Cobalt-catalyzed regio- and stereoselective intermolecular enyne coupling: an efficient synthesis of 1,3-diene derivatives

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Supporting Information

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Experimental section

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 4-phenylbut-3-yn-1-ol (**1f**), 3-(pent-1-ynyl)thiophene (**1d**) and hex-1-ynylbenzene (**1e**) were prepared according to the literature procedure.[2] Others were commercially available and used as purchased.

References.

1. D. D. Perrin, W. L. F. Armarego, *In Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.
2. C. Molinaro, T. F. Jamison, *J. Am, Chem, Soc*. **2003**, *125*, 8076.

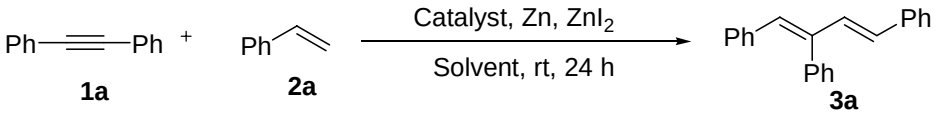
General procedure for the enyne coupling of alkyne with alkene. A sealed tube (20 mL) containing CoI_2 (0.0500 mmol, 5 mol%), dppp (0.0500 mmol), zinc powder (0.200 mmol) and ZnI_2 (0.200 mmol) were evacuated and purged with nitrogen gas three times. Freshly distilled CH_2Cl_2 (1.5 - 2.0 mL) was added and stirred well for 2 min. Then, alkyne (1.00 mmol) and alkene (1.20 mmol) were added via syringes. The reaction mixture was stirred at rt for 24 h and was diluted with dichloromethane and stirred in the air for 10 min. The mixture was filtered through a Celite and silica gel pad and washed with dichloromethane. The filtrate was concentrated and the residue was purified on a silica gel column using hexane or hexane/ethyl acetate as eluent to afford the desired product **3**.

For product **3k**, Co(dppe)Br_2 (0.0500 mmol, 5mol%) was used instead of CoI_2/dppp in the presence of zinc powder (0.200 mmol) and ZnI_2 (0.200 mmol) using DCE as solvent at 80 ºC for 20 h.

For products **3l**,**m**, the reactions were carried out using Co(dppe)Br_2 (0.0500 mmol, 5 mol%) using dichloromethane as solvent at rt for 36 h in the presence of zinc powder (0.200 mmol) and ZnI_2 (0.200 mmol). For products **3n-p**, reactions were carried out using Co(dppe)Br_2 (0.0500 mmol, 5 mol%) and 2,2-bipyridine (0.0500 mmol, 5 mol%) in the presence of zinc powder (0.200 mmol) and ZnI_2 (0.200 mmol) using dichloromethane as solvent at 50 ºC for 24 h. For product **3q**, the reaction was carried out using 5 mol%

$Co(dppe)Cl_2$ and 5 mol% $P(2\text{-furyl})_3$ in the presence of zinc powder (0.200 mmol) and ZnI_2 (0.200 mmol) using dichloromethane as solvent at 50 ºC for 36 h.

Optimization studies for cobalt-catalyzed coupling of diphenylacetylene with styrene.[a]

