
3.06
3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

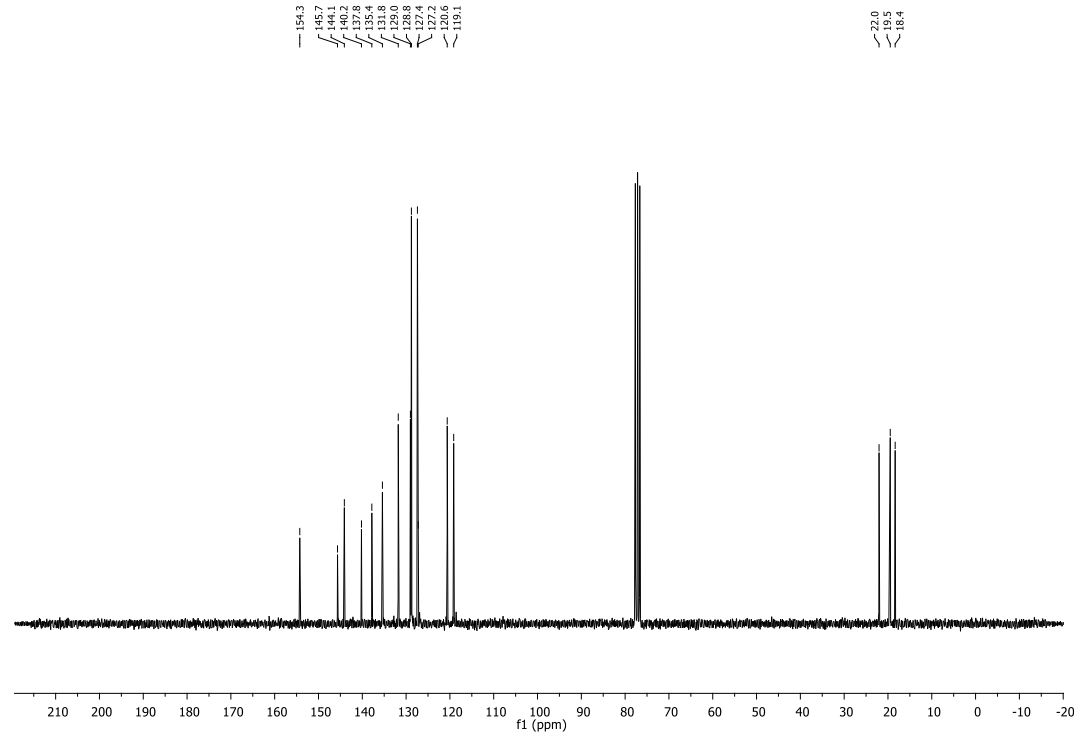

157.5
154.9
144.2
143.2
138.9
137.2
131.8
129.6
128.1
127.2
121.5
120.0
102.0
55.7
21.5
19.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

