Electronic Supplementary Material (ESI) for Chemical Communications

Synthesis of Biarylketones and Phthalides from Organoboronic Acids and Aldehydes Catalyzed by Cobalt Complexes

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Supporting Information

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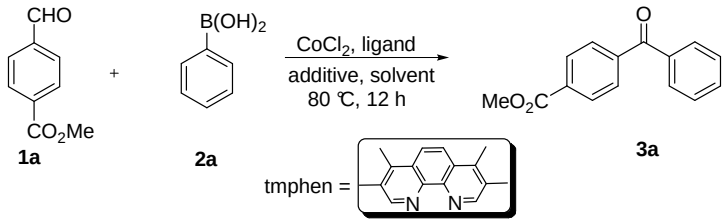
General. All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. All solvents were dried according to known methods and distilled prior to use.[1] Starting materials were commercially available and used as purchased.

General procedure for the cobalt-catalyzed synthesis of biarylketones. A seal tube (20 mL) containing $CoCl_2$ (0.10 mmol, 10 mol%), tmphen (0.015 mmol, 15 mol%) 4-methoxycarbonylbenzaldehyde (1.00 mmol) phenylboronic acid (1.50 mmol) and Cs_2CO_3 (2.00 mmol) were evacuated and purged with nitrogen gas three times. Freshly distilled acetonitrile (3.0 mL) and toluene (1.0 mL) were added and stirred well until the solution became deep blue. Then the reaction mixture was evacuated and filled with oxygen. The reaction mixture was heated with stirring at 80 °C for 14 h and then cooled, diluted with 30% *n*-hexane-ethyl acetate and stirred in air for 10 min. The mixture was filtered through a Celite and silica gel pad and washed with 30% *n*-hexane-ethyl acetate. The filtrate was concentrated and the residue was purified on a silica gel column using *n*-hexane-ethyl acetate as eluent to afford the desired product **3a**. Similar procedures were employed to prepare compounds **3b-t**. Similar procedures were also used for the preparation of **3u-w**, except that the reactions were carried out under nitrogen atmosphere.

Table 1. Optimization studies for the cobalt-catalyzed addition of organoboronic acids with aldehydes to give diarylketones.[a]

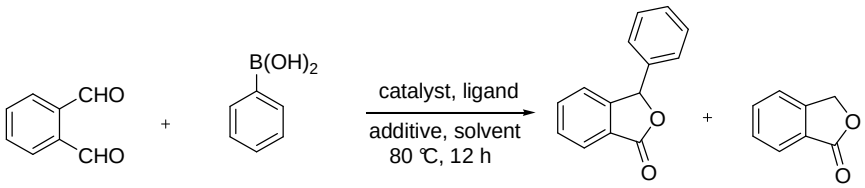


Entry	Catalyst	Ligand	Additive	Solvent	Yield (%)[b]
1	$CoCl_2$	dppe	Cs_2CO_3	CH_3CN:Tol (3:1)	N.R
2	$CoCl_2$	1,10-phen	Cs_2CO_3	CH_3CN:Tol (3:1)	58
3	$CoCl_2$	bipy	Cs_2CO_3	CH_3CN:Tol (3:1)	38
4	$CoCl_2$	tmeda	Cs_2CO_3	CH_3CN:Tol (3:1)	31
5	$CoCl_2$	2,9-dm-1,10-phen	Cs_2CO_3	CH_3CN:Tol (3:1)	47
6	$CoCl_2$	tmphen	Cs_2CO_3	CH_3CN:Tol (3:1)	64
7	$CoCl_2$	tmphen	Cs_2CO_3	CH_3CN	36
8	$CoCl_2$	tmphen	Cs_2CO_3	Toluene	17
9	$CoCl_2$	tmphen	Cs_2CO_3	1,2-DCE	12
10	$CoCl_2$	tmphen	Cs_2CO_3	THF	18
11	$CoCl_2$	tmphen	Cs_2CO_3	1,4-dioxane	N.R
12	$CoCl_2$	tmphen	K_2CO_3	CH_3CN:Tol (1:1)	27
13	$CoCl_2$	tmphen	Cs_2CO_3	CH_3CN:Tol (2:1)	82
14	**$CoCl_2$**	**tmphen**	**Cs_2CO_3**	**CH_3CN:Tol (3:1)**	**91**
15	$CoCl_2$	tmphen	Cs_2CO_3	CH_3CN:Tol (4:1)	85
16	$CoCl_2$	tmphen	Cs_2CO_3	CH_3CN:Tol (1:1)	54[c]

[a] Unless otherwise mentioned, all reactions were carried out using aldehyde **1** (1.00 mmol), arylboronic acid **2** (1.50 mmol), $CoCl_2$ (0.10 mmol) tmphen (0.15 mmol), Cs_2CO_3 (1.50 mmol) and CH_3CN/toluene (3:1, 4 mL) at 80 ºC for 12 h under O_2 (1 atm at room temperature). [b] Isolated yields. [c] The reaction was carried out under N_2.

General procedure for the cobalt-catalyzed synthesis of 3-arylphthalides. A seal tube (20 mL) containing CoI_2 (0.050 mmol, 5 mol%), dppe (0.050 mmol, 5 mol%), K_2CO_3 (1.50 mmol) phthalaldehyde (1.00 mmol) and phenylboronic acid (1.50 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled THF (3.0 mL) was added and the mixture was stirred until the solution became deep brown. The reaction mixture was heated with stirring at 80 °C for 14 h and was then cooled, diluted with 30% *n*-hexane-ethyl acetate and stirred in the air for 10 min. The mixture was filtered through a Celite and silica gel pad and washed with 30% *n*-hexane-ethyl acetate. The filtrate was concentrated and the residue was purified on a silica gel column using *n*-hexane-ethyl acetate as eluent to afford the desired product **4a**. Similar procedures were employed to prepare compounds **4b- 4k**.

Table 2. Optimization studies for the cobalt-catalyzed addition reaction of organoboronic acids with phthalaldehydes to give 3-arylphthalides.[a]



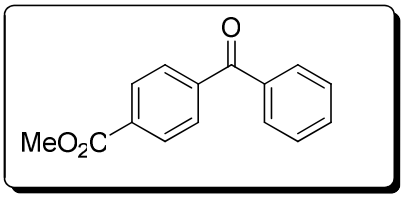
1p **2a** **4a** **5a**

Entry	Catalyst	Ligand	Additive	Solvent	Yield of 4a (%)[b]	Yield of 5a (%)[b]
1	$CoCl_2$	tmphen	Cs_2CO_3	CH_3CN:Tol (3:1)	62	28
2	$CoCl_2$	1,10-Phen	K_2CO_3	CH_3CN	36	65
3	CoI_2	dppe	K_2CO_3	CH_3CN	56	30
4	**CoI_2**	**dppe**	**K_2CO_3**	**THF**	**89**	**10**
5	CoI_2	dppe	K_2CO_3	THF	87[c]	10[c]
6	CoI_2	dppe	K_2CO_3	Toluene	48	41
7	CoI_2	dppe	K_2CO_3	1,2-DCE	35	60
8	CoI_2	dppe	K_2CO_3	1,4-Dioxane	-	-
9	CoI_2	dppe	CsF	THF	67	32
10	CoI_2	dppe	Cs_2CO_3	THF	78	18
11	CoI_2	dppe	Na_2CO_3	THF	80	14
12	CoI_2	dppe	K_3PO_4	THF	82	15

[a] Unless otherwise mentioned, all reactions were carried out using phthalaldehyde **1** (1.00 mmol), arylboronic acid **2** (1.50 mmol), CoI_2 (0.050 mmol), dppe (0.050 mmol), K_2CO_3 (1.50 mmol) and THF (4 mL) at 80 °C for 12 h under N_2. [b] Isolated yields. [c] The reaction was carried out under air.

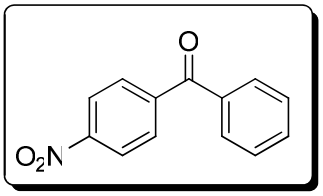
The spectral data and a copy of the ^{1}H and ^{13}C NMR spectra of compounds **3** are listed below.

4-Methoxycarbonylphenyl(phenyl)methanone (3a)



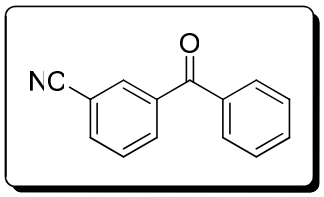
White solid m.p. 65-67 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.0 Hz, 2 H), 7.82 (d, *J* = 8.0 Hz, 2 H), 7.78 (d, *J* = 7.6 Hz, 2 H), 7.60 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 2 H), 3.94 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.0 (CO), 166.3 (*CO*-Ester), 141.3 (C), 136.9 (C), 133.2 (C), 132.9 (*C*H), 130.1 (2 *C*H), 129.7 (2 *C*H), 129.5 (2 *C*H), 128.5 (2 *C*H), 52.4 (CH_3); IR (neat) 1720 (ν_{CO}), 1655, 1438 and 1282 cm^{-1}; **HRMS** (EI^+) calcd for $C_{15}H_{12}O_3$ 240.0786, found 240.0780.

4-Nitrophenyl(phenyl)methanone (3b)



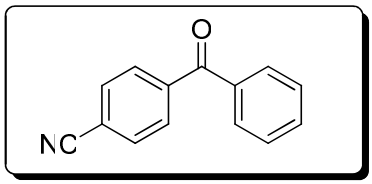
Light yellow solid m.p. 76-77 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 2 H), 7.92 (d, *J* = 8.8 Hz, 2 H), 7.80 (d, *J* = 7.6 Hz, 2 H), 7.63 (t, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.8 (CO), 149.8 (C), 142.8 (C), 136.3 (C), 133.5 (*C*H), 130.7 (2 *C*H), 130.1 (2 *C*H), 128.7 (2 *C*H), 123.5 (2 *C*H); IR (neat) 1650 (ν_{CO}), 1594, and 1513 cm^{-1}; **HRMS** (EI^+) calcd for $C_{13}H_9NO_3$ 227.0582, found 227.0590.

3-Cyanophenyl(phenyl)methanone (3c)



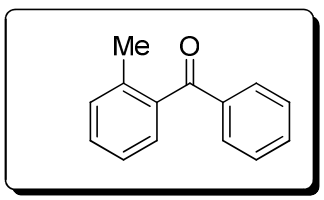
Pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 (s, 1 H), 8.02 (d, *J* = 8.4 Hz, 1 H), 7.85 (d, *J* = 7.6 Hz, 2 H), 7.75 (d, *J* = 7.6 Hz, 2 H), 7.64-7.59 (m, 2 H), 7.50 (t, *J* = 7.6 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.4 (CO), 138.6.(C), 136.3 (C), 135.3 (*C*H), 133.8 (*C*H), 133.4 (*C*H), 133.2 (*C*H), 129.9 (2 *C*H), 129.4 (*C*H), 128.7 (*C*H), 117.9 (CN), 112.8(C); IR (neat) 2231, 1664 (ν_{CO}), 1597and 1283 cm^{-1}; **HRMS** (EI^+) calcd for $C_{14}H_9NO$ 207.0684, found 207.0681.

4-Cyanophenyl(phenyl)methanone (3d)



Pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 8.4 Hz, 4 H), 7.60 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.9 (CO), 141.1.(C), 136.2 (C), 133.2 (*C*H), 132.1 (2 *C*H), 130.1 (2 *C*H), 129.9 (2 *C*H), 128.5 (2 *C*H), 117.9 (CN), 115.5(C); IR (neat) 2228, 1649 (ν_{CO}), 1596, and 1447 cm^{-1}; **HRMS** (EI^+) calcd for $C_{14}H_9NO$ 207.0684, found 207.0681.

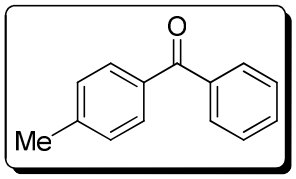
Phenyl(2-tolyl)methanone (3e)



Light yellow solid m.p. 114-116 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 7.6, *J* = 1.4 Hz, 2 H), 7.56 (tt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1 H), 7.37 (t, *J* = 7.6 Hz, 2 H), 7.37 (dt, *J* = 7.4 Hz, *J* = 1.2 Hz, 1 H), 7.30-7.21 (m, 3 H), 2.31 (s, 3 H). **^{13}C NMR** (100

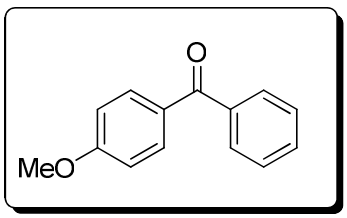
MHz, $CDCl_3$): δ 198.6 (CO), 138.6 (C), 137.7 (C), 136.7 (C), 133.1 (*C*H), 130.9 (*C*H), 130.2 (*C*H), 130.1 (2 *C*H), 128.5 (*C*H), 128.4 (2 *C*H), 125.2 (*C*H), 19.9 (CH_3); IR (neat) 1654 (ν_{CO}), 1598, and 840 cm^{-1}; **HRMS** (EI^+) calcd for $C_{14}H_{12}O$ 196.0888, found 196.0884.

Phenyl(4-tolyl)methanone (3f)



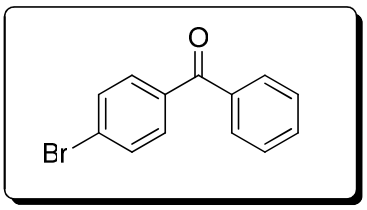
Pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 2 H),7.72 (d, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.28 (d, *J* = 7.6 Hz, 2 H),2.43 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.3 (CO), 143.0 (C), 137.7 (C), 134.7 (C), 131.9 (*C*H), 130.1 (2 *C*H), 129.7 (2 *C*H), 128.8 (2 *C*H), 128.0 (2 *C*H), 21.5 (CH_3); IR (neat) 1657 (ν_{CO}), 1605 and 833 cm^{-1}; **HRMS** (EI^+) calcd for $C_{14}H_{12}O$ 196.0888, found 196.0884.

4-Methoxyphenyl(phenyl)methanone (3g)



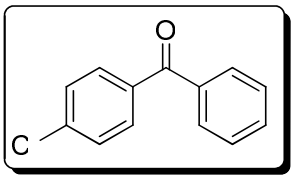
Pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 2 H),7.72 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 2 H), 7.51 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.2 Hz, 2 H), 6.90 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2 H), 3.84 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.0 (CO), 162.0 (C), 137.9 (C), 132.1 (2 *C*H), 131.5 (*C*H), 129.7 (C), 129.3 (2 *C*H), 127.8 (2 *C*H), 113.2 (2 *C*H), 55.1 (CH_3); IR (neat) 2839, 1651 (ν_{CO}), 1508 and 1318 cm^{-1}; **HRMS** (EI^+) calcd for $C_{14}H_{12}O_2$ 212.0837, found 212.0836.

4-Bromophenyl(phenyl)methanone (3h)



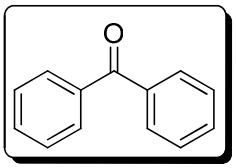
Pale pink solid m.p. 81-83 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76- 7.70 (m, 2 H) 7.67-7.50 (m, 5 H), 7.48-7.44 (m, 2 H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 195.6 (CO), 137.1 (C), 136.2(C), 132.6 (*C*H), 131.6 (2 *C*H), 131.5 (2 *C*H), 129.8 (2 *C*H), 128.3 (2 *C*H), 127.4 (C); IR (neat) 1648 (ν_{CO}), 1586 and 1279 cm^{-1}; **HRMS** (EI^+) calcd for $C_{13}H_9BrO$ 259.9837, found 259.9836.

4-Chlorophenyl(phenyl)methanone (3i)



Pale yellow solid m.p. 72-75 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (t, *J* = 8.0 Hz, 4 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 7.48-7.42 (m, 4 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.4 (CO), 138.8 (C), 137.1(C), 135.8(C), 132.5 (*C*H), 131.4 (2 *C*H), 129.8 (2 *C*H), 128.5 (2 *C*H), 128.3 (2 *C*H); IR (neat) 1649 (ν_{CO}), 1585, 1444 and 863 cm^{-1}; **HRMS** (EI^+) calcd for $C_{13}H_9ClO$ 216.0342, found 216.0338.

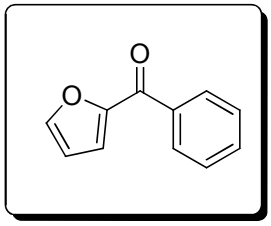
Benzophenone (3j)



White solid m.p. 48-50 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.6 Hz, 4 H),7.50 (t, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 8.0 Hz, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.4 (CO), 137.4 (2C), 132.2 (2 *C*H), 129.8 (4 *C*H), 128.0 (4 *C*H); IR (neat) 1651

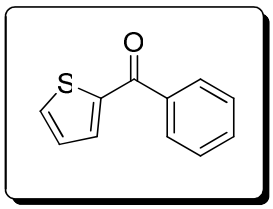
(ν_{CO}), 1598 and 1320 cm^{-1}; **HRMS** (EI^+) calcd for $C_{13}H_{10}O$ 182.0732, found 182.0736.

2-Furyl(phenyl)methanone (3k)



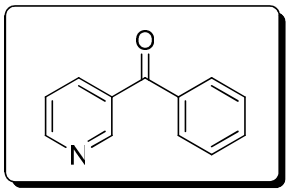
Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.2 Hz, 2 H), 7.68 (s, 1 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.20 (d, *J* = 2.8 Hz, 1 H), 6.57 (dd, *J* = 3.4 Hz, *J* = 1.2 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 182.5 (*CO*), 152.2 (C), 147.0 (*C*H), 137.2 (C), 132.5 (*C*H), 129.2 (2 *C*H), 128.3 (2 *C*H), 120.5 (*C*H), 112.1 (*C*H); IR (neat) 2839, 1651 (ν_{CO}), 1508 and 1318 cm^{-1}; **HRMS** (EI^+) calcd for $C_{11}H_8O_2$ 172.0524, found 172.0521.

Phenyl(2-thienyl)methanone (3l)



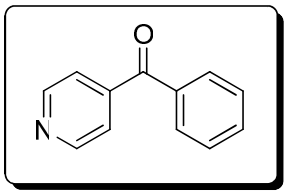
Brown oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.2 Hz, 2 H), 7.70 (d, *J* = 5.2 Hz 1 H), 7.62 (d, *J* = 3.6 Hz, 1 H), 7.57 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.14 (t, *J* = 4.4 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 188.1 (CO), 143.6 (C), 138.0(C), 134.8 (*C*H), 134.1 (*C*H), 132.2 (*C*H), 129.1 (2 *C*H), 128.3 (2 *C*H) 127.9 (*C*H); IR (neat) 1636 (ν_{CO}), 1598 and 1412 cm^{-1}; **HRMS** (EI^+) calcd for $C_{11}H_8OS$ 188.0296, found 188.0302.

Phenyl(3-pyridinyl)methanone (3m)



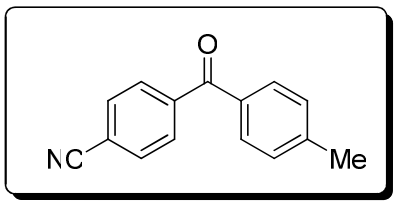
Colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.96 (s, 1 H), 8.79 (d, *J* = 4.8 Hz, 1 H), 8.15 (d, *J* = 7.6 Hz, 1 H), 7.79 (d, *J* = 7.6 Hz, 2 H), 7.62 (t, *J* = 7.6 Hz, 1 H),7.52-7.41 (m, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.4 (CO), 152.5 (*C*H), 150.5 (*C*H), 136.8(*C*H), 136.3 (C), 132.8 (*C*H), 132.7 (C), 129.7 (2 *C*H), 128.3 (2 *C*H), 123.0 (*C*H); IR (neat) 2231, 1664 (ν_{CO}), 1597 and 1283 cm^{-1}; **HRMS** (EI^+) calcd for $C_{13}H_9NO$ 183.0684, found 183.0677.

Phenyl(4-Pyridinyl)methanone (3n)



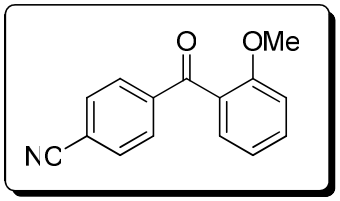
White solid m.p. 66-69 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 6.0 Hz, 2 H), 7.76 (d, *J* = 7.2 Hz, 2 H), 7.58 (t, *J* = 7.60 Hz, 2 H), 7.52 (d, *J* = 6.0 Hz, 2 H) 7.45 (t, *J* = 7.6 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.0 (CO), 150.2 (2 *C*H), 144.2(C), 135.7(C), 133.4 (*C*H), 130.0 (2 *C*H), 128.5 (2 *C*H), 122.7 (2 *C*H); IR (neat) 1652 (ν_{CO}), 1598, 1550 and 1408 cm^{-1}; **HRMS** (EI^+) calcd for $C_{13}H_9NO$ 183.0684, found 183.0683.

4-Cyanophenyl(4-tolyl)methanone (3o)



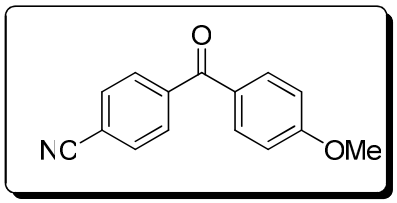
Yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.8 (*CO*), 144.4 (C), 141.6 (C), 133.6 (C), 132.1 (2 *C*H), 130.3 (2 *C*H), 130.1 (2 *C*H), 129.3 (2 *C*H), 118.1(CN), 115.4(C), 21.7 (CH_3); IR (neat) 2230, 1649 (ν_{CO}), 1603 and 1140 cm^{-1}; **HRMS** (EI^+) calcd for $C_{15}H_{11}NO$ 221.0841, found 221.0843.

4-Cyanophenyl(2-methoxyphenyl)methanone (3p)



Yellow solid m.p. 128-130 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.50 (t, *J* = 8.0 Hz, 1 H), 7.40 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.04 (t, *J* = 7.6 Hz, 1 H), 6.96 (d, *J* = 8.0 Hz, 1 H), 3.65 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.9 (*CO*), 157.5 (C), 141.4 (C), 133.0 (*C*H), 131.9 (2 *C*H), 130.0 (*C*H), 129.7 (2 *C*H), 127.3 (C), 130.8 (*C*H), 118.1(CN), 115.6(C), 111.4 (*C*H), 55.4 (CH_3); IR (neat) 2847, 2230, 1666 (ν_{CO}) and 1598 cm^{-1}; **HRMS** (EI^+) calcd for $C_{15}H_{11}NO_2$ 237.0790, found 237.0793.

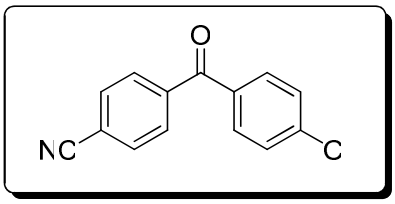
4-Cyanophenyl(4-methoxyphenyl)methanone (3r)



Yellow solid m.p. 131-134 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.81- 7.52 (m, 6 H), 6.97 (dd, *J* = 7.5 Hz, *J* = 2.0 Hz, 2 H), 3.88 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.7 (*CO*), 163.8 (C), 142.0 (C), 132.6 (2 *C*H), 132.0 (2 *C*H), 129.9 (2 *C*H), 128.9

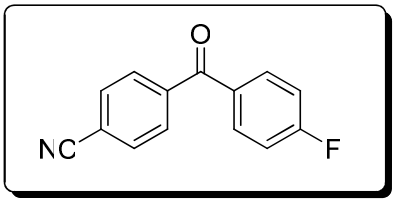
(C), 118.1(CN), 115.1(C), 113.9 (2 *C*H), 55.6 (CH_3); IR (neat) 2851, 2230, 1655 (ν_{CO}) and 1598 cm^{-1}; **HRMS** (EI^+) calcd for $C_{15}H_{11}NO_2$ 237.0790, found 237.0793.

4-Chlorophenyl(4-cyanophenyl)methanone (3s)



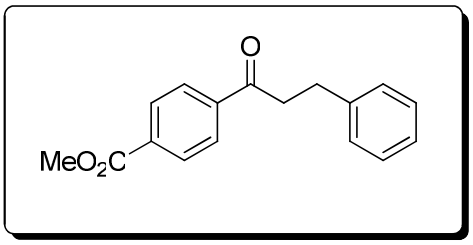
Yellow solid m.p. 137-140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.4 Hz, 2 H), 7.78 (d, *J* = 8.0 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.8 (*CO*), 140.8 (C), 139.9 (C), 134.6 (C), 132.2 (2 *C*H), 131.4 (C), 130.1 (2 *C*H), 129.0 (2 *C*H), 117.8(CN), 115.9(C); IR (neat) 2228, 1645 (ν_{CO}) and 1588 cm^{-1}; **HRMS** (EI^+) calcd for $C_{14}H_8ClNO$ 241.0294, found 241.0298.

4-Cyanophenyl(4-flourophenyl)methanone (3t)



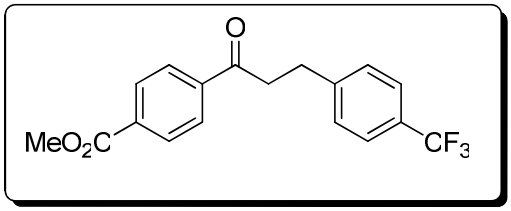
Yellow solid m.p. 92-95 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84- 7.76 (m, 6 H), 7.17 (t, *J* = 8.6 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.5 (*CO*), 165.8 (d, J_{CF} = 254.0 Hz, C), 141.1 (C), 133.3 (C), 132.7 (2 *C*H), 132.5 (2 *C*H), 130.0 (2 *C*H), 117.8(CN), 116.0 (*C*H), 115.8 (*C*H), 115.7(C); IR (neat) 2231, 1648 (ν_{CO}), 1598 and 860 cm^{-1}; **HRMS** (EI^+) calcd for $C_{14}H_8FNO$ 225.0590, found 225.0588.

4-Methoxycarbonylphenyl(Phenyl)proponone (3u)



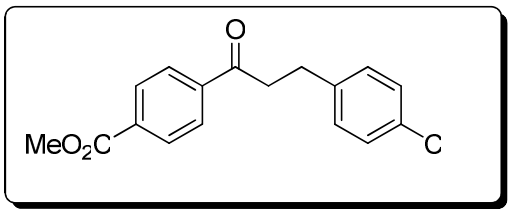
White solid; m.p. 78-82 °C **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 6.8 Hz, *J* = 2.0 Hz, 2 H), 8.00 (dd, *J* = 6.8 Hz, *J* = 2.0 Hz, 2 H), 7.32 -7.21 (m, 5 H), 3.94 (s, 3H), 3.33 (t, *J* = 7.6 Hz, 2 H), 3.07 (t, *J* = 7.6 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.6 (*CO*-ketone),166.1 (*CO*-Ester), 140.8 (C), 139.9 (C), 133.7 (C), 129.7 (2 *C*H), 128.5 (2 *C*H), 128.3 (2 *C*H), 127.8 (2 *C*H), 126.1 (*C*H), 52.4 (CH_3), 40.7 (CH_2), 29.8 (CH_2); IR (neat) 1712, 1684 (ν_{CO}), 1626 and 1576 cm^{-1}; **HRMS** (EI^+) calcd for $C_{17}H_{16}O_3$ 268.1099, found 268.1102.

4-Methoxycarbonylphenyl(4-trifluoromethylPhenyl)proponone (3v)



White solid m.p. 117-120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.0 Hz, 2 H), 7.97 (d, *J* = 8.4 Hz, 2 H), 7.52 (d, *J* = 7.6 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 3.91 (s, 3H), 3.32 (t, *J* = 7.6 Hz, 2 H), 3.11 (t, *J* = 7.6 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.0 (*CO*-ketone),166.1 (*CO*-Ester), 145.1 (C), 139.7 (C), 133.9 (C), 129.8 (2 *C*H), 128.7 (2 *C*H), 128.7 (2 *C*H), 127.8 (2 *C*H), 125.4 (q, $C_{C\text{-}F}$ J = 3.6Hz, C), 52.4 (CH_3), 40.1 (CH_2), 29.5 (CH_2); IR (neat) 2924, 1725, 1671 (ν_{CO}) and 1571 cm^{-1}; **HRMS** (EI^+) calcd for $C_{18}H_{15}F_3O_3$ 336.0973, found 336.0977.

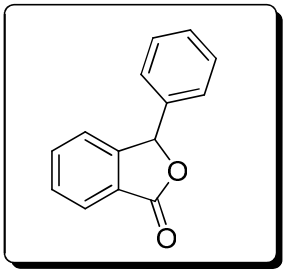
4-Methoxycarbonylphenyl(4-chloroPhenyl)proponone (3w)



White solid m.p. 104-106 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.4 Hz, 2 H), 8.17 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 4.11 (s, 3H), 3.48 (t, *J* = 7.6 Hz, 2 H), 3.21 (t, *J* = 7.6 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.6 (*CO*-ketone), 166.1 (*CO*-Ester), 140.8 (C), 139.9 (C), 133.7 (C), 129.7 (2 *C*H), 128.5 (2 *C*H), 128.3 (2 *C*H), 127.8 (2 *C*H), 126.1 (*C*H), 52.4 (CH_3), 40.7 (CH_2), 29.8 (CH_2); IR (neat) 1717 (ν_{CO}), 1681(ν_{CO}), 1618 and 1572 cm^{-1}; **HRMS** (EI^+) calcd for $C_{17}H_{15}ClO_3$ 302.0710, found 302.0712.