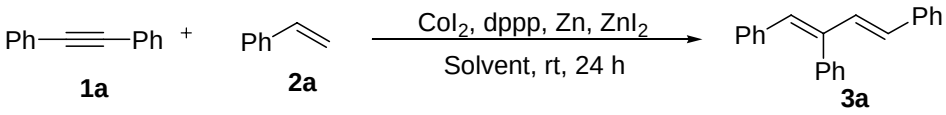


1a **2a** **3a**

Entry	Catalyst	Solvent	Yield(%)
1[b]	$Co(PPh_3)_2Cl_2$, EtOH	CH_3CN	0
2[b]	$Co(PPh_3)_2I_2$, EtOH	CH_3CN	0
3[b]	$Co(PPh_3)_2I_2$, EtOH	CH_2Cl_2	0
4[b]	$Co(PPh_3)_2I_2$/dppp, EtOH	CH_2Cl_2	92
5	$Co(PPh_3)_2I_2$/dppp	CH_2Cl_2	92
6	$Co(PPh_3)_2I_2$/dppe	CH_2Cl_2	12
7	$Co(PPh_3)_2I_2$/dppb	CH_2Cl_2	0
8	$Co(PPh_3)_2I_2$/dppm	CH_2Cl_2	0
9	$Co(dppe)Br_2$	CH_2Cl_2	76
10	$Co(dppe)I_2$	CH_2Cl_2	27
11	**CoI_2/dppp**	**CH_2Cl_2**	**97**
12	CoI_2/dppm	CH_2Cl_2	0
13	CoI_2/dppb	CH_2Cl_2	0
14	$Co(dppp)Cl_2$	CH_2Cl_2	0
15	$Co(dppe)Cl_2$	CH_2Cl_2	0
16	CoI_2/dppp (no ZnI_2)	CH_2Cl_2	0
17	No	CH_2Cl_2	0

[a]All reactions were carried out using alkyne **1a** (1.0 mmol), alkene **2a** (1.2 mmol), cobalt complex (0.0500 mmol), ligand (0.0500 mmol), Zn (0.2000 mmol) and ZnI_2 (0.0200 mmol). [b]0.0200 mmol of ethanol was used.

Table. Effect of solvents on cobalt-catalyzed coupling of diphenylacetylene with styrene.[a]



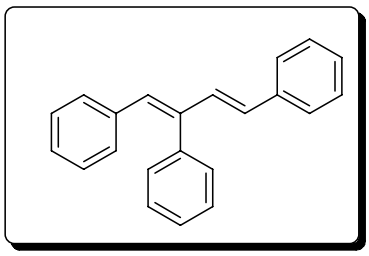
1a **2a** **3a**

Entry	Solvent	Yield(%)
1	CH_3CN	0
2	**CH_2Cl_2**	**97**
3	DCE[b]	73
4	THF	0
5	DMF	0
6	Toluene	18

[a]All reactions were carried out using alkyne **1a** (1.0 mmol), alkene **2a** (1.2 mmol), CoI_2 (0.0500 mmol), dppp (0.0500 mmol), Zn (0.2000 mmol) and ZnI_2 (0.0200 mmol). [b]1,2-dichloroethane.

The spectral data and copies of ^1H and ^{13}C NMR spectra of all compounds are listed below.

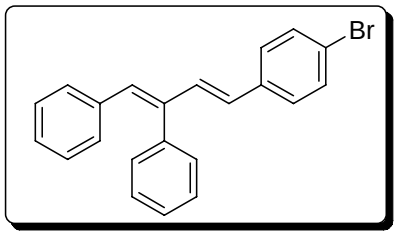
(*1Z*,*3E*)-Buta-1,3-diene-1,2,4-triyltribenzene (3a).



Semisolid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.39 (m, 3 H), 7.36 (d, *J* = 7.6 Hz, 2 H), 7.29 (t, *J* = 7.2 Hz, 2 H), 7.24 – 7.16 (m, 4 H), 7.09 – 7.08 (m, 3 H), 6.91 – 6.89 (m, 2 H), 6.73 (s, 1 H), 6.15 (d, *J* = 15.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6 (C),

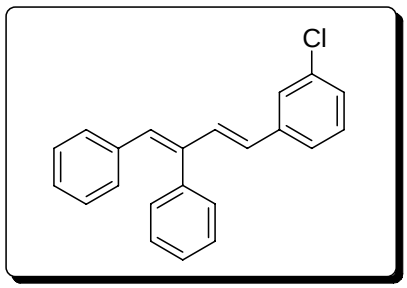
138.2 (C), 137.3 (C), 136.8 (C), 134.2 (CH), 131.9 (CH), 131.2 (CH), 129.5 (2 CH), 129.3 (2 CH), 128.9 (2 CH), 128.5 (2 CH), 127.9 (2 CH), 127.4 (CH), 127.4 (CH), 126.8 (CH), 126.4 (2 CH); HRMS: calcd for $C_{22}H_{18}$ 282.1409, found 282.1407.

1-Bromo-4-((1*E*,3*Z*)-3,4-diphenylbuta-1,3-dienyl)benzene (3b).