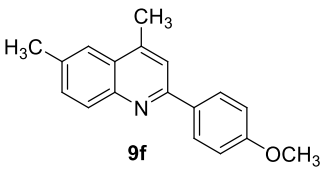

CH3
H3C
N
CH3

9e

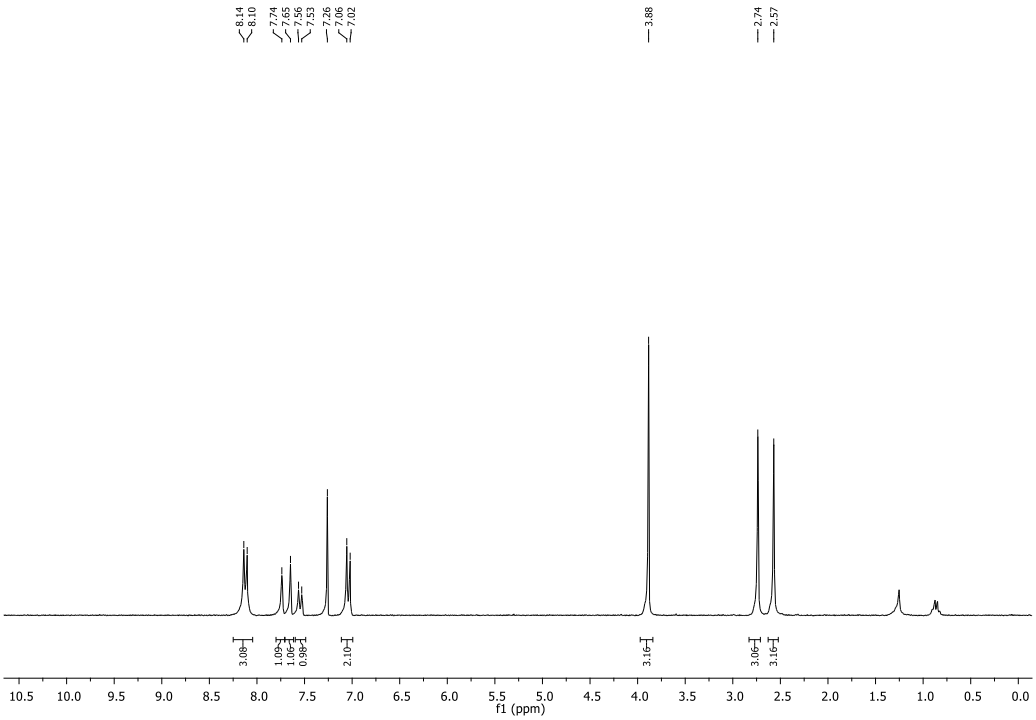

8.28
8.27
8.27
8.25
8.25
8.24
7.71
7.60
7.57
7.56
7.55
7.53
7.53
7.51
7.50
7.48
7.48
7.47
7.45
7.43
7.26
2.90
2.73
2.54

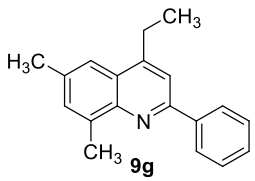

1.91
0.97
0.98
3.08
1.20
2.77
2.99
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.3
145.7
144.1
140.2
137.8
135.4
131.8
130.0
128.8
127.4
127.2
120.6
119.1
22.0
19.5
18.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


CH3
H3C
N
OCH3

9f


8.14
8.10
7.74
7.65
7.56
7.53
7.26
7.06
7.02
3.88
2.74
2.57
3.08
1.09
1.06
0.98
2.10
3.16
3.06
3.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CH3
H3C
N
CH3