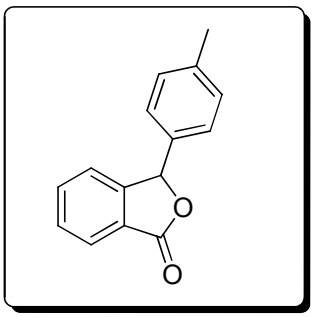
The spectral data and a copy of the ^{1}H and ^{13}C NMR spectra of compounds **4** are listed below.

3-Phenylisobenzofuran-1(3*H*)-one (4a)



White solid m.p. 112-113 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.6 Hz, 1 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.36-7.29 (m, 4 H), 7.26-7.24 (m,, 2 H), 6.38 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.4 (*CO-lactone*), 149.6 (C), 136.3 (C), 134.3 (C), 129.3 (*C*H), 129.2 (*C*H), 128.9 (2 *C*H), 126.9 (2 *C*H), 125.5 (*C*H), 125.4(C), 122.8 (*C*H), 82.6 (*C*H); IR (neat) 1764 (ν_{CO}), 1495, and 1285 cm^{-1}; **HRMS** (EI^{+}) calcd for $C_{14}H_{10}O_2$ 210.0681, found 210.0681.

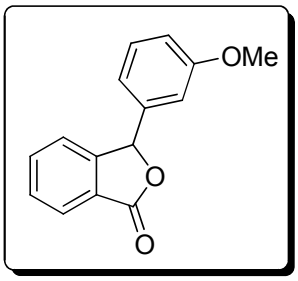
3-*p*-Tolylisobenzofuran-1(3*H*)-one (4b)



White solid m.p. 107-110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 1 H), 7.62 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.29 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1 H), 7.17-7.11 (m, 4 H), 6.35 (s, 1 H), 2.32 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.5 (*CO-lactone*), 149.7 (C), 136.2 (C), 134.2 (*C*H), 133.3 (C), 129.5 (2 *C*H), 129.2 (*C*H), 126.9 (2 *C*H), 125.6 (C), 125.4(*C*H), 122.8 (*C*H), 82.7

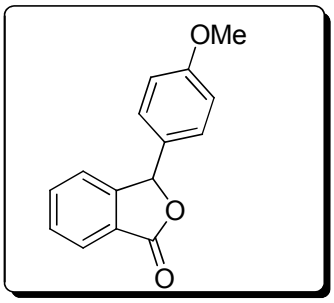
(*C*H), 21.1 (CH_3); IR (neat) 1754 (ν_{CO}), 1513 and 1463 cm^{-1}; **HRMS** (EI^+) calcd for $C_{15}H_{12}O_2$ 224.0837, found 224.0835.

3-(3-Methoxyphenyl)isobenzofuran-1(3*H*)-one (4c)



White solid m.p. 118-120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (td, *J* = 7.6 Hz, *J* = 0.8 Hz, 1 H), 7.61 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.32 (qd, *J* = 8.0 Hz, *J* = 0.2 Hz, 1 H), 7.32 (t, *J* = 8.0 Hz, 1H), 6.88-6.75 (m, 3 H), 6.38 (s, 1 H), 3.74 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.4 (*CO-lactone*), 159.9 (C), 149.5 (C), 137.9 (C), 134.3 (*C*H), 129.9 (*C*H), 129.3 (*C*H), 125.5 (*C*H), 125.3 (C), 122.8(*C*H), 118.9 (*C*H), 114.5 (*C*H), 112.3 (*C*H), 82.4 (*C*H), 55.2 (CH_3); IR (neat) 2837, 1766 (ν_{CO}), and 1600 cm^{-1}; **HRMS** (EI^+) calcd for $C_{15}H_{12}O_3$ 240.0786, found 240.0785.

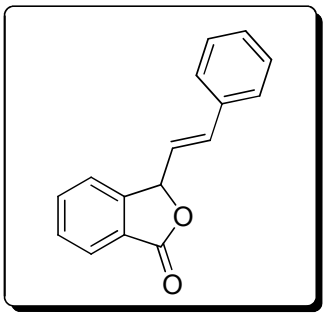
3-(4-Methoxyphenyl)isobenzofuran-1(3*H*)-one (4d)



White solid m.p. 110-112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.62 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.52 (dt, *J* = 7.6 Hz, *J* = 0.8 Hz, 1 H), 7.28 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.86 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 2H), 6.34 (s, 1 H), 3.77 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ

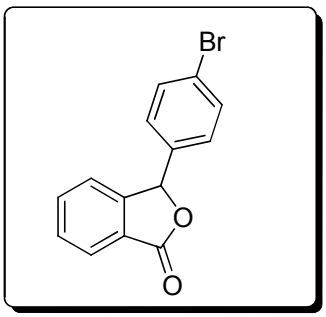
170.5 (*CO-lactone*), 160.4 (C), 149.7 (C), 134.2 (*C*H), 129.2 (*C*H), 129.2 (*C*H), 128.7 (2 *C*H), 128.2 (C), 125.8(C), 125.5 (*C*H), 122.9 (*C*H), 114.3 (2 *C*H), 82.7 (*C*H), 55.3 (CH_3); IR (neat) 2840, 1753 (ν_{CO}), 1612 and 1286 cm^{-1}; **HRMS** (EI^+) calcd for $C_{15}H_{12}O_3$ 240.0786, found 240.0782.

(*E*)-3-Styrylisobenzofuran-1(3*H*)-one (4e)



White solid m.p. 98-100 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.5 Hz, 1 H), 7.68 (t, *J* = 7.5 Hz, 1 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 2 H), 7.31-7.25 (m, 3 H), 6.90 (d, *J* = 15.0 Hz, 1 H), 6.12 (dd, *J* = 15.0 Hz, *J* = 7.0 Hz, 1 H), 5.99 (d, *J* = 7.5 Hz, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.3 (*CO-lactone*), 148.8 (C), 136.3 (C), 135.4 (C), 135.2 (*C*H), 134.2 (*C*H), 129.4 (*C*H), 128.7 (2 *C*H), 128.6 (*C*H), 126.9 (2 *C*H), 125.7 (*C*H), 123.8 (C), 122.6 (*C*H), 82.1 (*C*H); IR (neat) 1760 (ν_{CO}), 1598 and 1284 cm^{-1}; **HRMS** (EI^+) calcd for $C_{16}H_{12}O_2$ 236.0837, found 236.0836.

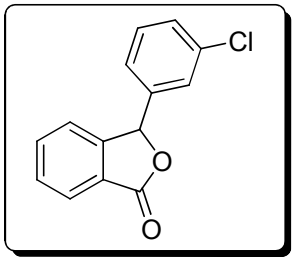
3-(4-Bromophenyl)isobenzofuran-1(3*H*)-one (4f)



White solid m.p. 157-159 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 1 H), 7.66 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.56 (dt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1 H), 7.50

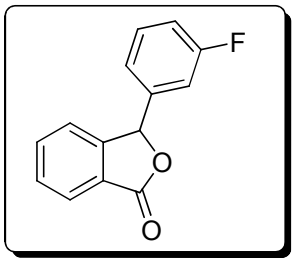
(d, *J* = 6.8 Hz, 2 H), 7.31 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.16 (d, *J* = 8.8 Hz, 1 H), 6.36 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.2 (*CO-lactone*), 149.1 (C), 135.4 (C), 134.4 (*C*H), 132.1 (2 *C*H), 129.5 (*C*H), 128.6 (2 *C*H), 125.7 (*C*H), 123.4 (C), 122.7 (*C*H), 81.8 (*C*H); IR (neat) 1768 (ν_{CO}), 1598 and 1284 cm^{-1}; **HRMS** (EI^+) calcd for $C_{14}H_9BrO_2$ 287.9786, found 287.9786.

3-(3-Chlorophenyl)isobenzofuran-1(3*H*)-one (4g)



White solid m.p. 132-134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.6 Hz, 1 H), 7.62 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.56 (dt, *J* = 7.6 Hz, *J* = 0.8 Hz, 1 H), 7.35- 7.29 (m, 3 H), 7.25 (s, 1 H), 7.20- 7.17 (m, 1 H), 6.39 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.1 (*CO-lactone*), 148.9 (C), 138.4 (C), 134.8 (*C*), 134.5 (*C*H), 130.3 (*C*H), 129.6 (*C*H), 129.4 (*C*H), 126.9 (*C*H), 125.7 (*C*H), 125.3 (C), 125.0 (*C*H), 122.7 (*C*H) 81.6 (*C*H); IR (neat) 1764 (ν_{CO}), 1597 and 1284 cm^{-1}; **HRMS** (EI^+) calcd for $C_{14}H_9ClO_2$ 244.0291, found 244.0287.

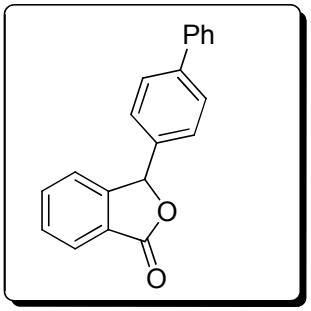
3-(3-Fluorophenyl)isobenzofuran-1(3*H*)-one (4h)



White solid m.p. 85-87 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.6 Hz, 1 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.36- 7.31 (m, 2 H), 7.09 (d, *J* = 7.6 Hz, 1 H), 7.03 (td, *J* = 8.4 Hz, *J* = 2.8 Hz, 1 H), 6.94 (td, *J* = 8.8 Hz, *J* = 2.0 Hz,

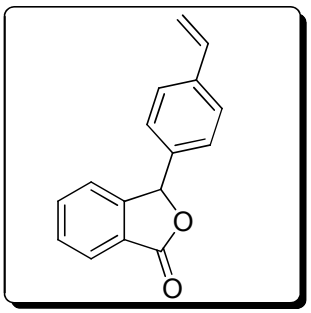
1 H), 6.36 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.1 (*CO-lactone*), 163.1 (d, J_{C-F} =986.8 Hz, C), 149.0 (C), 138.8 (d, J_{C-F} =7.4 Hz, C), 134.4 (*C*H), 130.6 (d, J_{C-F} =8.1 Hz, *C*H), 129.5 (*C*H), 125.7 (*C*H), 125.3 (C), 122.7 (*C*H), 122.5 (d, J_{C-F} =3.7 Hz, *C*H), 116.2 (d, J_{C-F} =21.2 Hz, *C*H), 113.7 (d, J_{C-F} =22.6 Hz, *C*H), 81.6 (*C*H); IR (neat) 1772, 1762 (ν_{CO}) and 1466 cm^{-1}; **HRMS** (EI^+) calcd for $C_{14}H_{10}FO_2$ 228.0587, found 228.0583.

3-(4-Biphenyl)isobenzofuran-1(3*H*)-one (4i)



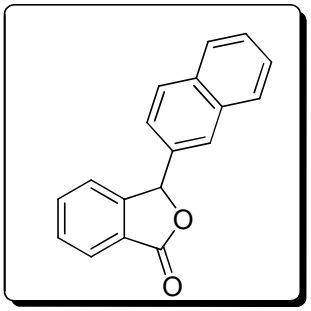
White solid m.p. 211-213 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.6 Hz, 1 H), 7.66 (t, *J* = 7.6 Hz, 1 H), 7.59- 7.54 (m, 5 H), 7.42 (m, 4 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 7.35- 7.25 (m, 4 H), 6.38 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.6 (*CO-lactone*), 149.6 (C), 142.3 (C), 140.2 (C), 135.2 (C), 134.4 (*C*H), 129.4 (*C*H), 128.8 (2 *C*H), 128.3 (2 *C*H), 127.7 (2 *C*H), 127.4(2 *C*H), 126.7 (*C*H), 125.6 (C), 122.7 (*C*H), 115.7 (*C*H), 82.6 (*C*H); IR (neat) 1750 (ν_{CO}), 1598 and 1464 cm^{-1}; **HRMS** (EI^+) calcd for $C_{20}H_{14}O_2$ 286.0994, found 286.0996.

3-(4-Vinylphenyl)isobenzofuran-1(3*H*)-one (4j)



White solid m.p. 116-118 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 1 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.41 (d, *J* = 7.6 Hz, 2 H), 7.32 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 6.70 (dd, *J* = 17.6 Hz, *J* = 10.8 Hz, 1 H), 6.40 (s, 1 H), 5.76 (d, *J* = 17.6 Hz, 1 H), 5.26 (d, *J* = 11.2 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.5 (*CO-lactone*), 149.6 (C), 138.3 (C), 135.9 (*C*H), 135.7 (C), 134.3 (*C*H), 129.4 (*C*H), 127.2 (2 *C*H), 126.7 (2 *C*H), 125.6 (*C*H), 125.5 (C), 122.8 (*C*H), 114.9 (CH_2), 82.5 (*C*H); IR (neat) 1756 (ν_{CO}), 1598 and 1284 cm^{-1}; **HRMS** (EI^+) calcd for $C_{16}H_{12}O_2$ 236.0837, found 236.0835.

3-(Naphthalen-2-yl)isobenzofuran-1(3*H*)-one (4k)

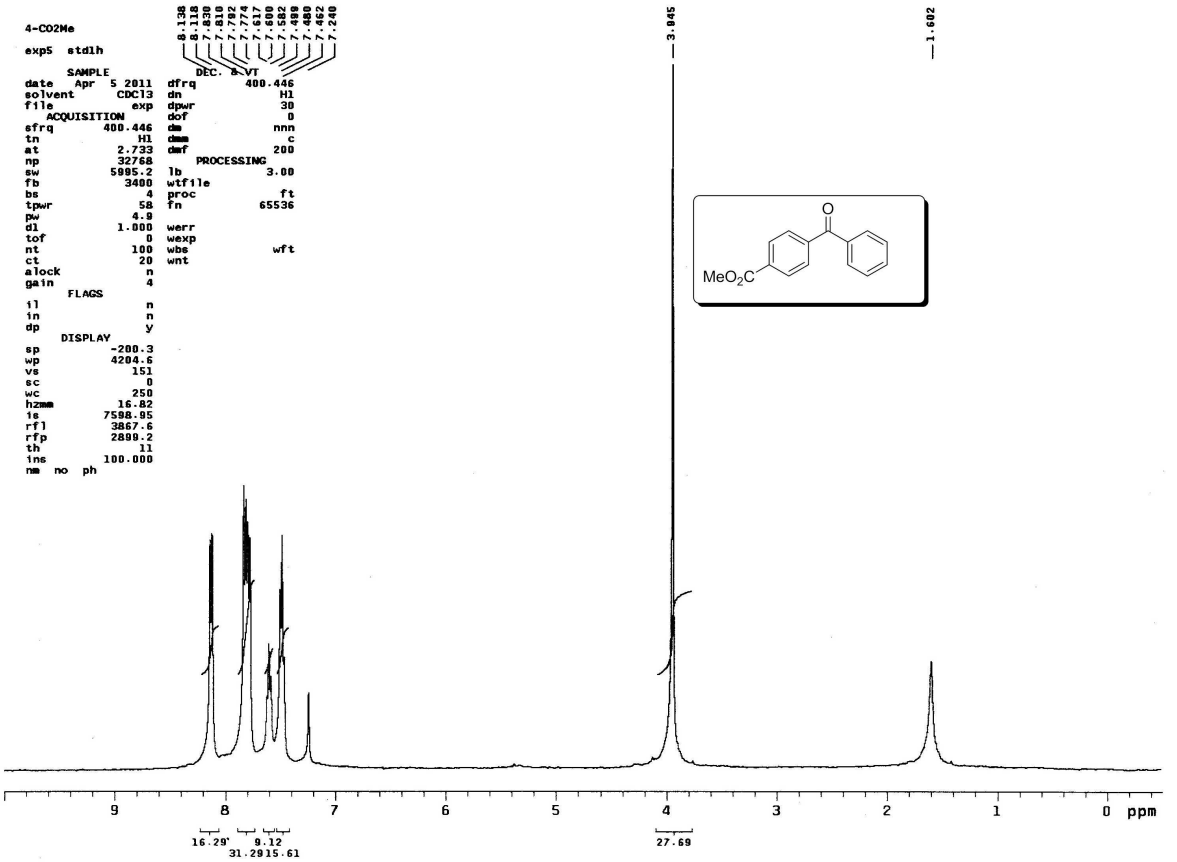


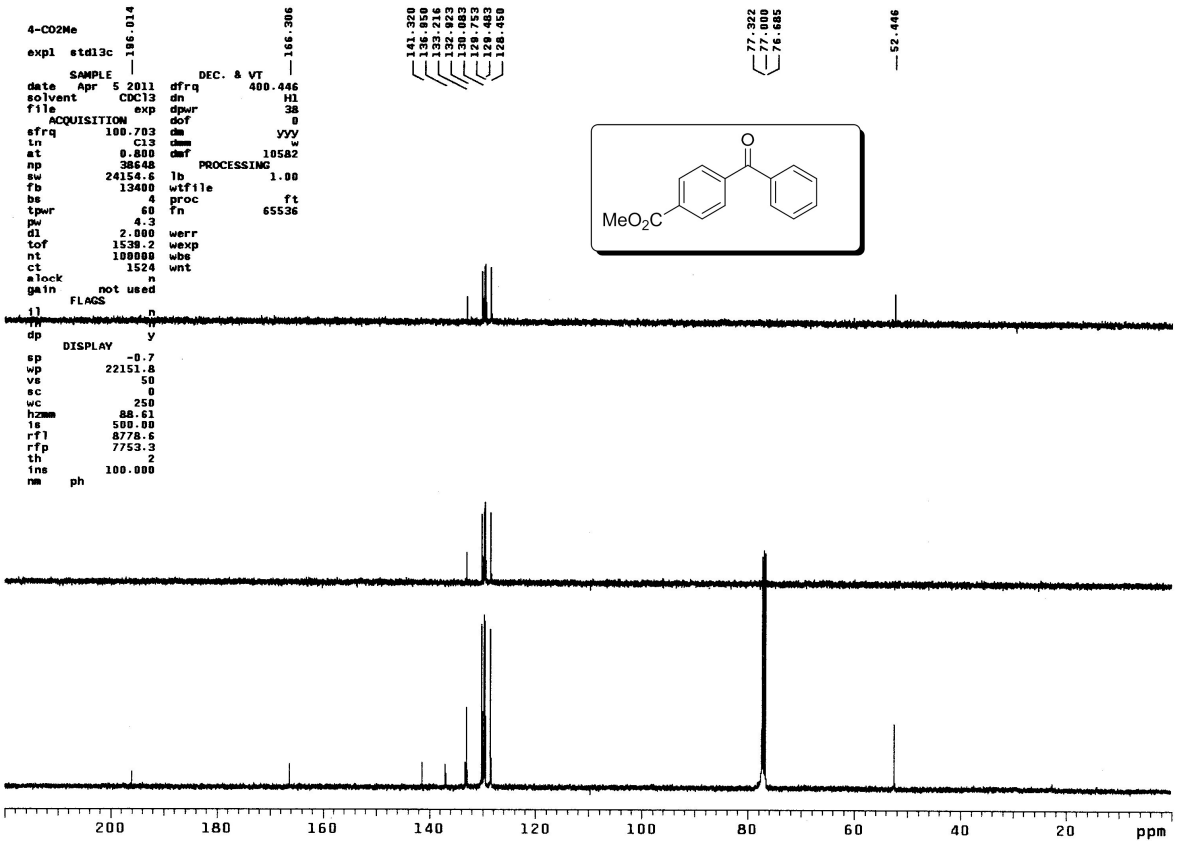
White solid m.p. 148-150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 1 H), 7.83- 7.78 (m, 4 H), 7.61 (t, *J* = 7.6 Hz, 1 H), 7.55- 7.47 (m, 3 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 7.21 (d, *J* = 8.4 Hz, 1 H), 6.53 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.5 (*CO-lactone*), 149.6 (C), 134.3 (*C*H), 133.6 (C), 133.5 (C), 132.9 (C), 129.4 (*C*H), 128.9 (*C*H), 128.0 (*C*H), 127.7 (*C*H),126.8 (*C*H), 126.7 (*C*H), 126.6 (*C*H), 125.6 (*C*H), 125.5(C), 123.7 (*C*H), 122.9 (*C*H), 82.8 (*C*H); IR (neat) 1764 (ν_{CO}), 1599, 1465 and 1285 cm^{-1}; **HRMS** (EI^+) calcd for $C_{18}H_{12}O_2$ 260.0837, found 260.0836.

References:

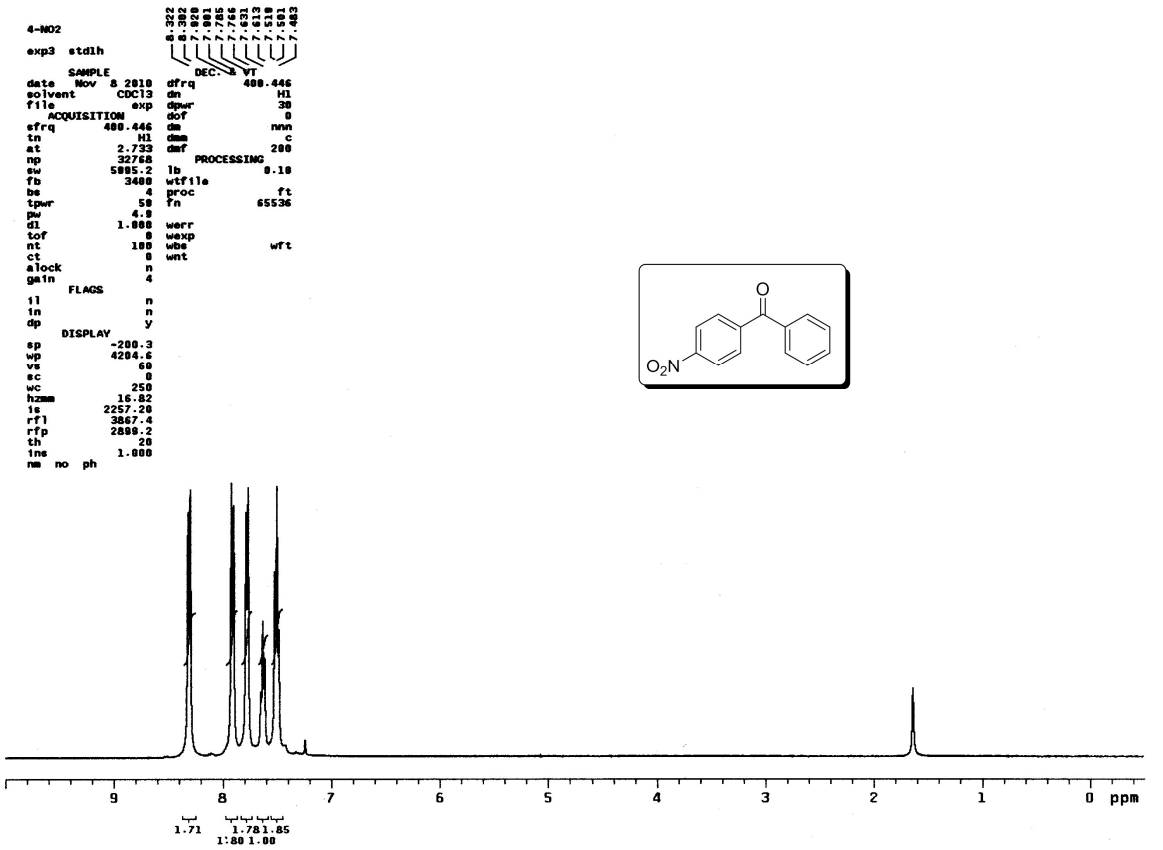
1. Perrin, D. D.; Armarego, W. L. F. *In Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

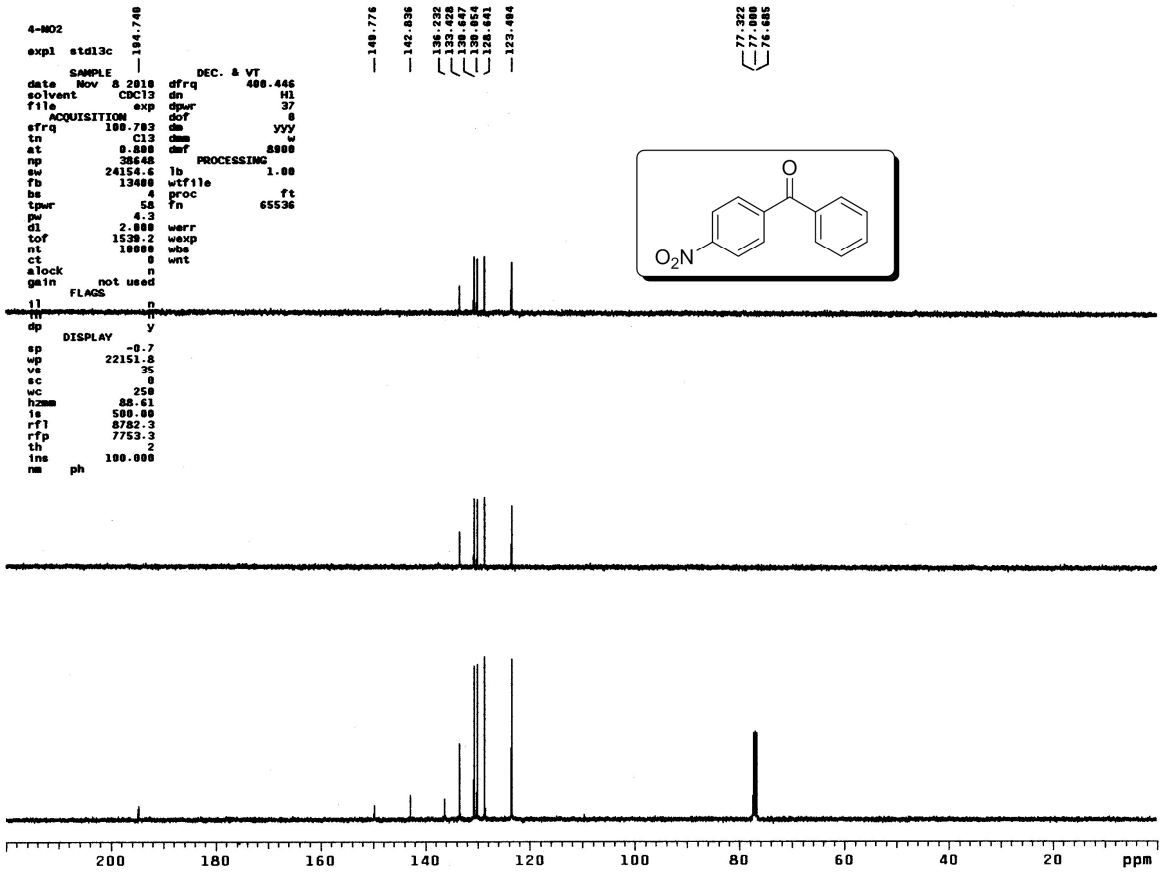
^{1}H and ^{13}C NMR spectra of compound **3a**



