CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Cobalt-Catalyzed Regioselective Synthesis of Indenamine from *o*-Iodobenzaldimine and Alkyne: Intriguing Difference with the Nickel-Catalyzed Reaction

Chuan-Che Liu,[a] Rajendra Prasad Korivi[a] and Chien-Hong Cheng*,[a]

[a] Department of Chemistry, National Tsing Hua University
Hsinchu, 30043 Taiwan.
Fax: (+)886-35724698
E-mail: chcheng@mx.nthu.edu.tw

Cobalt-Catalyzed Regioselective Synthesis of Indenamine from *o*-Iodobenzaldimine and Alkyne: Intriguing Difference with the Nickel-Catalyzed Reaction

Chuan-Che Liu, Rajendra Prasad Korivi, Chien-Hong Cheng*

Department of Chemistry, National Tsing Hua University, Hsinchu, 30013 Taiwan

chcheng@mx.nthu.edu.tw

Supporting Information

Table of Contents

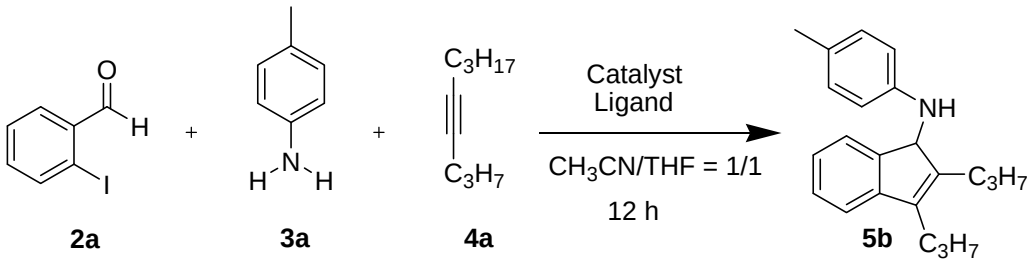
General procedures for preparation of substituted indenamine derivatives (5 or 6): A screw cap seal tube initially fitted with a septum containing aldehyde **2** (0.3 mmol) and amine **3** (0.3 mmol) was evacuated and purged with nitrogen gas three times. Then alkyne **4** (0.60 mmol), a mixture of CH_3CN and THF (2.0 mL, 1:1) were added to the system via a syringe. The septum was removed and [$CoCl_2$(dppe)] (0.012 g, 0.0210 mmol) and zinc (0.040 g, 0.60 mmol) were added to the system and the seal tube was quickly capped by a screw cap. The resultant reaction mixture was stirred at 100 °C for 12 h. The reaction mixture was cooled to room temperature and diluted with dichloromethane. The mixture was filtered through a silica gel pad (0.5 cm) and washed thoroughly with dichloromethane. The filtrate was concentrated in a rotary evaporator to get the crude product. Further separation of the crude product on a silica gel column using a mixture of hexanes and ethyl acetate as eluent afforded the desired pure product **5**. Compounds **5a-t** were synthesized according to this procedure and their spectral data were given below. For the the preparation of indene-enamine derivatives **6a-c**, the same procedure was employed except that Hacac (0.021 mmol) was added along with the alkyne.

General procedure for synthesis of indenimine derivatives (7): A solution of 1M TBAF in THF (1.0 mL) was added to the indenamine derivative **5** or indene-enamine **6** (0.25 mmol) prepared according to the above procedure. The

resulted mixture was stirred at 40 °C under nitrogen for 1 h. The reaction mixture was cooled to room temperature and diluted with dichloromethane. The mixture was filtered through small silica gel column and washed with dichloromethane. The solvent was removed under vacuum to give pure product **7**. Compounds **7a-e** were synthesized according to this procedure and the spectral data of these compounds were given below.

General procedure for synthesis of indenone derivatives (8): To a solution of indenamine **7** (0.25 mmol) in dichloromethane (20 mL) was added HCl (35% in H_2O, 10 mg) and H_2O (50mg). After the mixture was stirred for 1 h, the solution was filtered through small silica gel column. The solvent was removed under vacuum to give pure product **8**.

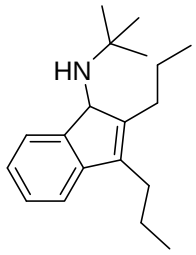
Table 1. Studies for the formation of compound 5b under various catalytic conditions



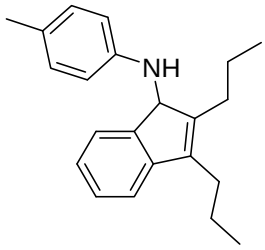
2a **3a** **4a** **5b**

entry	2a:3a:4a	Catalyst	ligand	Zn	T(^{o}C)	yield(%)[a]
1[b]	1:1:1	$Co(acac)_2$ (7%)		1 eq	100	0
2[b]	1:1:1	$Co(acac)_2$ (7%)	dppe (14%)	1 eq	100	46
3	1:1:1	$Co(acac)_2$ (7%)	dppe (7%)	1 eq	100	51
3	1:1:1	$Co(acac)_2$ (7%)	dppe (14%)	1 eq	100	55
4[c]	1:1:1	$Co(acac)_2$ (7%)	dppe (14%)	1 eq	100	0
5	1:1:2	$Co(acac)_2$ (7%)	dppe (14%)	1 eq	100	63
6	1:1:2	$Co(acac)_2$ (7%)	dppe (14%)	2 eq	100	87
7	1:1:2	$Co(acac)_2$ (7%)	dppe (7%)	2 eq	100	74
8	1:1:2	$Co(acac)_2$ (7%)	dppe (14%)	3 eq	100	91
9	1:1:2	$CoCl_2$(dppe) (7%)		2 eq	100	>99
10[b]	1:1:2	$CoCl_2$(dppe) (7%)		2 eq	100	80
11	1:1:2	$CoCl_2$(dppe) (7%)	acac (7%)	2 eq	100	92
12	1:1:2	CoI_2(dppe) (7%)		2 eq	100	>99
13	1:1:2	$CoBr_2$(dppp) (7%)		2 eq	100	75

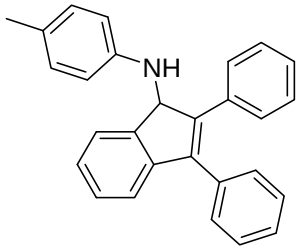
[a] Yields were measured from crude products by the ^{1}H NMR integration method using mesitylene as an internal standard. All reaction were carried out in MeCN+THF (2.0 mL, 1:1) under one nitrogen atmosphere using aldehyde **2** (0.30 mmol), amine **3** (0.30 mmol) at 100 $^\circ$C for 12 h. [b] MeCN (2.0 mL) was used as solvent. [c] H_2O (2.0 eq.) was added. [eq. = equivalents to aldehyde]



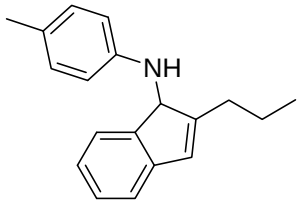
***N-tert*-Butyl-2,3-dipropyl-1H-inden-1-amine (5a)**: viscous liquid; R_f = 0.45 (10% ethyl acetate in hexanes); ^{1}H NMR δ 0.97-1.01 (m, 6H), 1.30 (s, 9H), 1.42-1.50 (m, 1H), 1.52-1.63 (m, 3H), 2.36-2.45 (m, 4 H), 4.23 (s, 1H), 7.12 (t, *J* = 7.0 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.0 Hz, 1H) and 7.48 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR δ 14.4, 14.5, 22.0, 23.6, 27.6, 27.7, 30.9, 50.7, 60.7, 118.5, 123.0, 124.3, 127.0, 136.0, 145.1, 147.2 and 148.5; HRMS (EI^+) 271.2300 (cal. for $C_{19}H_{29}N$ 271.2300); IR 1226, 1465, 1604, 1704, 2869, 2931, 2954 and 3355 cm^{-1}.



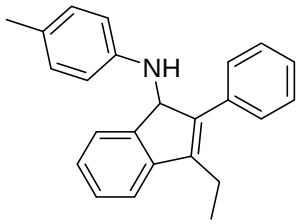
2,3-Dipropyl-*N*-*p*-tolyl-*1H*-inden-1-amine (5b): viscous liquid; R_f = 0.80 (10% ethyl acetate in hexanes); ^{1}H NMR δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H), 1.43-1.52 (m, 1H), 1.58-1.67 (m, 3H), 2.24 (s, 3H), 2.30-2.42 (m, 2H), 2.50 (t, *J* = 7.7 Hz, 2H), 3.67 (s, 1H), 4.95 (s, 1H), 6.56 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 7.04 (dt, *J* = 1.8 and 7.3 Hz, 1H), 7.23-7.27 (m, 2H) and 7.37 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR δ 14.3, 14.4, 20.4, 21.9, 23.2, 27.4, 28.1, 61.6, 113.7, 118.7, 122.8, 124.5, 126.6, 127.5, 129.7, 137.7, 144.5, 144.8, 145.4 and 145.6; HRMS (EI^+) 305.2142 (cal. for $C_{22}H_{27}N$ 305.2143); IR 1457, 1519, 1612, 1704, 2861, 2923 and 3417 cm^{-1}.



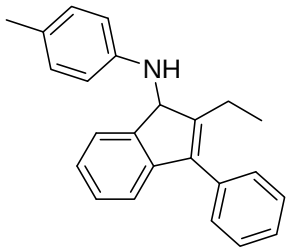
2,3-Diphenyl-*N*-*p*-tolyl-*1H*-inden-1-amine (5c): yellow solid; melting point 137 °C; R_f = 0.67 (10% ethyl acetate in hexanes); ^{1}H NMR δ 2.12 (s, 3H), 5.49 (s, 1H), 6.52 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 7.01-7.29 (m, 13H) and 7.41 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR δ 20.4, 62.4, 113.9, 120.7, 123.3, 126.0, 126.9, 127.1, 127.6, 127.9, 128.0, 128.8, 129.2, 129.4, 129.8, 134.3, 135.1, 140.1, 143.1, 144.0, 145.3 and 145.5; HRMS (EI^+) 373.1825 (cal. for $C_{28}H_{23}N$ 373.1830); IR 1272, 1612, 1704, 1882, 1951, 2923, 3054 and 3409 cm^{-1}.



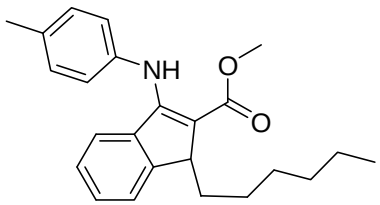
2-Propyl-*N*-*p*-tolyl-*1H*-inden-1-amine (5d): viscous liquid; R_f = 0.80 (10% ethyl acetate in hexanes); ^{1}H NMR δ 1.02 (t, *J* = 7.5 Hz, 3H), 1.65-1.75 (m, 2H), 2.28 (s, 3H), 2.48 (t, *J* = 7.3 Hz, 2H), 5.09 (s, 1H), 6.27 (d, *J* = 1.5 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 7.19 (td, *J* = 2.0 and 7.5, 1H), 7.29-7.34 (m, 2H) and 7.48 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 14.2, 20.4, 20.8, 29.6, 60.6, 113.9, 119.3, 123.3, 125.6, 127.1, 127.8, 129.8, 130.4, 144.2, 145.1, 145.6 and 146.2; HRMS (EI^+) 363.1667 (cal. for $C_{19}H_{21}N$ 363.1674); IR 1265, 1519, 1612, 1727, 2923, 3046 and 3409 cm^{-1}.



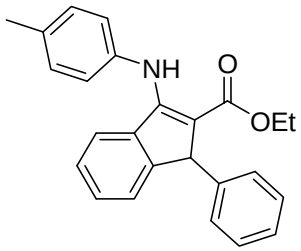
3-Ethyl-2-phenyl-*N*-*p*-tolyl-*1H*-inden-1-amine (5e): viscous liquid; R_f = 0.75 (10% ethyl acetate in hexanes); ^{1}H NMR (CD_2Cl_2) δ 1.31 (t, *J* = 7.5 Hz, 3H), 2.18 (s, 3H), 2.67-2.75 (m, 2H), 3.92(s, 1H, NH), 5.42 (s, 1H), 6.47 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 7.14 (td, *J* = 1.0 and 7.0 Hz, 1H), 7.26-7.29 (m, 1H), 7.32-7.38 (m, 5H), and 7.40-7.45 (m, 2H); ^{13}C NMR (CD_2Cl_2) δ 13.7, 19.7, 20.4, 63.0, 114.1, 120.2, 123.3, 125.9, 127.0, 127.3, 128.1, 128.6, 129.3, 129.9, 135.9, 141.7, 142.6, 144.1, 145.6 and 145.8; HRMS (EI^+) 325.1829 (cal. for $C_{24}H_{23}N$ 325.1830); IR 1286, 1457, 1519, 1612, 2923, 2969, 3023 and 3417 cm^{-1}.



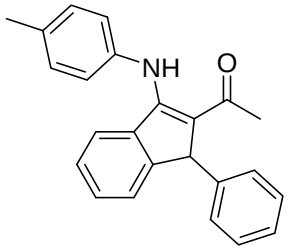
2-Ethyl-3-phenyl-*N*-*p*-tolyl-*1H*-inden-1-amine (5e'): yellow liquid; R_f = 0.80 (10% ethyl acetate in hexanes); ^{1}H NMR (CD_2Cl_2) δ 1.13 (t, *J* = 8.0 Hz, 3H), 2.21 (s, 3H), 2.33-2.52 (m, 2H), 3.97 (s, 1H, NH), 5.13 (s, 1H), 6.56 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 7.09 (td, *J* = 1.5 and 7.5 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.37-7.43 (m, 4H) and 7.47-7.50 (m, 2H); ^{13}C NMR (CD_2Cl_2) δ 14.9, 20.0, 20.4, 62.0, 114.1, 120.1, 123.3, 125.3, 127.1, 127.7, 127.9, 128.9, 129.2, 130.0, 135.3, 138.4, 144.5, 145.4, 145.8 and 149.1; HRMS (EI^+) 325.1823 (cal. for $C_{24}H_{23}N$ 325.1830); IR 1265, 1457, 1519, 1612, 2869, 2923, 2969, 3039 and 3417 cm^{-1}.



Methyl 3-(*p*-tolylamino)-1-hexyl-*1H*-indene-2-carboxylate (6a): yellow solid; melting point 80 °C; R_f = 0.76 (10% ethyl acetate in hexanes); ^{1}H NMR δ 0.80 (t, *J* = 7.3 Hz, 3H),1.16-1.25 (m, 8H) , 2.02-2.06 (m, 2H), 2.36 (s, 3H), 3.81 (s, 3H), 3.85 (t, *J* = 4.8 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.28 (td, *J* = 1.2 and 7.6 Hz, 1H), 7.41 (d, *J* = 7.0 Hz, 1H) and 9.24 (s, 1H, NH); ^{13}C NMR δ 14.0, 21.0, 22.6, 24.0, 29.6, 31.2, 31.6, 45.5, 50.5, 105.6, 123.6, 123.9, 124.8, 125.7, 128.3, 129.5, 134.8, 137.1, 137.9, 150.0, 156.0 and 168.6; HRMS (EI^+) 363.2206 (cal. for $C_{24}H_{29}NO_2$ 363.2198); IR 1195, 1257, 1442, 1565, 1658, 2923 and 3278 cm^{-1}.

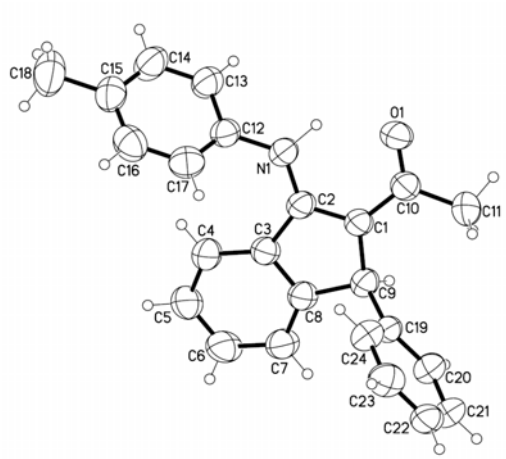


Ethyl 3-(*p*-tolylamino)-1-phenyl-*1H*-indene-2-carboxylate (6b): yellow solid; melting point 111 °C; R_f = 0.75 (10% ethyl acetate in hexanes); ^{1}H NMR δ 1.04 (t, *J* = 7.0 Hz, 3H), 2.40 (s, 3H), 4.00-4.13 (m, 2H), 4.85 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 7.13-7.18 (m, 8H), 7.20-7.24 (m, 3H) and 9.38(s, 1H, NH); ^{13}C NMR δ 14.2, 21.0, 52.1, 59.0, 106.9, 123.9, 124.9, 125.0, 126.0, 126.2, 127.9, 128.1, 128.9, 129.6, 135.1, 136.5, 137.5, 141.6, 150.3, 156.4 and 168.0; HRMS (EI^+) 369.1723 (cal. for $C_{25}H_{23}NO_2$ 369.1729); IR 1435, 1511, 1604, 1643, 2861, 2923, 3023 and 3278 cm^{-1}.



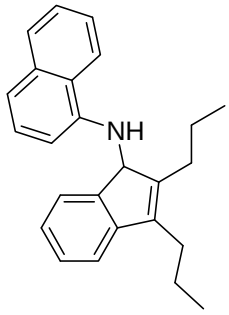
1-(3-(*p*-Tolylamino)-1-phenyl-*1H*-inden-2-yl)ethanone (6c): yellow solid; melting point 164 °C; R_f = 0.27 (10% ethyl acetate in hexanes); ^{1}H NMR δ 1.95 (s, 3H), 2.40 (s, 3H), 4.86 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.18-7.28 (m, 10H) and 11.45(s, 1H, NH); ^{13}C NMR δ 21.1, 28.5, 52.6, 114.6, 124.7, 125.1, 126.0, 126.4, 126.8, 127.6, 128.8, 129.7, 129.9, 135.2, 136.3, 136.6, 141.5, 150.9, 158.5 and 195.2; HRMS (EI^+) 339.1628 (cal. for $C_{24}H_{21}NO$ 339.1623); IR 1612, 1704, 1897, 1951, 2923, 3031, 3054 and 3185 cm^{-1}.

X-ray crystallographic data of compound **6c**

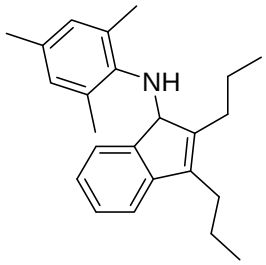


C(1)-C(2)		1.386(3)	
C(1)-C(10)		1.433(3)	
C(1)-C(9)		1.513(3)	
C(2)-N(1)	1.348(2)		
C(2)-C(3)	1.477(3)		
C(3)-C(4)	1.392(3)		
C(3)-C(8)	1.395(3)		
C(8)-C(9)	1.515(3)		
C(2)-C(1)-C(10)	123.25(17)		
C(2)-C(1)-C(9)	110.61(17)		

C(10)-C(1)-C(9)	126.02(18)
N(1)-C(2)-C(1)	123.26(18)
N(1)-C(2)-C(3)	127.50(17)
C(1)-C(2)-C(3)	109.08(17)

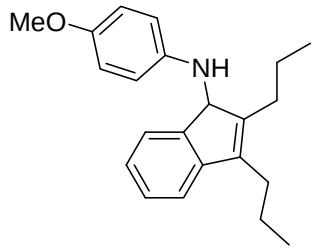


***N*-(2,3-Dipropyl-*1H*-inden-1-yl)naphthalen-1-amine (5h):** yellow liquid; R_f = 0.67 (10% ethyl acetate in hexanes); ^{1}H NMR δ 0.93 (t, *J* = 7.0 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H), 1.48-1.53 (m, 1H), 1.61-1.70 (m, 3H), 2.37-2.46 (m, 2H), 2.54-2.58 (m, 2H), 4.64 (s, br, 1H, NH), 5.27 (s, 1H), 6.75 (d, *J* = 7.0 Hz, 1H), 7.04-7.07 (m, 1H), 7.23-7.31 (m, 4H), 7.39-7.46 (m, 3H) and 7.77-7.80 (m, 2H); ^{13}C NMR δ 14.3, 14.4, 22.0, 23.3, 27.5, 28.2, 61.2, 105.3, 117.2, 118.9, 119.9, 122.9, 123.5, 124.6, 124.7, 125.6, 126.6, 127.7, 128.7, 134.5, 138.1, 142.8, 144.5 (2C), and 145.1; HRMS (EI^+) 341.2137 (cal. for $C_{25}H_{27}N$ 341.2143); IR 1288, 1527, 1581,1704, 1905, 2954, 3062 and 3440 cm^{-1}.

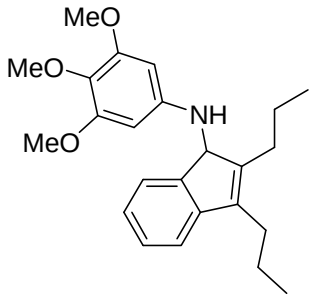


***N*-Mesityl-2,3-dipropyl-*1H*-inden-1-amine (5i):** viscous liquid; R_f = 0.90 (10% ethyl acetate in hexanes); ^{1}H NMR δ 0.92 (t, *J* = 7.0 Hz, 3H), 0.99(t, *J* = 7.0 Hz, 3H), 1.40-1.51 (m, 1H) , 1.54-1.68 (m, 3H), 2.15 (s, 6H), 2.27 (s, 3H), 2.39-2.51 (m, 4H), 2.85 (s, 1H, NH), 4.73 (s, 1H), 5.71 (d, *J* = 7.5 Hz, 1H), 6.84 (s, 2H), 6.89-7.92 (m, 1H) and 7.18-7.21 (m, 2H); ^{13}C NMR δ 14.3 (2C), 18.8, 20.6, 22.0, 23.4, 27.3, 28.3,

60.3, 118.7, 123.1, 124.2, 127.2, 129.2, 129.6, 131.1, 137.7, 142.2, 144.3, 145.3 and 145.8; HRMS (EI^+) 322.2453 (cal. for $C_{24}H_{31}N$ 322.2457); IR 1481, 1727,2869, 2931, 2954, 3016 and 3363 cm^{-1}.