9g


8.27
8.26
8.25
8.24
8.23
8.23
7.73
7.65
7.56
7.55
7.54
7.52
7.52
7.51
7.50
7.49
7.47
7.46
7.46
7.44
7.41
7.26
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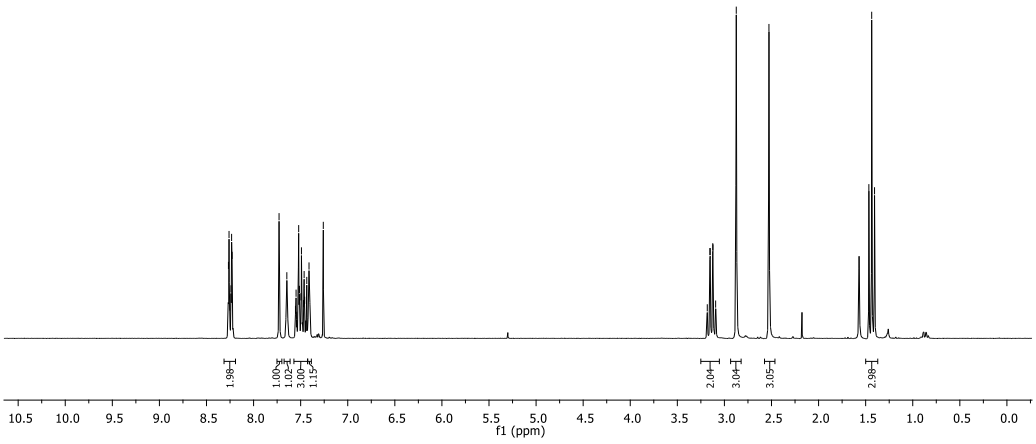
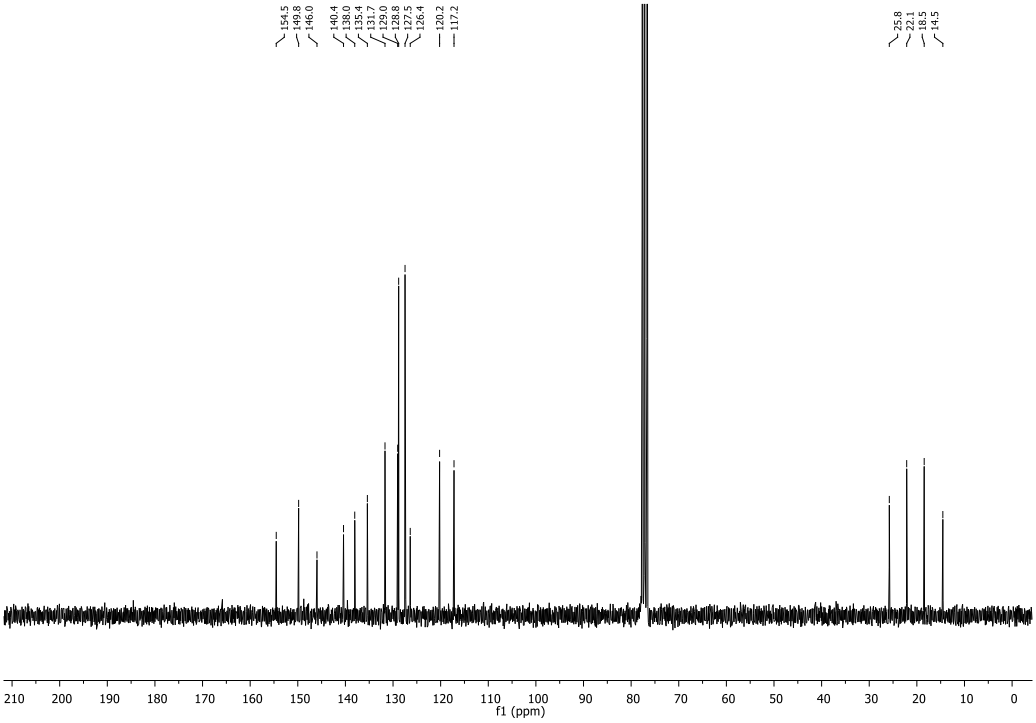
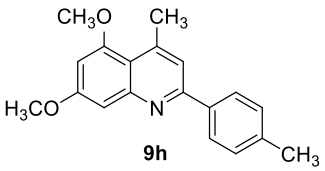
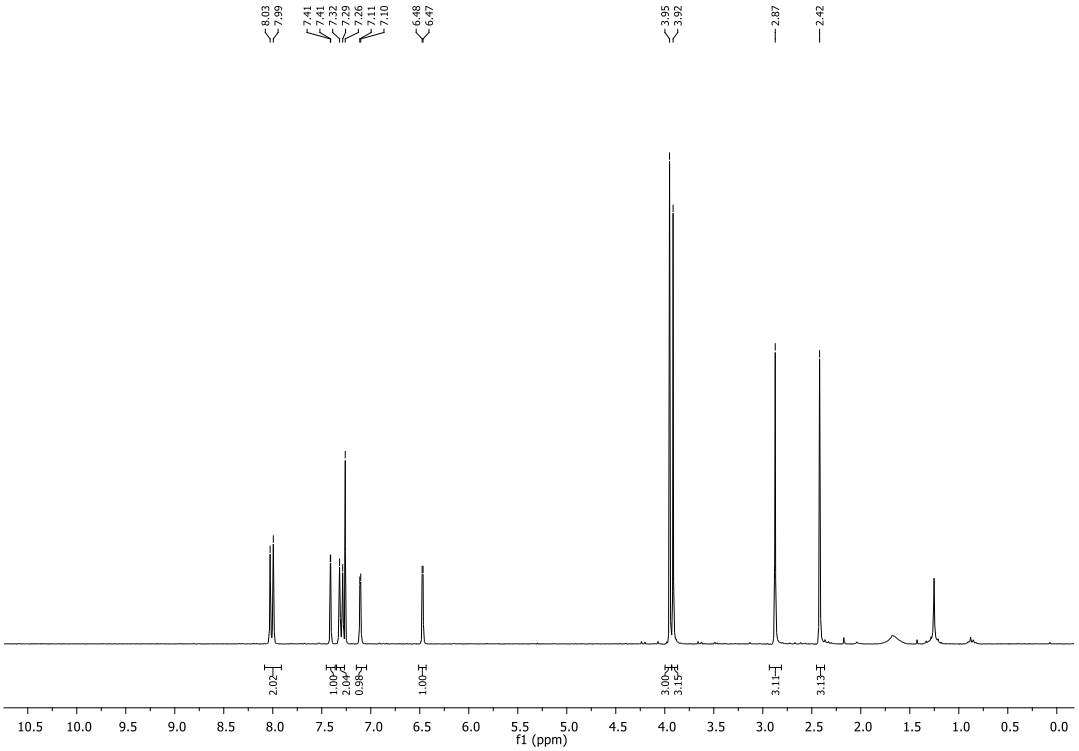
3.09
2.87
2.53
1.47
1.44
1.41