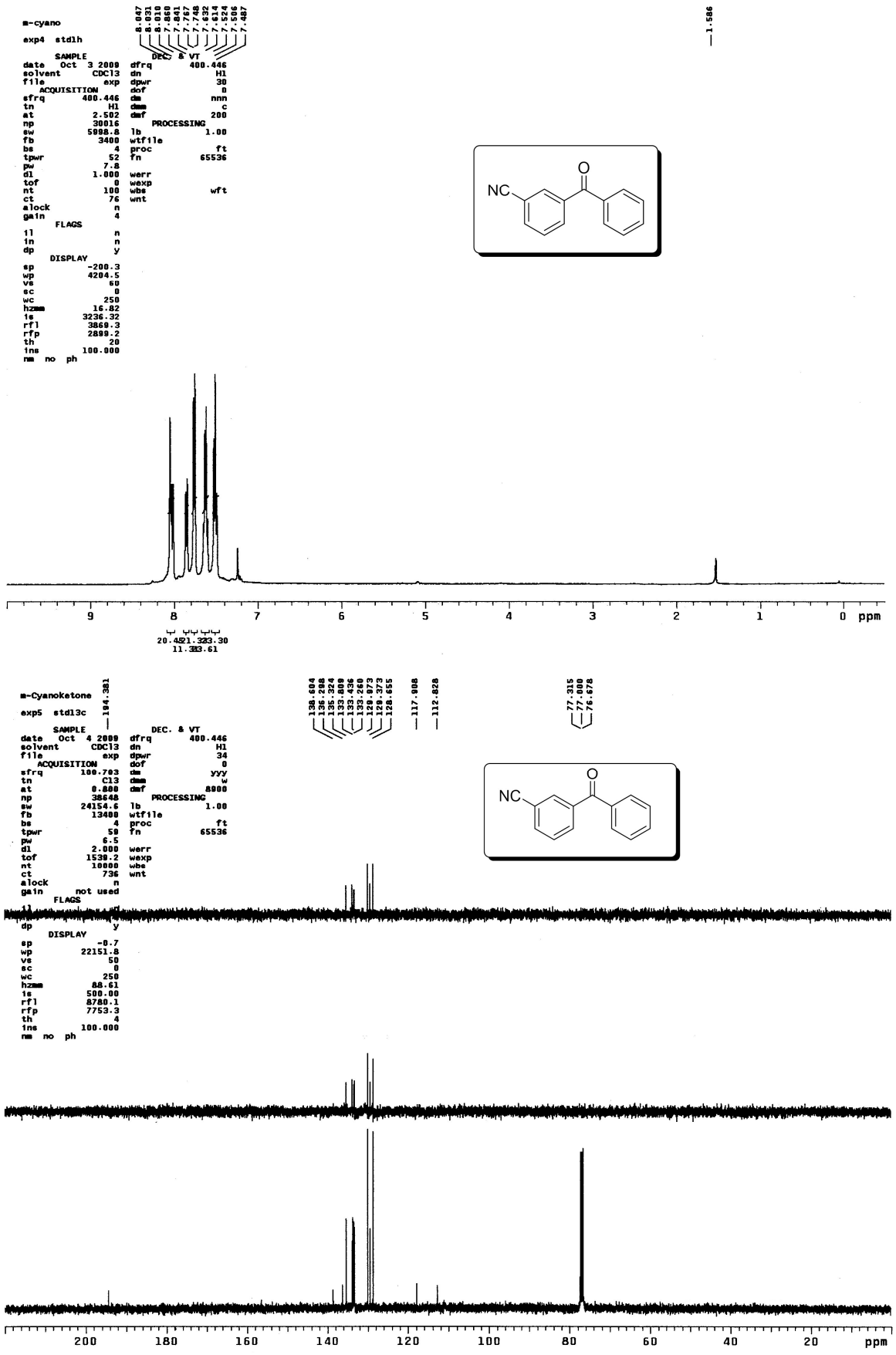


^{1}H and ^{13}C NMR spectra of compound **3b**

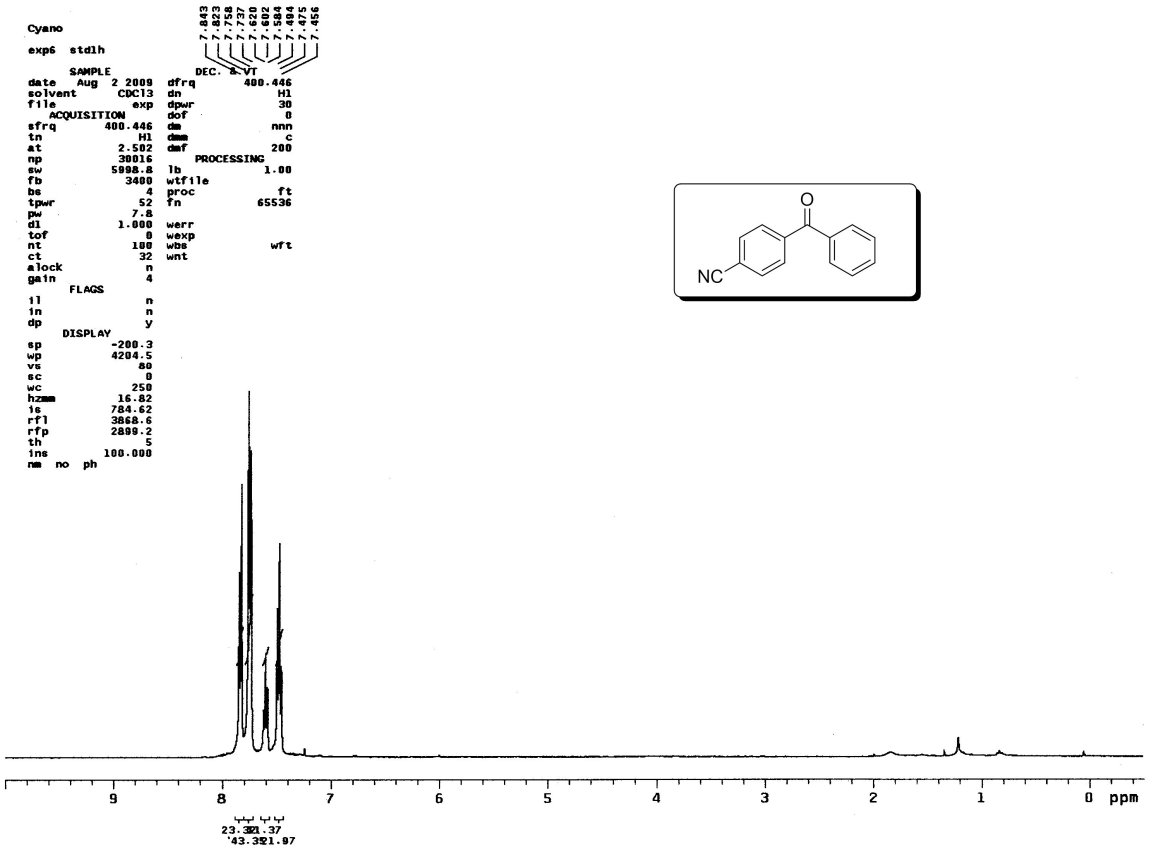


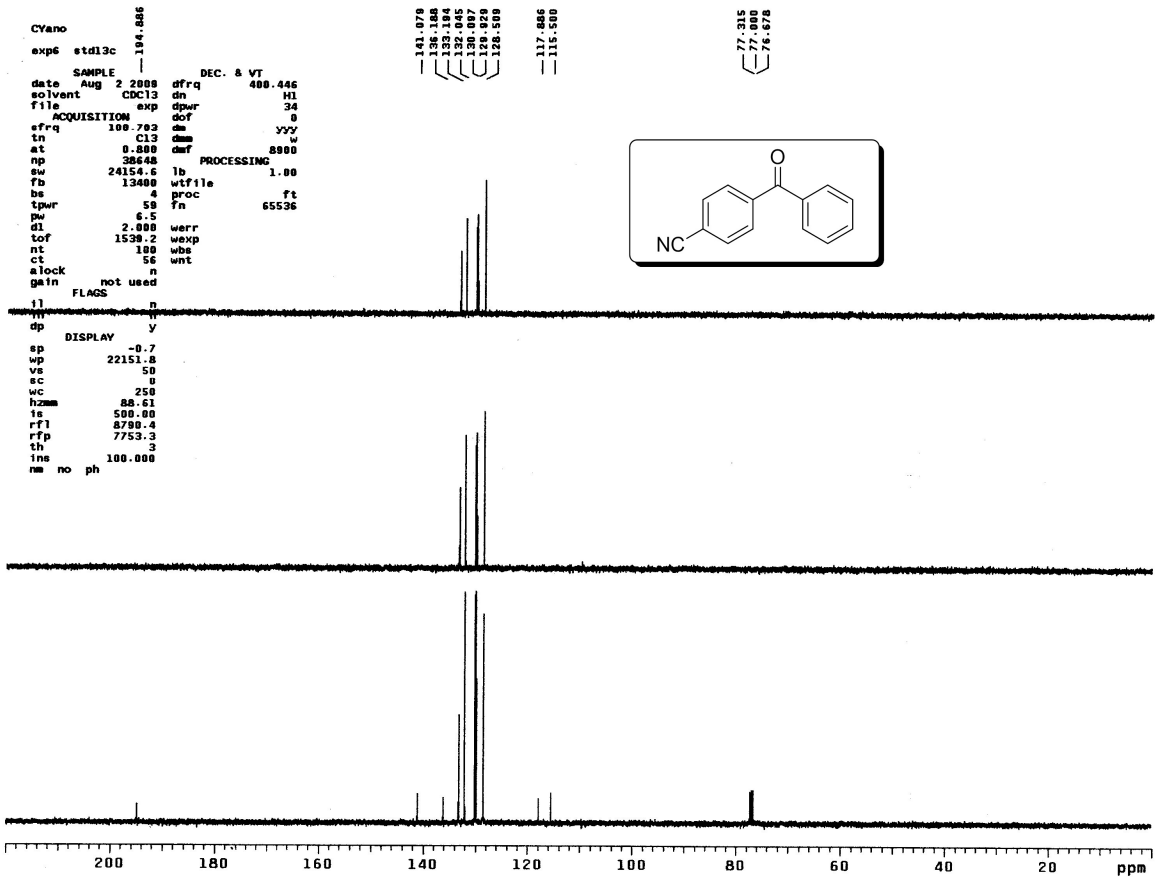


^{1}H and ^{13}C NMR spectra of compound **3c**

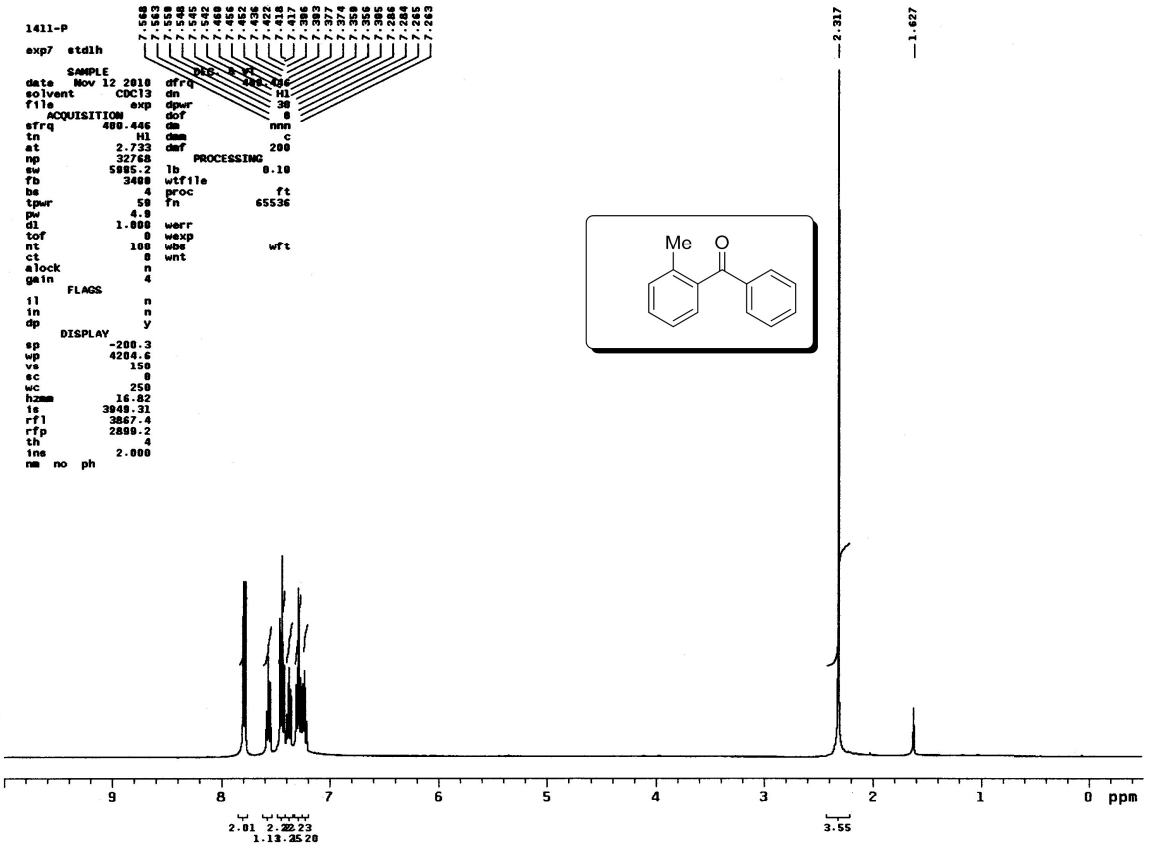


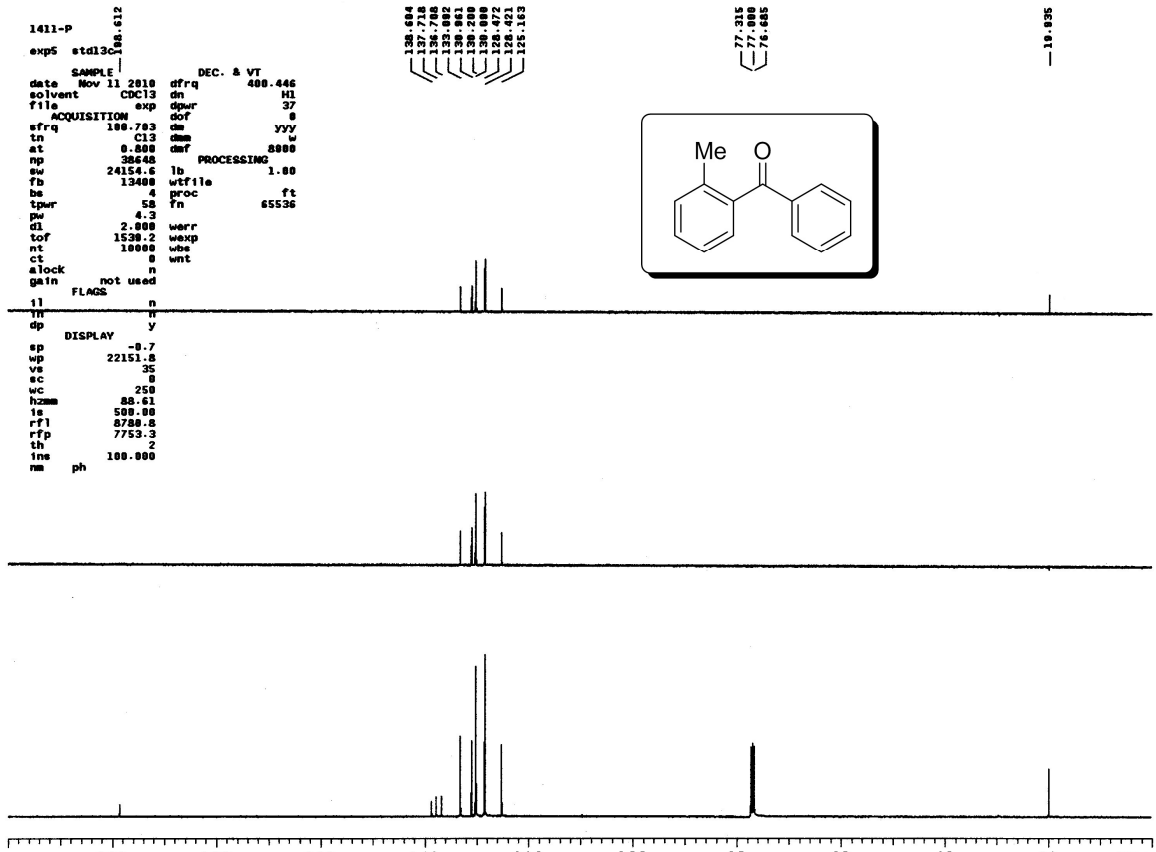
^{1}H and ^{13}C NMR spectra of compound **3d**



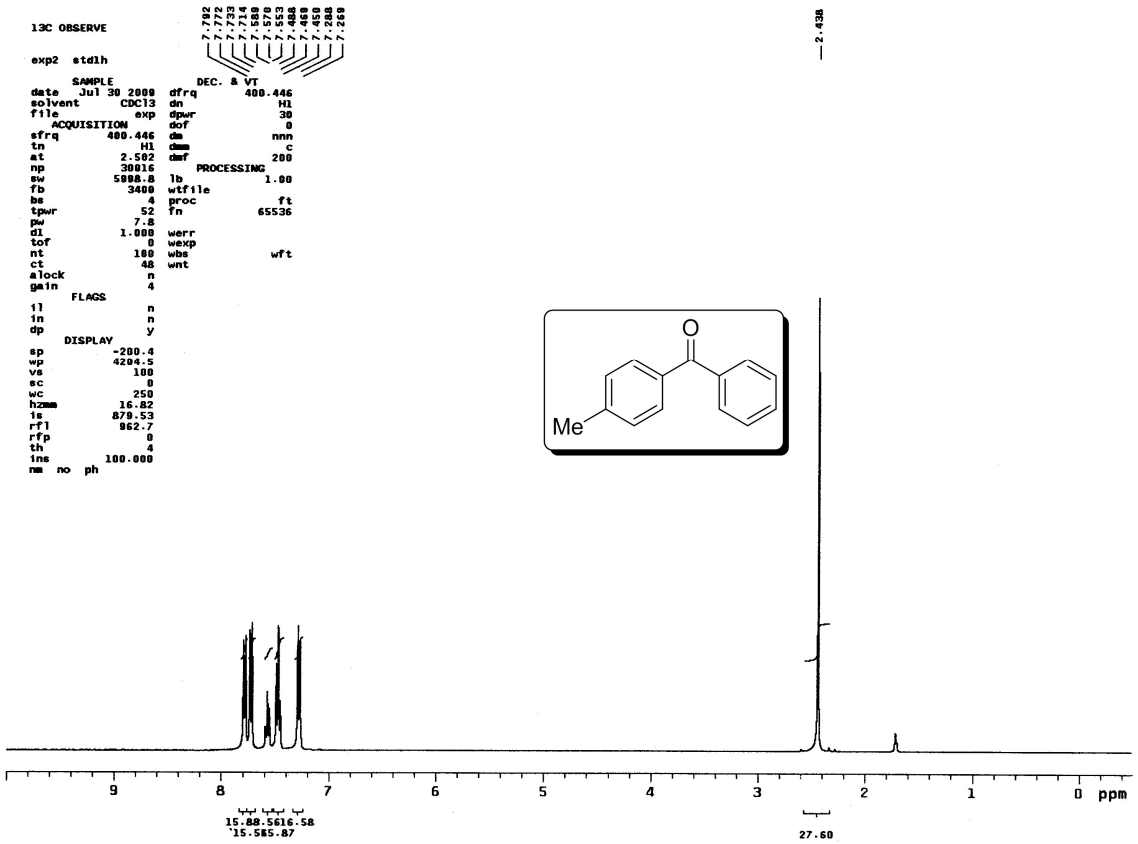


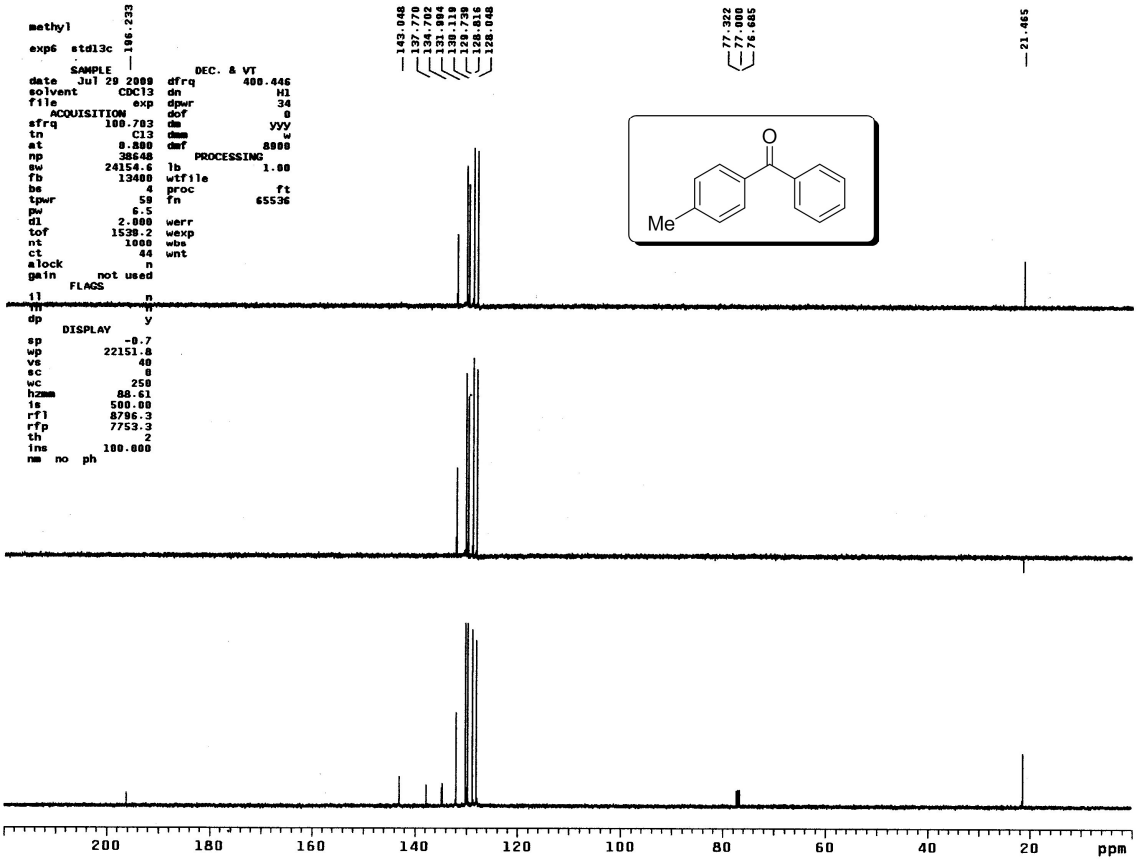
^{1}H and ^{13}C NMR spectra of compound **3e**



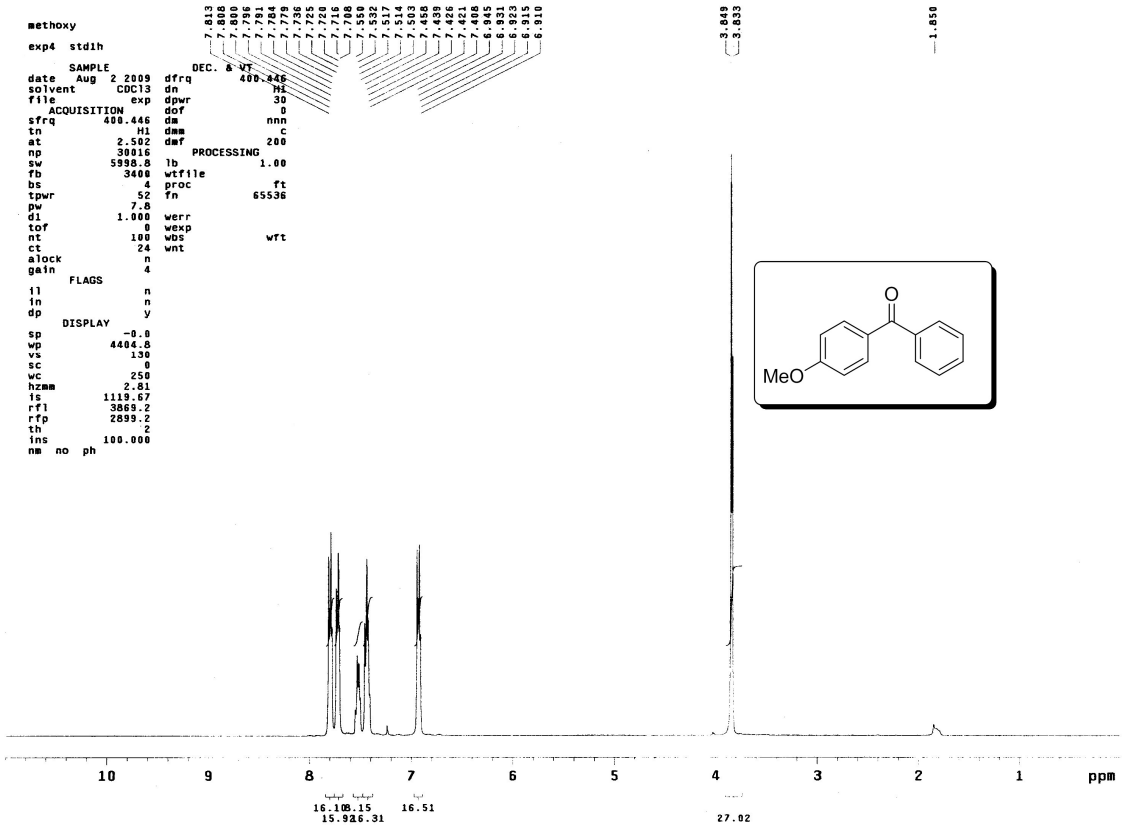


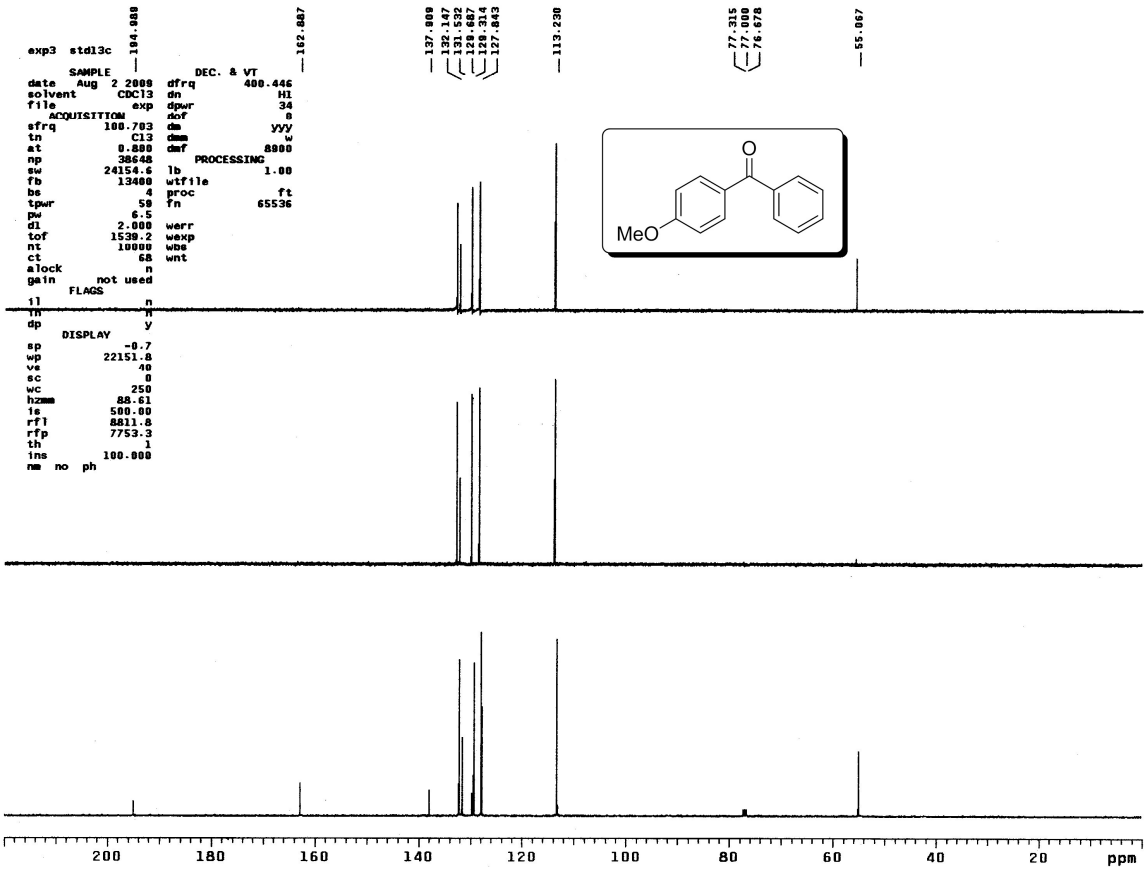
^{1}H and ^{13}C NMR spectra of compound **3f**