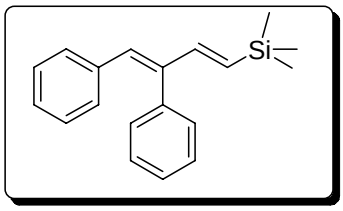
Colorless highly viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 5 H), 7.22 – 7.20 (m, 4 H), 7.12 (d, *J* = 16.0 Hz, 1 H), 7.11 – 7.08 (m, 3 H), 6.90 – 6.89 (m, 2 H), 6.73 (s, 1 H), 6.06 (d, *J* = 16.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3 (C), 138.0 (C), 136.6 (C), 136.3 (C), 134.9 (CH), 132.5 (CH), 131.6 (2 CH), 129.8 (CH), 129.5 (2 CH), 129.4 (2 CH), 128.9 (2 CH), 128.0 (2 CH), 127.8 (2 CH), 127.5 (CH), 127.0 (CH), 121.0 (C); HRMS: calcd for $C_{22}H_{17}Br$ 360.0514, found 360.0509.

(1-Chloro-3-((*1E,3Z*)-3,4-diphenylbuta-1,3-dienyl)benzene (3c).



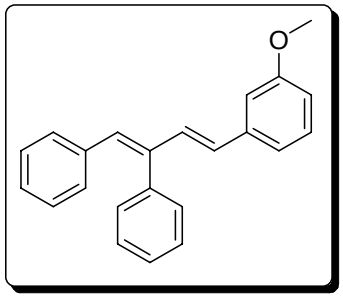
White solid; mp: 82 – 85 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.40 (m, 3 H), 7.37 (s, 1 H), 7.25 – 7.16 (m, 6 H), 7.12 – 7.11 (m, 3 H), 6.93 (dd, *J* = 6.4 Hz, 2.0 Hz, 2 H), 6.76 (s, 1 H), 6.09 (d, *J* = 16.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2 (C), 139.3 (C), 137.9 (C), 136.5 (C), 135.5 (CH), 134.4 (C), 132.8 (CH), 129.7 (CH), 129.6 (CH), 129.5 (2 CH), 129.4 (2 CH), 128.9 (2 CH), 128.0 (2 CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 126.2 (CH), 124.5 (CH); HRMS: calcd for $C_{22}H_{17}Cl$ 316.1019, found 316.1016.

((*1E,3Z*)-3,4-Diphenylbuta-1,3-dienyl)trimethylsilane (3d).



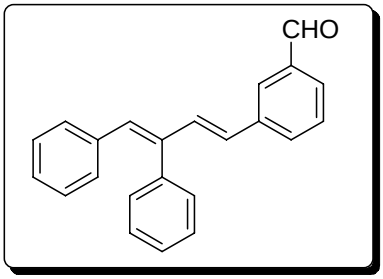
Colorless viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.27 – 7.26 (m, 3 H), 7.19 (d, *J* = 6.0 Hz, 2 H), 7.14 – 7.13 (m, 3 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.91 (d, *J* = 14.4 Hz, 1 H), 6.69 (s, 1 H), 5.74 (d, *J* = 14.0 Hz, 1 H), 0.16 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6 (CH), 142.3 (C), 139.1 (C), 136.7 (C), 132.6 (CH), 129.5 (2 CH), 129.3 (2 CH), 128.4 (2 CH), 128.3 (CH), 128.0 (2 CH), 127.4 (CH), 126.8 (CH), 0.5 (3 CH_3); HRMS: calcd for $C_{19}H_{22}Si$ 278.1491, found 278.1493.

1-((*1E,3Z*)-3,4-Diphenylbuta-1,3-dienyl)-3-methoxybenzene (3e).