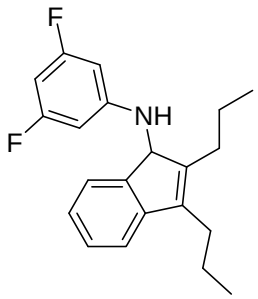


***N*-(4-Methoxyphenyl)-2,3-dipropyl-*1H*-inden-1-amine (5j):** viscous liquid; R_f = 0.85 (10% ethyl acetate in hexanes); ^1H NMR δ 0.93 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H),1.40-1.51 (m, 1H), 1.56-1.64 (m, 3H), 2.30-2.41 (m, 2H), 2.48 (t, *J* = 7.5 Hz, 2H), 3.73 (s, 3H), 4.88 (s, 1H), 6.58 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 7.04 (td, *J* = 1.5 and 7.3 Hz, 1H), 7.21-7.26 (m, 2H) and 7.34 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR δ 14.30, 14.33, 21.94, 23.2, 27.4, 28.1, 55.7, 62.4, 114.8, 115.3, 118.8, 122.9, 124.5, 127.5, 137.8, 141.7, 144.5, 144.7, 145.3 and 152.3; HRMS (EI^+) 321.2090 (cal. for $C_{22}H_{27}NO$ 321.2093); IR 1041, 1234, 1512, 2931 and 3409 cm^{-1}.

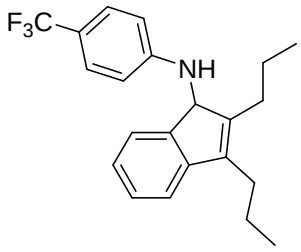


***N*-(3,4,5-Trimethoxyphenyl)-2,3-dipropyl-*1H*-inden-1-amine (5k)**: viscous liguid; R_f = 0.24 (10% ethyl acetate in hexanes); ^1H NMR δ 0.94 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H), 1.41-1.51 (m, 1H),1.55-1.66 (m, 3H), 2.28-2.33 (m, 1H), 2.36-2.42 (m, 1H), 2.43-2.53 (m, 2H), 3.67 (s, 6H), 3.73 (s, 3H), 4.87 (s, 1H), 5.77 (s, 2H), 7.07 (dt, *J* = 1.5 and 7.3 Hz, 1H), 7.22-7.27 (m, 2H) and 7.39 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR δ 14.3, 14.4, 22.0, 23.3, 27.5, 28.1, 55.7(2C), 61.0, 61.8, 91.1, 118.7, 122.8,

124.7, 127.6, 129.9, 137.8, 144.3(2C), 144.6, 144.8 and 153.7; HRMS (EI^+) 381.2306 (cal. for $C_{24}H_{31}NO_3$ 381.2304); IR 1010, 1126, 1234, 1457, 1511, 1604, 2931, 2954 and 3394 cm^{-1}.

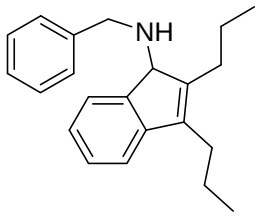


***N*-(3,5-Difluorophenyl)-2,3-dipropyl-*1H*-inden-1-amine (5l)**: viscous liquid; R_f = 0.83 (10% ethyl acetate in hexanes); ^{1}H NMR δ 0.95 (t, *J* = 7.5 Hz, 3H), 1.01(t, *J* = 7.3 Hz, 3H), 1.42-1.51 (m, 1H),1.55-1.67 (m, 3H), 2.23-2.29 (m, 1H), 2.38-2.44 (m, 1H), 2.51 (t, *J* = 7.8 Hz, 2H), 4.11 (s, 1H, NH), 4.88 (s, 1H), 6.06-6.13 (m, 3H). 7.10 (td, *J* = 1.5 and 7.5 Hz, 1H), 7.24-7.31 (m, 2H) and 7.37 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR δ 14.3 (2C), 21.9, 23.2, 27.5, 28.0, 61.2, 92.5 (t, *J* = 26.62 Hz), 96.1 (d, *J* = 28.87 Hz), 119.1, 122.7, 124.9, 127.9, 138.6, 143.4, 144.0, 144.4, 150.1 (t, *J* = 13 Hz), 163.1 (d, *J* = 15 Hz) and 165.1 (d, *J* = 15.50 Hz); HRMS (EI^+) 327.1805 (cal. for $C_{21}H_{23}F_2N$ 327.1799); IR 1110, 1211, 1481, 1635, 2868, 2962 and 3424 cm^{-1}.

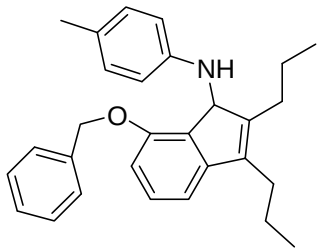


***N*-(4-(Trifluoromethyl)phenyl)-2,3-dipropyl-*1H*-inden-1-amine (5m):** viscous liquid; R_f = 0.76 (10% ethyl acetate in hexanes); ^{1}H NMR δ 0.92 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.0 Hz, 3H), 1.40-1.49 (m, 1H), 1.52-1.65 (m, 3H), 2.21-2.26 (m, 1H), 2.35-2.41 (m,1 H), 2.50 (t, *J* = 7.5 Hz, 2H), 4.23 (s, 1H, NH), 4.96 (d, *J* = 7.0 Hz, 1H), 6.55 (d, *J* = 9.0 Hz, 2H), 7.07 (td, *J* = 1.5 and 7.5 Hz, 1H) and 7.24-7.35 (m, 5H); ^{13}C

NMR δ 14.3, 14.4, 21.9, 23.2, 27.5, 28.0, 60.9, 112.5, 119.0, 122.7, 124.8, 126.6 (2C), 127.9, 138.5, 143.6, 144.1, 144.4 and 150.3; HRMS (EI^+) 359.1865 (cal. for $C_{22}H_{24}F_3O$ 359.1861); IR 1110,1326, 1612, 2931, 2962 and 3424 cm^{-1}.

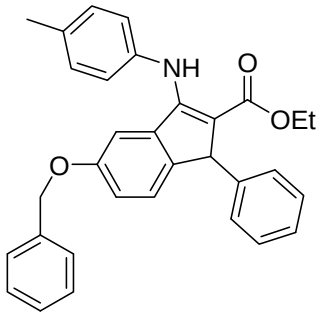


***N*-Benzyl-2,3-dipropyl-*1H*-inden-1-amine (5o):** viscous liquid ; R_f = 0.47 (10% ethyl acetate in hexanes); ^1H NMR δ 0.97 (t, *J* = 7.5 Hz, 6H), 1.42-1.51 (m, 1H), 1.57-1.68 (m, 3H), 2.34-2.39 (m, 1H), 2.42-2.47 (m, 1H), 2.50 (t, *J* = 7.5 Hz, 2H), 3.35-3.44 (m, 2H), 4.40 (s, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.20-7.31 (m, 7H) and 7.49 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR δ 14.3, 14.4, 22.0, 23.2, 27.4, 28.1, 47.7, 64.7, 118.6, 122.8, 124.2, 126.8, 127.3, 128.3 (2C), 138.0, 140.9, 144.7, 144.8 and 145.4; HRMS (EI^+) 305.2149 (cal. for $C_{22}H_{27}N$ 305.2143); IR 1465, 1604, 1712, 2923, 2954, 3031, 3062 and 3409 cm^{-1}.

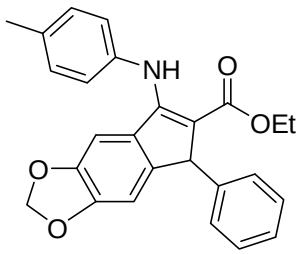


17-(Benzyloxy)-2,3-dipropyl-*N*-*p*-tolyl-*1H*-inden-1-amine (5q): viscous liquid; R_f = 0.67 (10% ethyl acetate in hexanes); ^1H NMR δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H), 1.41-1.49 (m, 1H), 1.55-1.64 (m, 3H), 2.25 (s, 3H), 2.28-2.37 (m, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 4.91 (s, 1H), 4.98 (s, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.87 (dd, *J* = 2.0 and 8.0 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 2H), 7.08 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H) and 7.28-7.38 (m, 5H); ^{13}C NMR δ 14.3 (2C), 20.4, 21.9, 23.2, 27.5, 28.1, 61.4, 70.2,

110.9, 113.3, 113.7, 119.0, 126.5, 127.5, 127.8, 128.5, 129.7, 137.2 (2C), 137.7, 142.7, 145.5, 147.2 and 156.9; HRMS (EI^+) 411.2571 (cal. for $C_{29}H_{33}NO$ 411.2562); IR 1612, 1697, 1866, 2869, 2931, 2954, 3031 and 3417 cm^{-1}.

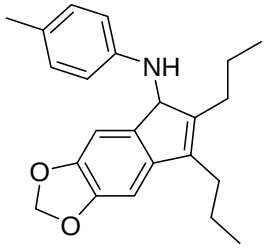


Ethyl-3-(p-tolylamino)-5-(benzyloxy)-1-phenyl-1H-indene-2-carboxylate (6d): yellow solid; melting point 154 °C; R_f = 0.53 (10% ethyl acetate in hexanes); ^1H NMR δ 1.04 (t, *J* = 7.2 Hz, 3H), 2.39 (s, 3H), 4.00-4.11 (m, 2H), 4.74 (s, 2H), 4.77 (s, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.85-6.88 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.08-7.26 (m, 11H), 7.29-7.35 (m, 3H) and 9.33(s, 1H, NH); ^{13}C NMR δ 14.1, 20.9, 51.4, 58.9, 69.8, 108.0, 109.4, 116.8, 125.0, 125.3, 126.1, 127.2, 127.4, 127.7, 128.0, 128.4, 129.4, 135.0, 136.7, 137.3, 137.4, 141.7, 142.9, 156.0, 157.1 and 167.8; HRMS (EI^+) 475.2145 (cal. for $C_{32}H_{29}NO_3$ 475.2147); IR 1172, 1218, 1249, 1565, 1643, 2854, 2923, 2969 and 3278 cm^{-1}.



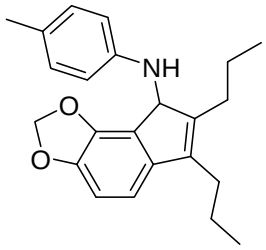
Ethyl 7-(*p*-tolylamino)-5-phenyl-*5H*-indeno[5,6-d][1,3]dioxole-6-carboxylate (6e): yellow solid; melting point 152 °C; R_f = 0.50 (10% ethyl acetate in hexanes); ^1H NMR δ 1.01 (t, *J* = 7.0 Hz, 3H), 2.37 (s, 3H), 4.00-4.07 (m, 2H), 4.71 (s, 1H), 5.85 (dd, *J* = 2.0 and 16.0 Hz, 2H), 6.29 (s, 1H), 6.59 (s, 1H), 7.09-7.23 (m, 9H) and 9.33 (s, 1H, NH); ^{13}C NMR δ 14.2, 21.0, 51.9, 58.8, 101.3, 104.1, 105.6, 106.3, 125.2,

126.3, 127.8, 128.1, 129.7, 135.3, 137.3 , 141.7, 146.2 (2C), 149.0, 156.6 and 167.6; HRMS (EI^+) 413.1621 (cal. for $C_{26}H_{23}NO_4$ 413.1627); IR 1218, 1457, 1573, 1643, 2900, 2977, 3023 and 3227 cm^{-1}.



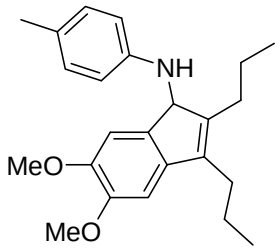
174

6,7-Dipropyl-*N*-*p*-tolyl-*5H*-indeno[5,6-d][1,3]dioxol-5-amine (5r): viscous liquid; R_f = 0.57 (10% ethyl acetate in hexanes); ^1H NMR δ 0.91 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H), 1.39-1.47 (m, 1H), 1.54-1.62 (m, 3H), 2.22 (s, 3H), 2.23-2.36 (m, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 3.69 (s, 1H, NH), 4.80 (s, 1H), 5.88 (dd, *J* = 1.5 and 4.5 Hz, 2H), 6.50 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 1H), 6.88 (s, 1H) and 6.92 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR δ 14.3 (2C), 20.3, 21.9, 23.4, 27.5, 28.2, 61.3, 100.3, 100.8, 104.9, 113.7, 126.6, 129.7, 137.0, 138.5, 138.9, 143.8, 145.2, 145.4 and 147.2; HRMS (EI^+) 349.2042 (cal. for $C_{23}H_{27}NO_2$ 349.2042); IR 1511, 1612, 1866, 2869, 2954 and 3417 cm^{-1}.

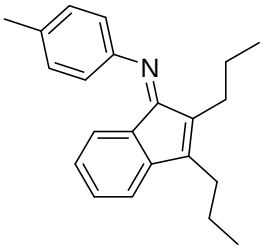


6,7-Dipropyl-*N*-*p*-tolyl-8H-indeno[5,4-d][1,3]dioxol-8-amine (5s): viscous liquid; R_f = 0.60 (10% ethyl acetate in hexanes); ^1H NMR δ 0.89 (t, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H), 1.37-1.44 (m, 1H), 1.53-1.62 (m, 3H), 2.19 (s, 3H), 2.20-2.25 (m, 1H), 2.29-2.35 (m, 1H), 2.43 (t, *J* = 7.5 Hz, 2H), 3.79 (s, 1H, NH), 4.96 (s, 1H), 5.84 (dd, *J* = 1.5 and 15.3 Hz, 1H), 6.46 (d, *J* = 8.5 Hz, 2H), 6.67-6.72 (m, 2H) and 6.88 (d,

J = 8.0 Hz, 2H); ^{13}C NMR δ 14.3, 14.4, 20.4, 22.0, 23.1, 27.6, 28.0, 60.2, 101.1, 106.8, 111.3, 113.9, 123.9, 126.6, 129.5, 137.6, 140.3, 142.9, 143.0, 145.3 and 146.2; HRMS (EI^+) 349.2040 (cal. for $C_{23}H_{27}NO_2$ 349.2042); IR 1049, 1241, 1519, 2931 and 3417 cm^{-1}.

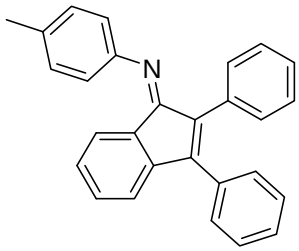


5,6-Dimethoxy-2,3-dipropyl-*N*-*p*-tolyl-*1H*-inden-1-amine (5t): viscous liquid; R_f = 0.25 (10% ethyl acetate in hexanes); ^{1}H NMR δ 0.89 (t, *J* = 7.5 Hz, 3H), 0.98(t, *J* = 7.5 Hz, 3H), 1.38-1.45 (m, 1H), 1.50-1.63 (m, 3H), 2.21 (s, 3H), 2.22-2.35 (m, 2H), 2.45 (t, *J* = 7.5 Hz, 2H), 3.70 (s, 1H, NH), 3.76 (s, 3H), 3.90 (s, 3H), 4.83 (s, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 6.92 (d, *J* = 8.5 Hz, 2H) and 6.97 (s, 1H); ^{13}C NMR δ 14.3 (2C), 20.4, 22.1, 23.4, 27.5, 28.2, 56.3, 61.6 (2C), 103.1, 107.7, 113.7, 126.5, 129.7, 137.1, 137.2, 137.5, 143.6, 145.5, 146.9 and 148.9; HRMS (EI^+) 365.2355 (cal. for $C_{22}H_{27}NO$ 365.2355); IR 1095, 1288, 1612, 2931 and 3394 cm^{-1}.



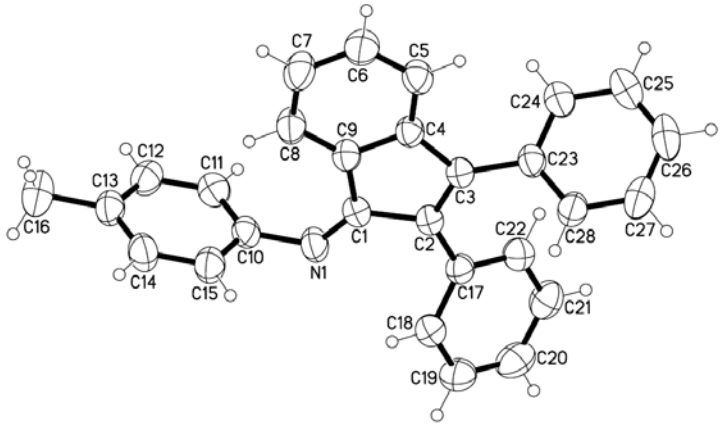
***(E+Z)*-*N*-(2,3-Dipropyl-1H-inden-1-ylidene)-4-methylbenzenamine (7a)** viscous liquid; R_f = 0.77 (10% ethyl acetate in hexanes); ^{1}H NMR δ 0.97 (t, *J* = 7.5 Hz, 3H), 1.03 (t, *J* = 7.5 Hz, 3H), 1.57-1.67 (m, 4H), 2.37 (s, 3H), 2.47 (t, *J* = 7.8 Hz, 2H), 2.53 (t, *J* = 7.8 Hz, 2H), 6.35 (d, *J* = 7.5 Hz, 1H), 6.75 (dd, *J* = 1.0 and 8.0 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 1H) and 7.13-7.16 (m, 3H); ^{13}C NMR δ 14.4,

14.5, 21.0, 21.7, 23.4, 26.0, 27.9, 118.1, 118.5, 125.1, 125.8, 128.7, 129.5, 130.4, 133.0, 137.8, 146.3, 148.3, 149.5 and 166.9; HRMS (EI^+) 303.1985 (cal. for $C_{22}H_{27}NO$ 303.1987); IR 910, 1457, 1643, 1869, 2923 and 2954 cm^{-1}.



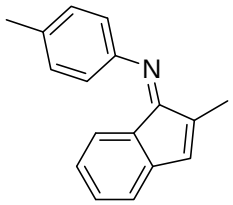
(*E*+*Z*)-4-Methyl-N-(2,3-diphenyl-1H-inden-1-ylidene)benzenamine (7b): orange solid; melting point 178 °C; R_f = 0.67 (10% ethyl acetate in hexanes); ^1H NMR δ 2.40 (s, 3H), 6.57 (d, *J* = 7.2 Hz, 1H), 6.84-6.87 (m, 2H), 6.92 (t, *J* = 7.0 Hz, 1H), 7.18-7.29 (m, 7H) and 7.33-7.39 (m, 7H); ^{13}C NMR δ 21.0, 117.9, 120.7, 125.9, 126.6, 127.1, 127.2, 127.7, 128.2, 128.5, 129.1, 129.6, 130.6, 131.1, 132.8, 133.3, 133.7, 136.7, 145.4, 148.4, 149.5 and 166.2; HRMS (EI^+) 371.1671 (cal. for $C_{28}H_{21}N$ 371.1674); IR 1272, 1612, 1704, 1882, 1951, 2923, 3054 and 3409 cm^{-1}.

X-ray crystallographic data of compound **7b:**

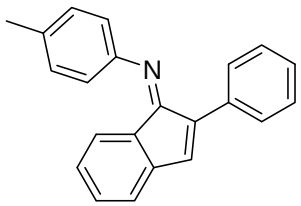


C(1)-N(1)	1.282(2)
C(1)-C(2)	1.493(3)
C(1)-C(9)	1.498(3)
C(2)-C(3)	1.359(3)
C(3)-C(4)	1.475(3)

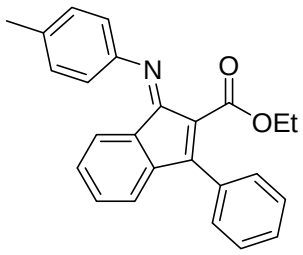
C(4)-C(9) 1.404(3)
N(1)-C(1)-C(2) 122.90(19)
N(1)-C(1)-C(9) 130.4(2)
C(2)-C(1)-C(9) 106.51(16)
C(1)-N(1)-C(10) 120.17(18)



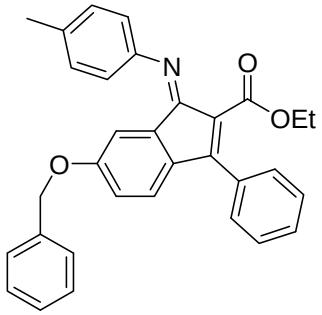
(*E*+*Z*)-4-Methyl-N-(2-methyl-1H-inden-1-ylidene)benzenamine (7c): yellow liquid; R_f = 0.55 (10% ethyl acetate in hexanes); ^{1}H NMR δ 2.09 (s, 3H), 2.37 (s, 3H), 6.36 (d, *J* =7.2 Hz, 1H), 6.73 (t, *J* =7.4 Hz, 1H), 6.80-6.82 (m, 3H), 6.96 (d, *J* =7.2 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H) and 7.15 (d, *J* =8.0 Hz, 2H); ^{13}C NMR δ 11.9, 21.0, 118.1, 120.5, 125.4, 125.8, 128.5, 129.6, 130.9, 133.5, 136.0, 139.6, 145.3, 149.1 and 167.8; HRMS (EI^+) 233.1203 (cal. for $C_{17}H_{15}N$ 233.1204); IR 1450, 1504, 1604, 1643, 1720, 2854, 2923, 3023 and 3062 cm^{-1}.



(*E*+*Z*)-4-Methyl-N-(2-phenyl-*1H*-inden-1-ylidene)benzenamine (7d); red solid; melting point 82 °C; R_f = 0.63 (10% ethyl acetate in hexanes); ^{1}H NMR δ 2.39 (s, 3H), 6.55 (d, *J* = 7.6 Hz, 1H), 6.82-6.88 (m, 4H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.15-7.20 (m, 6H) and 7.41 (dd, *J* = 2.0 and 7.6 Hz, 2H); ^{13}C NMR δ 21.0, 117.9, 121.4, 125.8, 127.1, 127.7, 127.8, 127.9, 129.6, 129.9, 130.9, 132.9, 133.6, 139.4, 142.1, 143.7, 149.2 and 165.5; HRMS (EI^+) 295.1348 (cal. for $C_{22}H_{17}N$ 295.1361); IR 1226, 1450, 1635, 1712, 2854 and 3054 cm^{-1}.

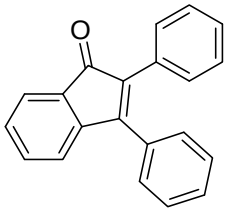


(*1E*+*Z*)-Ethyl 1-(*p*-tolylimino)-3-phenyl-1H-indene-2-carboxylate (7e): orange solid; melting point 80 °C; R_f = 0.50 (10% ethyl acetate in hexanes); ^{1}H NMR δ 1.14 (t, *J* = 7.2 Hz, 3H), 2.37 (s, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 2H), 6.91 (td, *J* = 1.2 and 7.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.27 (td, *J* = 1.2 and 7.6 Hz, 1H), 7.33-7.41 (m, 3H), 7.46-7.49 (m, 2H) and 7.65 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR δ 13.8, 14.1, 21.0, 22.6, 29.7, 31.6, 60.9, 117.5, 122.1, 126.0, 127.0, 127.3, 127.5, 128.4, 129.7, 130.4, 131.4, 132.2, 134.0, 137.3, 142.3, 144.8, 149.2, 164.9 and 166.1; HRMS (EI^+) 367.1561 (cal. for $C_{25}H_{23}NO_2$ 367.1572); IR 1203, 1635, 1712, 2923 and 2923 cm^{-1}.