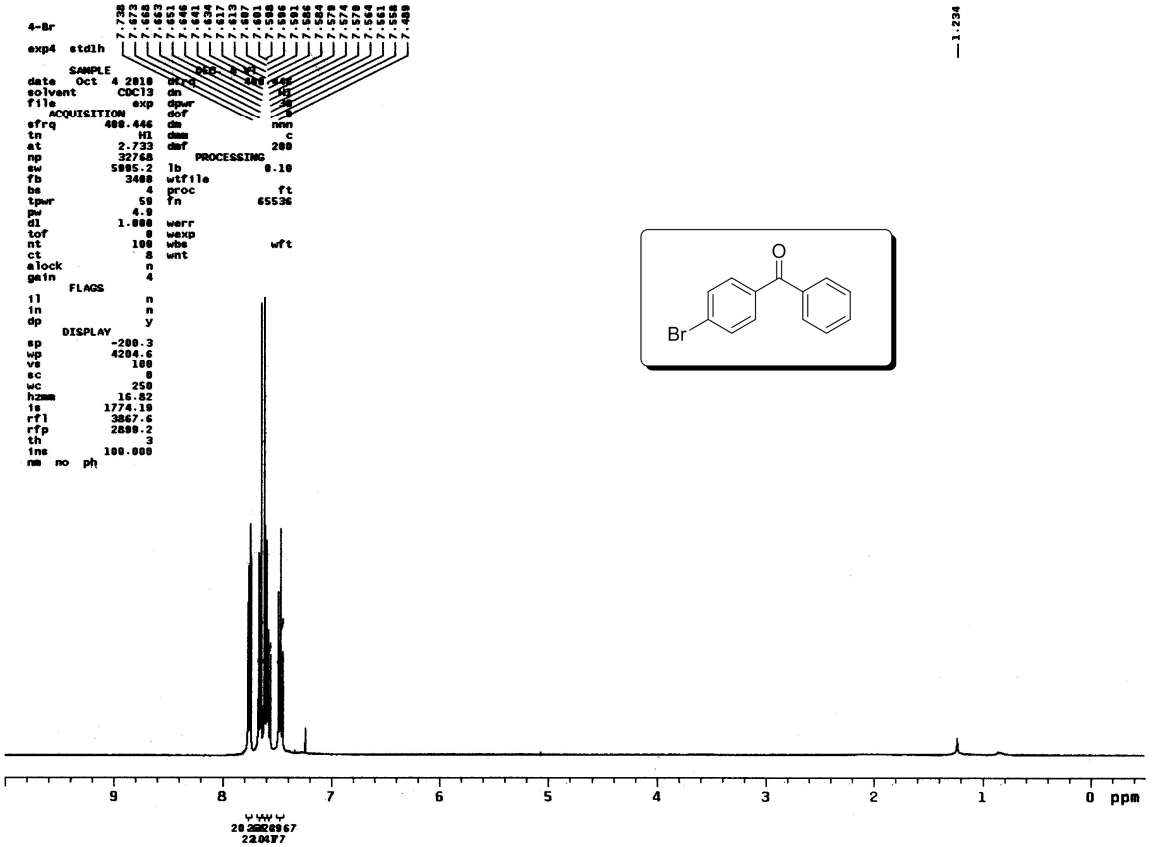


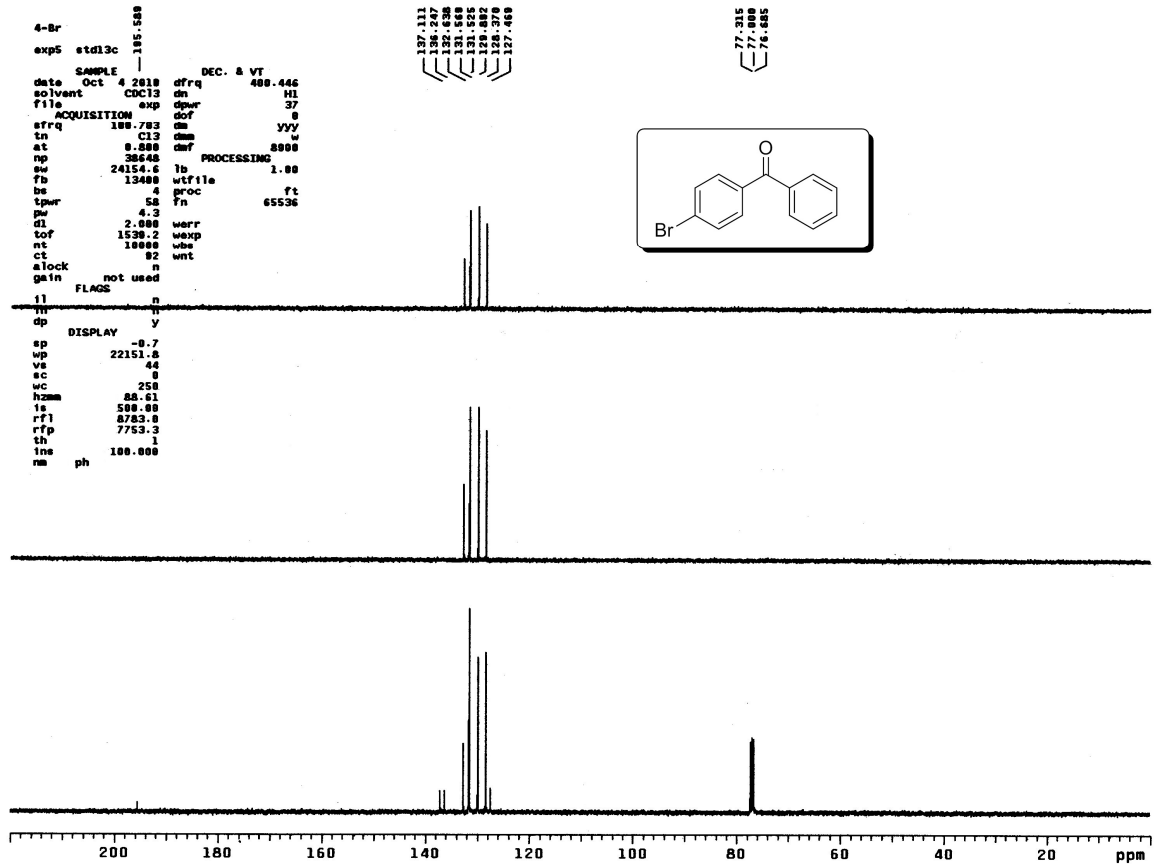
^{1}H and ^{13}C NMR spectra of compound **3g**



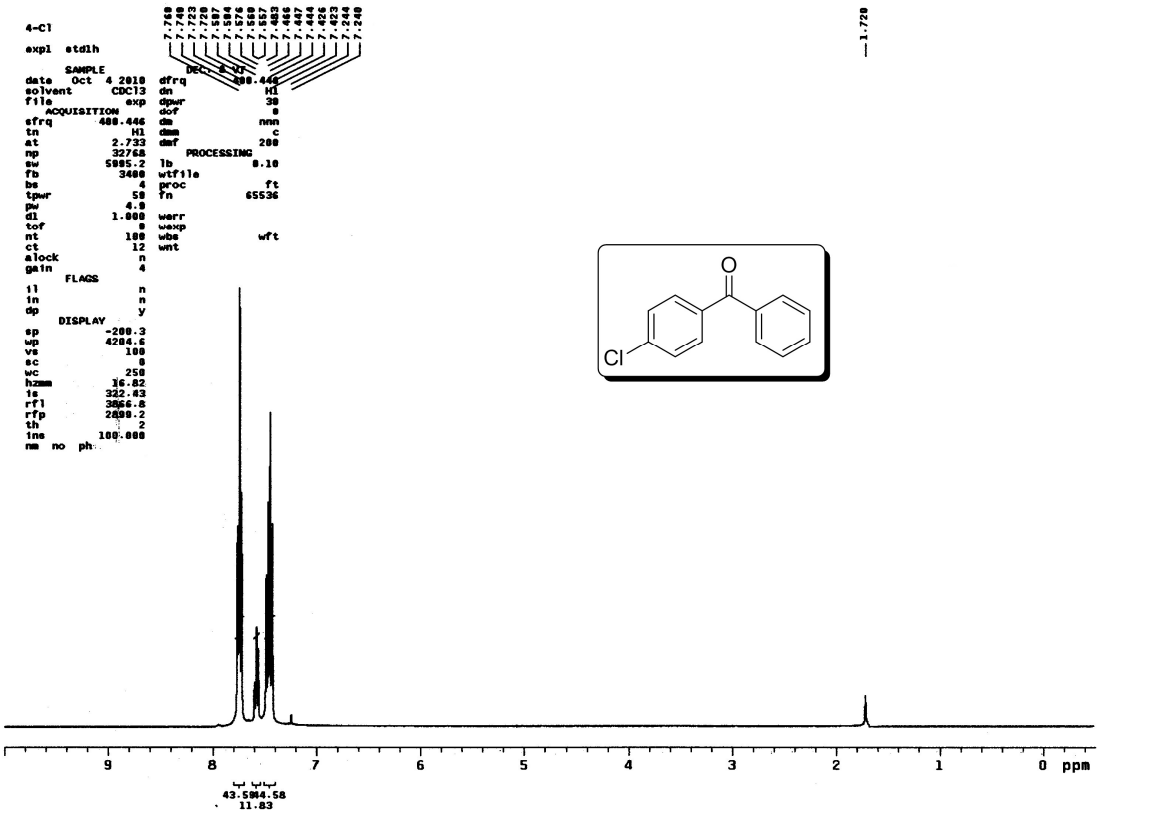


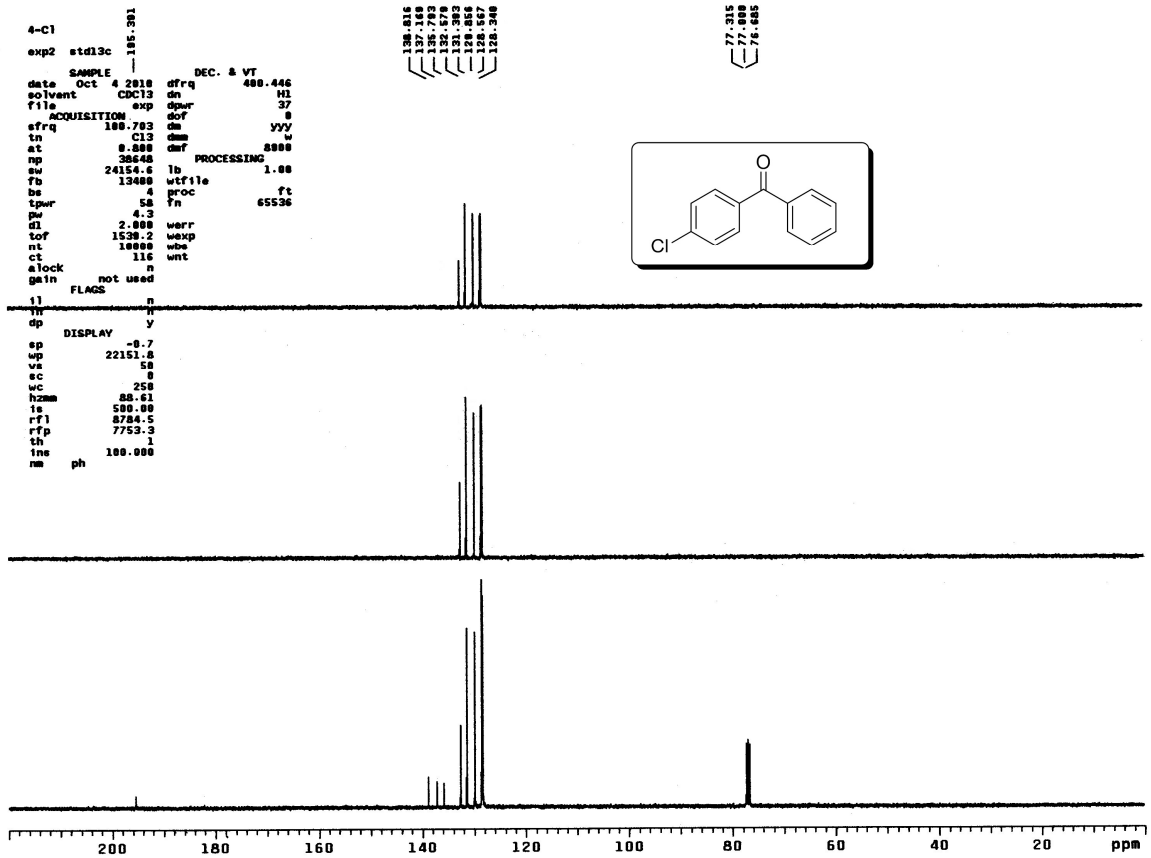
^{1}H and ^{13}C NMR spectra of compound **3h**



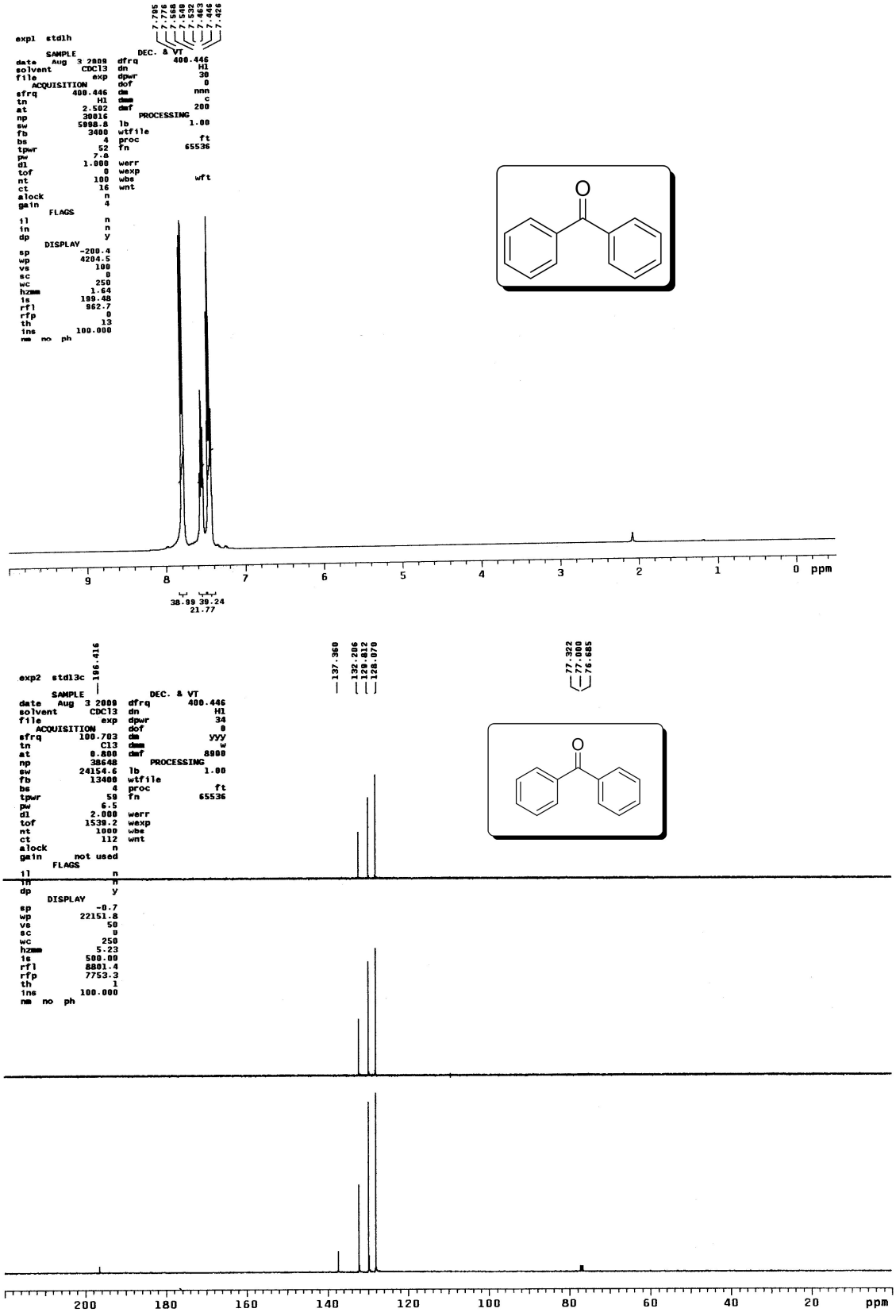


^{1}H and ^{13}C NMR spectra of compound **3i**

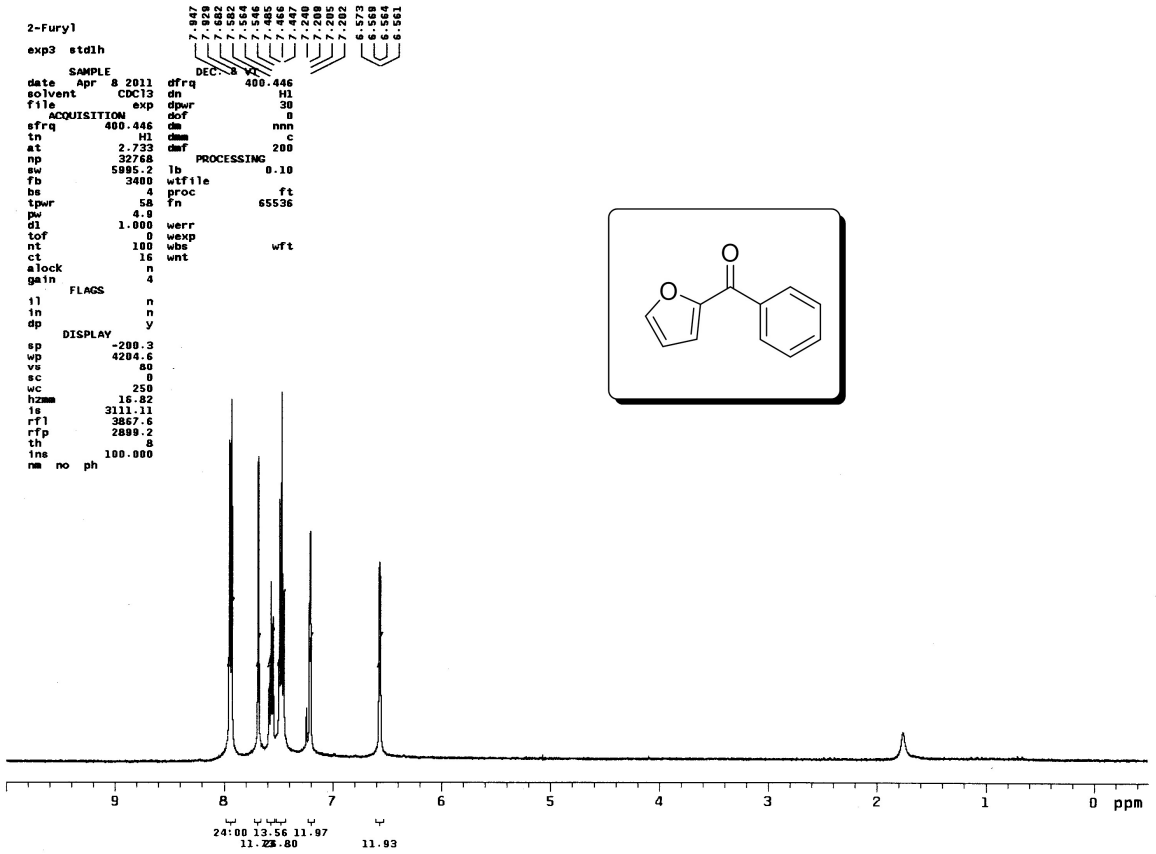


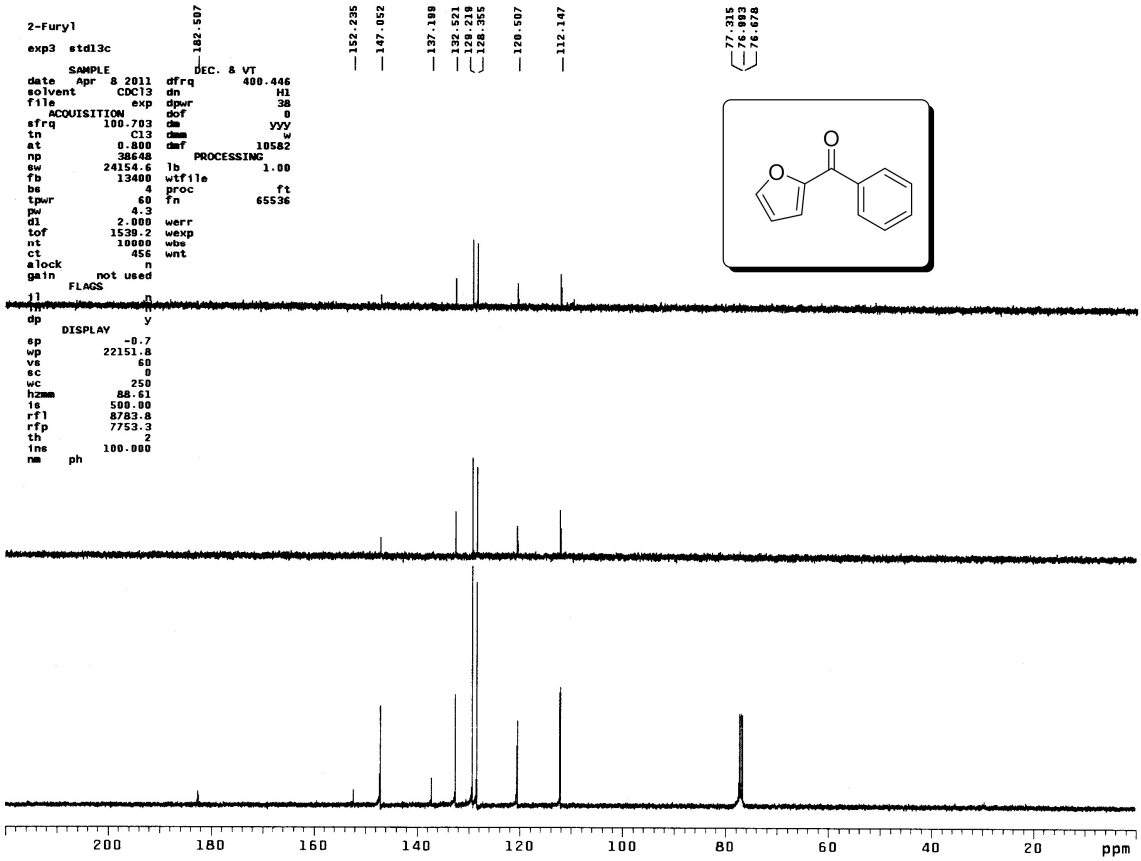


^{1}H and ^{13}C NMR spectra of compound **3j**

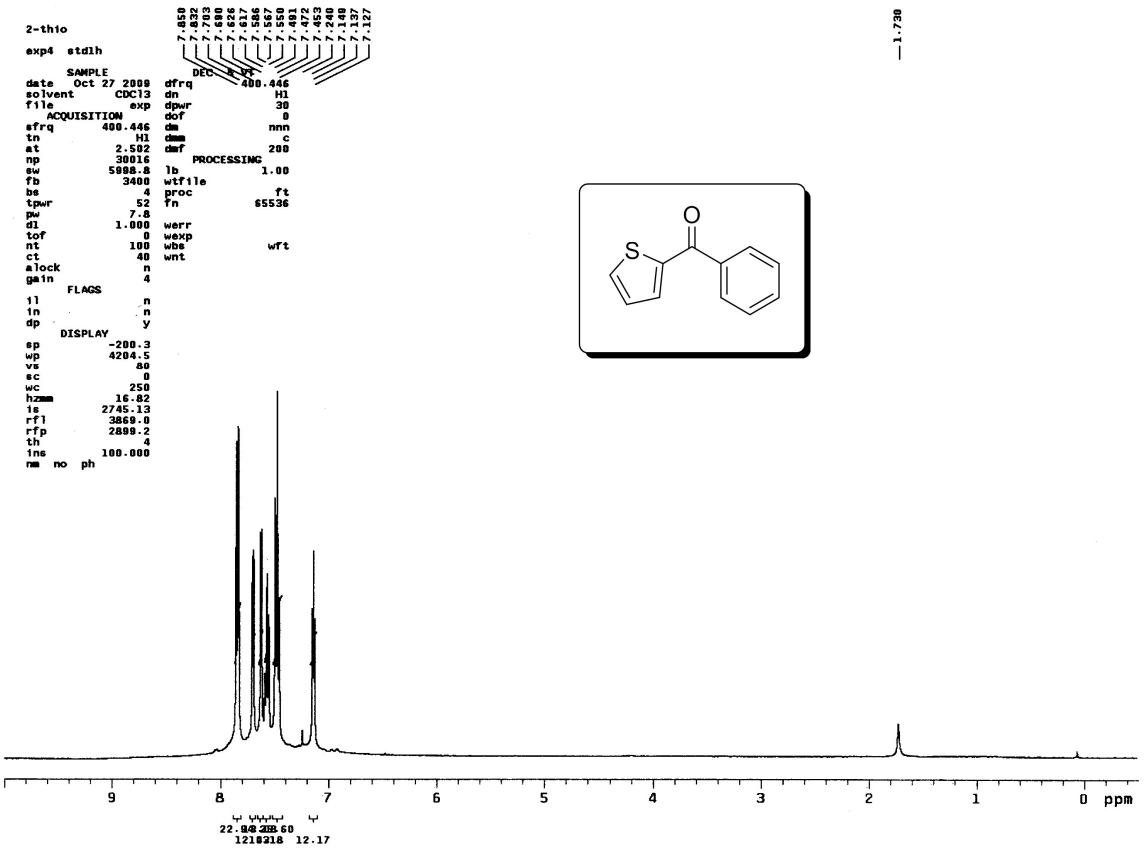


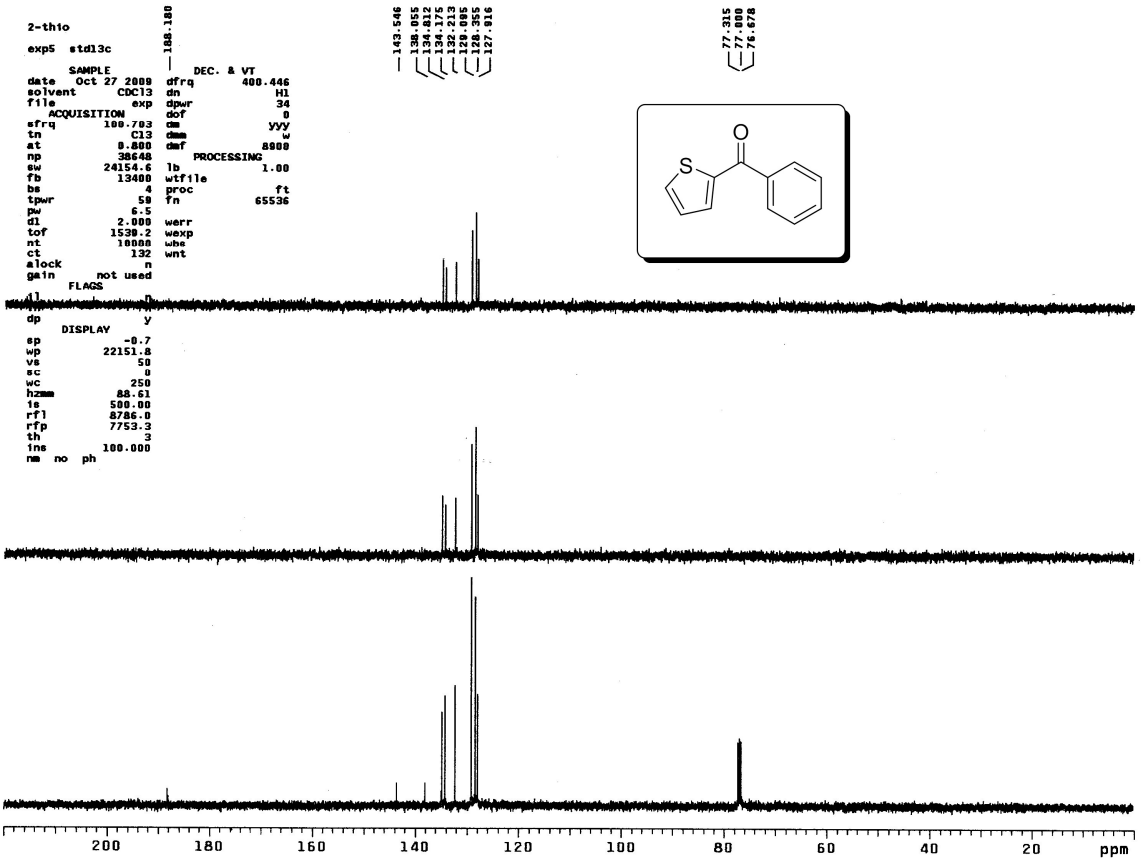
^{1}H and ^{13}C NMR spectra of compound **3k**