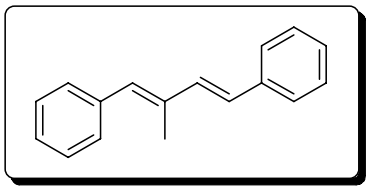
Colorless highly viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.40 (m, 3 H), 7.24 (d, *J* = 7.6 Hz, 2 H), 7.20 (d, *J* = 7.6 Hz, 1 H), 7.18 (d, *J* = 15.6 Hz, 1 H), 7.10 – 7.09 (m, 3 H), 6.97 (d, *J* = 7.6 Hz, 1 H), 6.90 (s, 3 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 6.74 (s, 1 H), 6.13 (d, *J* = 16.0 Hz, 1 H), 3.80 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7 (C), 141.5 (C), 138.8 (C), 138.2 (C), 136.7 (C), 134.5 (CH), 132.1 (CH), 131.1 (CH), 129.5 (2 CH), 129.4 (CH), 129.3 (2 CH), 128.9 (2 CH), 127.9 (2 CH), 127.4 (CH), 126.8 (CH), 119.1 (CH), 113.3 (CH), 111.4 (CH), 55.1 (CH_3); HRMS: calcd for $C_{23}H_{20}O$ 312.1514, found 312.1519.

3-((*1E,3Z*)-3,4-Diphenylbuta-1,3-dienyl)benzaldehyde (3f).



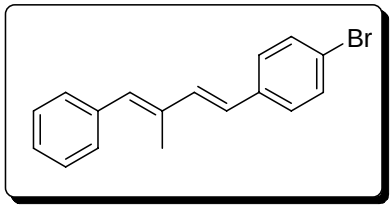
Colorless highly viscous oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1 H), 7.85 (s, 1 H), 7.68 (d, *J* = 7.2 Hz, 1 H), 7.59 (d, *J* = 7.6 Hz, 1 H), 7.45 – 7.40 (m, 4 H), 7.28 – 7.21 (m, 3 H), 7.09 – 7.08 (m, 3 H), 6.91 (m, 2 H), 6.77 (s, 1 H), 6.16 (d, *J* = 16.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3 (CHO), 141.2 (C), 138.4 (C), 137.9 (C), 136.6 (C), 136.5 (C), 135.9 (CH), 133.1 (CH), 132.1 (CH), 129.5 (CH), 129.4 (2 CH), 129.4 (2 CH), 129.2 (CH), 129.0 (2 CH), 128.5 (CH), 128.0 (2 CH), 127.6 (CH), 127.3 (CH), 127.1 (CH); HRMS: calcd for $C_{23}H_{18}O$ 310.1358, found 310.1359.

((*1E,3E*)-2-Methylbuta-1,3-diene-1,4-diyl)dibenzene (3g).



White solid; mp: 56–58 °C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.0 Hz, 2 H), 7.39 – 7.33 (m, 6 H), 7.24 (m, 2 H), 7.00 (d, *J* = 16.0 Hz, 1 H), 6.67 (d, *J* = 16.0 Hz, 1 H), 6.80 (s, 1 H), 2.14 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8 (C), 137.6 (C), 135.8 (C), 134.1 (CH), 132.2 (CH), 129.2 (2 CH), 128.6 (2 CH), 128.1 (2 CH), 127.9 (CH), 127.2 (CH), 126.6 (CH), 126.3 (2 CH), 13.9 (CH_3); HRMS: calcd for $C_{17}H_{16}$ 220.1252, found 220.1258.

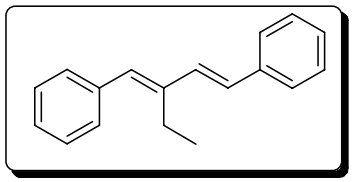
1-Bromo-4-((*1E,3E*)-3-methyl-4-phenylbuta-1,3-dienyl)benzene (3h).



White solid; mp: 112 – 115 °C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43(d, *J* = 8.4 Hz, 2 H), 7.37 – 7.29 (m, 6 H), 7.24 – 7.23 (m, 1 H), 6.95 (d, *J* = 15.6 Hz, 1 H), 6.66 (s, 1 H), 6.56

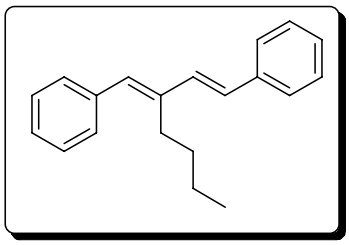
(d, *J* = 16.0 Hz, 1 H), 2.10 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6 (C), 136.5 (C), 135.5 (C), 134.8 (CH), 132.9 (CH), 131.7 (2 CH), 129.2 (2 CH), 128.1 (2 CH), 127.8 (2 CH), 126.7 (CH), 126.6 (CH), 120.9 (C), 13.9 (CH_3); HRMS: calcd for $C_{17}H_{15}Br$ 298.0357, found 298.0364.