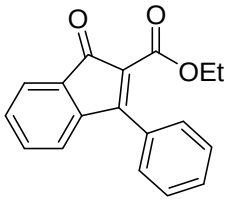


(*E*+*Z*)-Ethyl-1-(p-tolylimino)-6-(benzyloxy)-3-phenyl-1H-indene-2-carboxylate (7f):viscous liquid; R_f = 0.27 (10% ethyl acetate in hexanes); ^{1}H NMR δ 0.82 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H), 2.31 (s, 3H), 2.37 (s, 3H), 3.37-4.42 (m, 2H), 4.14-4.19 (m, 2H), 4.71 (s, 2H), 5.15 (s, 2H), 6.23 (d, *J* = 2.4 Hz, 1H), 6.77 (dd, *J* = 8.4,2.4 Hz, 1H), 6.85-6.93 (m, 6H), 7.05-7.21 (m, 8H), 7.27-7.49 (m, 17H) and 7.55 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR δ 13.5, 13.8, 60.7, 69.8, 70.4, 109.1, 113.6, 116.6, 117.0, 118.0, 120.8, 121.6, 123.2, 123.3, 127.2, 127.4, 128.0, 128.1, 128.3, 128.5, 128.6, 129.2, 129.4, 129.7, 132.2, 132.8, 133.7, 134.4, 134.7, 136.0, 136.2, 136.5, 137.8,

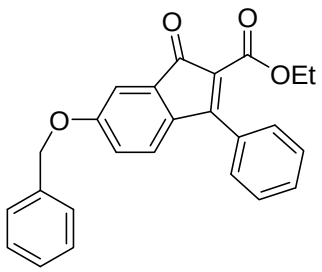
148.3, 148.9, 155.4, 157.6, 159.5, 160.4, 161.5, 163.4. 164.5 and 165.5; HRMS (EI^+) 473.1992 (cal. for $C_{32}H_{27}NO_3$ 473.1991); IR 1018, 1118, 1180, 1218, 1349, 1373, 1720, 2923, 2977 and 3031cm^{-1}.



2,3-Diphenyl-1H-inden-1-one (8b): pale red solid; melting point 152 °C; R_f = 0.55 (10% ethyl acetate in hexanes); ^1H NMR δ 7.11 (d, *J* = 7.5 Hz, 1H), 7.21-7.26 (m, 6H), 7.31-7.39 (m, 6H) and 7.55 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR δ 121.2, 122.9, 127.7, 128.0, 128.4, 128.6, 128.7, 128.9, 129.2, 129.9, 130.7, 132.3, 132.7, 133.4, 145.2, 155.3 and 196.4; HRMS (EI^+) 282.1037 (cal. for $C_{21}H_{14}O$ 282.1045); IR 1079, 1180, 1349, 1450, 1604, 1704, 2923 and 3062 cm^{-1}.

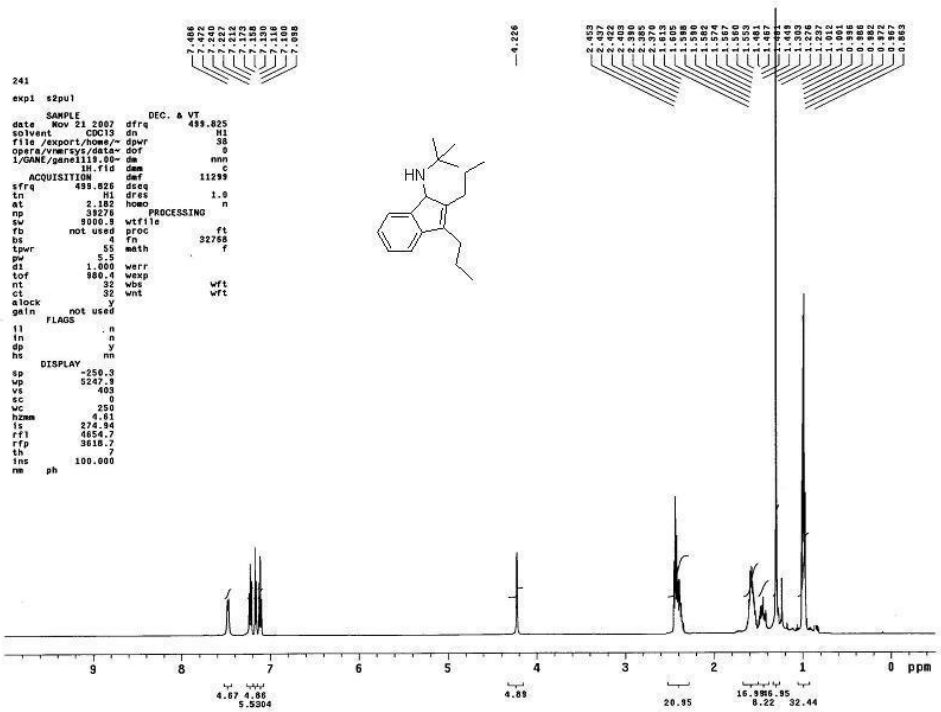


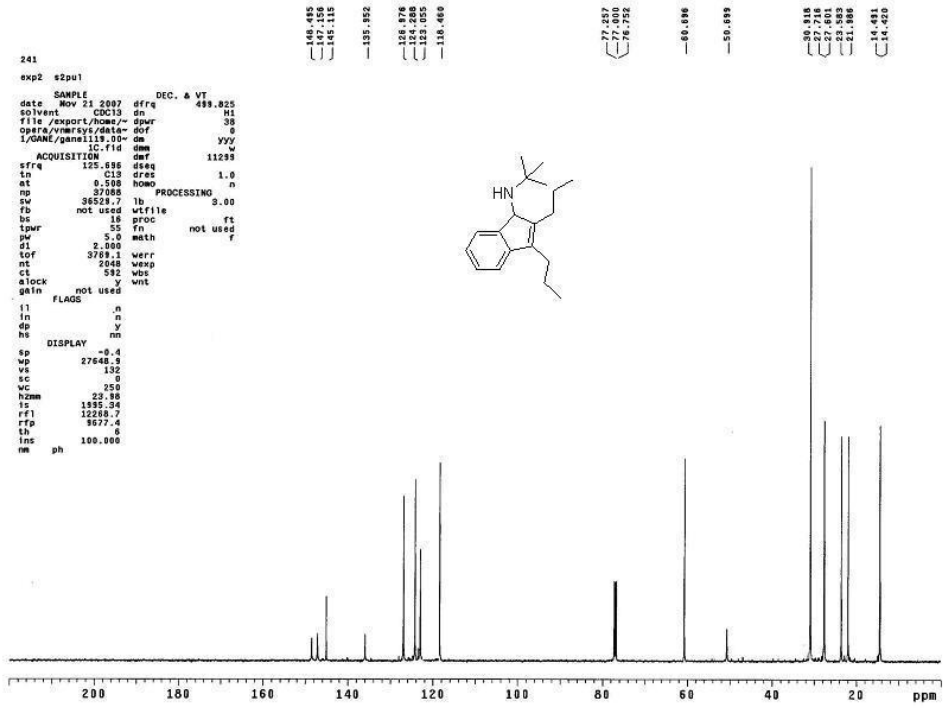
Ethyl 1-oxo-3-phenyl-1H-indene-2-carboxylate (8e): yellow solid; melting point 84 °C; R_f = 0.17 (10% ethyl acetate in hexanes); ^1H NMR δ 1.15 (t, *J* = 7.0 Hz, 3H), 4.16-4.21 (m, 2H), 7.17-7.19 (m, 1H), 7.37-7.42 (m, 2H), 7.47-7.53 (m, 5H) and 7.58-7.60 (m, 1H); ^{13}C NMR δ 13.9, 60.9, 123.4, 123.5, 124.4, 128.1, 128.4, 130.4, 130.5, 131.0, 131.5, 133.5, 143.2, 163.0, 164.9 and 191.1; HRMS (EI^+) 278.0943 (cal. for $C_{18}H_{14}O_3$ 278.0943); IR 1226, 1334, 1573, 1604, 1712, 1727, 2854, 2923, 2977 and 3062 cm^{-1}.



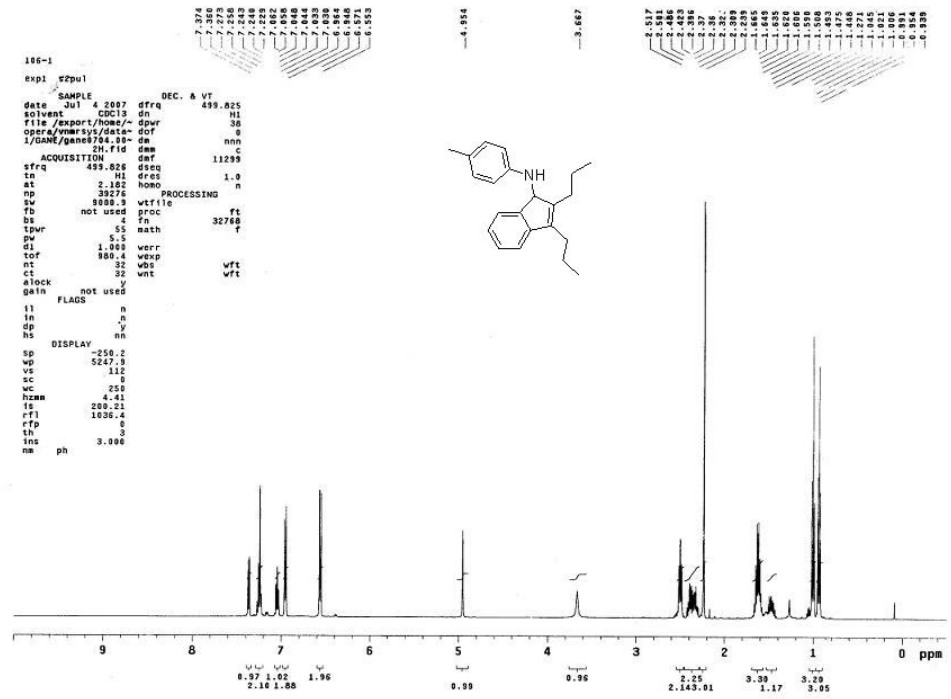
Ethyl-6-(benzyloxy)-1-oxo-3-phenyl-1H-indene-2-carboxylate (9): red solid; melting point 126 °C; R_f = 0.13 (10% ethyl acetate in hexanes); ^{1}H NMR δ 1.16 (t, *J* = 6.8 Hz, 3H), 4.16-4.21 (m, 2H), 5.11 (s, 2H), 6.88 (dd, *J* = 2.0 and 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.30-7.41 (m, 5H) and 7.49(s, 5H); ^{13}C NMR δ 13.9, 60.6, 70.5, 111.4, 117.7, 122.7, 124.8, 127.4, 128.0, 128.2(2C), 128.6, 130.3, 131.7, 132.9, 134.8, 135.9, 161.8, 162.8, 166.9 and 191.7; HRMS (EI^+) 384.1350 (cal. for $C_{25}H_{20}O_4$ 384.1362); IR 1110, 1218, 1288, 1349, 1727, 2923 and 2969 cm^{-1}.