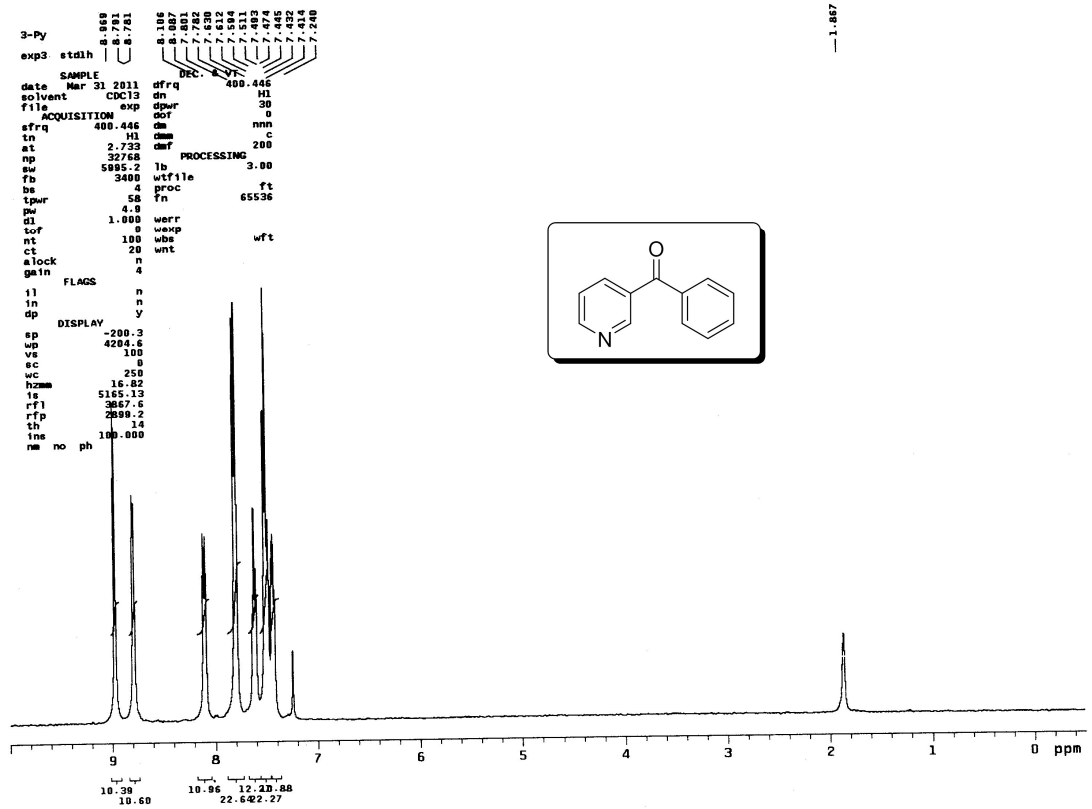


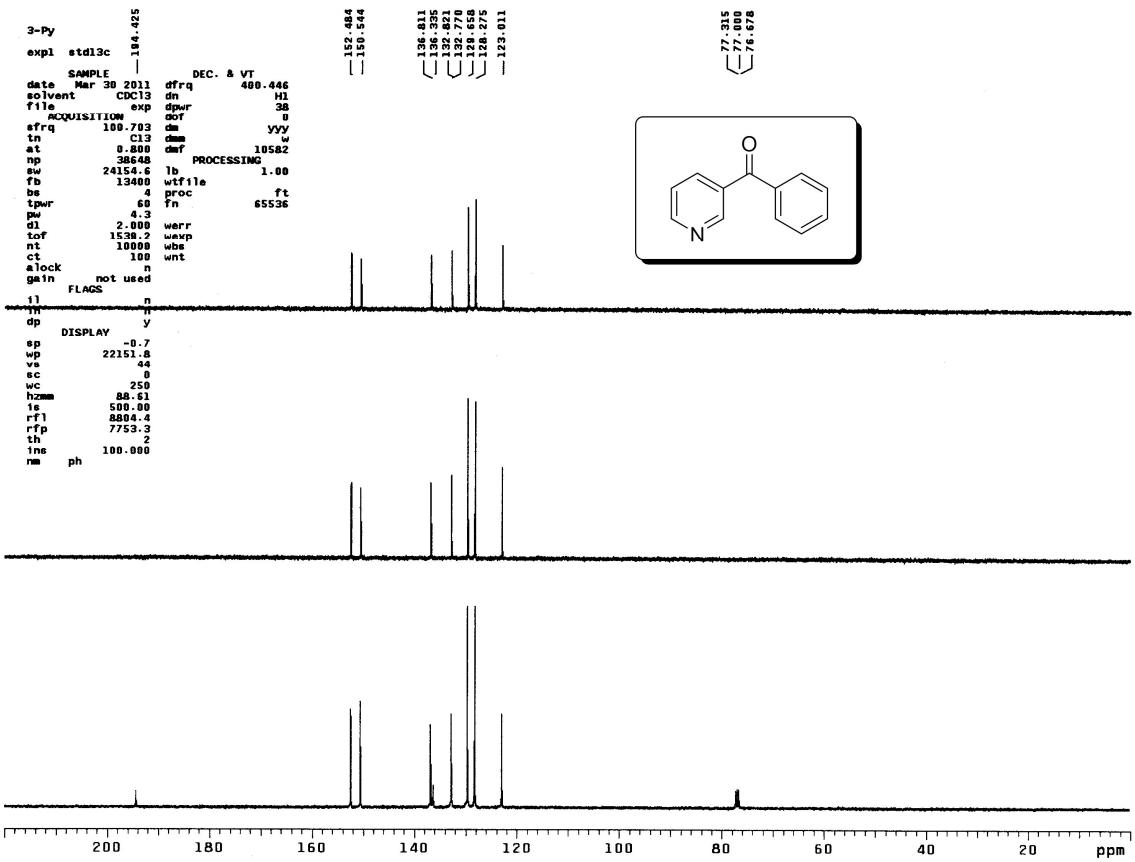
^{1}H and ^{13}C NMR spectra of compound **3l**



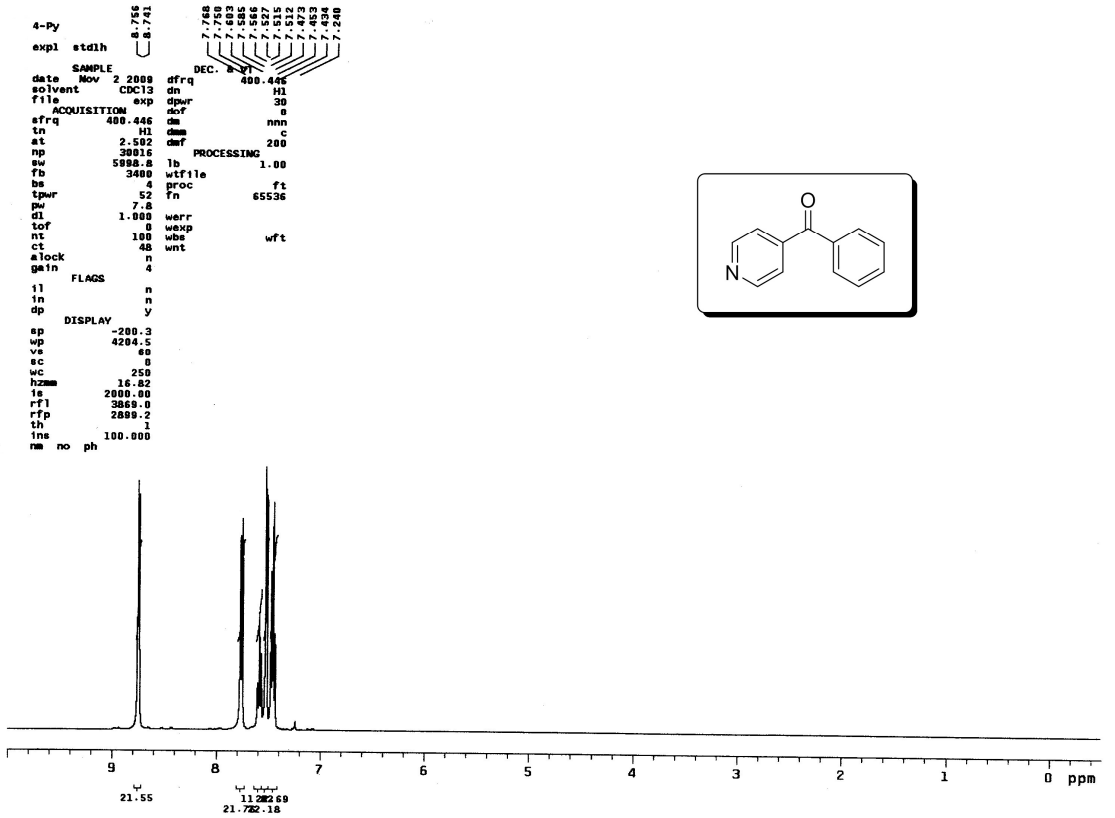


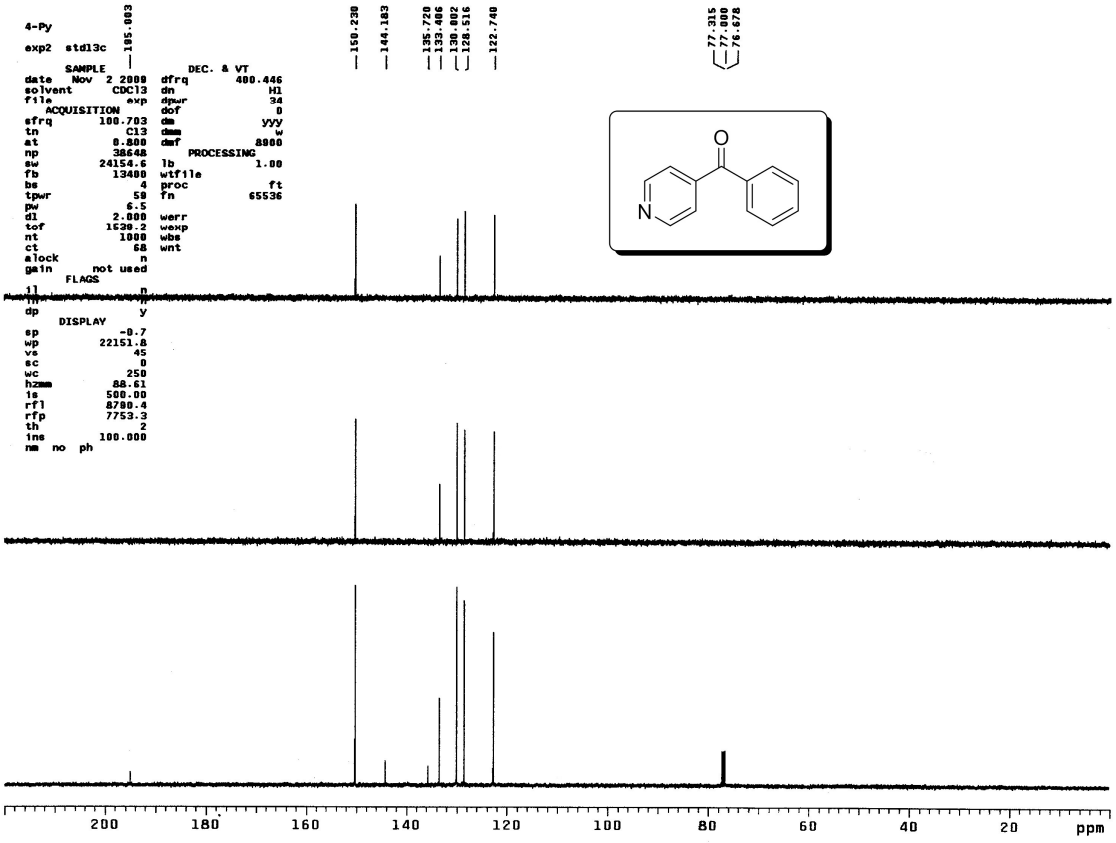
^{1}H and ^{13}C NMR spectra of compound **3m**



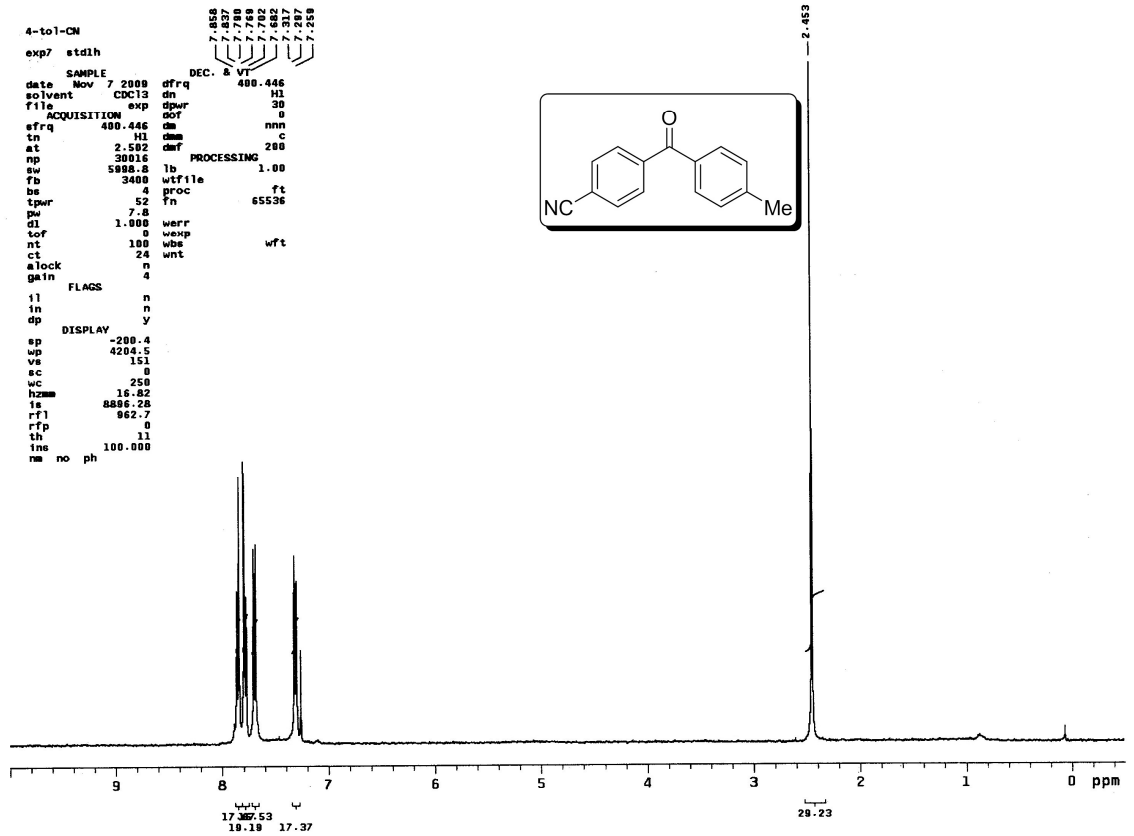


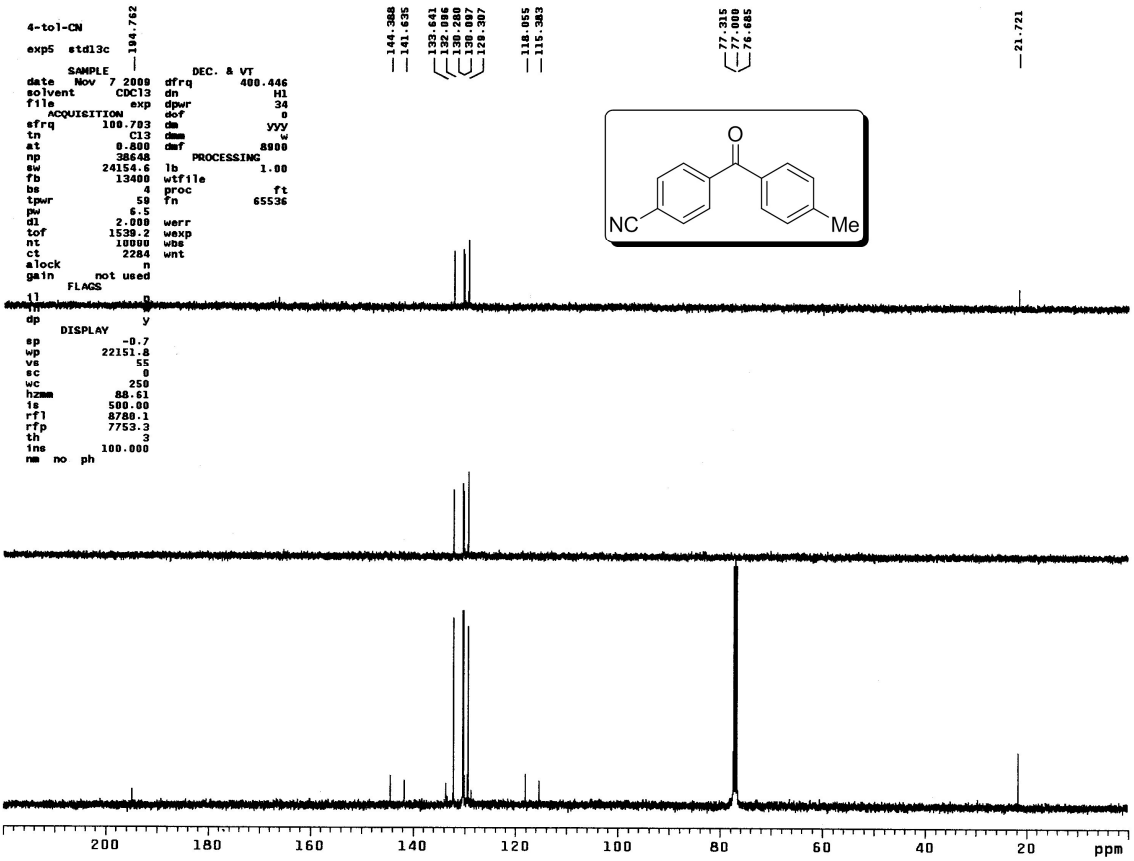
^{1}H and ^{13}C NMR spectra of compound **3n**



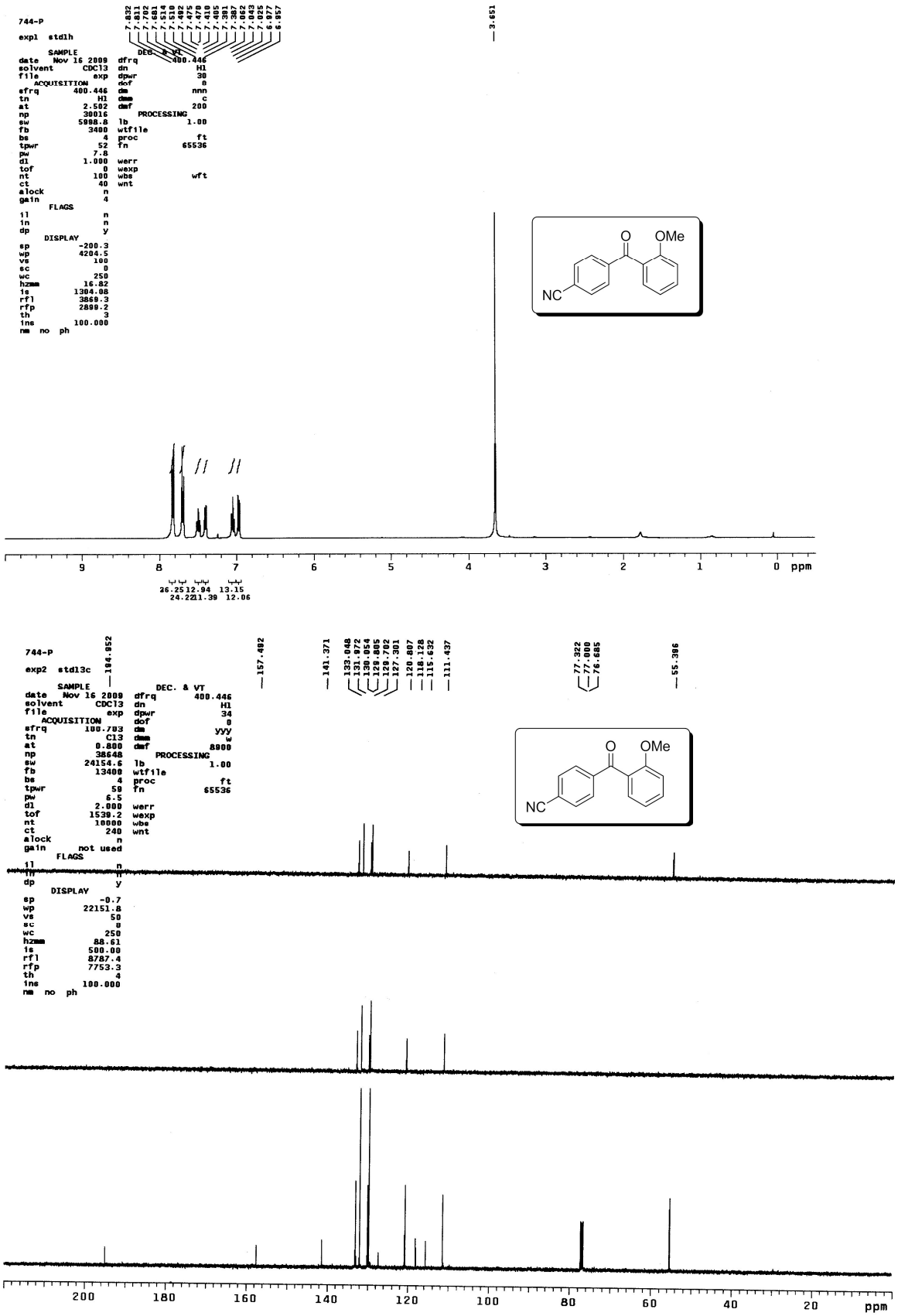


^{1}H and ^{13}C NMR spectra of compound **3o**

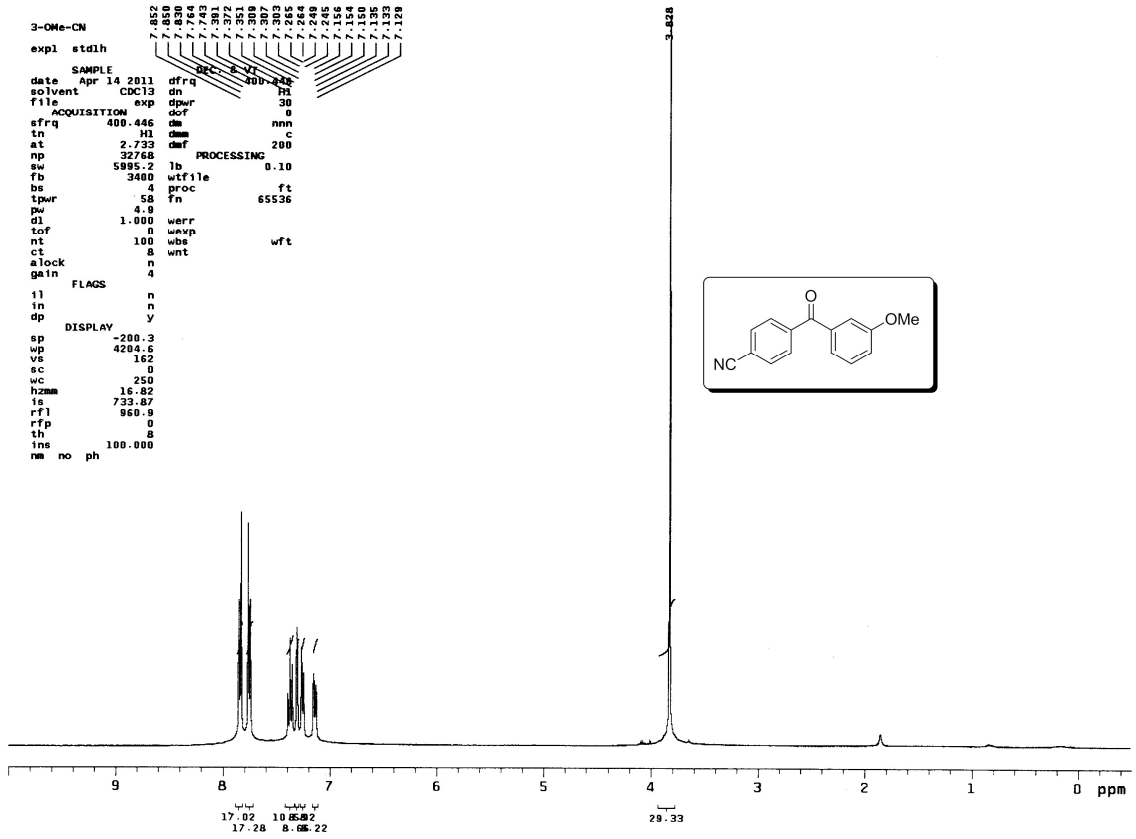


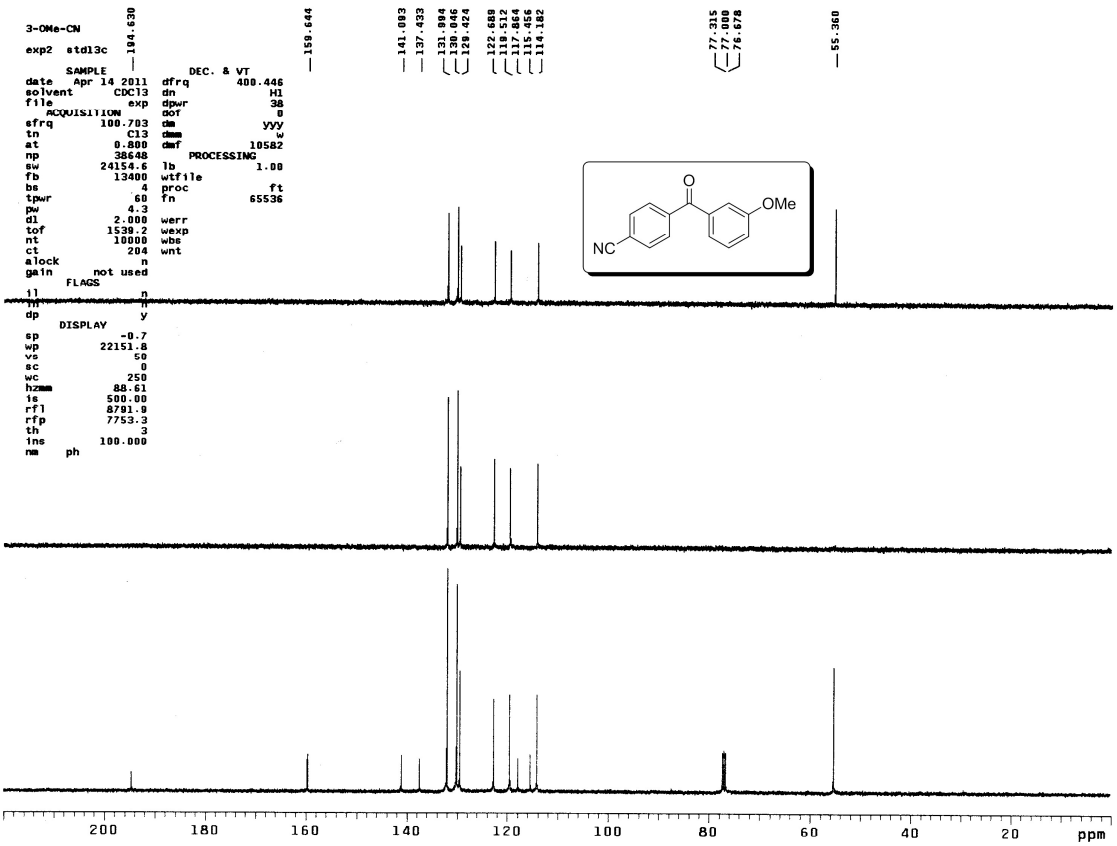


^{1}H and ^{13}C NMR spectra of compound **3p**

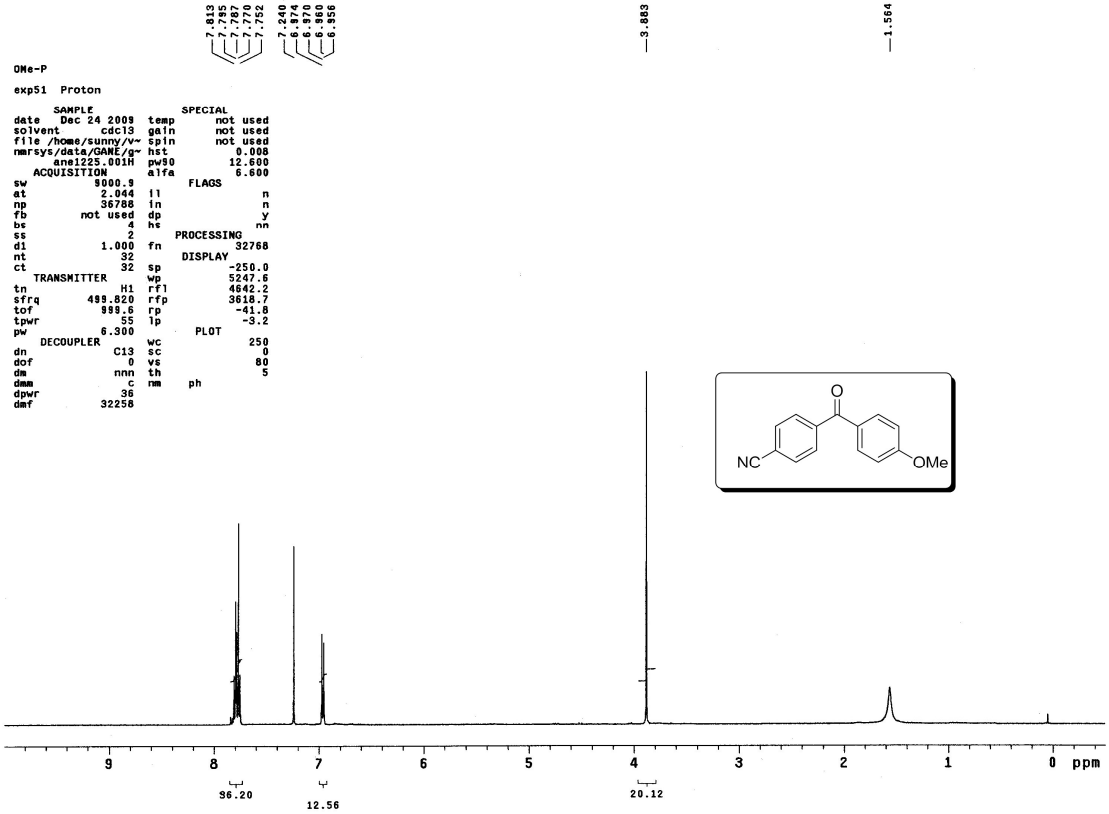


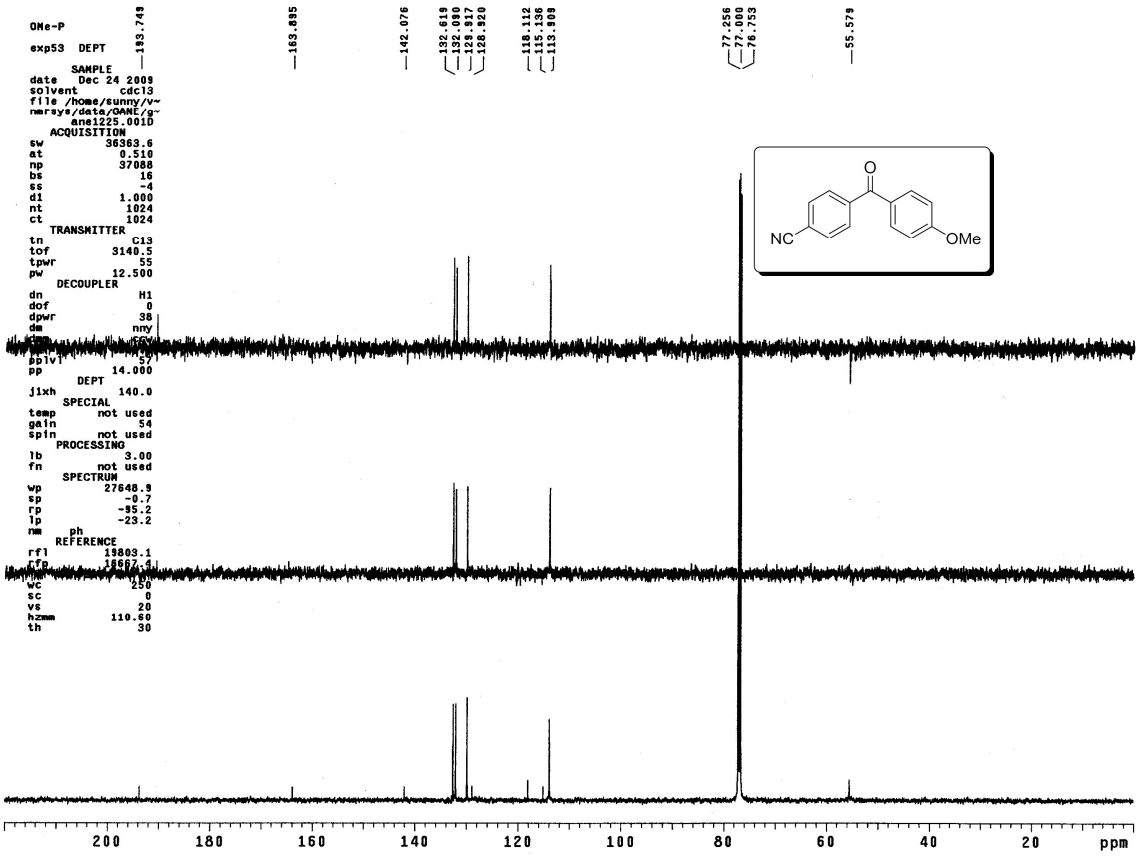
^{1}H and ^{13}C NMR spectra of compound **3q**