((*1E*,*3E*)-2-Ethylbuta-1,3-diene-1,4-diyl)dibenzene (3i).



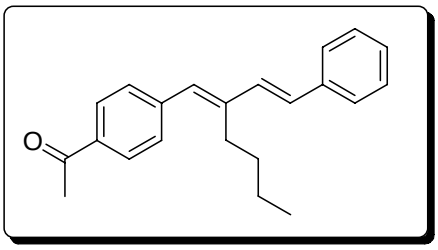
White solid; mp: 75 – 78 °C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.6 Hz, 2 H), 7.39 – 7.33 (m, 6 H), 7.27 – 7.22 (m, 2 H), 6.88 (d, *J* = 16.4 Hz, 1 H), 6.70 (d, *J* = 16.4 Hz, 1 H), 6.61 (s, 1 H), 2.63 (q, *J* = 8.0 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0 (C), 137.7 (C), 137.6 (C), 132.7 (CH), 131.5 (CH), 128.7 (2 CH), 128.6 (2 CH), 128.2 (2 CH), 127.6 (CH), 127.2 (CH), 126.6 (CH), 126.3 (2 CH), 20.3 (CH_2), 13.9 (CH_3); HRMS: calcd for $C_{18}H_{18}$ 234.1409, found 243.1411.

((*1E*,*3E*)-2-Butylbuta-1,3-diene-1,4-diyl)dibenzene (3j).



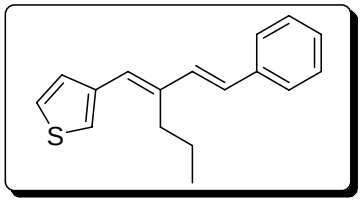
Colorless highly viscous oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.6 Hz, 2 H), 7.37 – 7.31 (m, 6 H), 7.26 – 7.20 (m, 2 H), 6.87 (d, *J* = 16.4 Hz, 1 H), 6.66 (d, *J* = 16.4 Hz, 1 H), 6.61 (s, 1 H), 2.56 (t, *J* = 8.0 Hz, 2 H), 1.66 – 1.58 (m, 2 H), 1.50 – 1.42 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8 (C), 137.7 (C), 137.6 (C), 133.2 (CH), 131.7 (CH), 128.7 (2 CH), 128.6 (2 CH), 128.2 (2 CH), 127.6 (CH), 127.2 (CH), 126.6 (CH), 126.3 (2 CH), 31.4 (CH_2), 27.1 (CH_2), 23.0 (CH_2), 13.9 (CH_3); HRMS: calcd for $C_{20}H_{22}$ 262.1722, found.262.1725.

1-(4-((*E*)-2-((*E*)-Styryl)hex-1-enyl)phenyl)ethanone (3k).



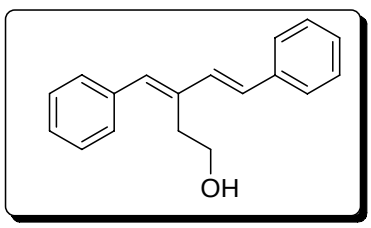
White solid; mp: 61–63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 7.6 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 7.6 Hz, 2 H),7.25 – 7.21 (m, 1 H), 6.85 (d, *J* = 16.0 Hz, 1 H), 6.70 (d, *J* = 16.0 Hz, 1 H), 6.60 (s, 1 H), 2.59 (s, 3 H), 2.56 (t, *J* = 6.8 Hz, 2 H), 1.64 – 1.56 (m, 2 H), 1.48 – 1.39 (m, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5 (CO), 143.1(C), 142.7 (C), 137.3 (C), 135.0 (C), 132.7 (CH), 130.4 (CH), 128.9 (CH), 128.8 (2 CH), 128.6 (2 CH), 128.4 (2 CH), 127.6 (CH), 126.5 (2 CH), 31.4 (CH_2), 27.3 (CH_2), 26.5 (CH_3), 23.0 (CH_2), 13.9 (CH_3); HRMS: calcd for $C_{22}H_{24}O$ 304.1827, found. 304.1825.