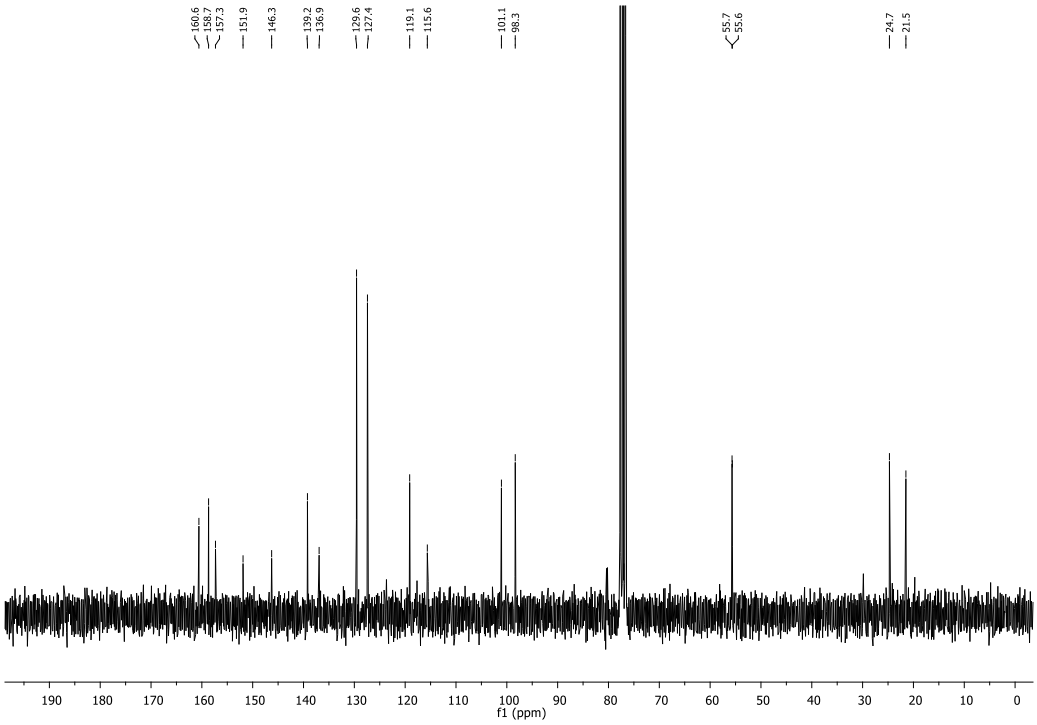

1.98
1.00
1.02
3.00
1.15
2.04
3.04
3.05
2.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.5
149.8
146.0
140.4
138.0
135.4
131.7
129.0
128.8
127.5
126.4
120.2
117.2
25.8
22.1
18.5
14.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CH3O
CH3
H3CO
N
CH3

9h


8.03
7.99
7.41
7.41
7.32
7.29
7.26
7.11
7.10
6.48
6.47
3.95
3.92
2.87
2.42
2.02
1.00
2.04
0.98
1.00
3.00
3.15
3.11
3.13
f1 (ppm)


160.6
158.7
157.3
151.9
146.3
139.2
136.9
129.6
127.4
119.1
115.6
101.1
98.3
55.7
55.6
24.7
21.5
f1 (ppm)