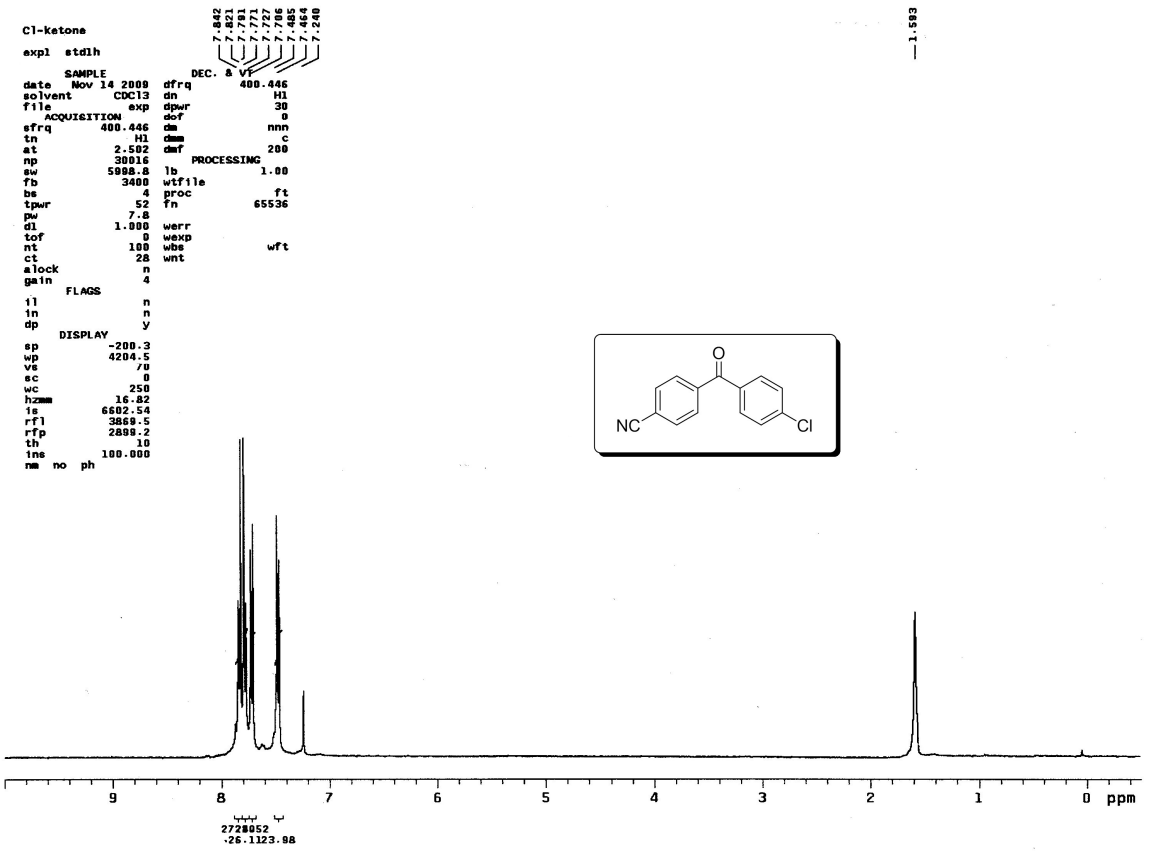


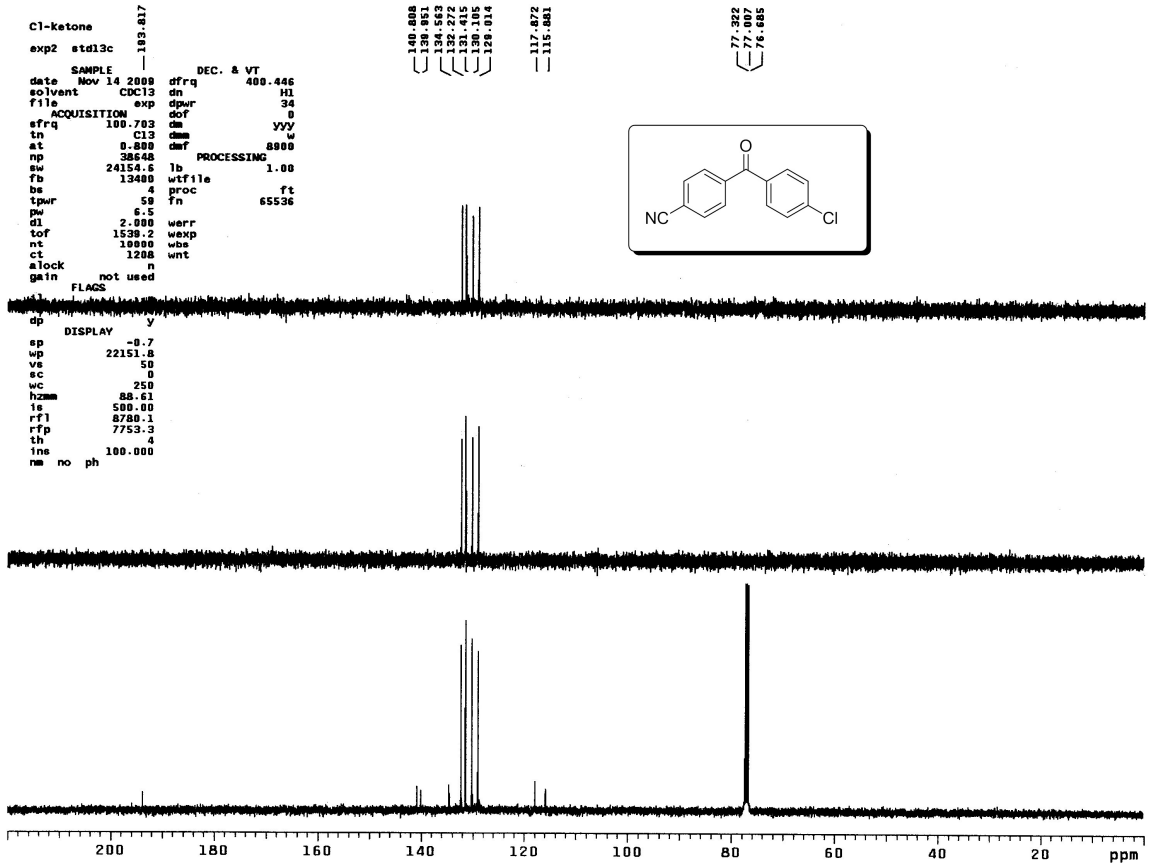
^{1}H and ^{13}C NMR spectra of compound **3r**



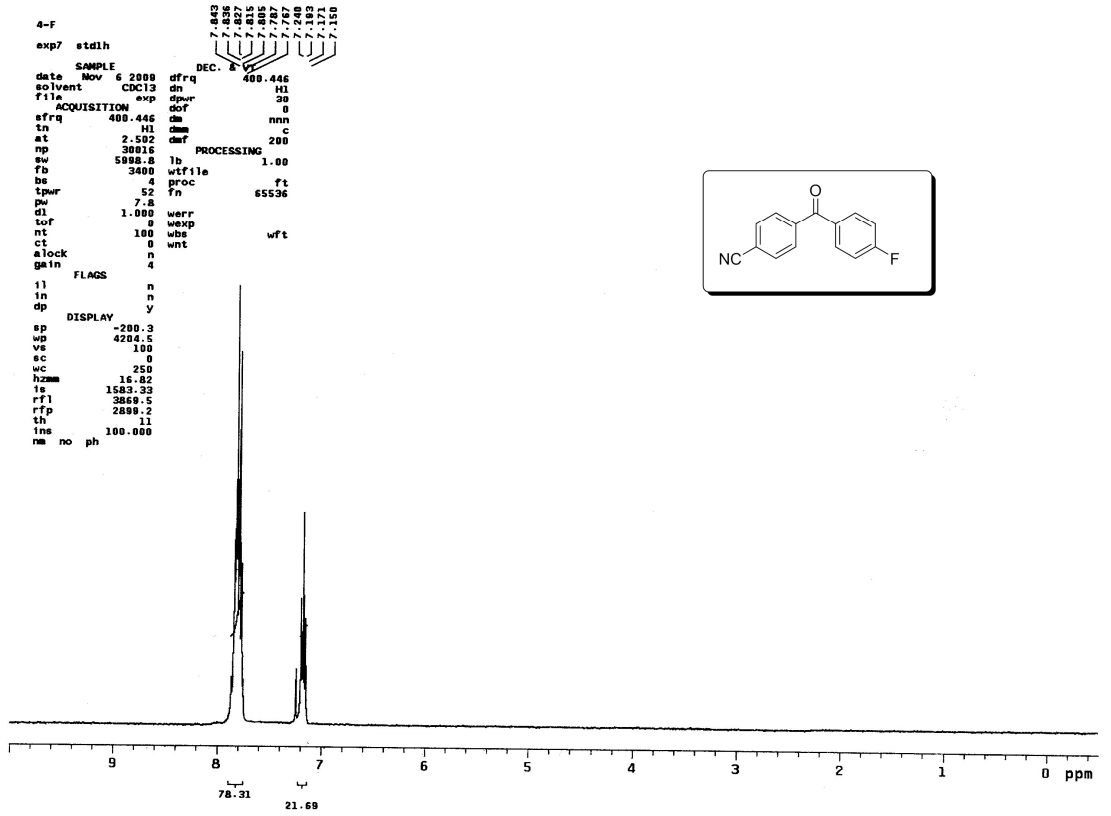


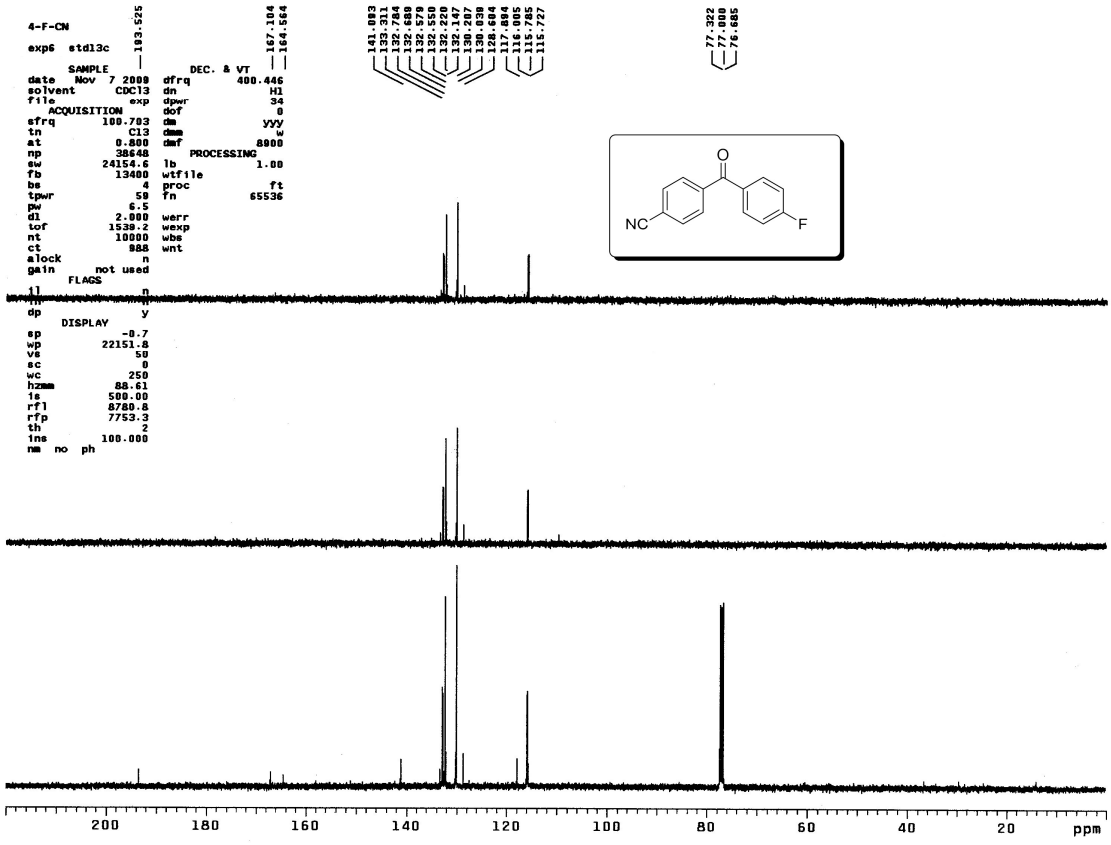
^{1}H and ^{13}C NMR spectra of compound **3s**



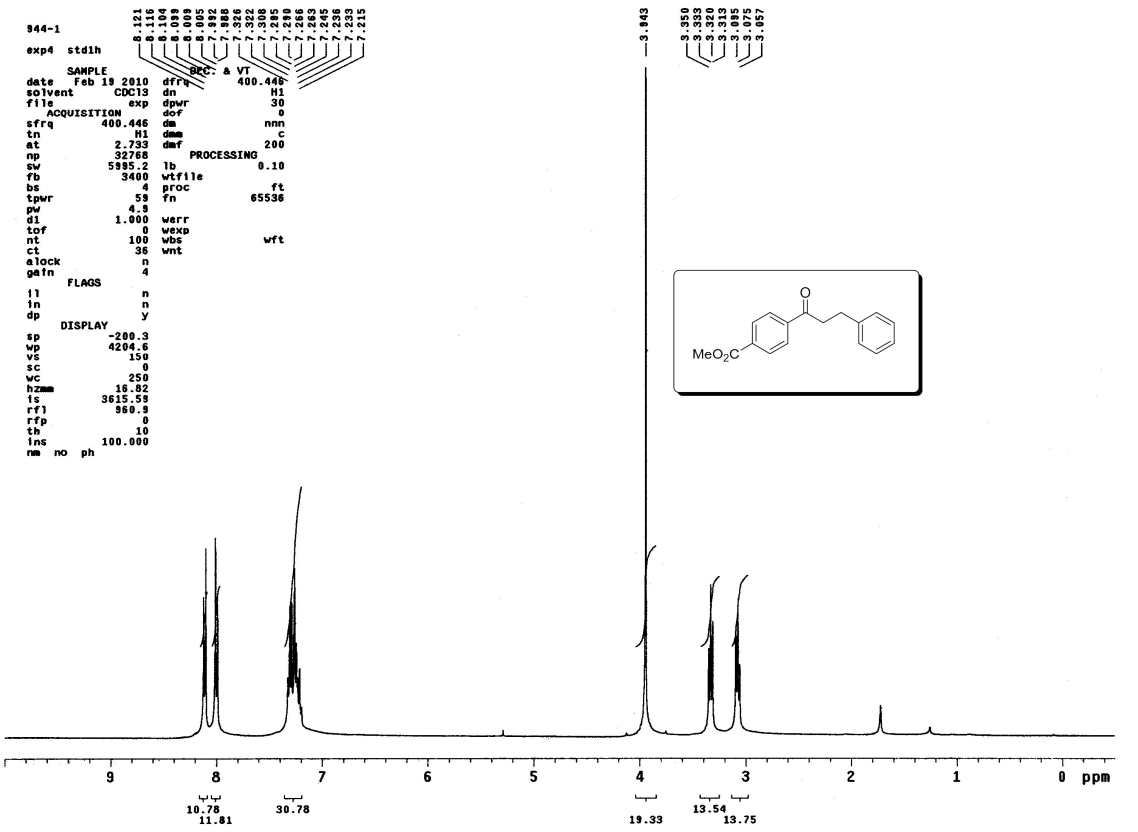


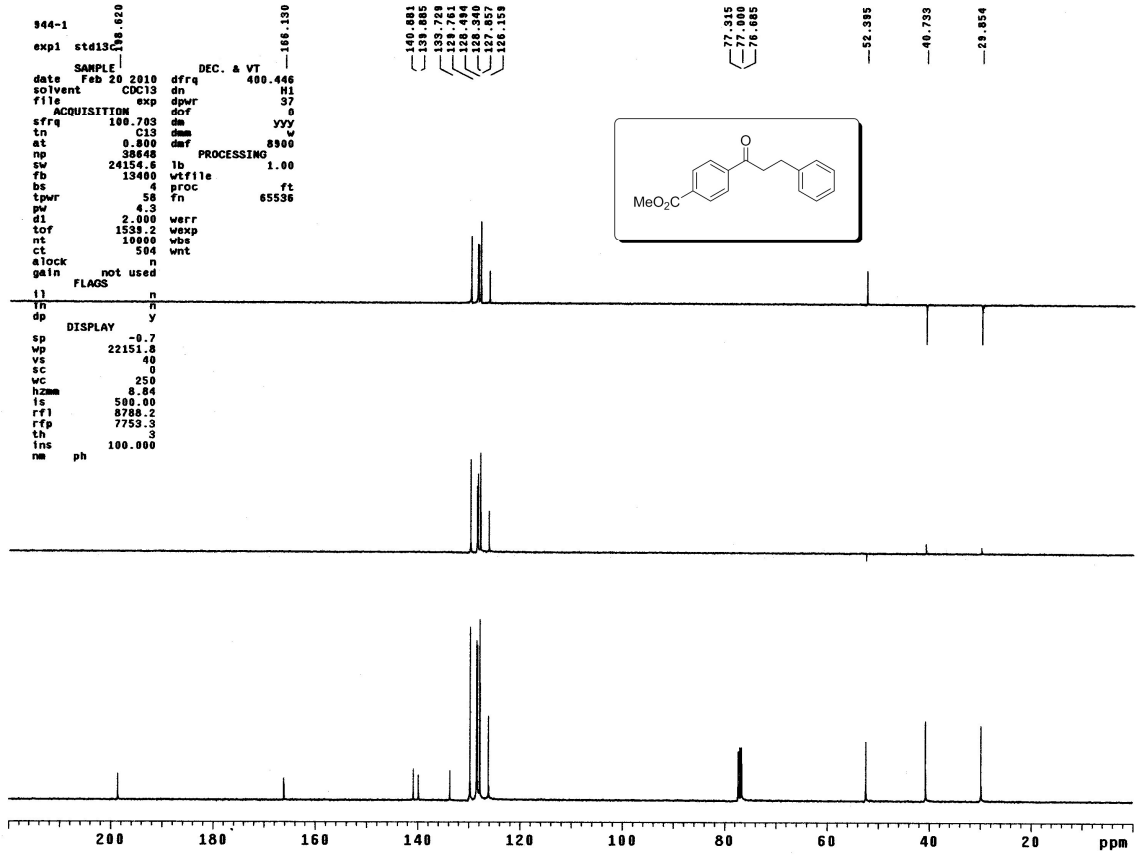
^{1}H and ^{13}C NMR spectra of compound **3t**