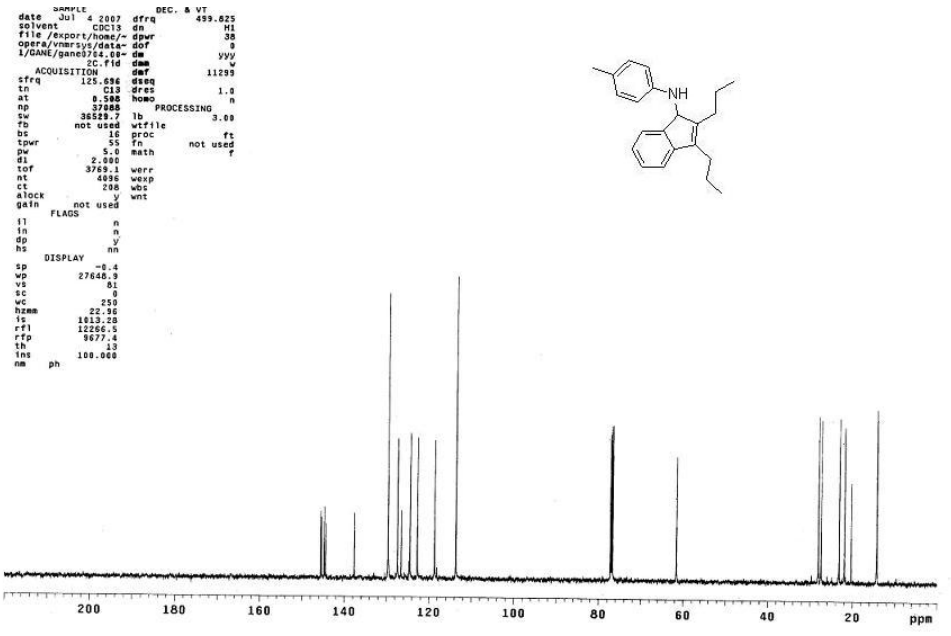
^{1}H and ^{13}C spectra of compound 5a



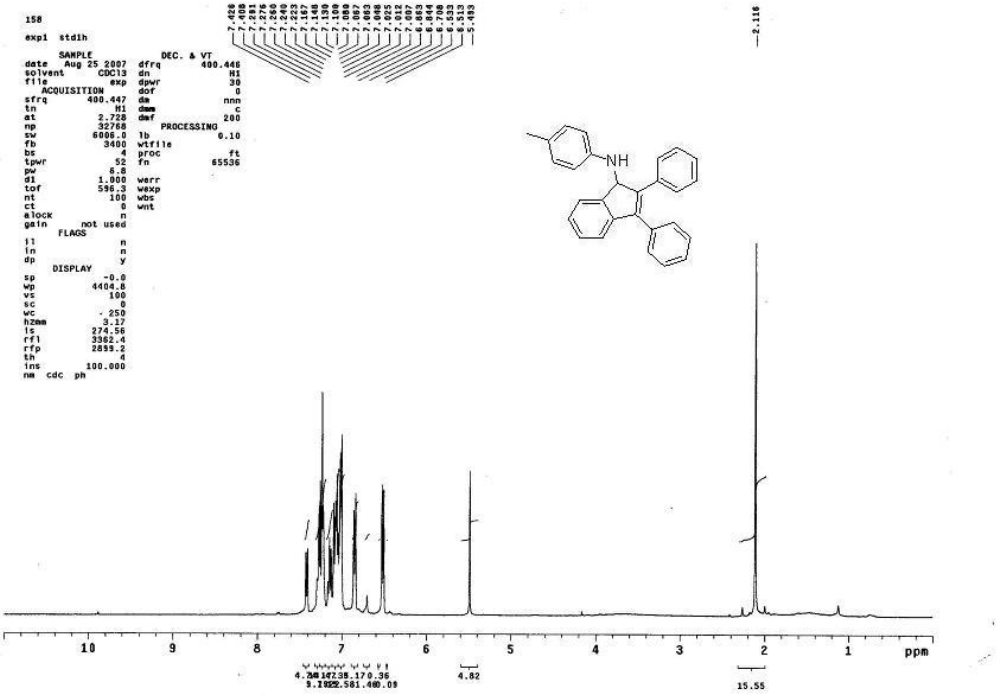


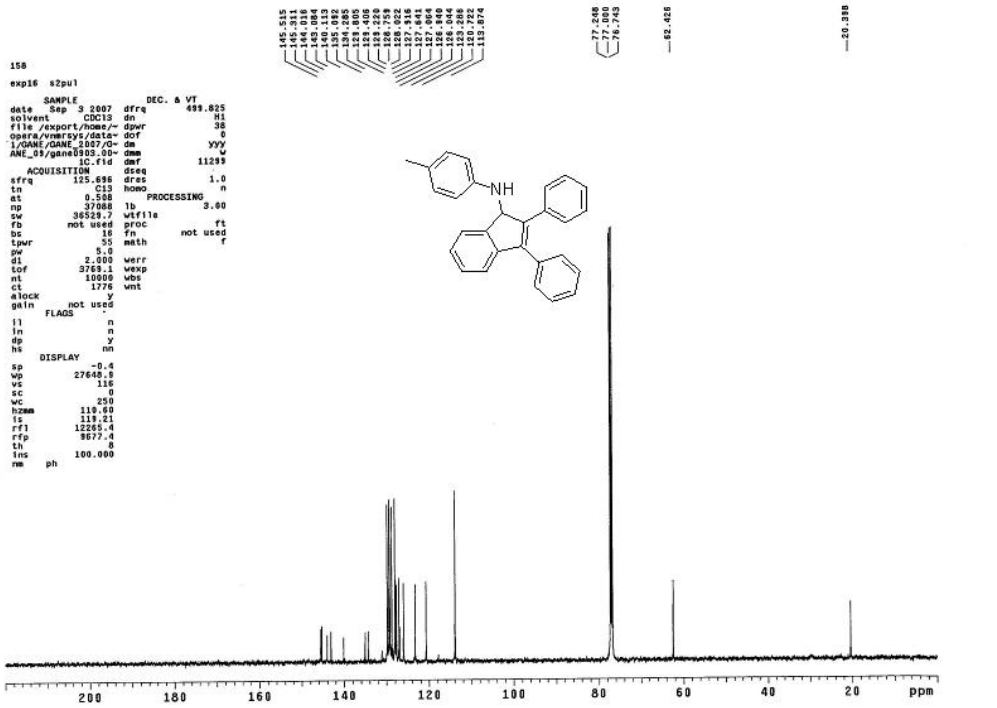
^{1}H and ^{13}C spectra of compound 5b



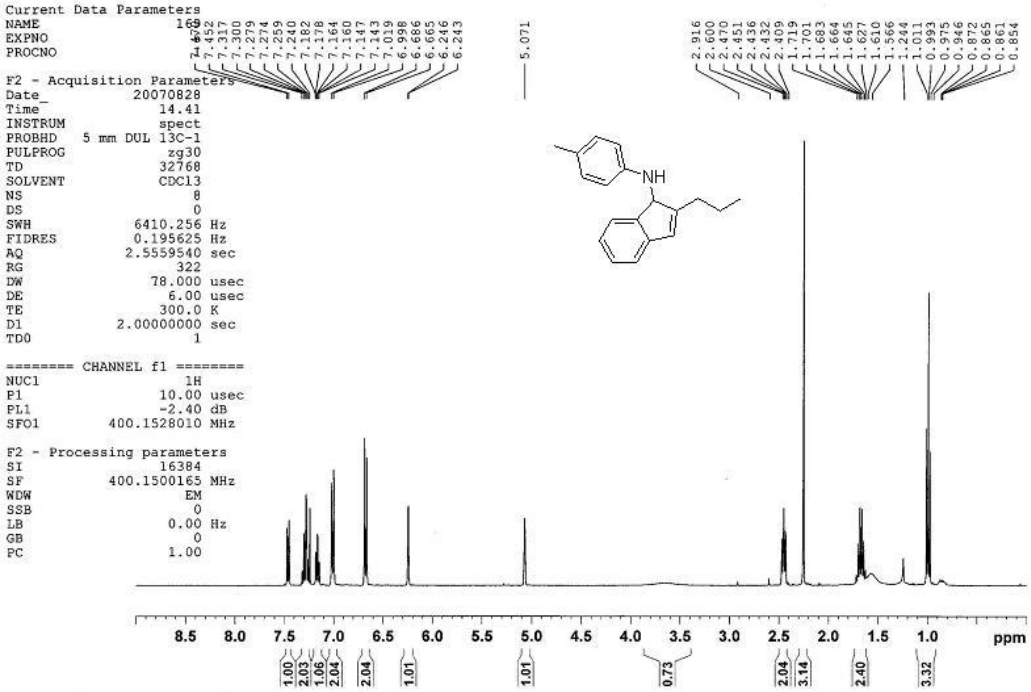


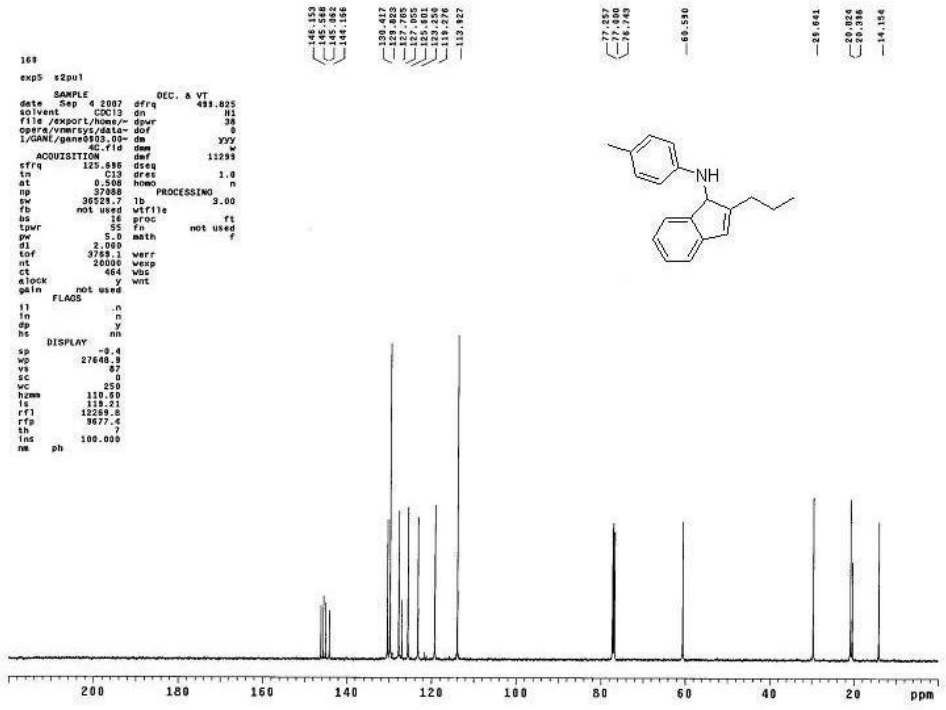
^{1}H and ^{13}C spectra of compound 5c



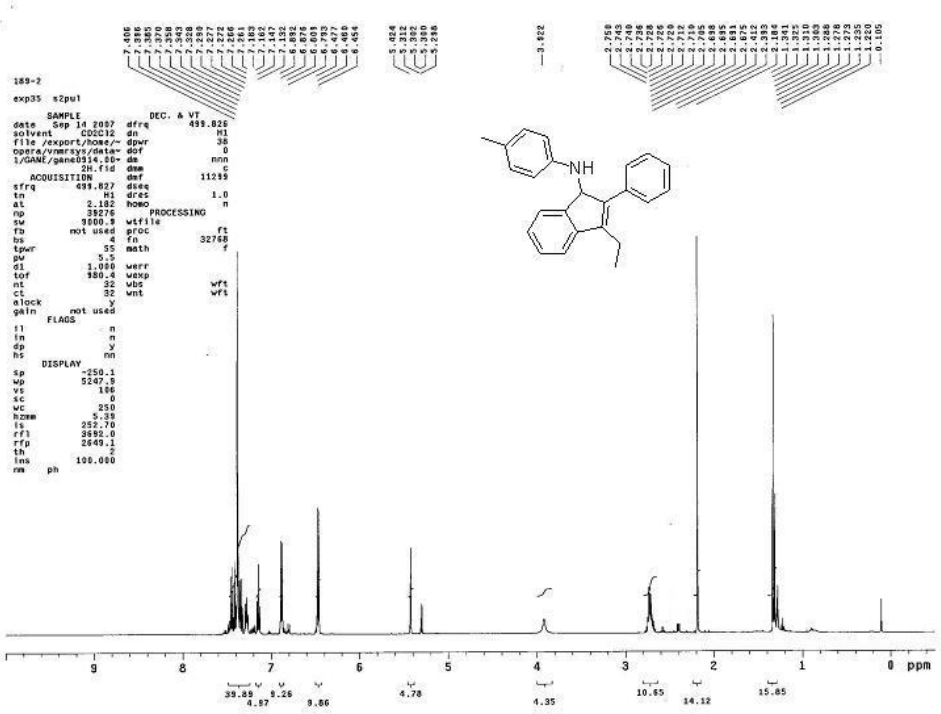


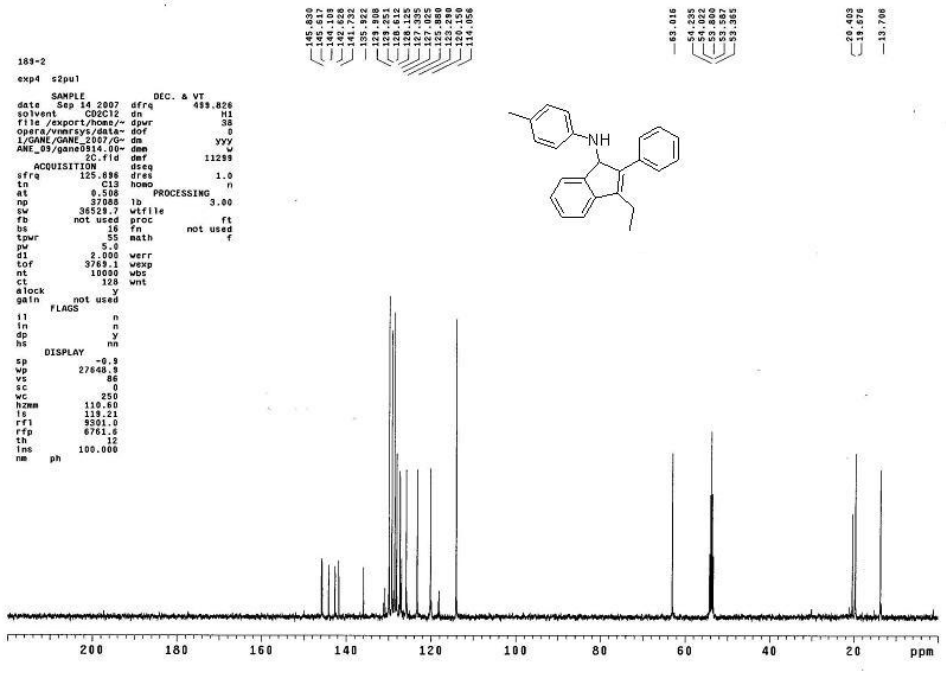
^{1}H and ^{13}C spectra of compound 5d



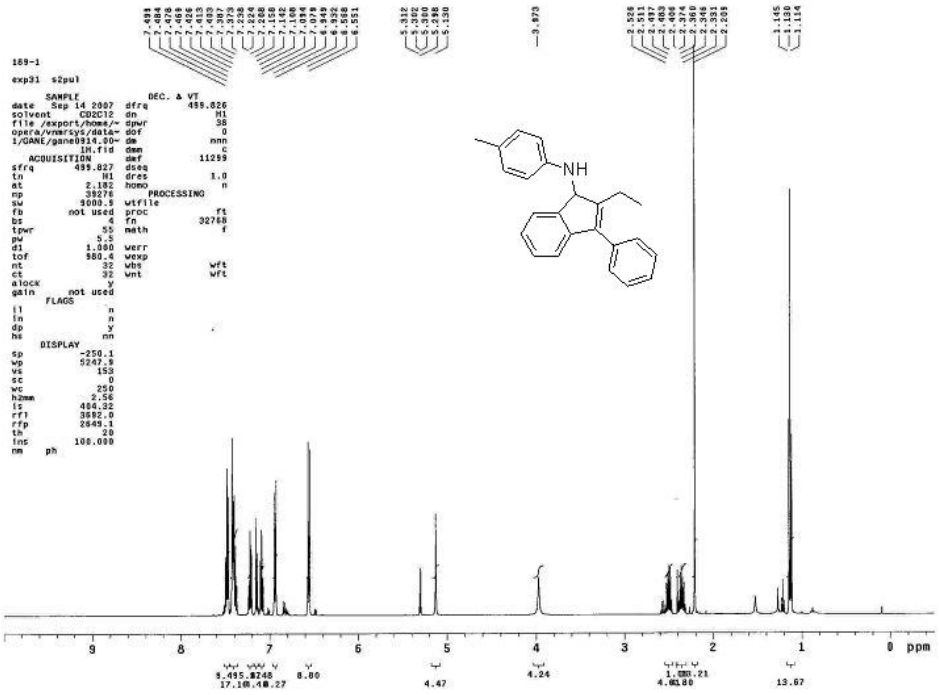


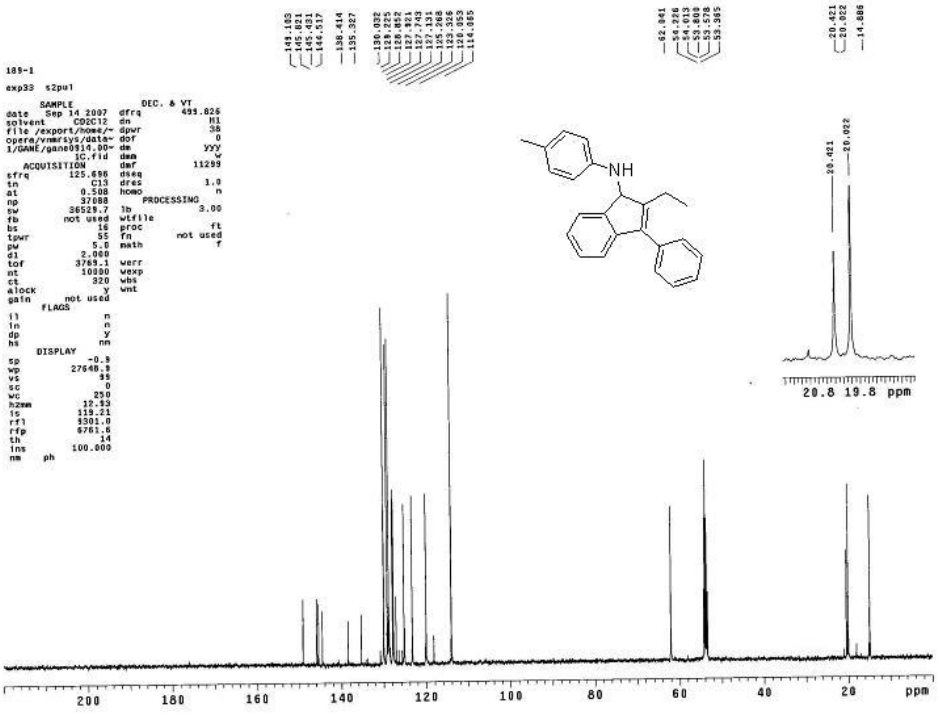
^{1}H and ^{13}C spectra of compound 5e



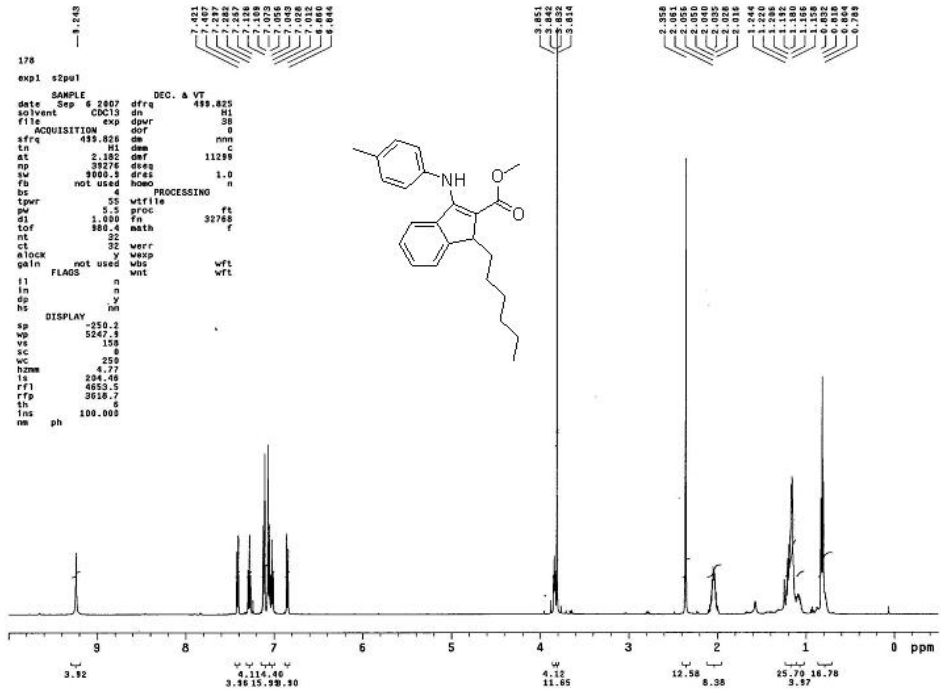


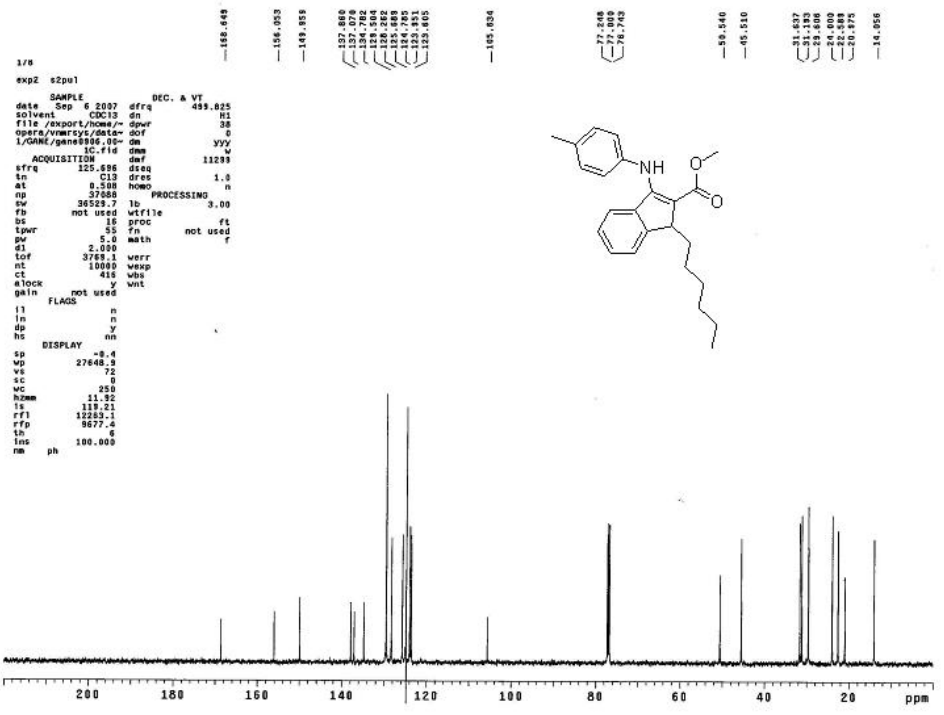
^{1}H and ^{13}C spectra of compound 5e’