3-((*E*)-2-((*E*)-Styryl)pent-1-enyl)thiophene (3l).



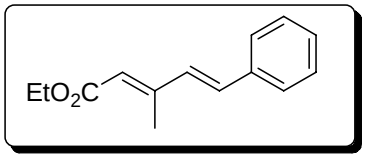
White solid; mp: 101– 103 °C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.6 Hz, 2 H), 7.34 – 7.20 (m, 3 H), 7.22 – 7.20 (m, 2 H), 7.13 (d, *J* = 5.2 Hz, 1 H), 6.85 (d, *J* = 16.0 Hz, 1 H), 6.63 (d, *J* = 16.4 Hz, 1 H), 6.56 (s, 1 H), 2.60 – 2.56 (m, 2 H), 1.69 – 1.60 (m, 2 H), 1.07 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8 (C), 138.8 (C), 137.7 (C), 133.2 (CH), 128.7 (CH), 128.6 (2 CH), 127.3 (CH), 127.1 (CH), 126.5 (2 CH), 126.3 (CH), 125.1 (CH), 122.8 (CH), 29.8 (CH_2), 22.1 (CH_2), 14.4 (CH_3); HRMS: calcd for $C_{17}H_{18}S$ 254.1129, found 254.1130.

(*3E*,*4E*)-3-Benzylidene-5-phenylpent-4-en-1-ol. (3m).



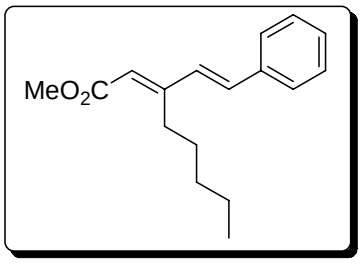
White solid; mp: 71–73 °C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.2 Hz, 3 H), 7.33 (t, *J* = 8.0 Hz, 3 H), 7.26 – 7.21 (m, 2 H), 6.90 (d, *J* = 16.4 Hz, 1 H), 6.77 (s, 1 H), 6.71 (d, *J* = 16.0 Hz, 1 H), 3.88 (t, *J* = 7.2 Hz, 2 H), 2.91 (t, *J* = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3 (C), 137.1 (C), 136.0 (C), 134.2 (CH), 132.7 (CH), 128.8 (2 CH), 128.6 (2 CH), 128.4 (2 CH), 128.0 (CH), 127.5 (CH), 127.0 (CH), 126.3 (2 CH), 61.7 (CH_2), 30.5 (CH_2); HRMS: calcd for $C_{18}H_{18}O$ 250.1358, found 250.1365.

(*2E*,*4E*)-Ethyl 3-methyl-5-phenylpenta-2,4-dienoate (3n).



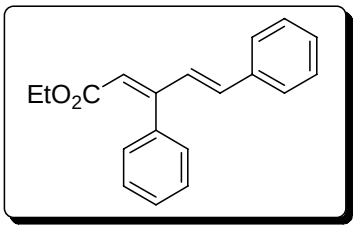
Colorless highly viscous oil,^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.6 Hz, 2 H), 7.33 (t, *J* = 7.6 Hz, 2 H), 7.27 (d, *J* = 6.8 Hz, 1 H), 6.91 (d, *J* = 16.0 Hz, 1 H), 6.79 (d, *J* = 16.0 Hz, 1 H), 5.90 (s, 1 H), 4.18 (q, *J* = 6.8 Hz, 2 H), 2.40 (s, 3 H), 1.29 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8 (CO_2Et), 151.8 (C), 136.2 (C), 133.9 (CH), 131.7 (CH), 128.6 (2 CH), 128.4 (CH), 126.9 (2 CH), 119.7 (CH), 59.6 (CH_2), 14.2 (CH_3), 13.6 (CH_3); HRMS: calcd for $C_{14}H_{16}O_2$ 216.1150, found 216.1150.