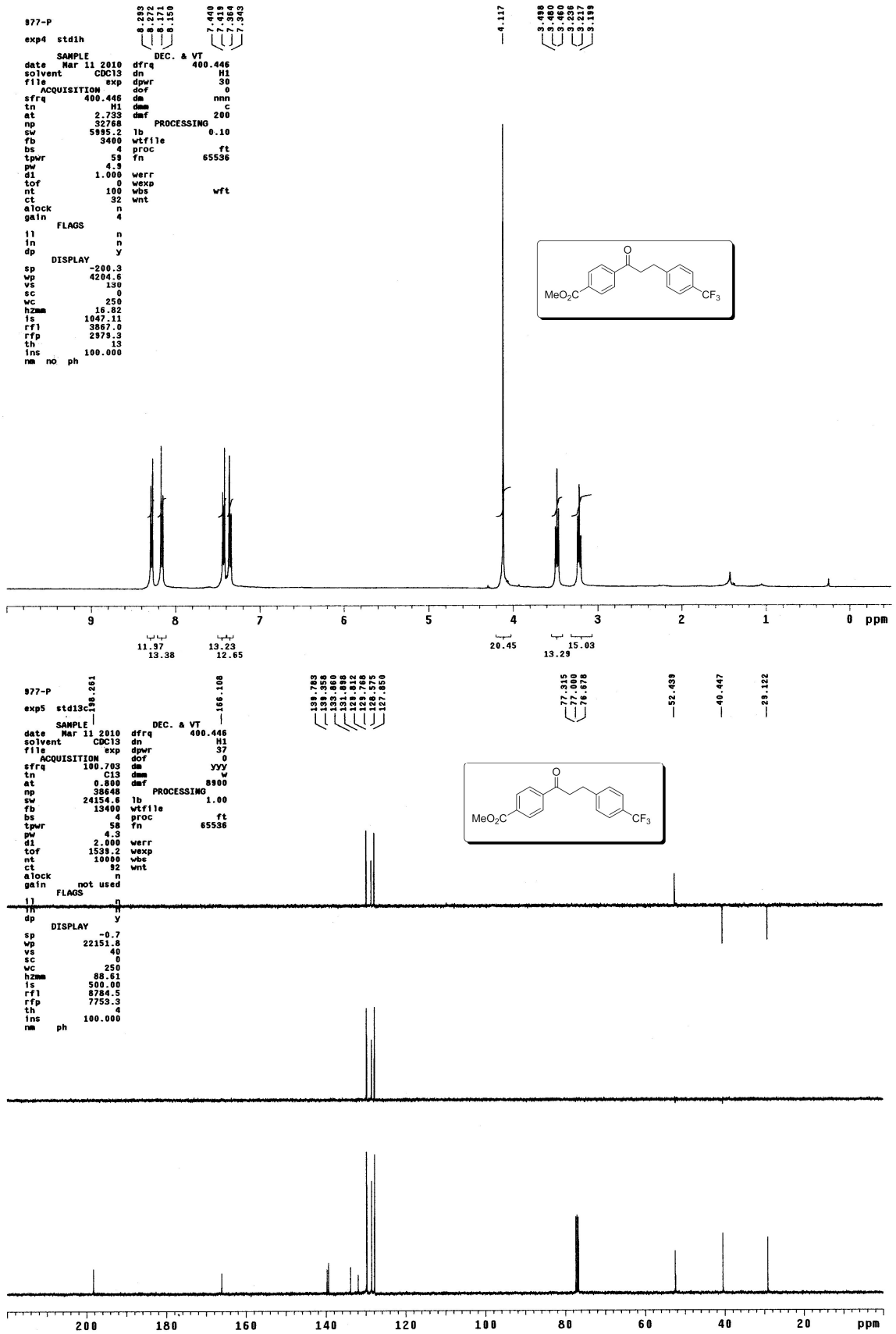


^{1}H and ^{13}C NMR spectra of compound **3u**

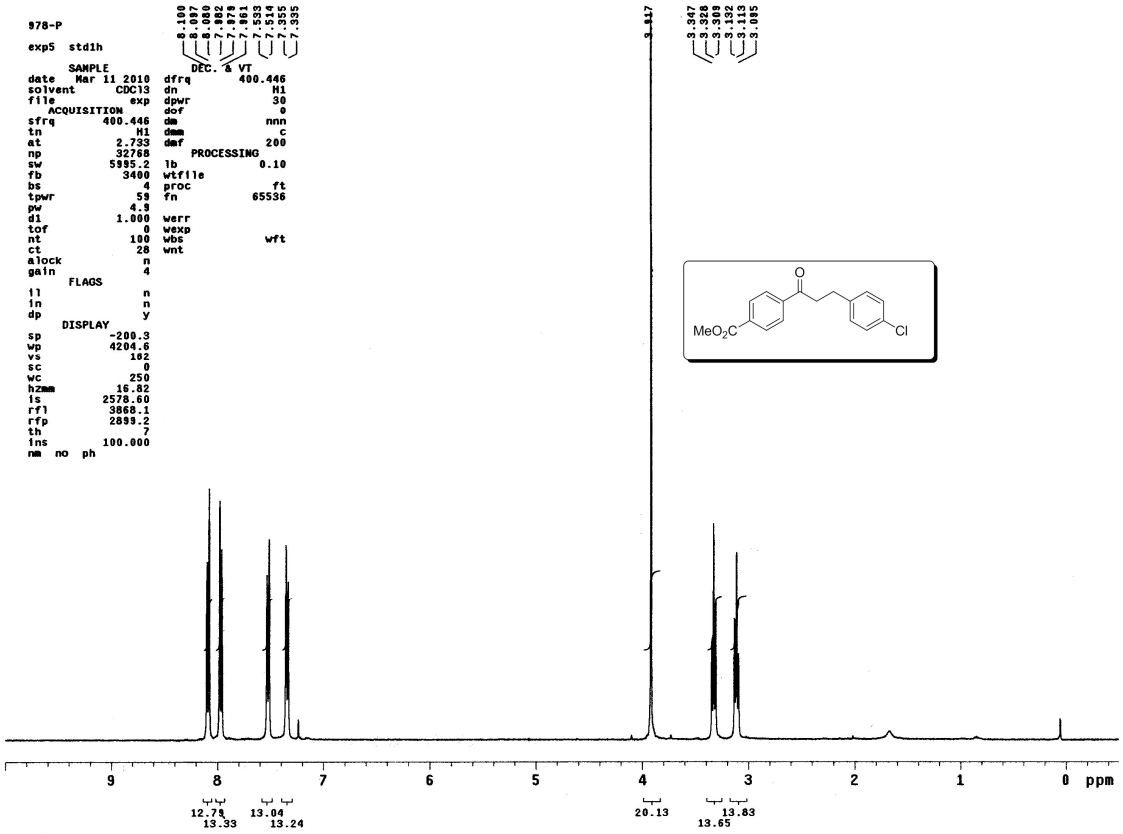


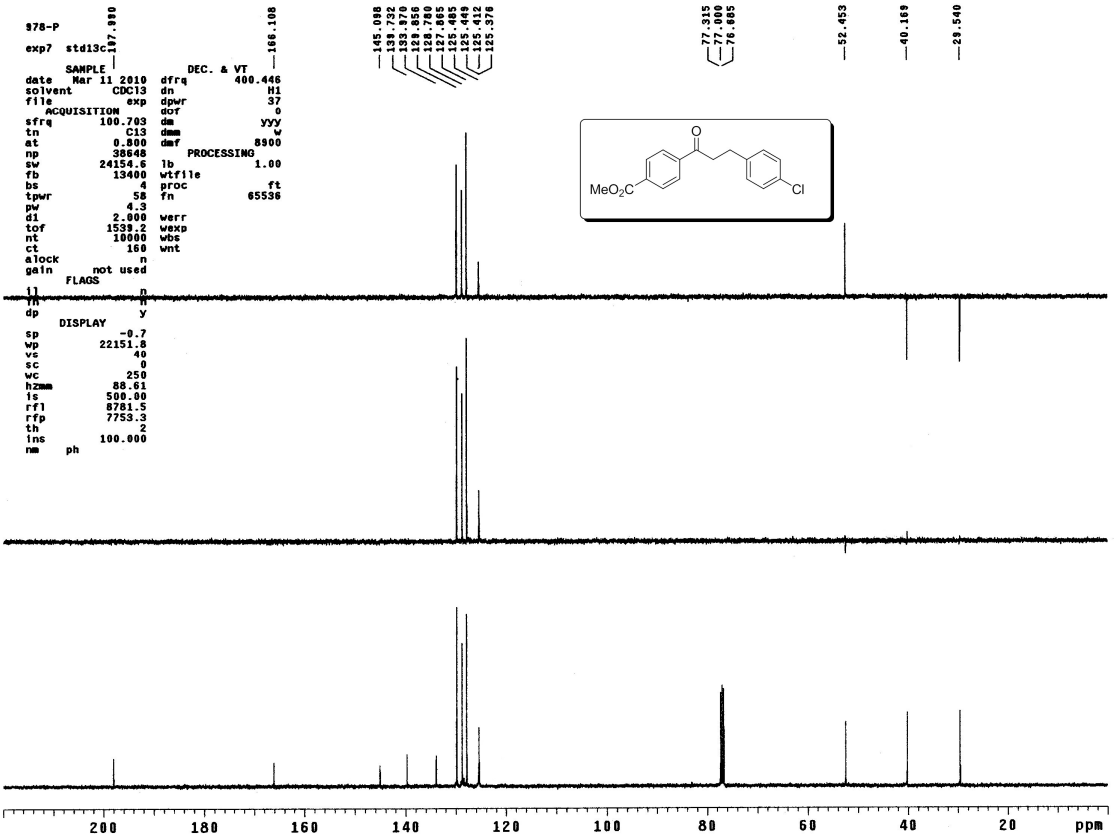


^{1}H and ^{13}C NMR spectra of compound **3v**

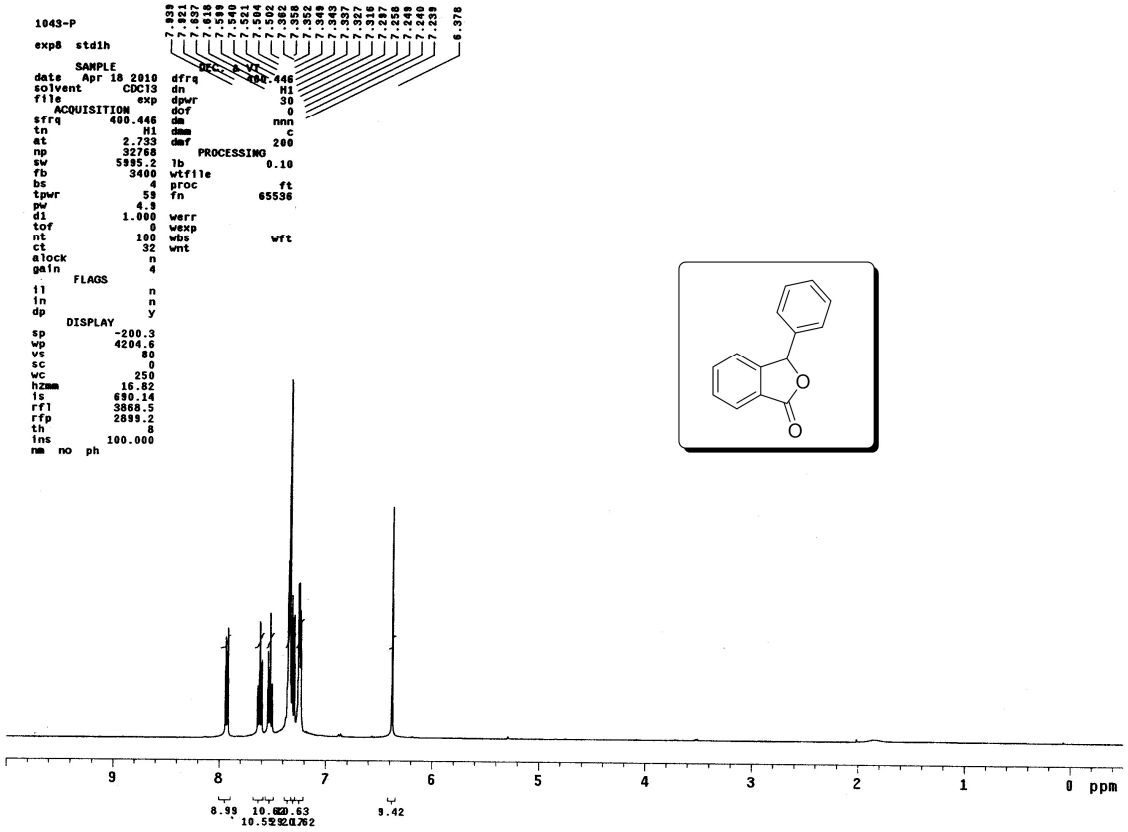


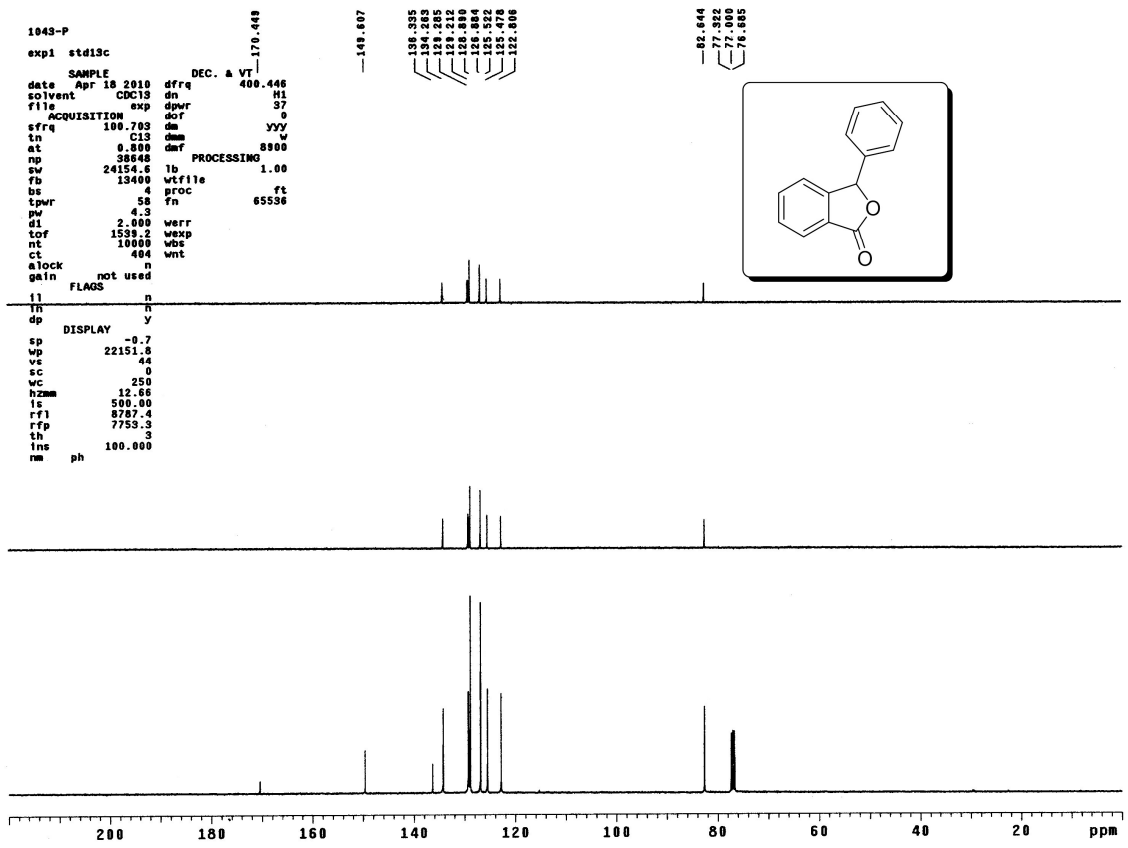
^{1}H and ^{13}C NMR spectra of compound **3w**



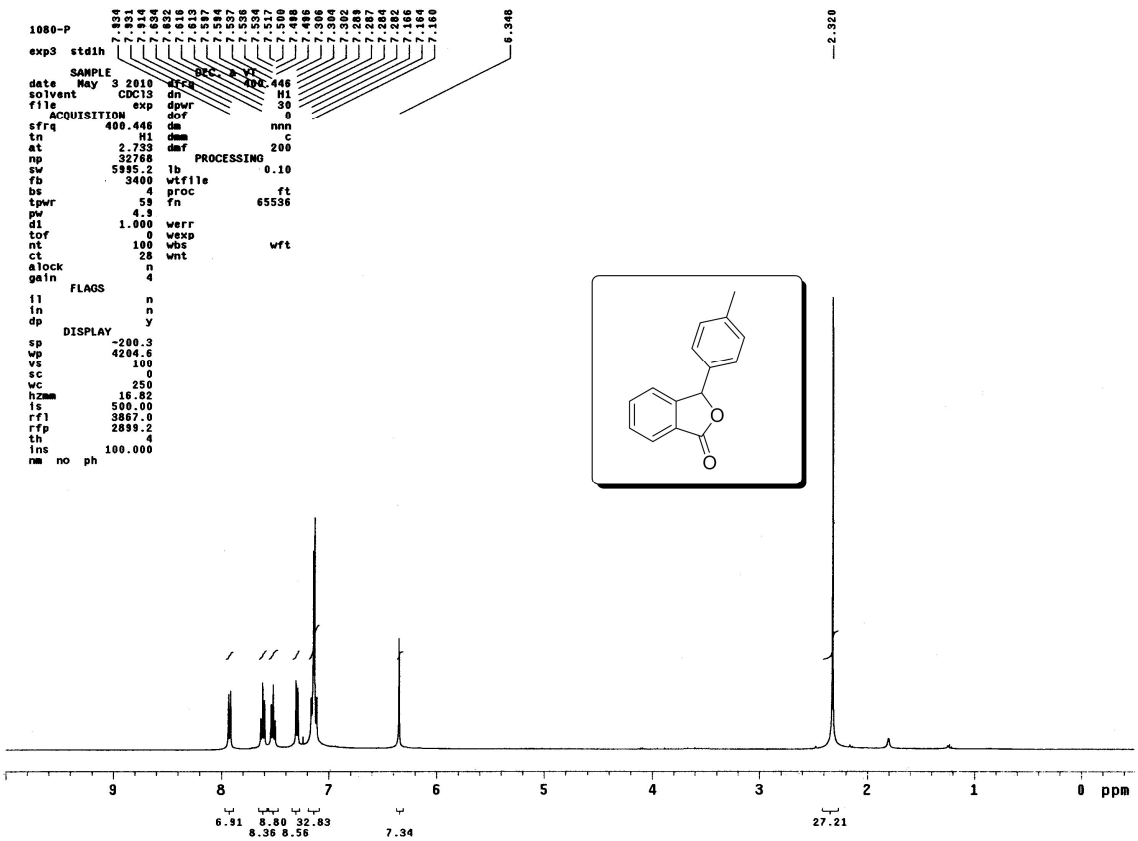


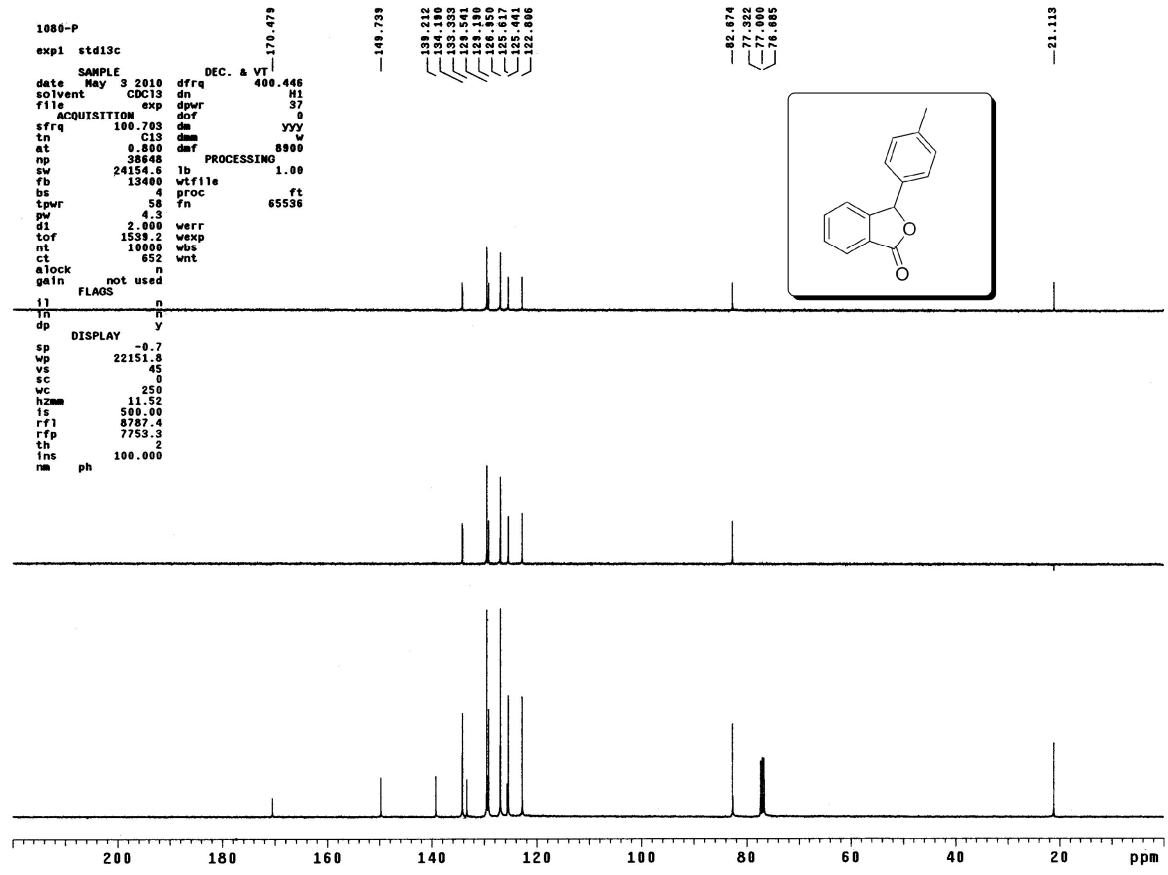
^{1}H and ^{13}C NMR spectra of compound **4a**



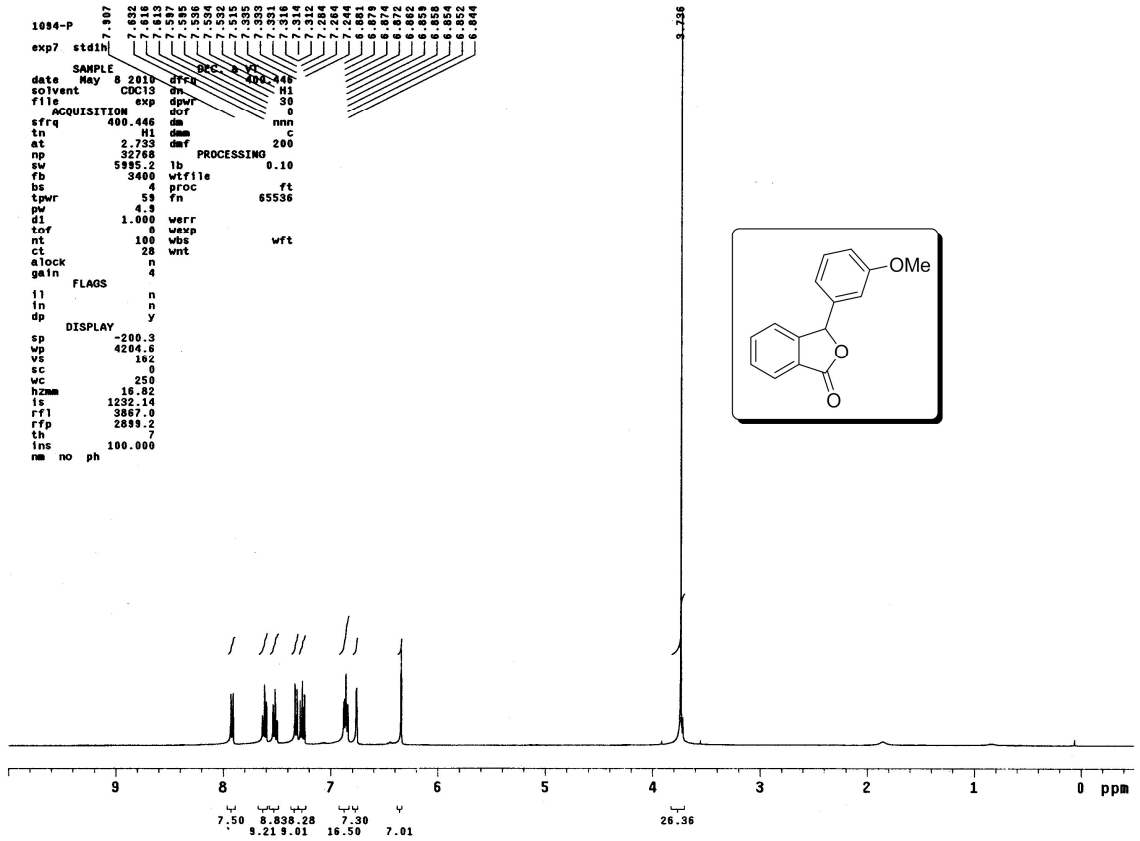


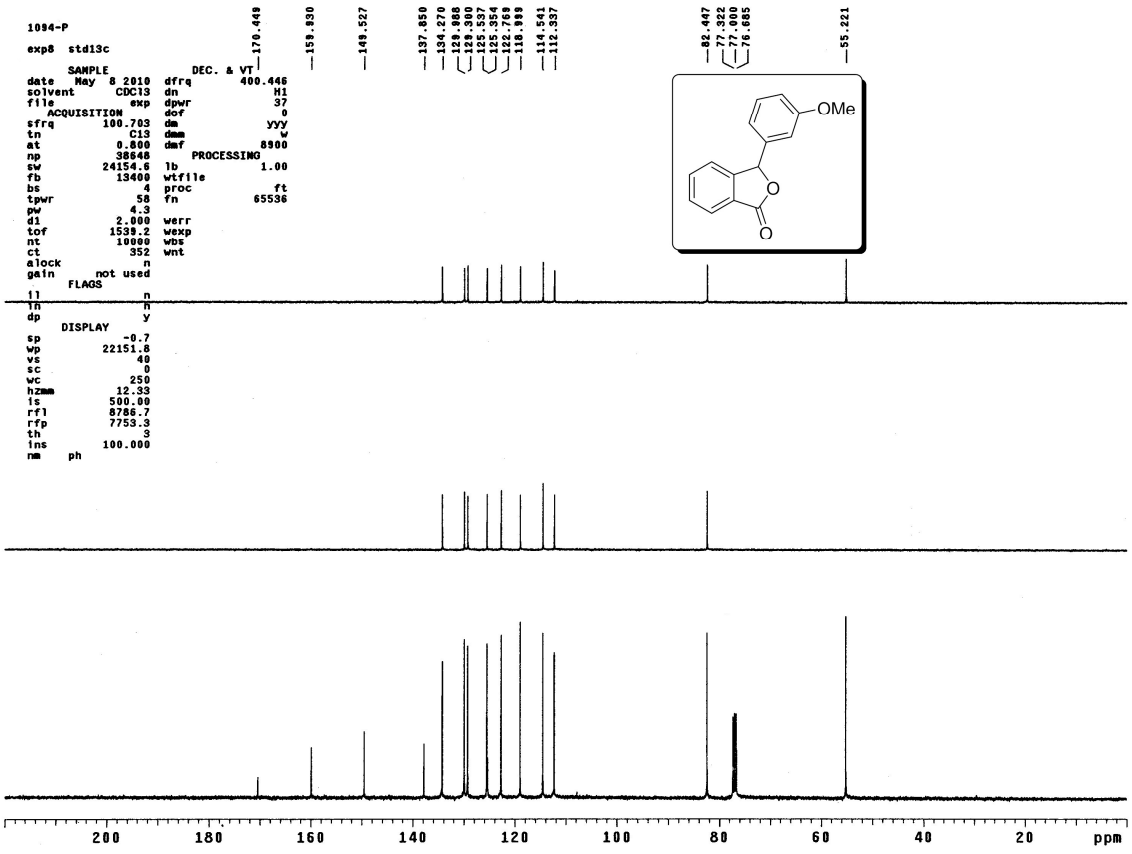
^{1}H and ^{13}C NMR spectra of compound **4b**



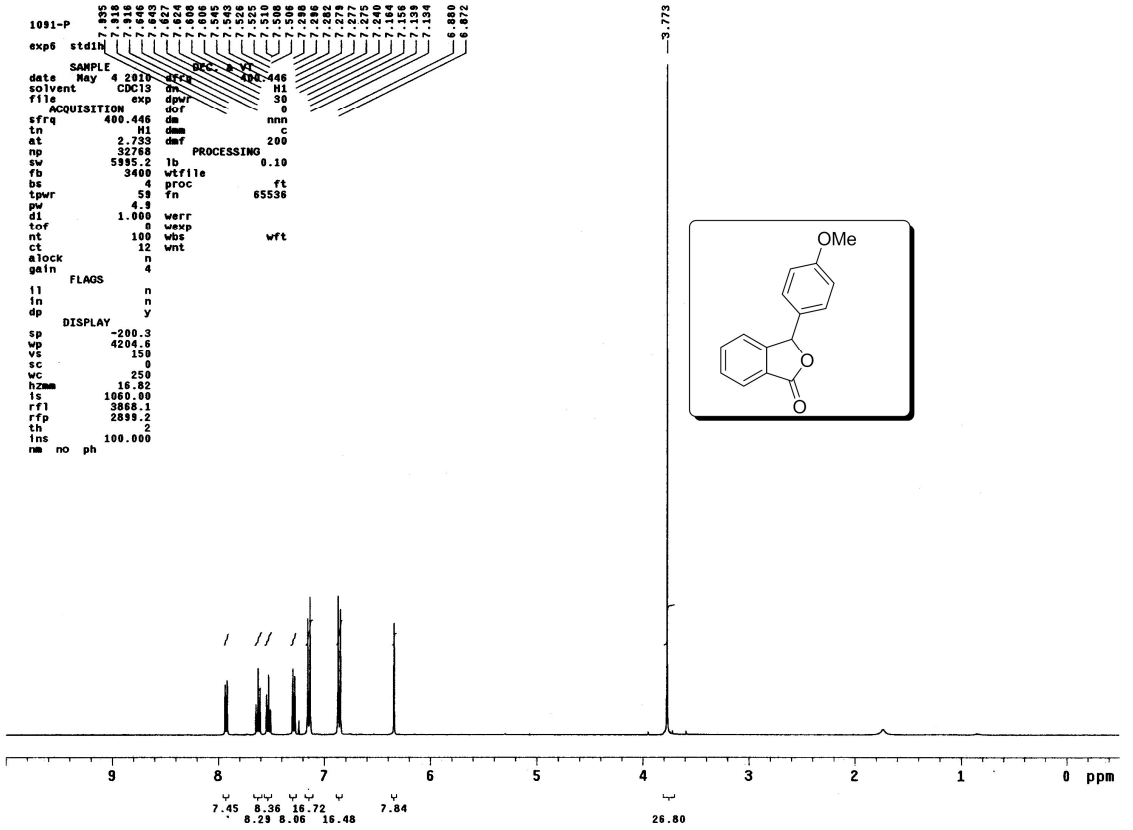


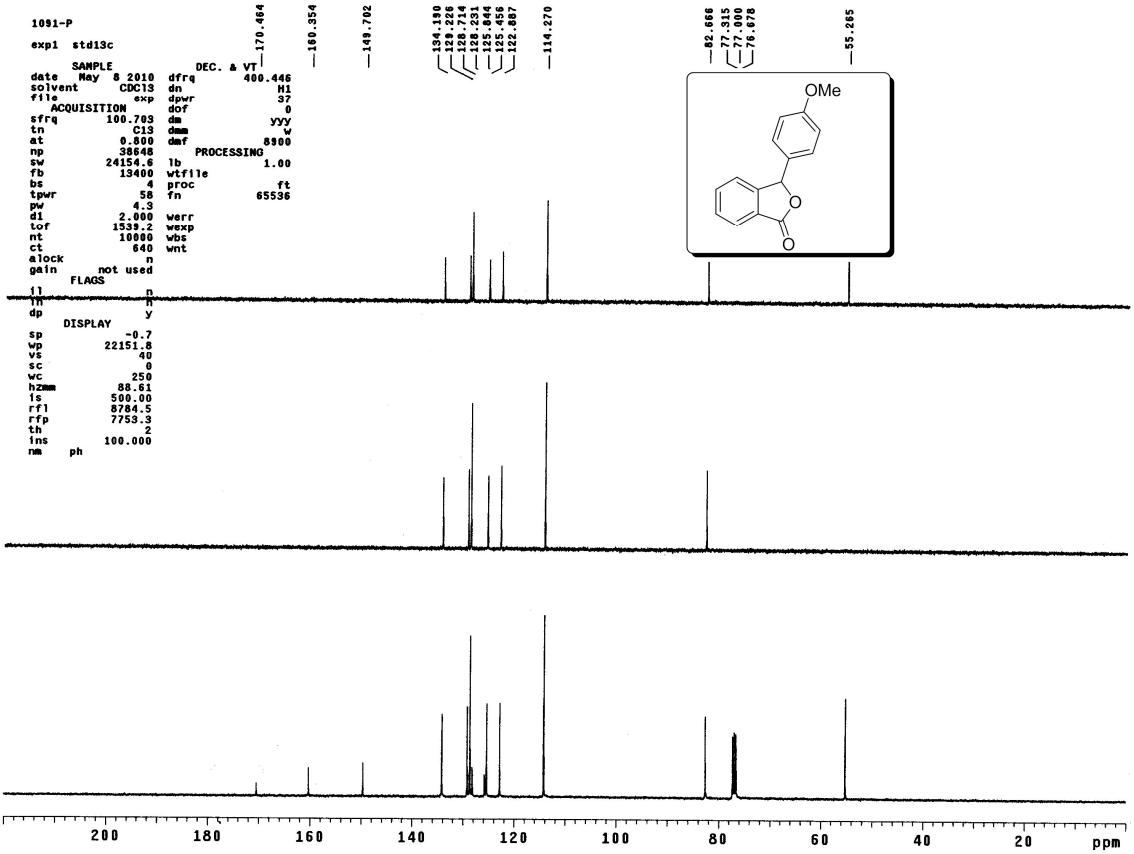
^{1}H and ^{13}C NMR spectra of compound **4c**



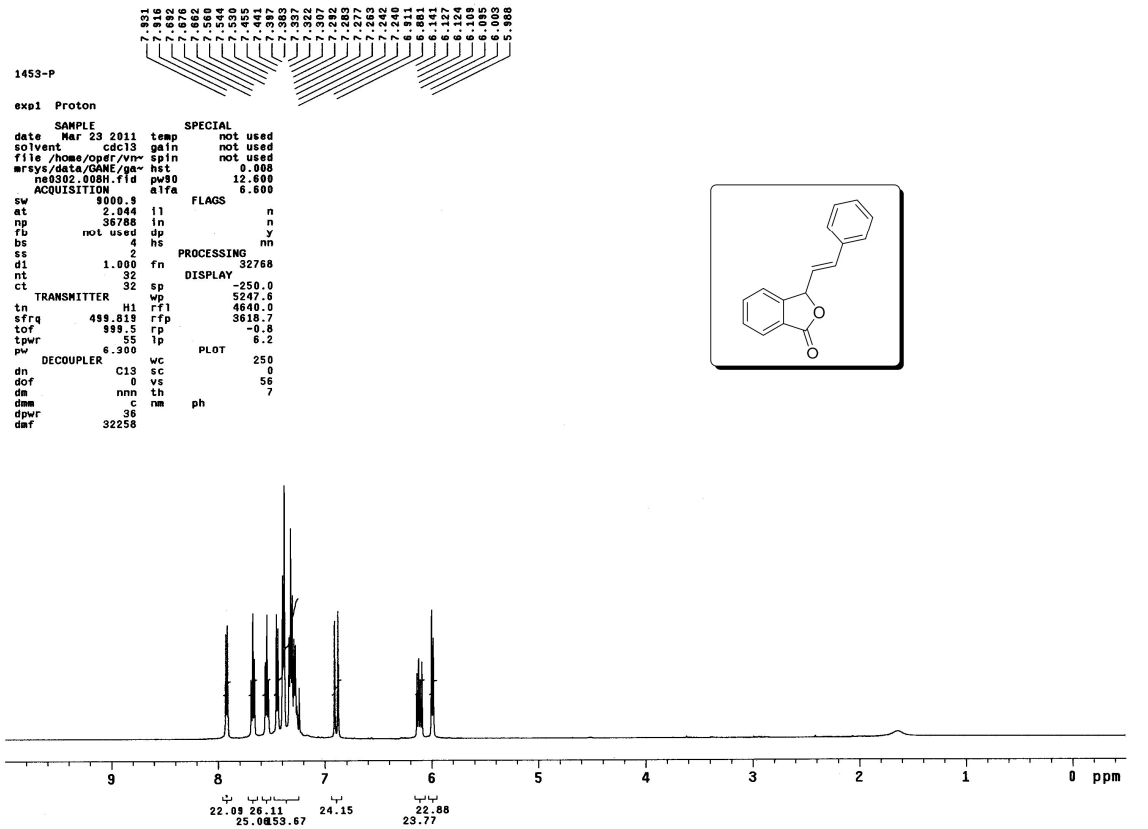


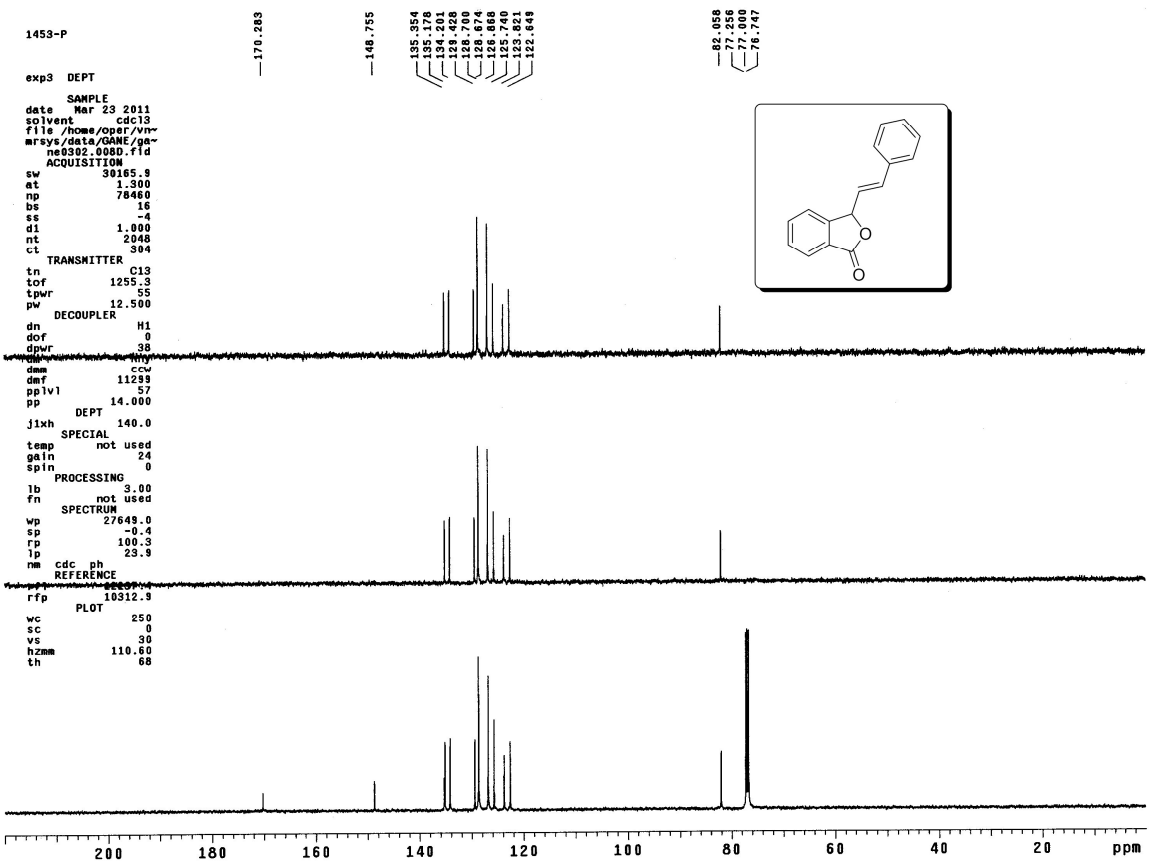
^{1}H and ^{13}C NMR spectra of compound **4d**