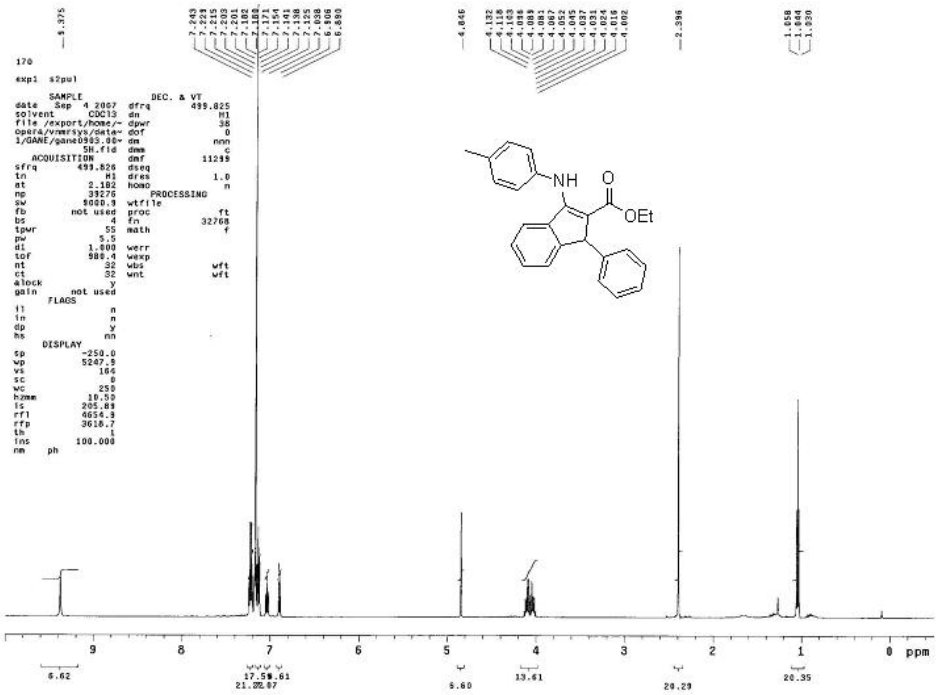


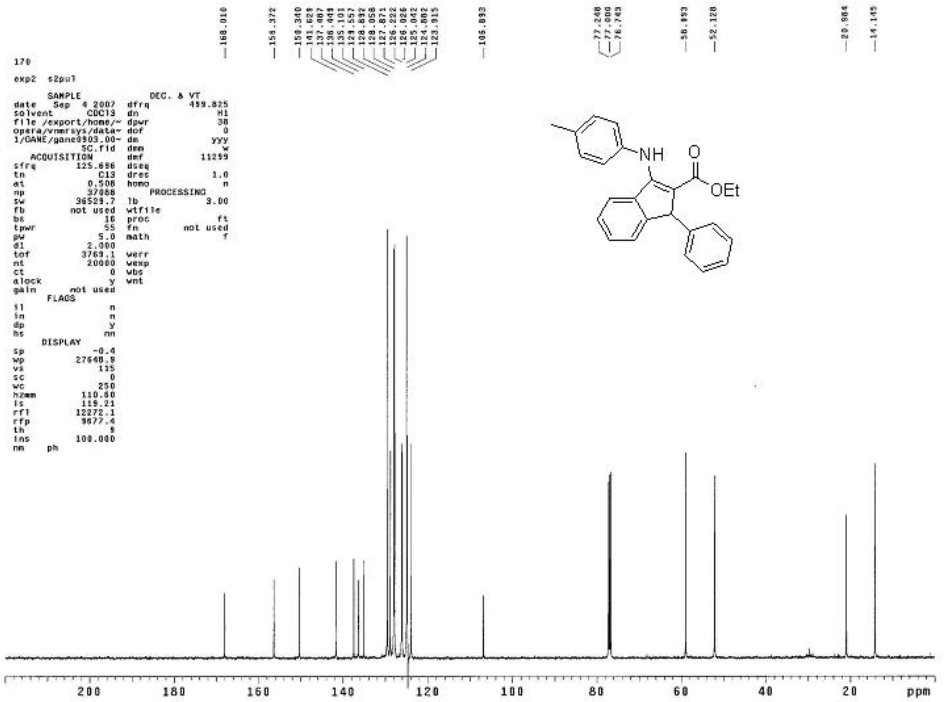
^{1}H and ^{13}C spectra of compound 6a



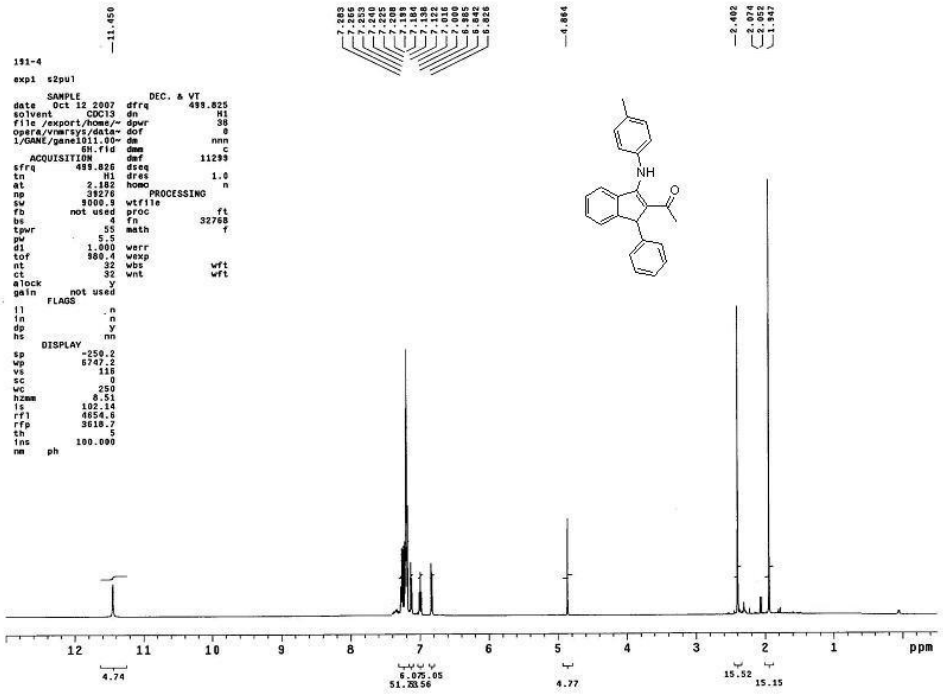


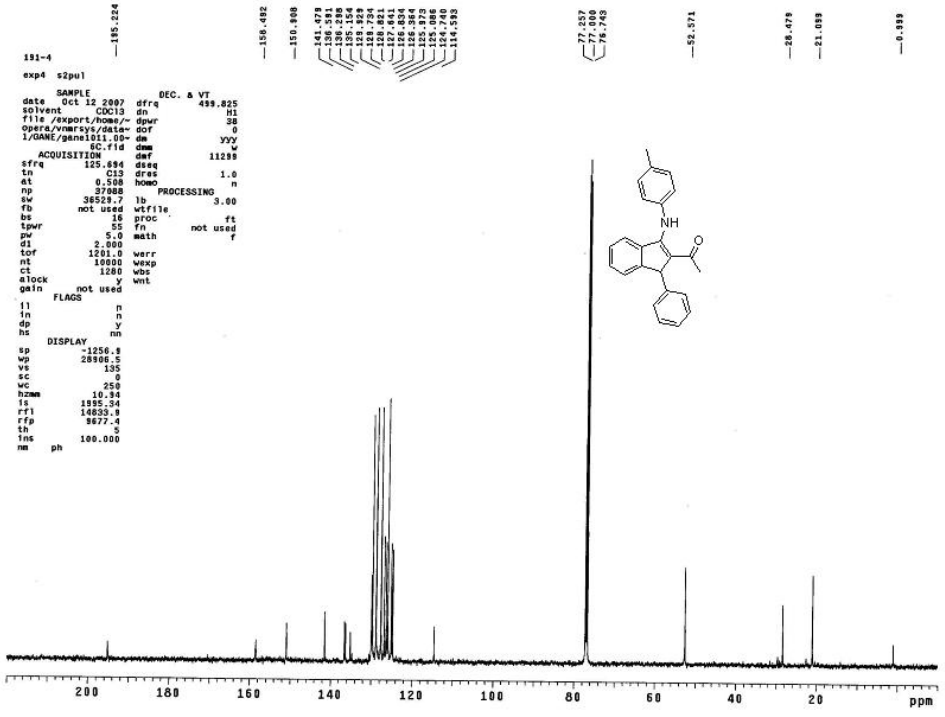
^{1}H and ^{13}C spectra of compound 6b



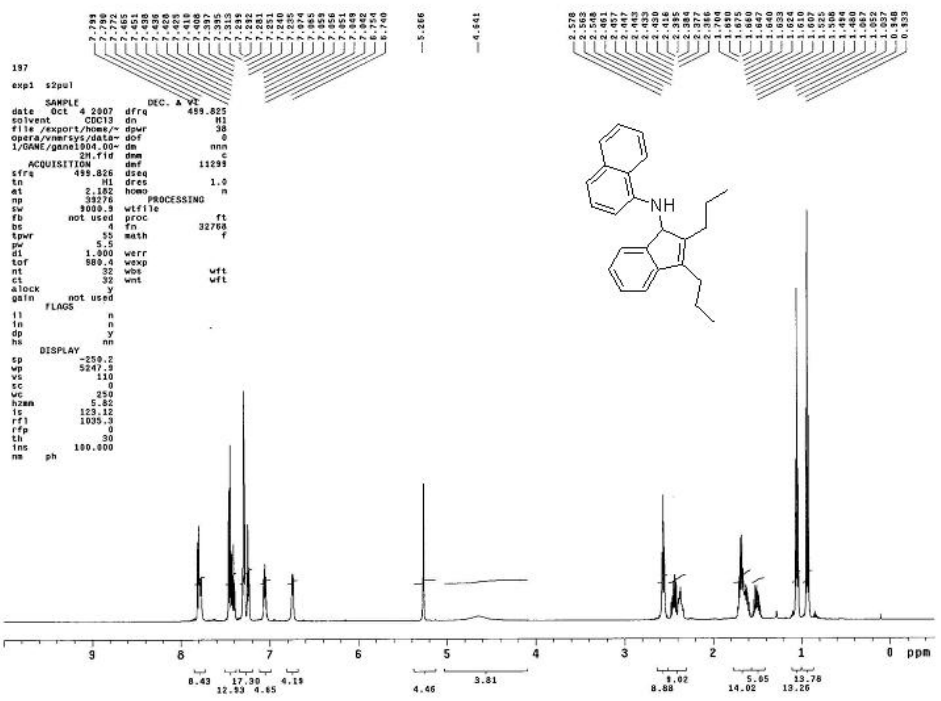


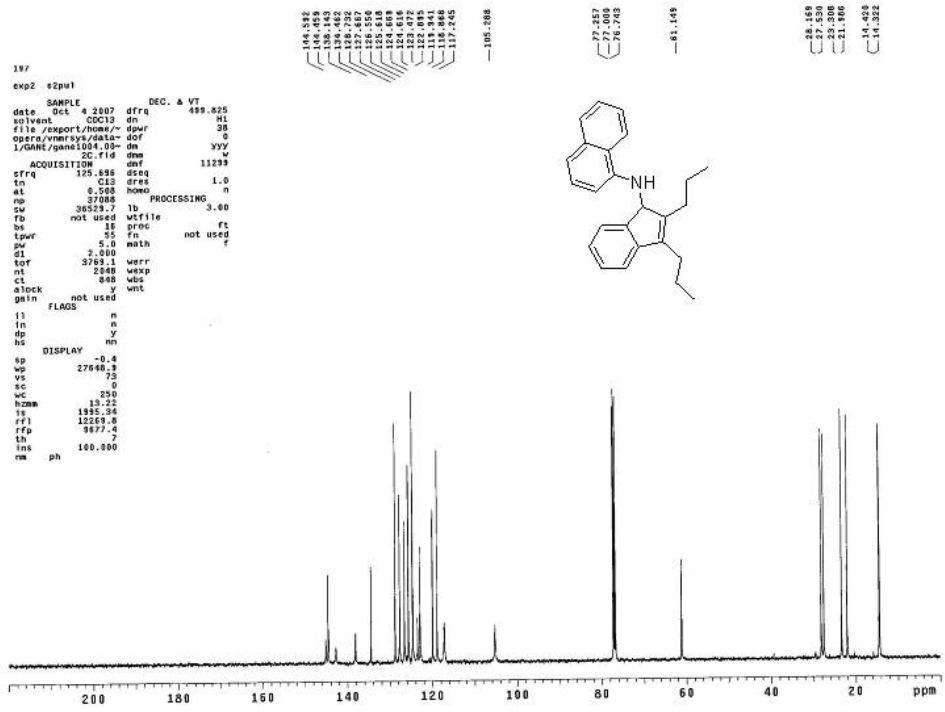
^{1}H and ^{13}C spectra of compound 6c



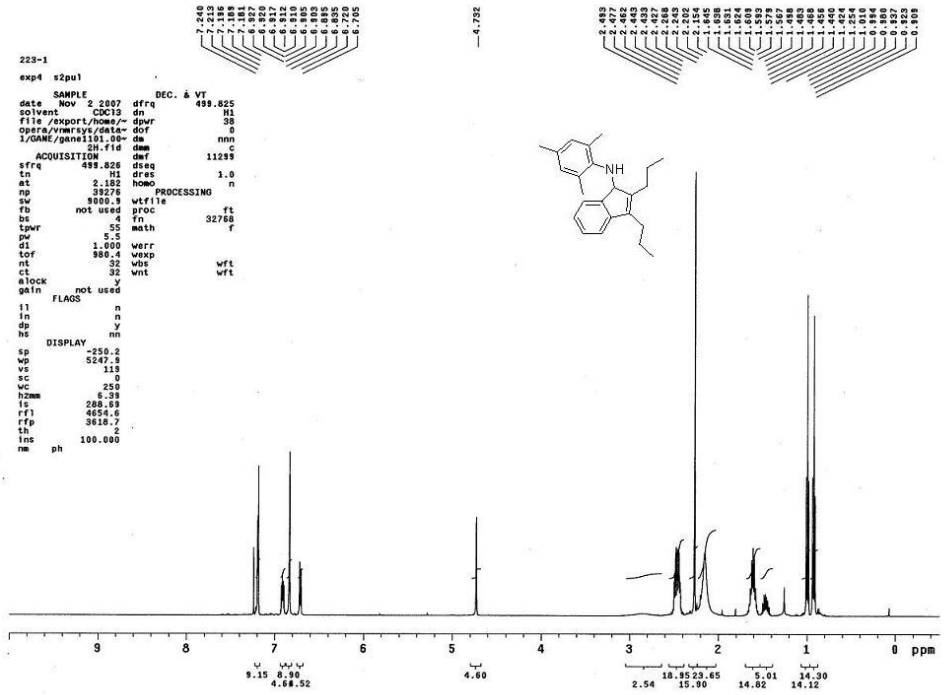


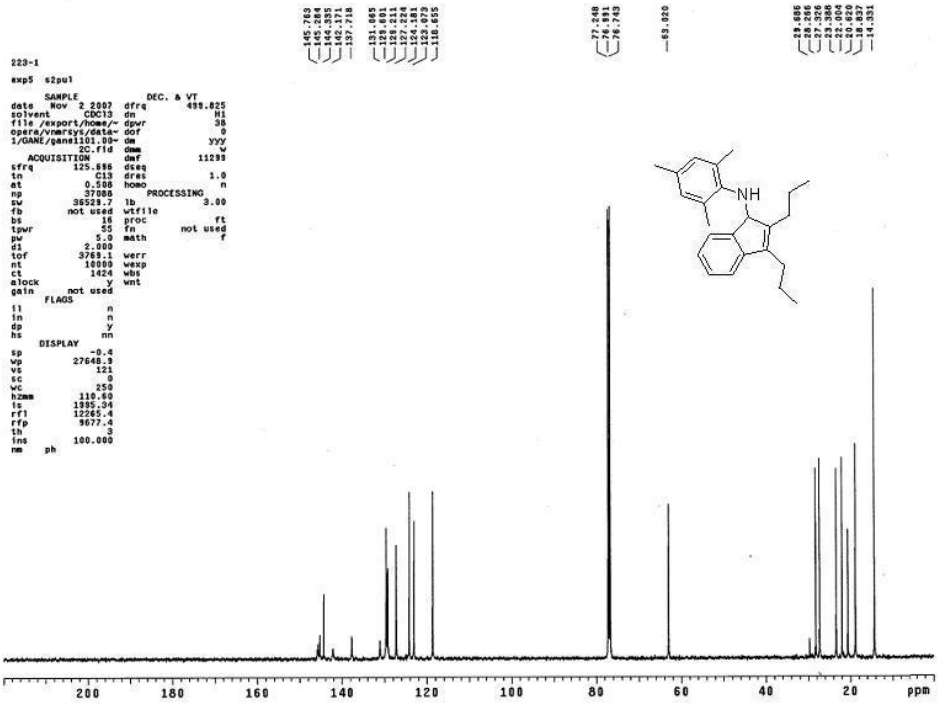
^{1}H and ^{13}C spectra of compound 5h



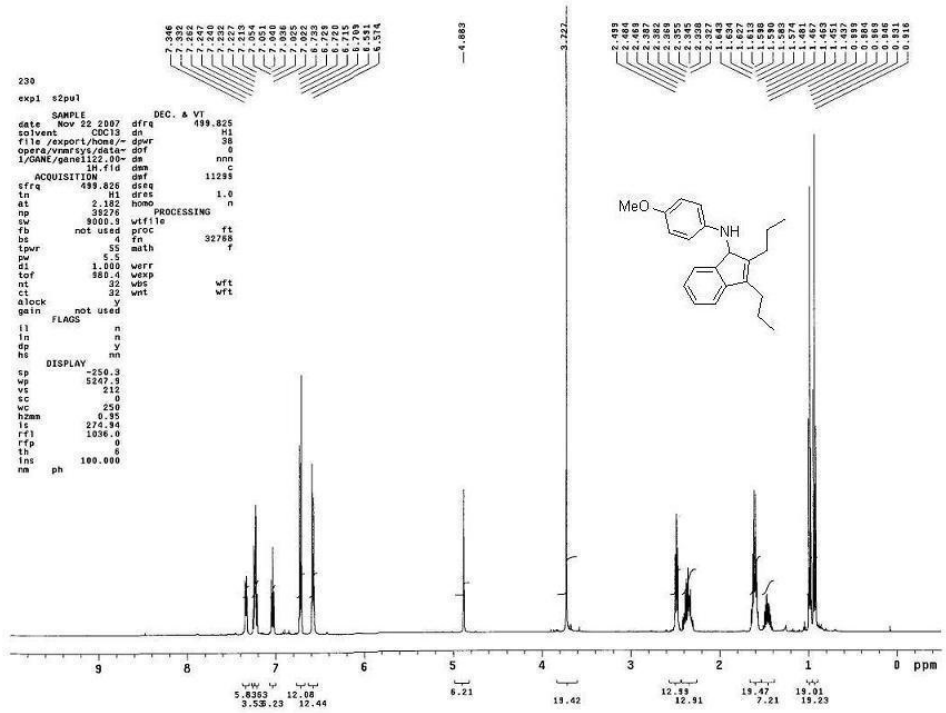


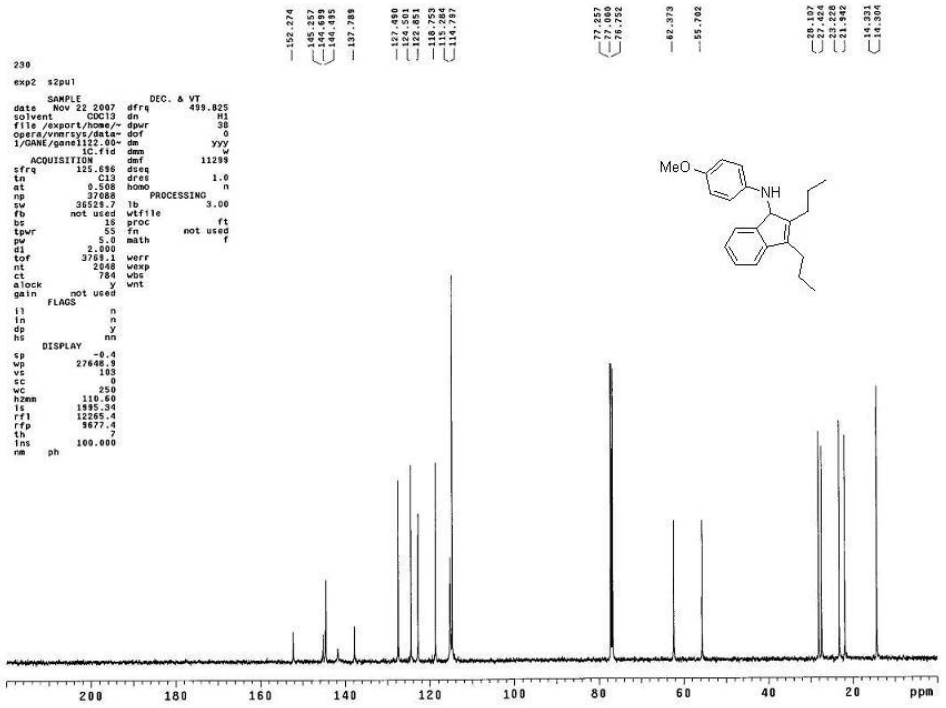
^{1}H and ^{13}C spectra of compound 5i



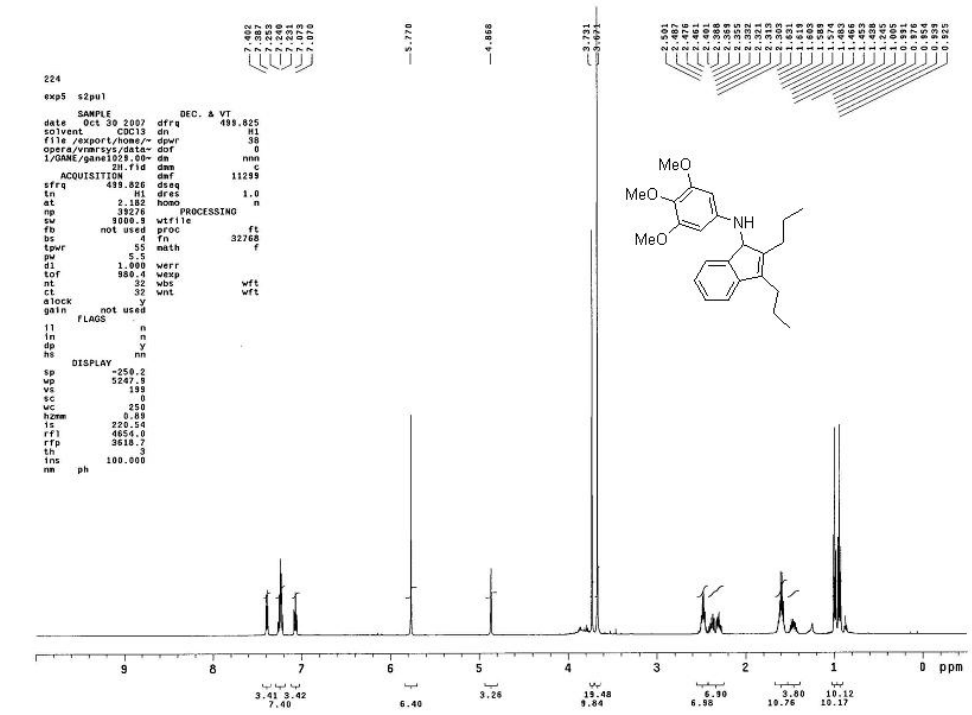


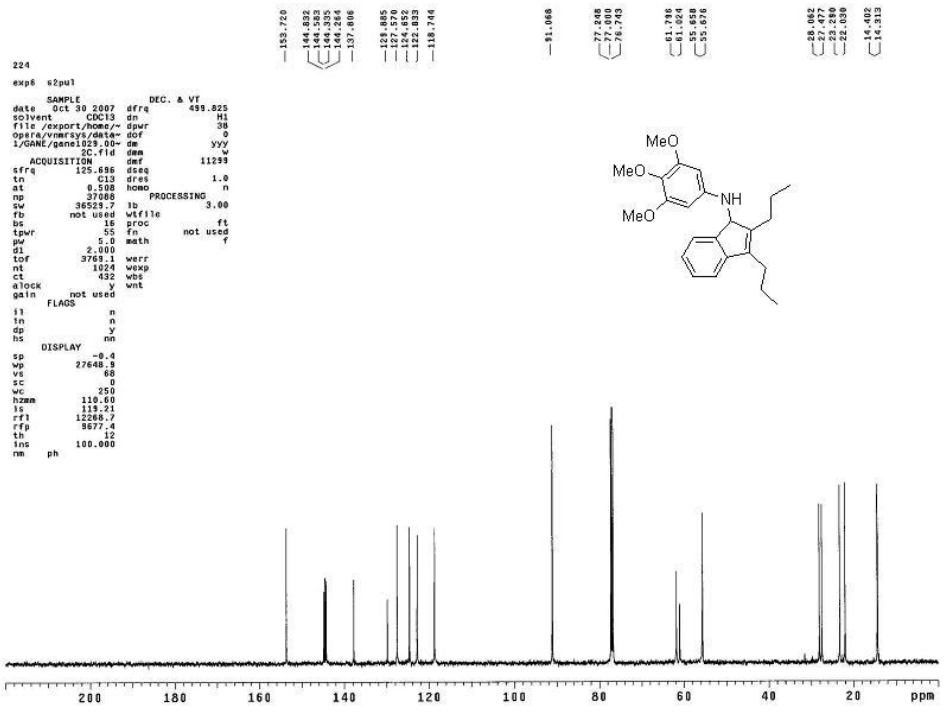
^{1}H and ^{13}C spectra of compound 5j



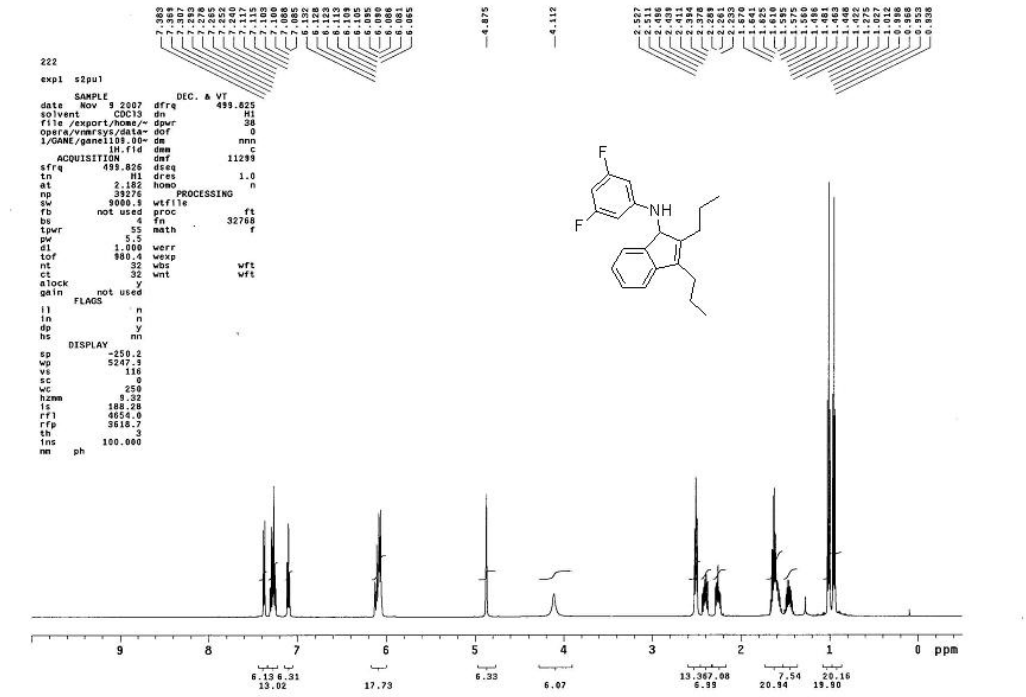


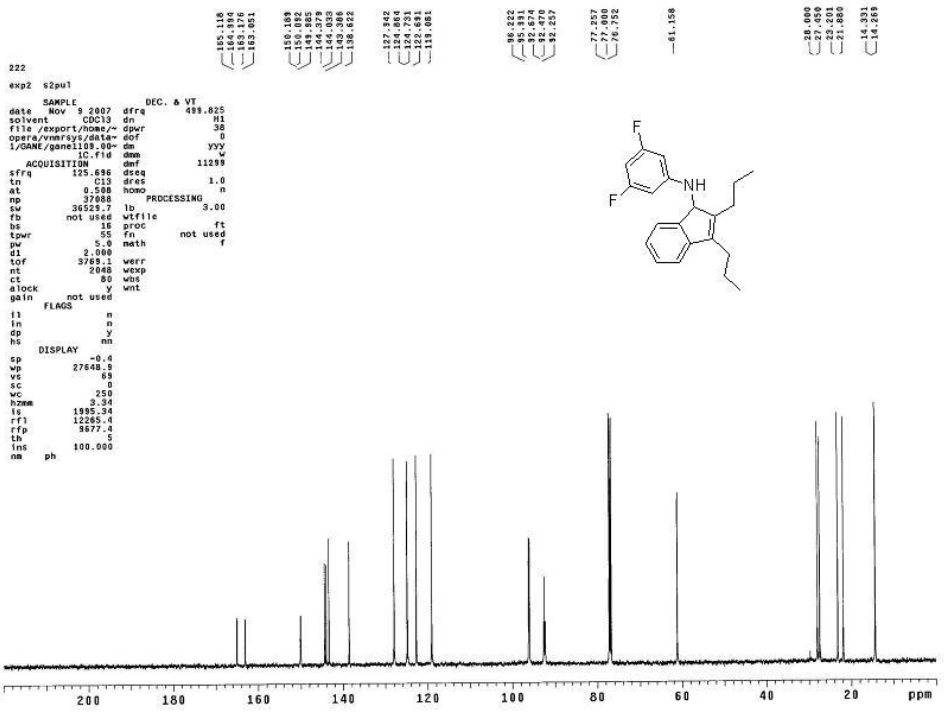
^{1}H and ^{13}C spectra of compound 5k



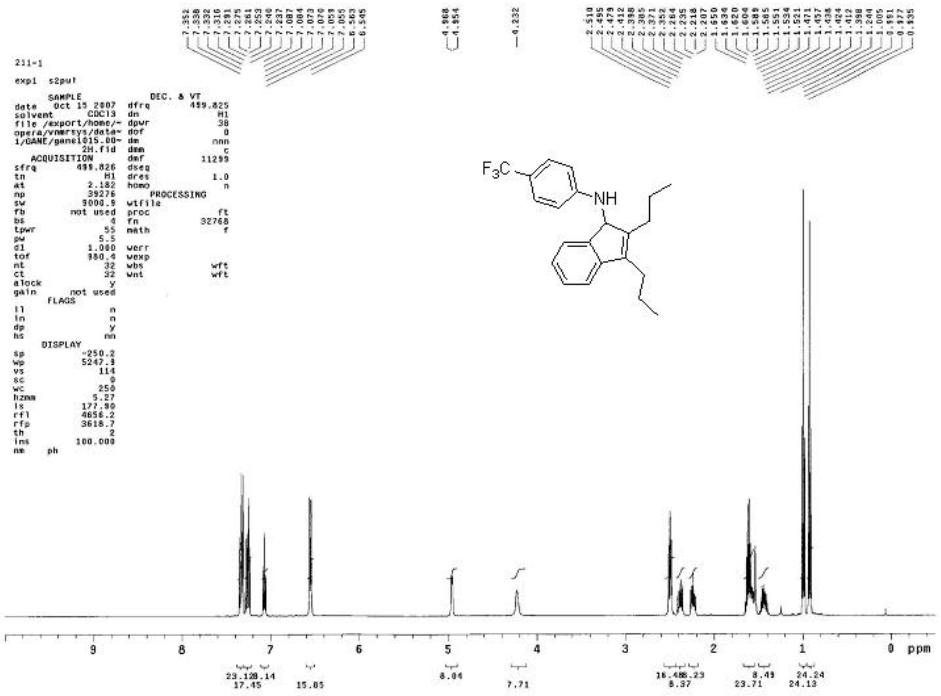


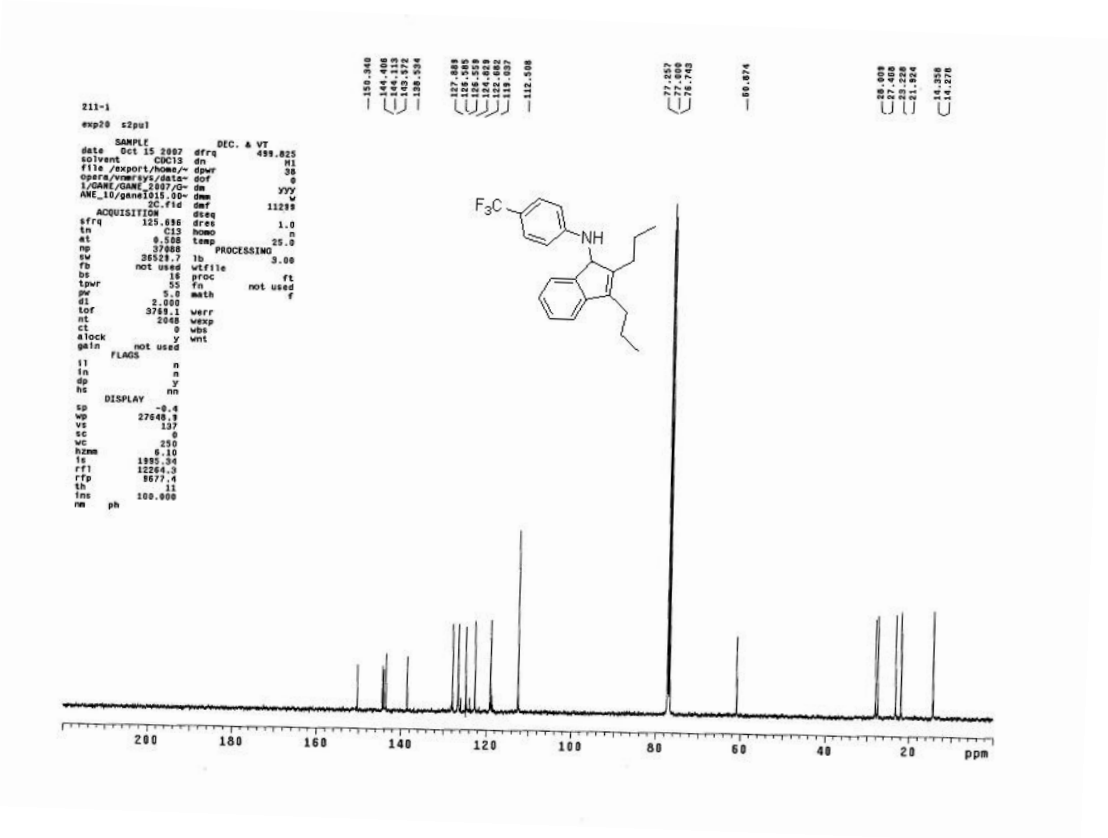
^{1}H and ^{13}C spectra of compound 5l



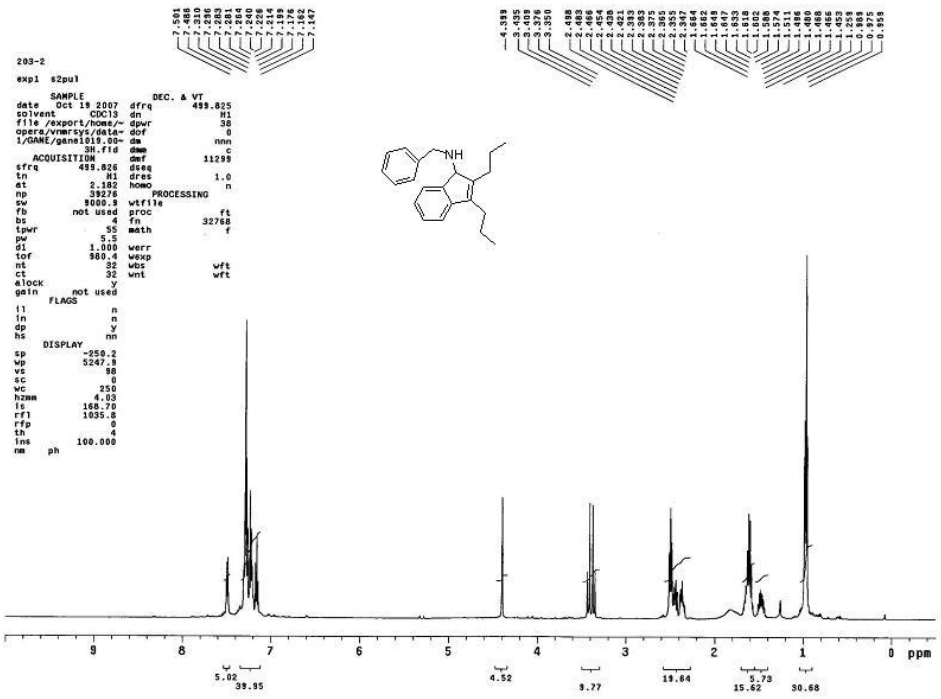


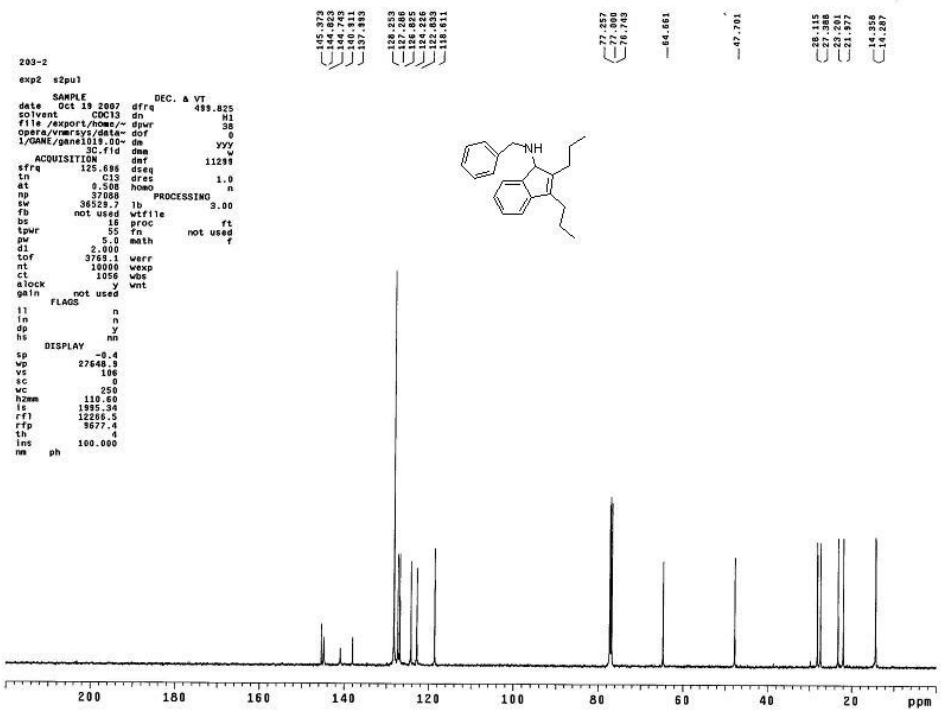
^{1}H and ^{13}C spectra of compound 5m



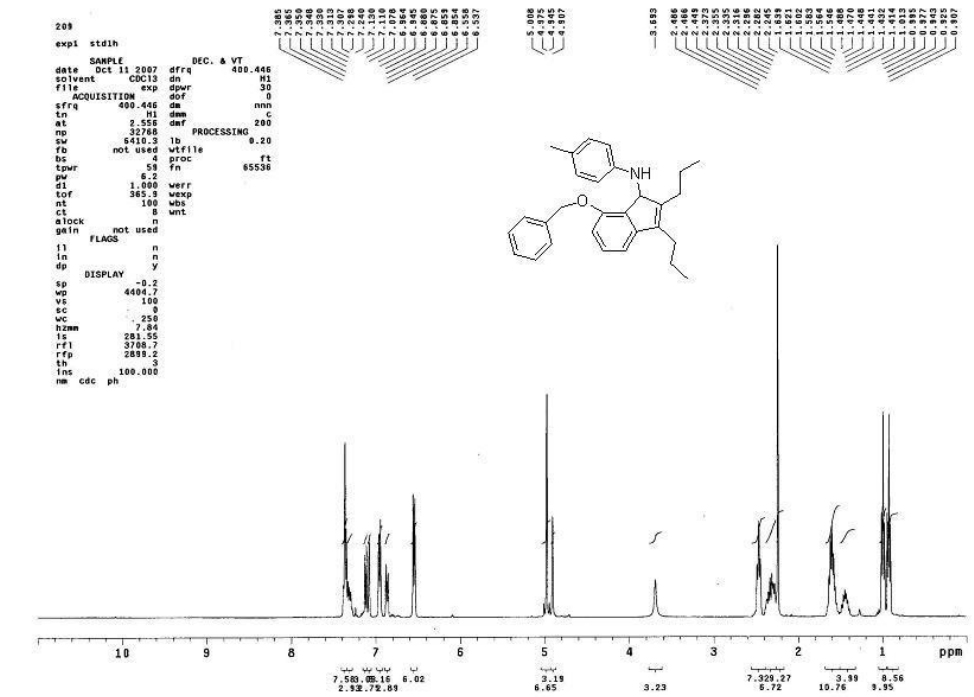


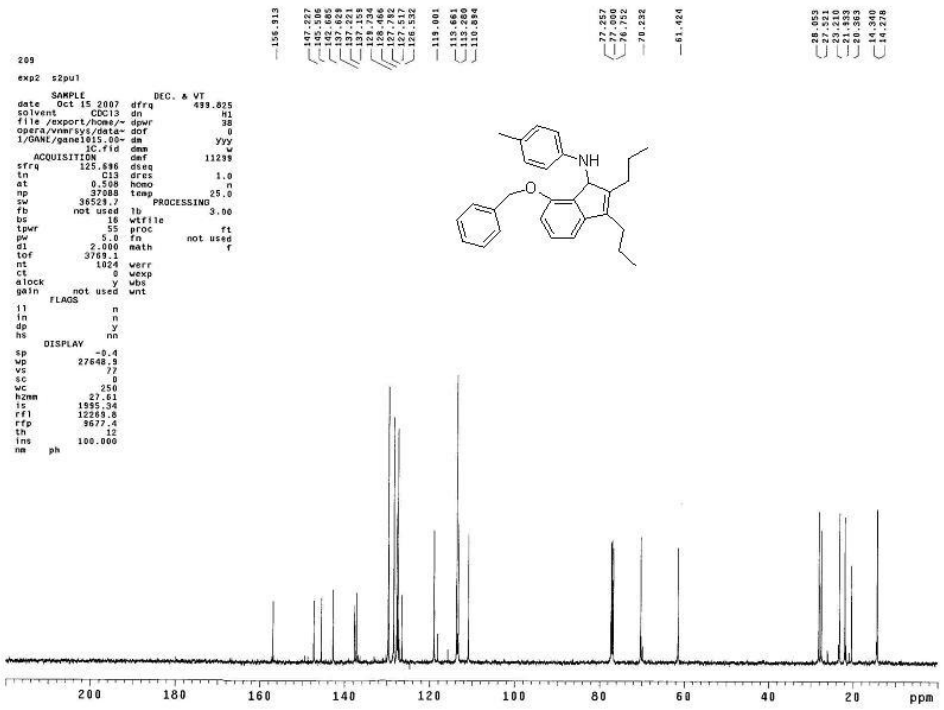
^{1}H and ^{13}C spectra of compound 5o



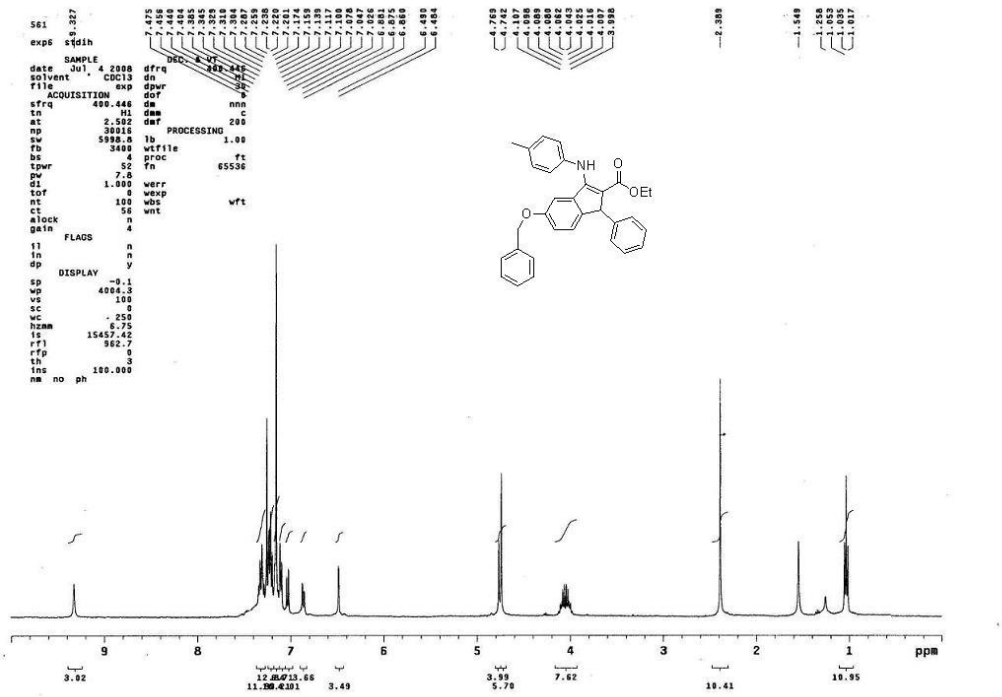


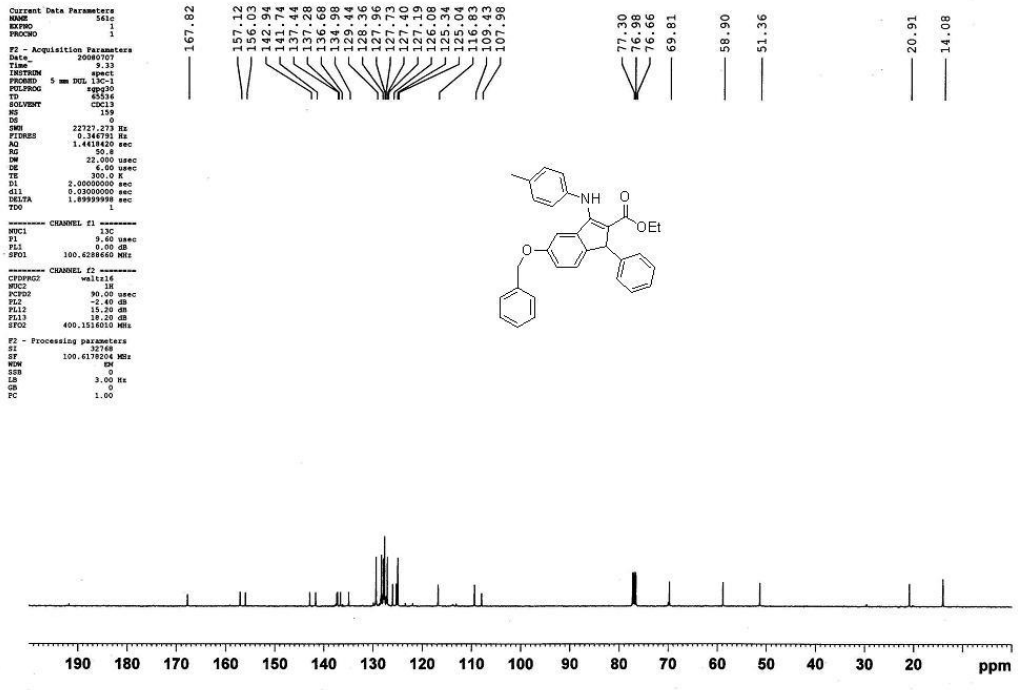
^{1}H and ^{13}C spectra of compound 5q



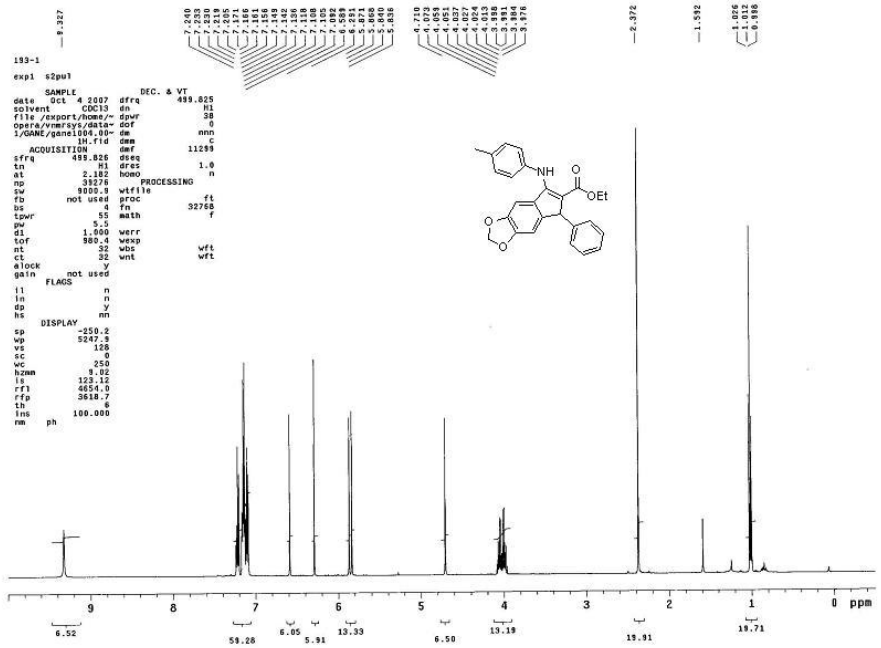


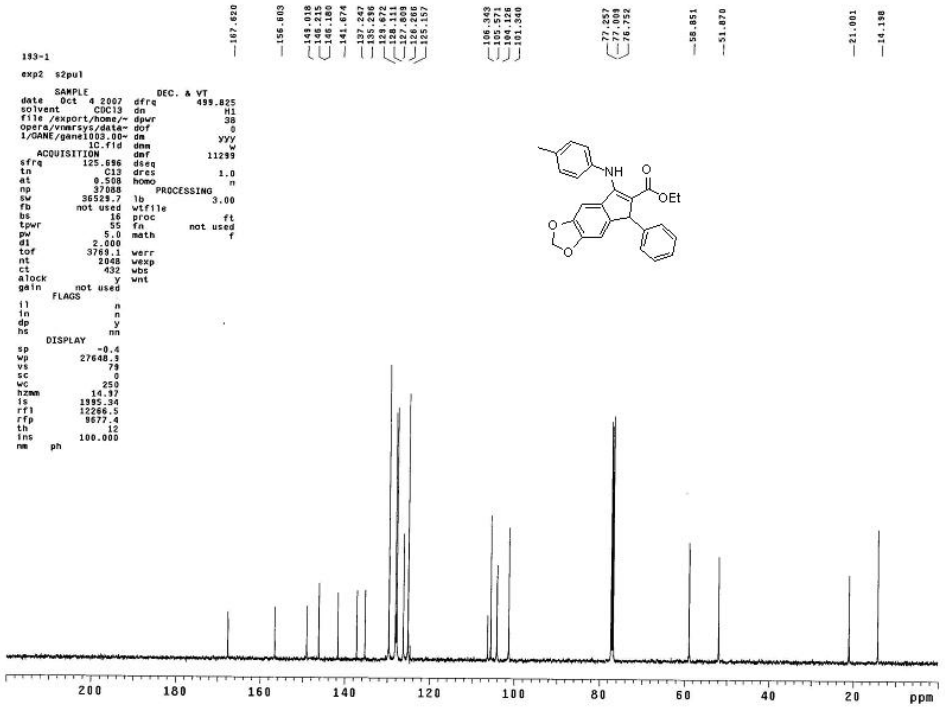
^{1}H and ^{13}C spectra of compound 6d