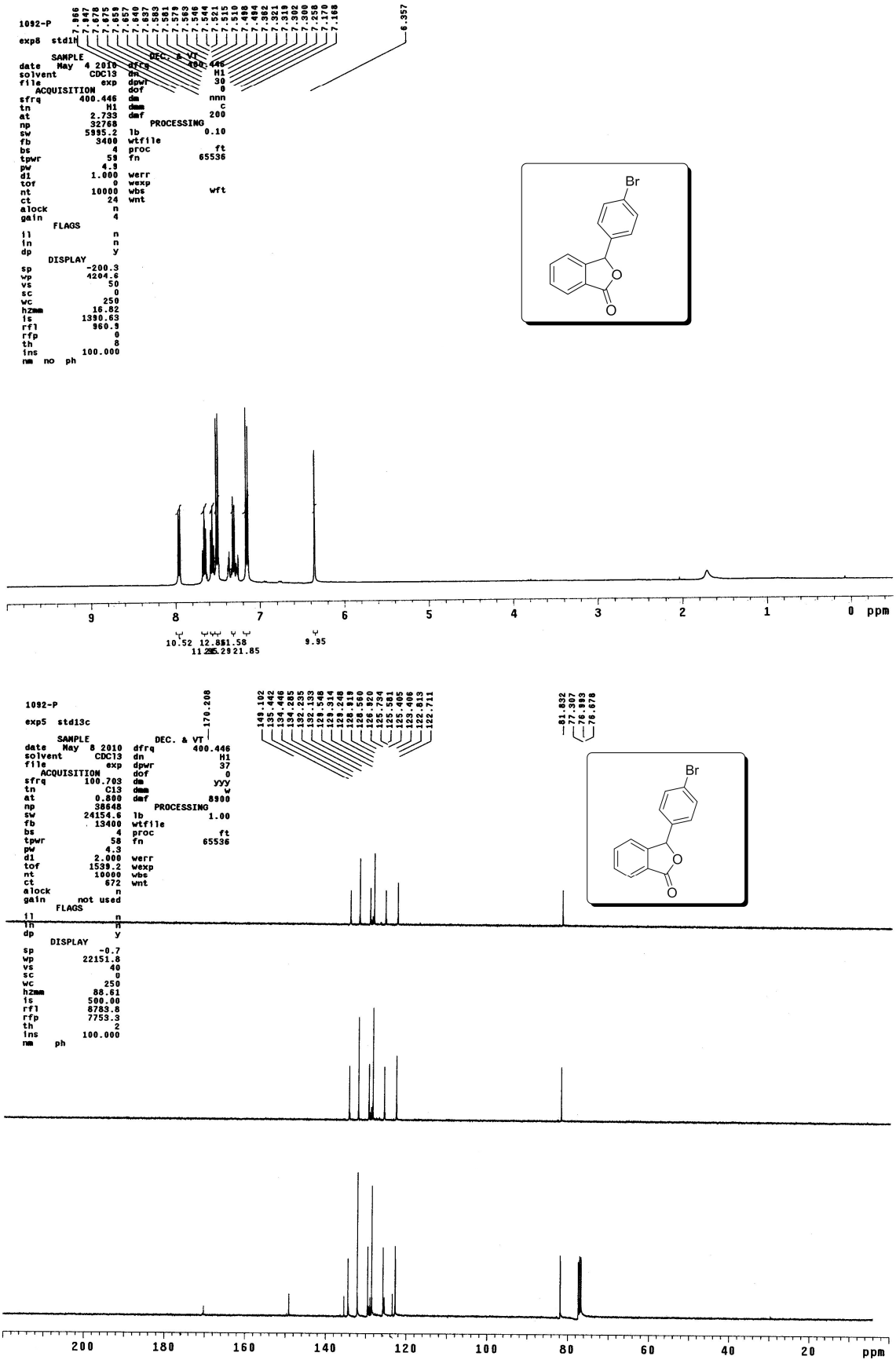


^{1}H and ^{13}C NMR spectra of compound **4e**

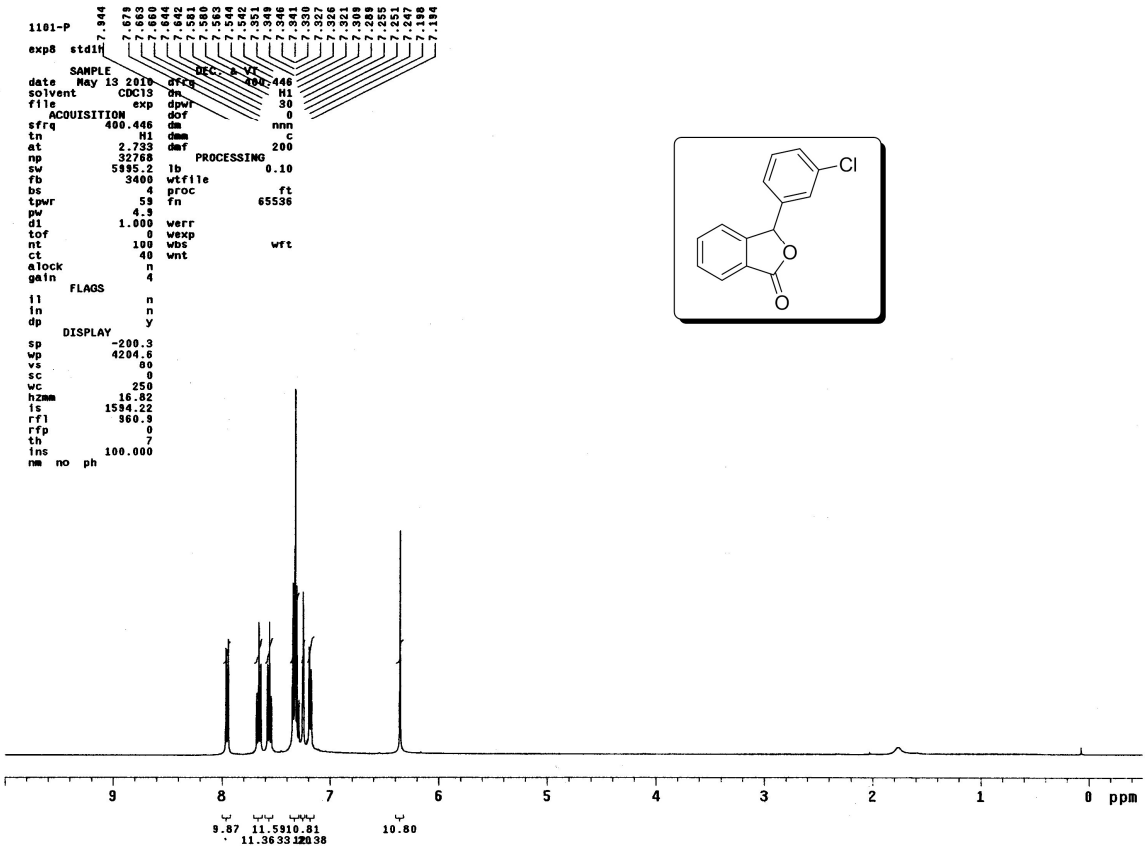


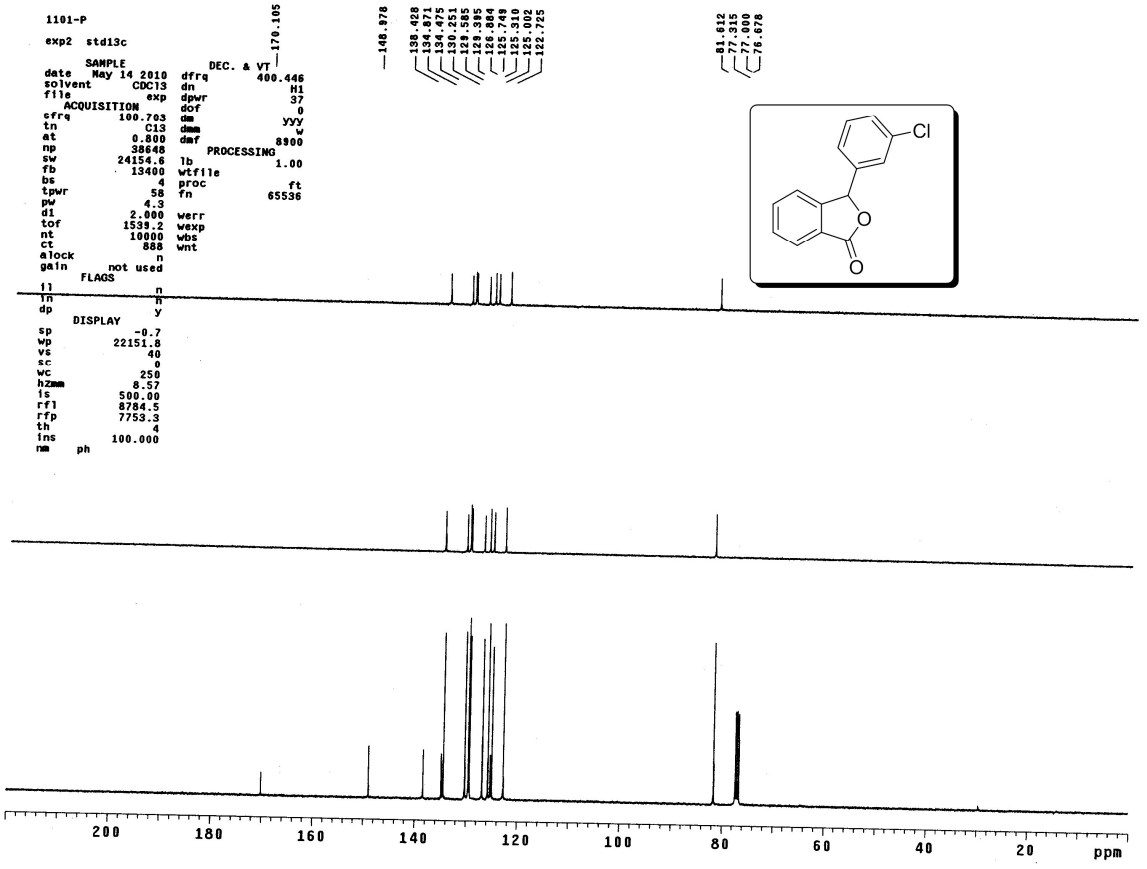


^{1}H and ^{13}C NMR spectra of compound **4f**

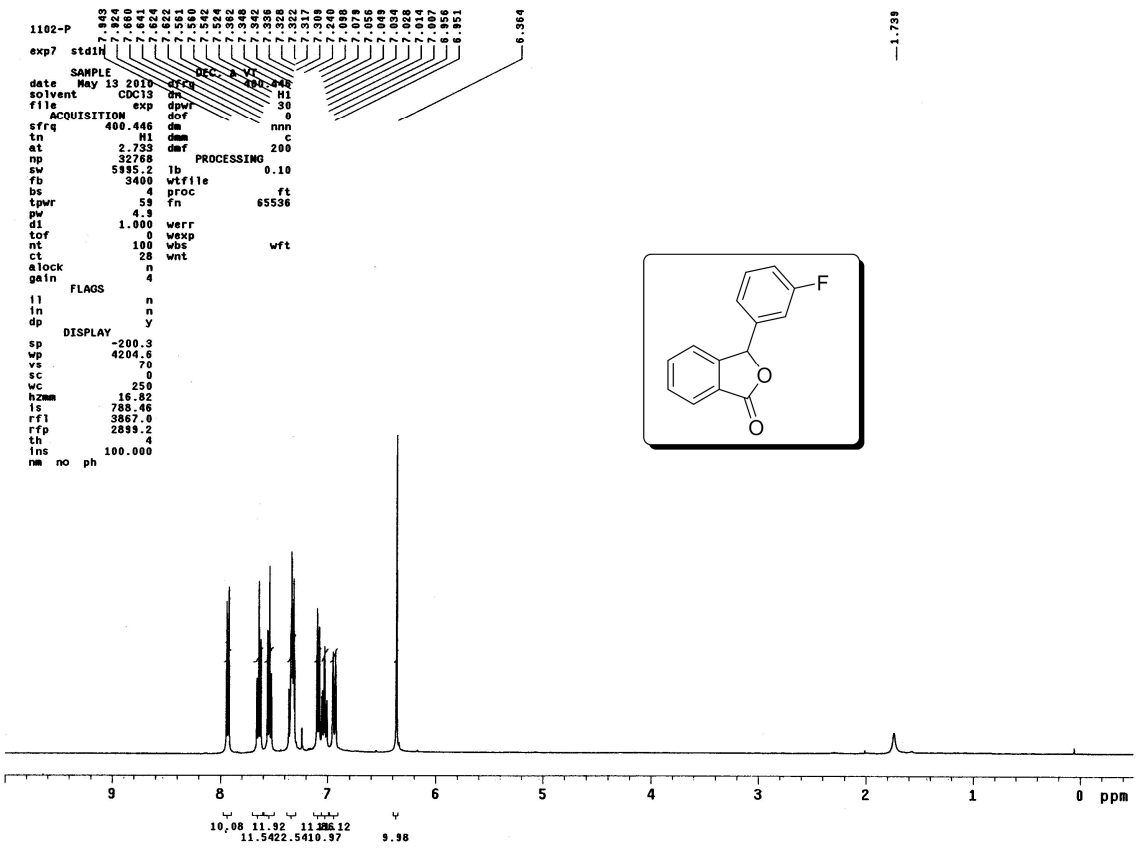


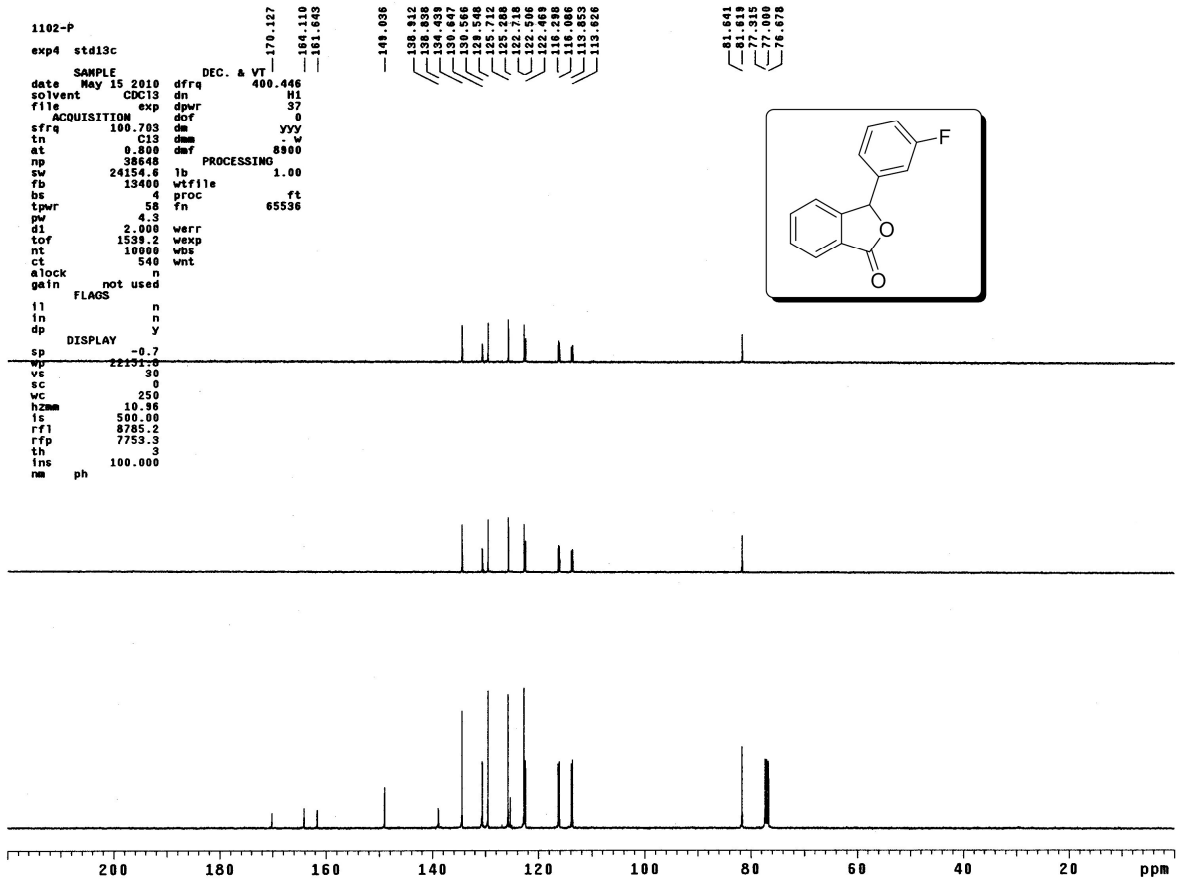
^{1}H and ^{13}C NMR spectra of compound **4g**



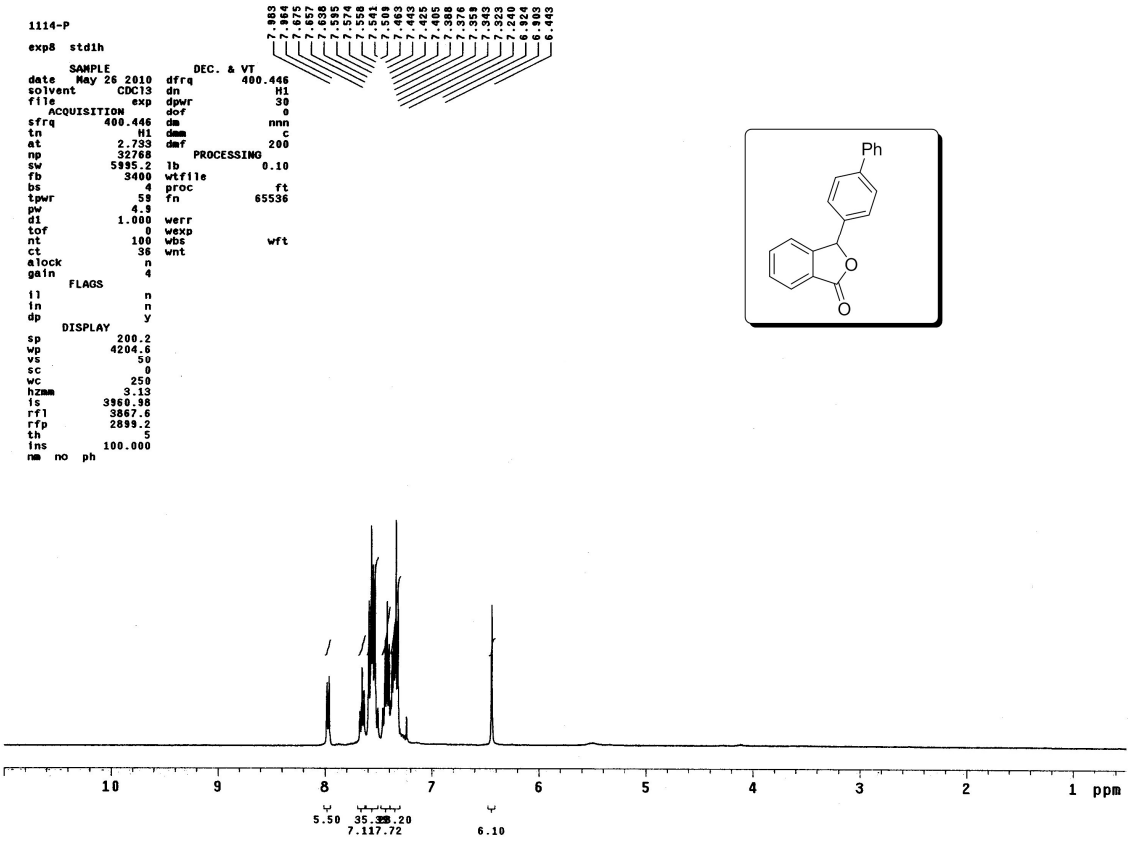


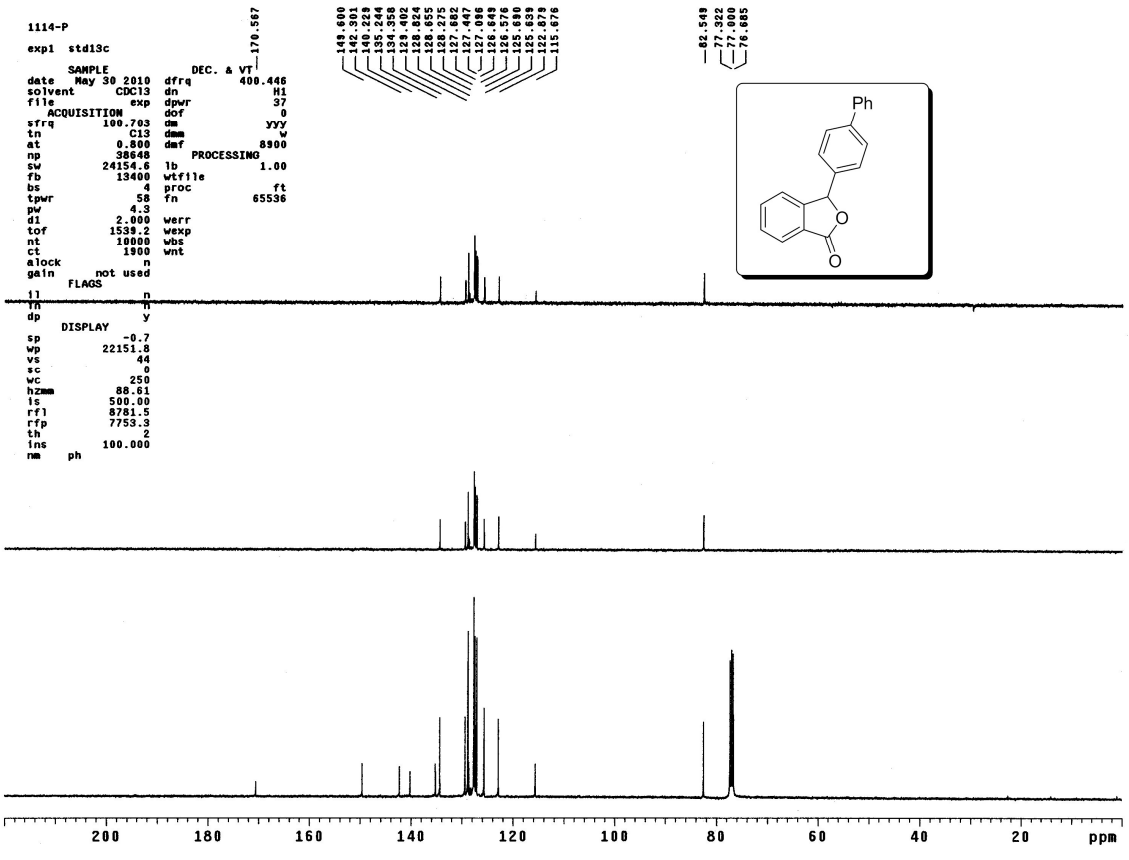
^{1}H and ^{13}C NMR spectra of compound **4i**



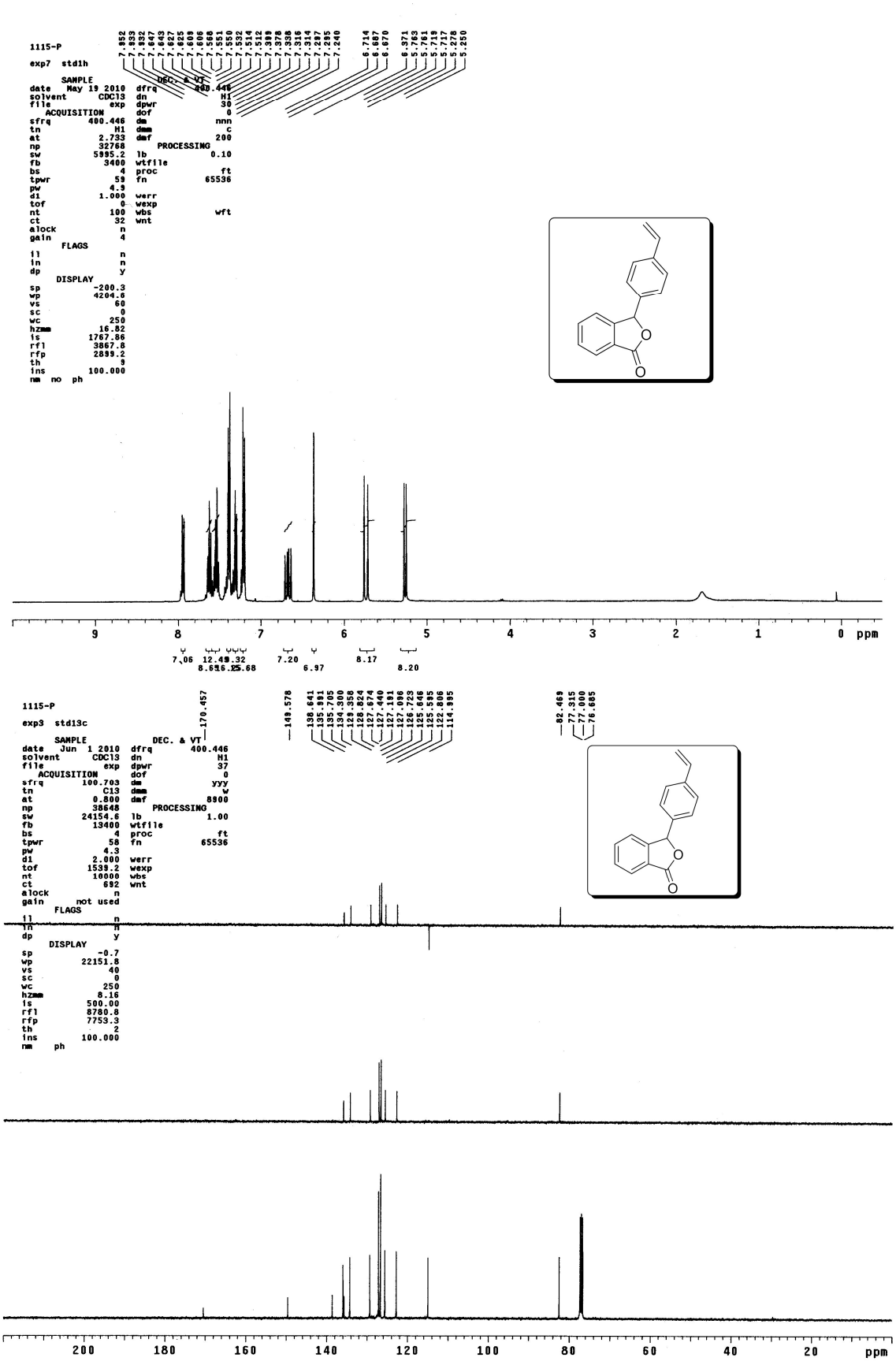


^{1}H and ^{13}C NMR spectra of compound **4j**





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



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