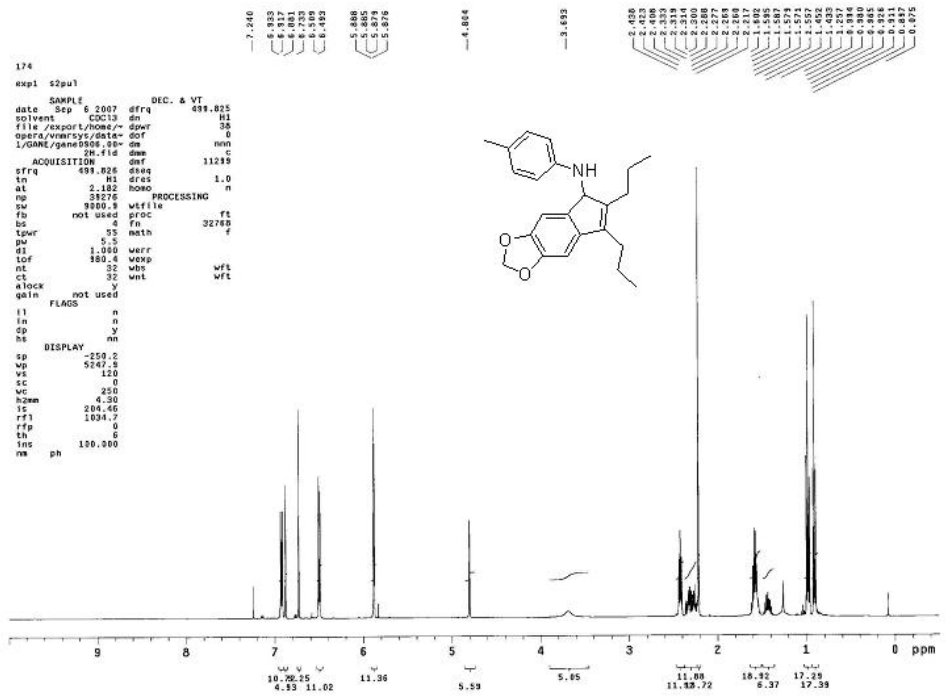


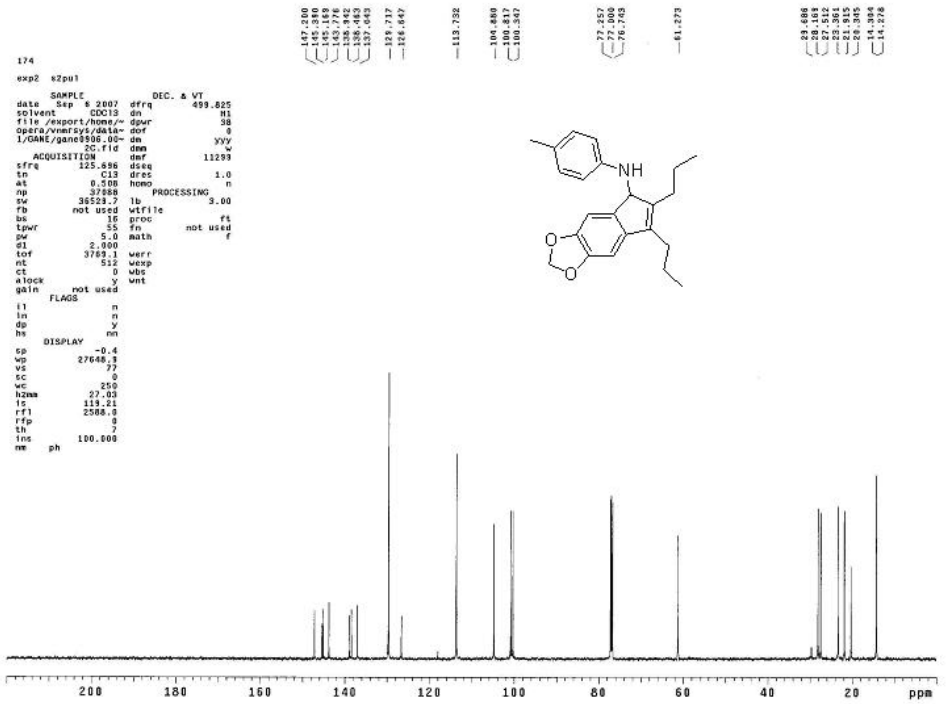
^{1}H and ^{13}C spectra of compound 6e



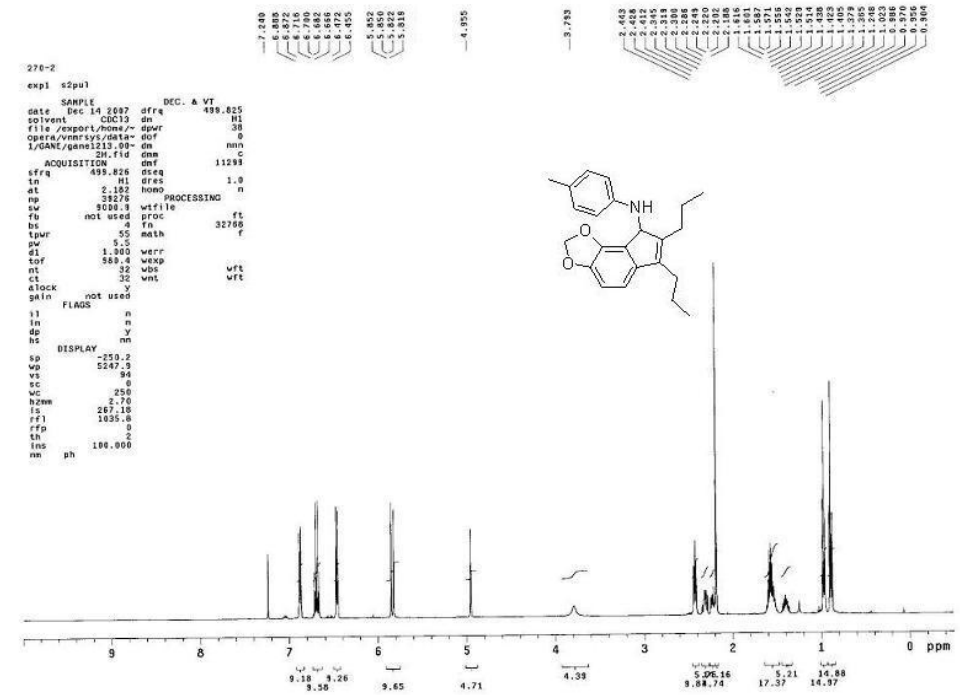


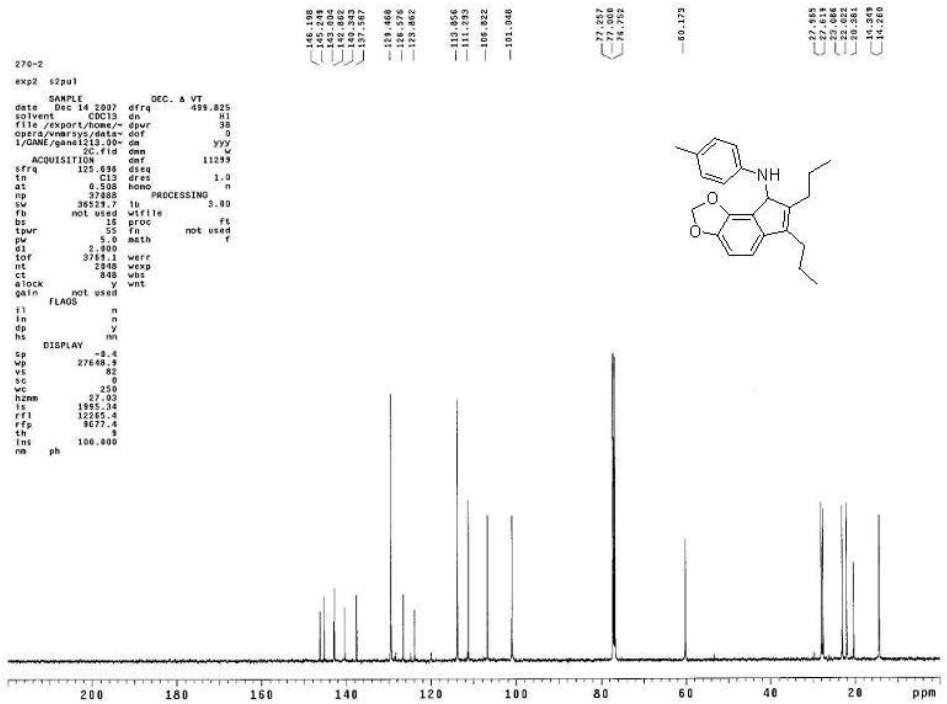
^{1}H and ^{13}C spectra of compound 5r



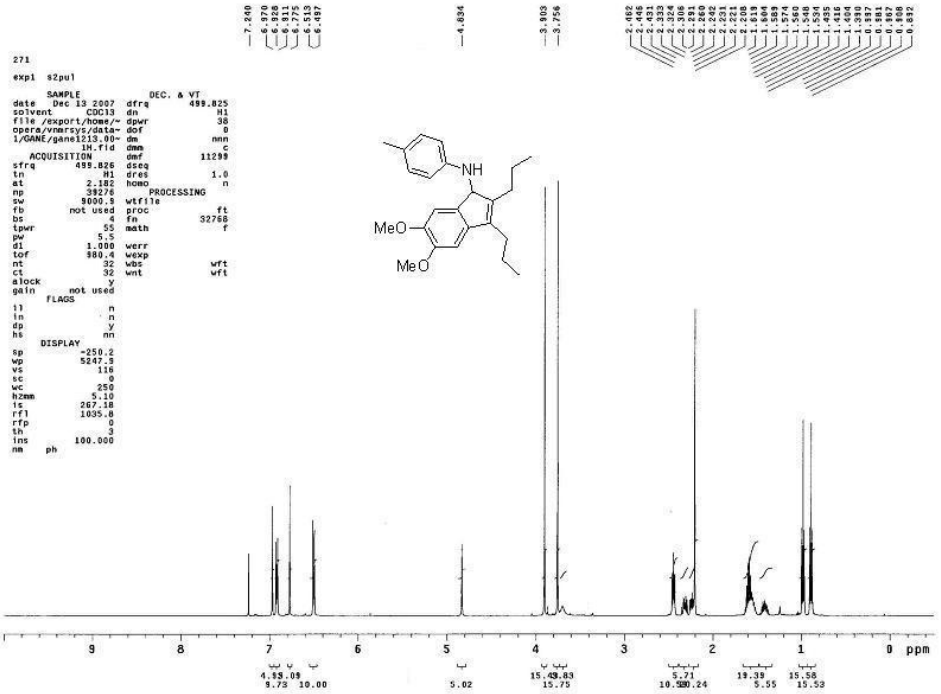


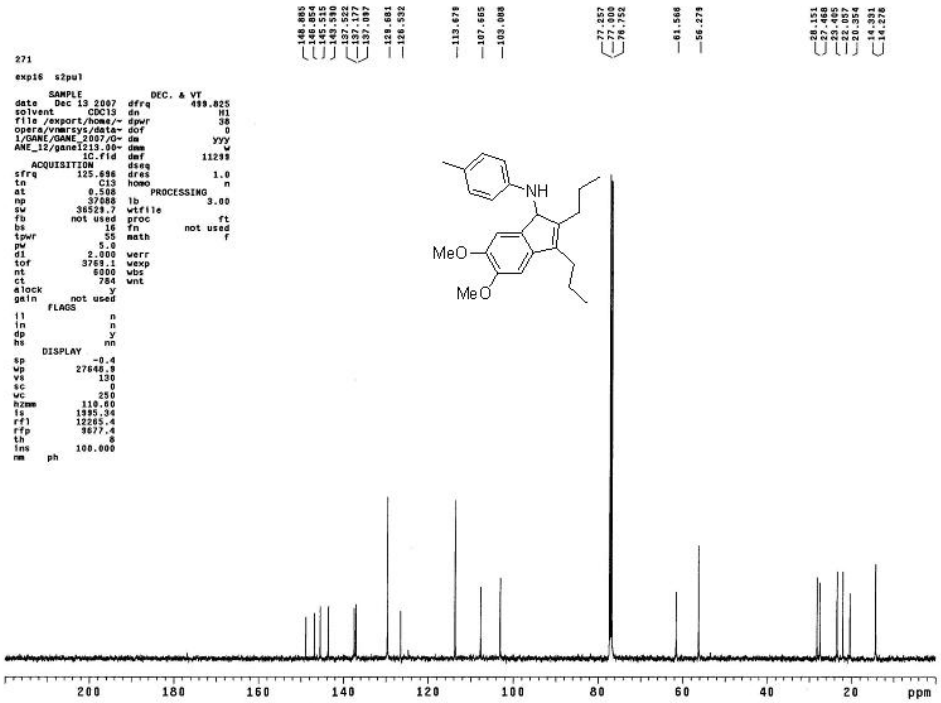
^{1}H and ^{13}C spectra of compound 5s



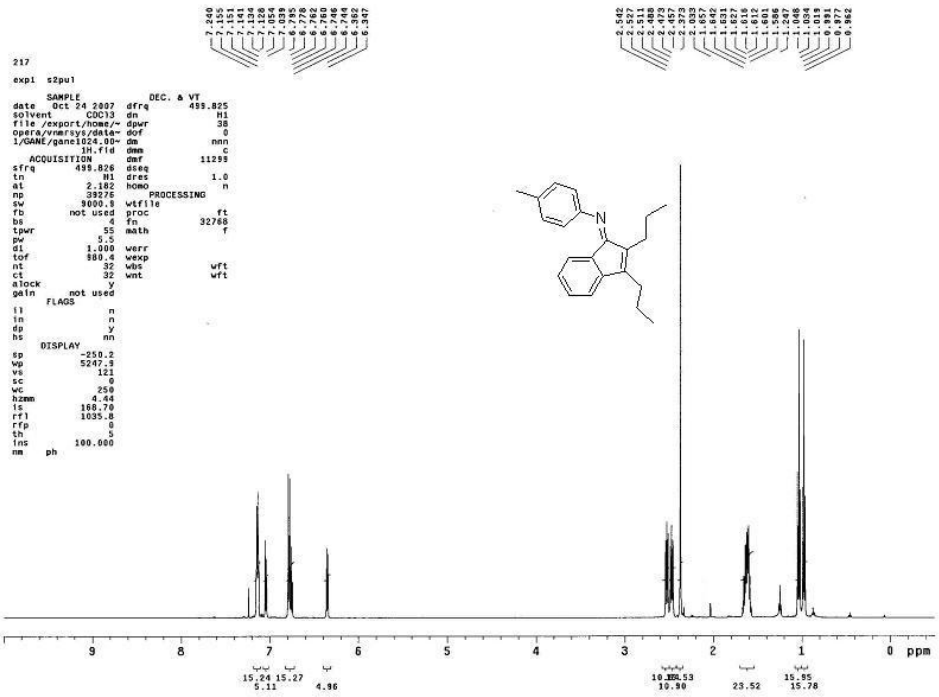


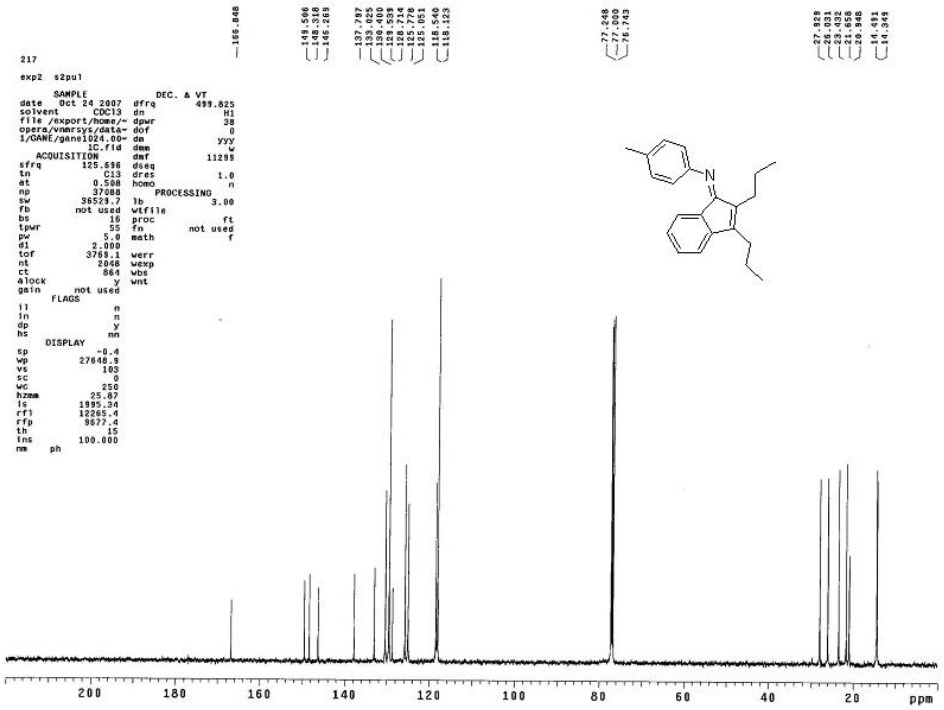
^{1}H and ^{13}C spectra of compound 5t



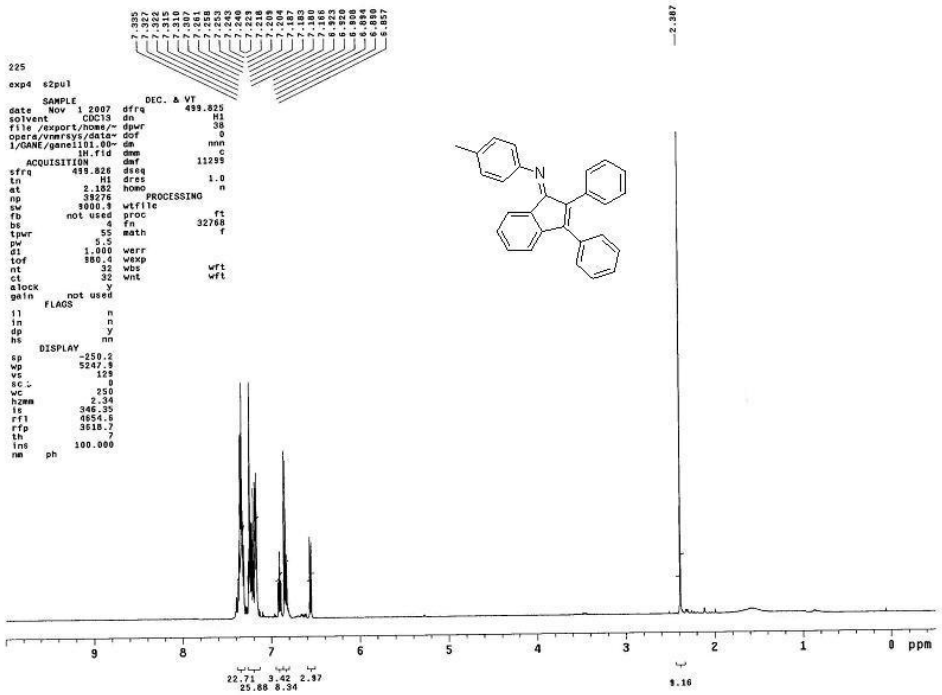


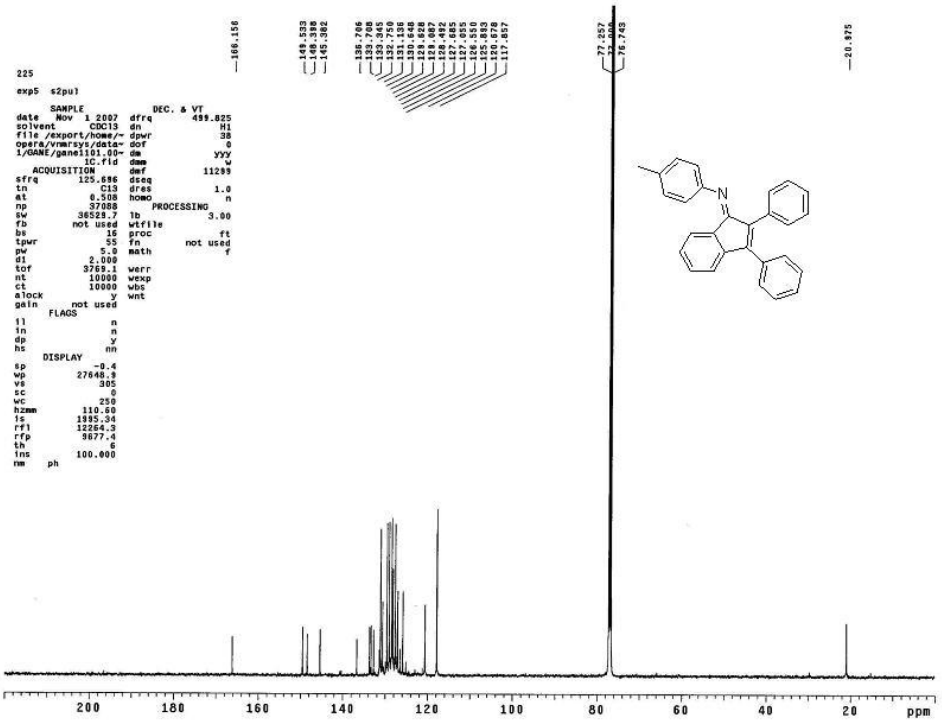
^{1}H and ^{13}C spectra of compound 7a



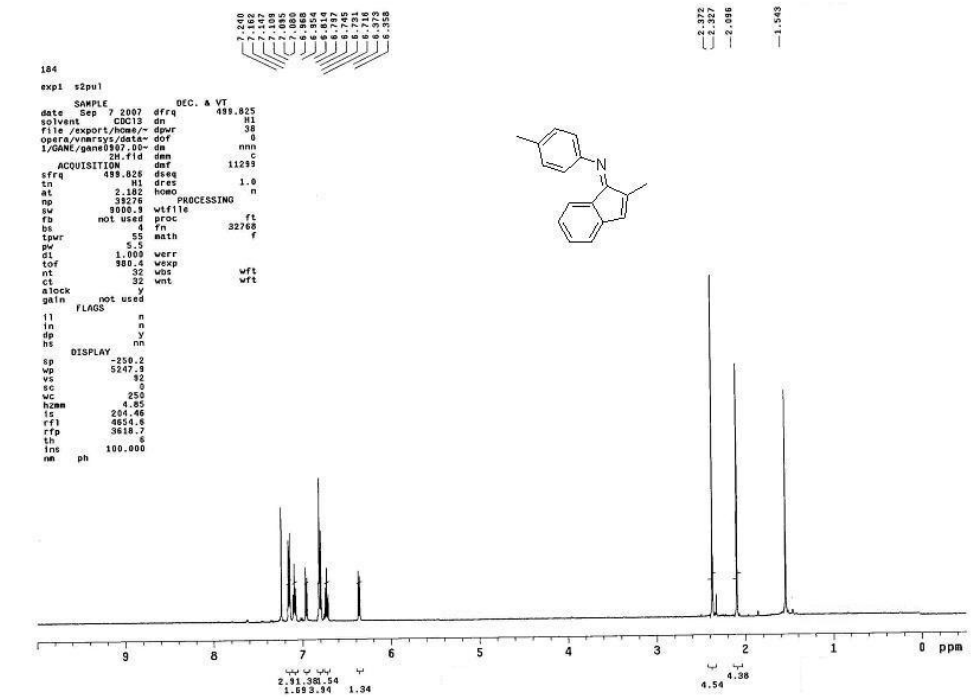


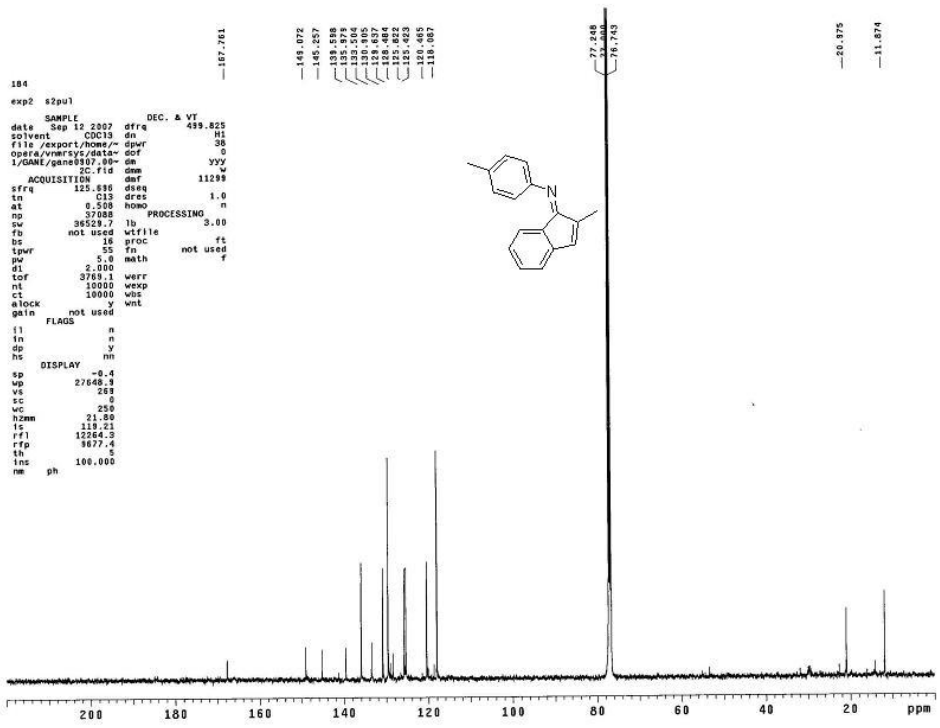
^{1}H and ^{13}C spectra of compound 7b



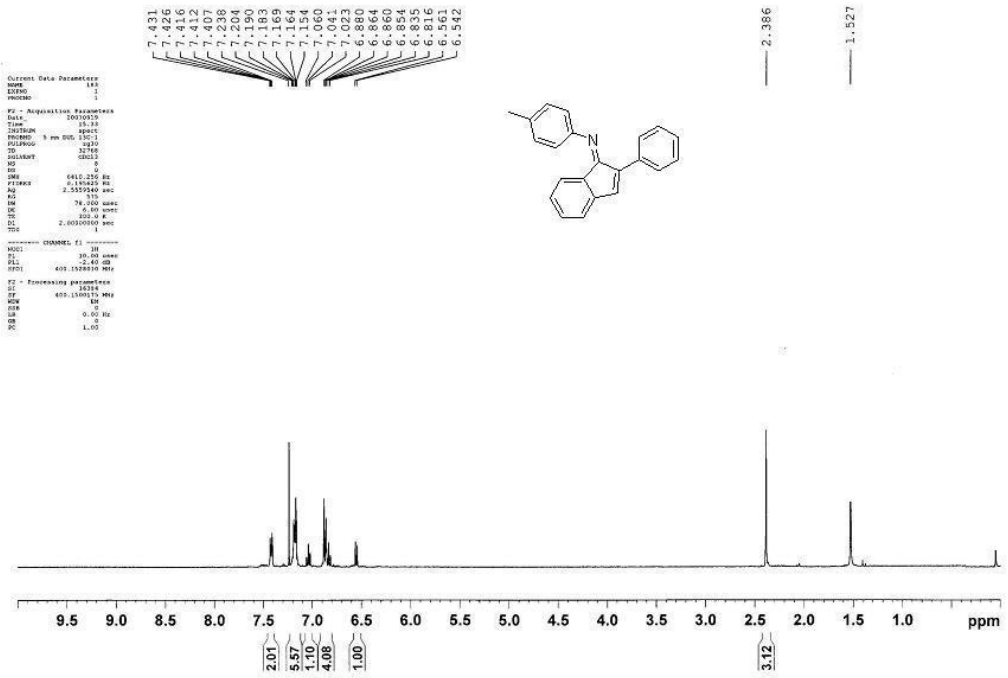


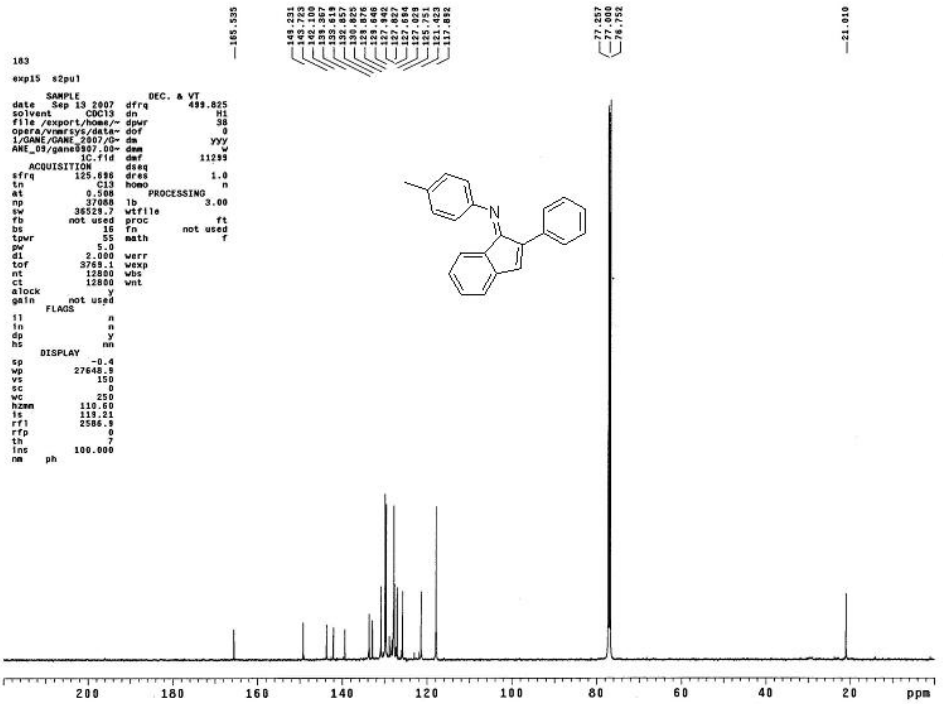
^{1}H and ^{13}C spectra of compound 7c



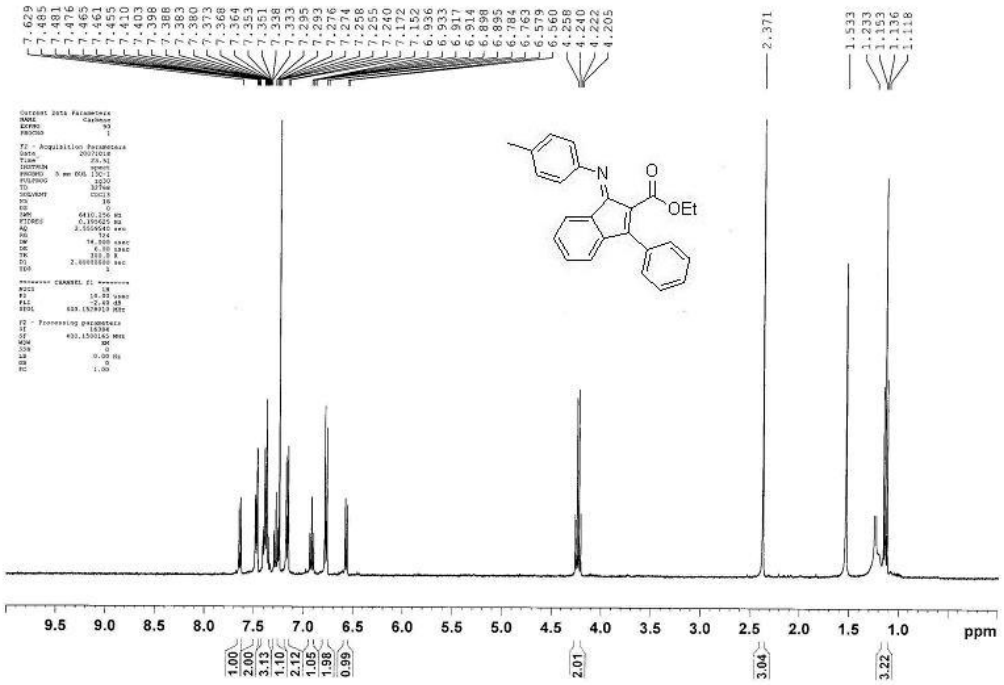


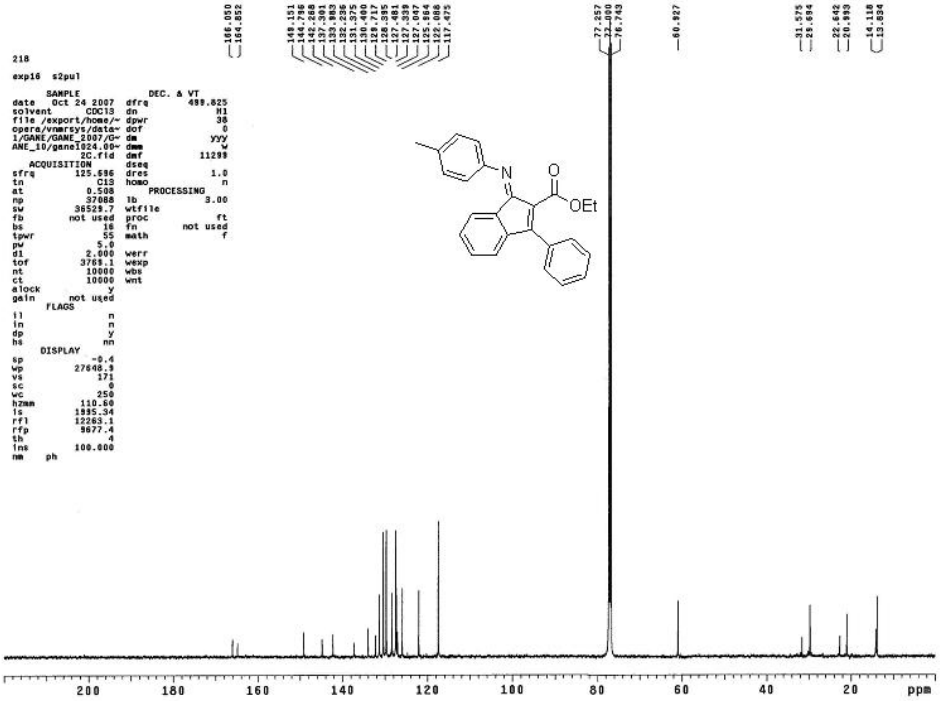
^{1}H and ^{13}C spectra of compound 7d



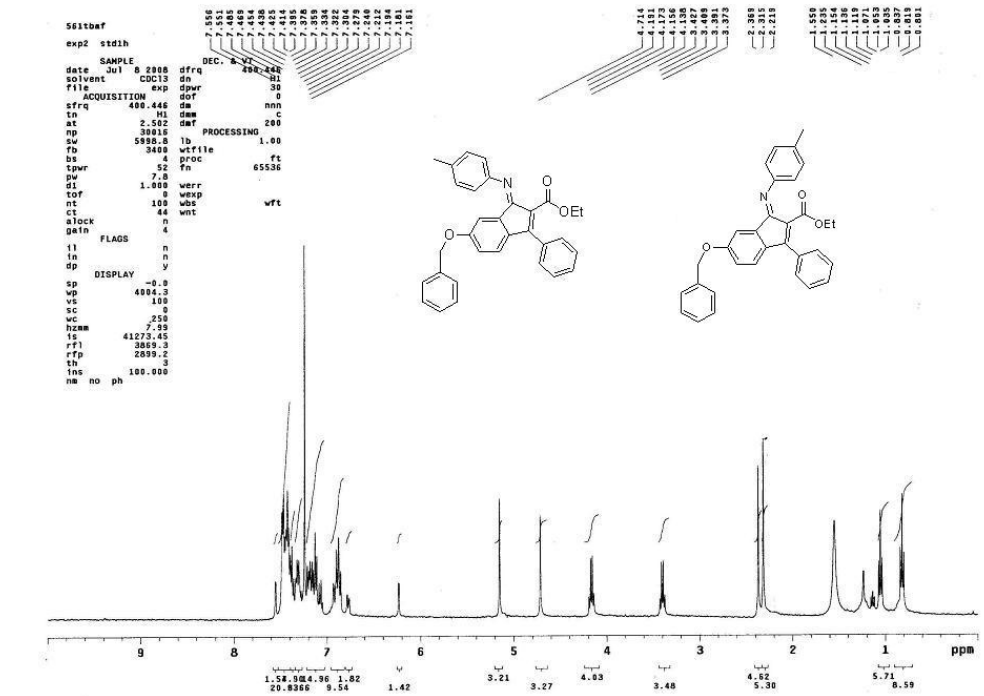


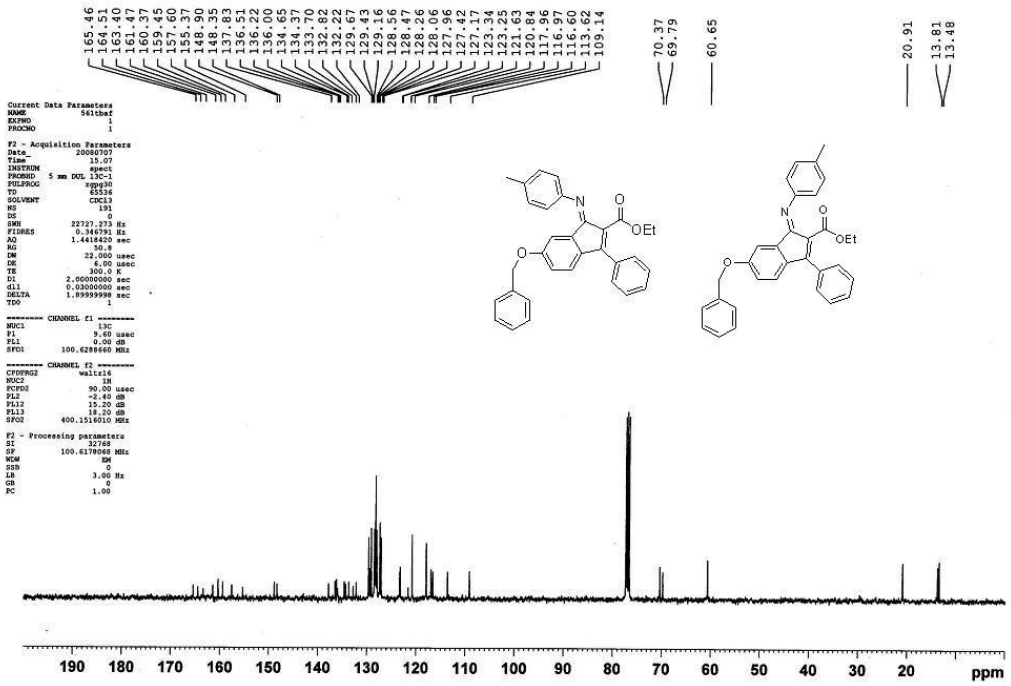
^{1}H and ^{13}C spectra of compound 7e



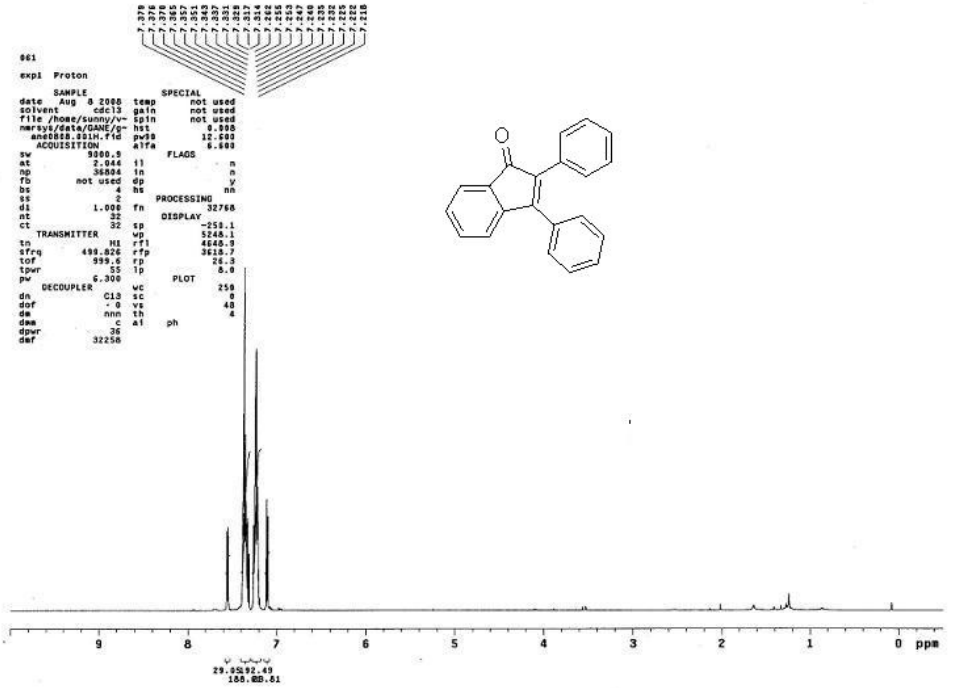


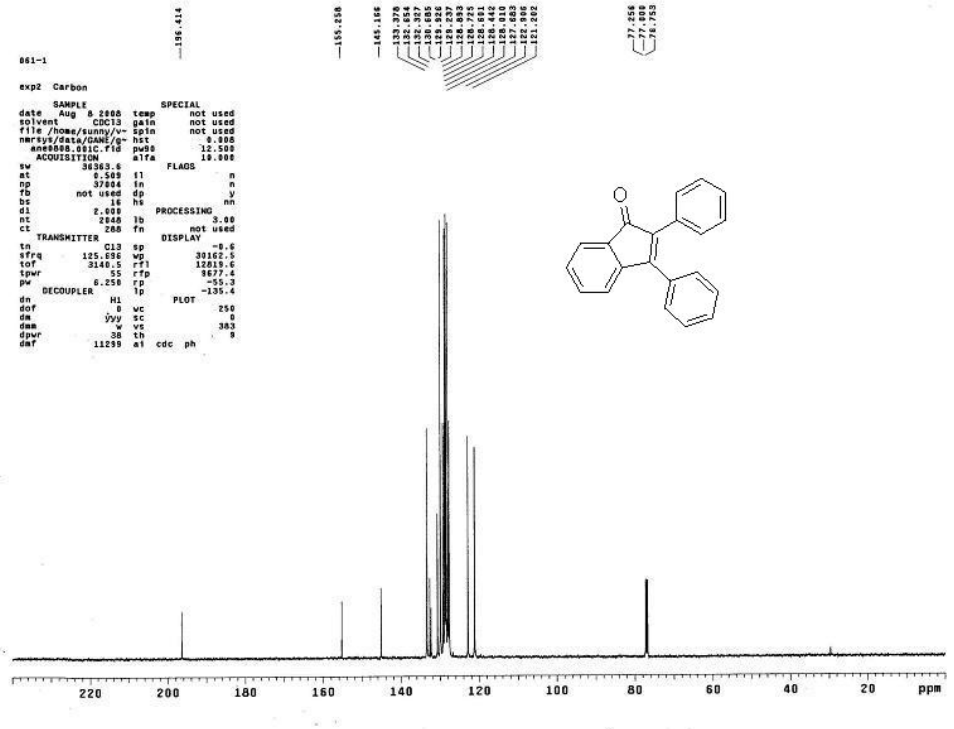
^{1}H and ^{13}C spectra of compound 7f



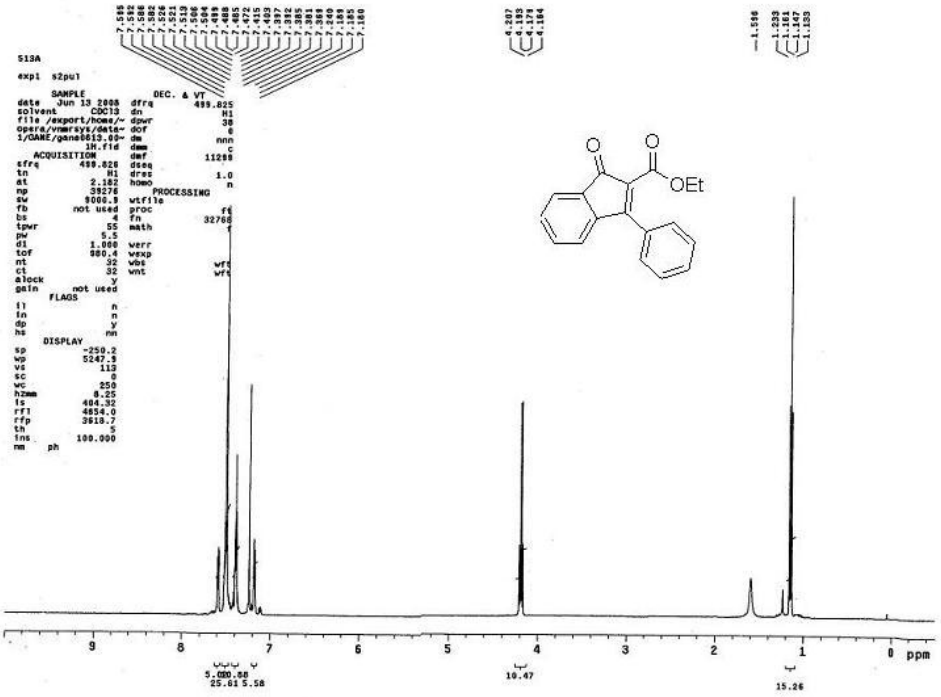


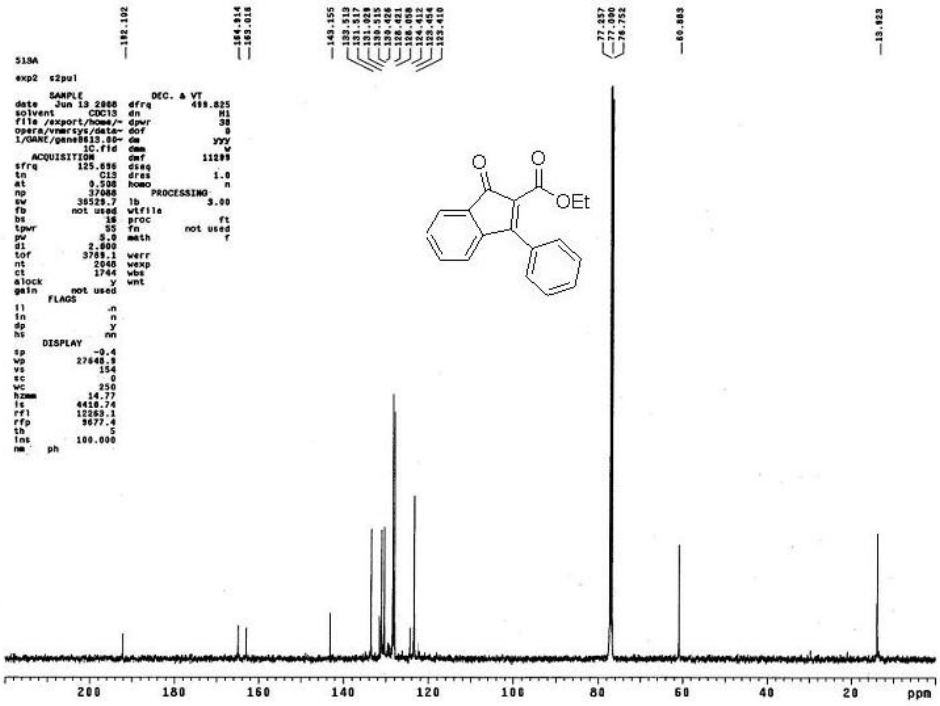
^{1}H and ^{13}C spectra of compound 8b





^{1}H and ^{13}C spectra of compound 8e





^{1}H and ^{13}C spectra of compound 9