(*E*)-Methyl 3-((*E*)-styryl)oct-2-enoate (3o).



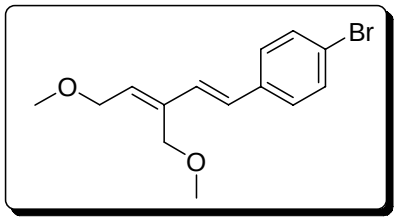
Colorless highly viscous oil,^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.6 Hz, 2 H), 7.33 (t, *J* = 7.2 Hz, 2 H), 7.27 (d, *J* = 7.2 Hz, 1 H), 6.93 (d, *J* = 16.4 Hz, 1 H), 6.70 (d, *J* = 16.0 Hz, 1 H), 5.86 (s, 1 H), 3.71 (s, 3 H), 2.90 (t, *J* = 8.0 Hz, 2 H), 1.56 – 1.51 (m, 2 H), 1.46 – 1.33 (m, 4 H), 0.91 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8 (CO_2Me), 157.4 (C), 136.2 (C), 133.6 (CH), 130.6 (CH), 128.6 (2 CH), 128.4 (CH), 126.9 (2 CH), 118.4 (CH), 50.8 (CH_3), 32.1 (CH_2), 29.4 (CH_2), 27.5 (CH_2), 22.4 (CH_2), 13.9 (CH_3); HRMS: calcd for $C_{17}H_{22}O_2$ 258.1620, found 258.1622.

(*2Z,4E*)-Ethyl 3,5-diphenylpenta-2,4-dienoate (3p).



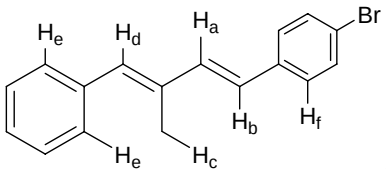
Colorless highly viscous oil,^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.39 (m, 3 H), 7.37 – 7.34 (m, 2 H), 7.31 – 7.24 (m, 3 H), 7.18 (dd, *J* = 7.6 Hz, 2.0 Hz, 2 H), 7.03 (d, *J* = 16.0 Hz, 1 H), 6.35 (d, *J* = 15.6 Hz, 1 H), 6.06 (s, 1 H), 3.98 (q, *J* = 7.2 Hz, 2 H), 1.06 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9 (CO_2Et), 154.9 (C), 138.4 (C), 136.9 (C), 136.1 (C), 131.4 (CH), 128.7 (CH), 128.6 (2 CH), 128.3 (2 CH), 127.8 (2 CH), 127.6 (CH), 127.1 (2 CH), 120.1 (CH), 58.4 (CH_2), 13.9 (CH_3); HRMS: calcd for $C_{19}H_{18}O_2$ 278.1307, found 278.1310.

1-Bromo-4-((*1E,3Z*)-5-methoxy-3-(methoxymethyl)penta-1,3-dienyl)benzene (3q).



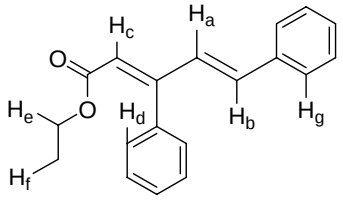
Colorless highly viscous oil,^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 6.70 (d, *J* = 16.8 Hz, 1 H), 6.65 (d, *J* = 16.4 Hz, 1 H), 5.93 (t, *J* = 6.4 Hz, 1 H), 4.20 (s, 2 H), 4.15 (d, *J* = 6.8 Hz, 2 H), 3.35 (s, 3 H), 3.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6 (C), 136.3 (C), 132.9 (CH), 131.6 (2 CH), 130.7 (CH), 127.9 (2 CH), 127.7 (CH), 121.1 (C), 68.6 (CH_2), 66.9 (CH_2), 58.2 (CH_3), 57.8 (CH_3); HRMS: calcd for $C_{14}H_{17}BrO_2$ 296.0412, found 296.0409

NOE data of compounds 3h and 3p.



3h

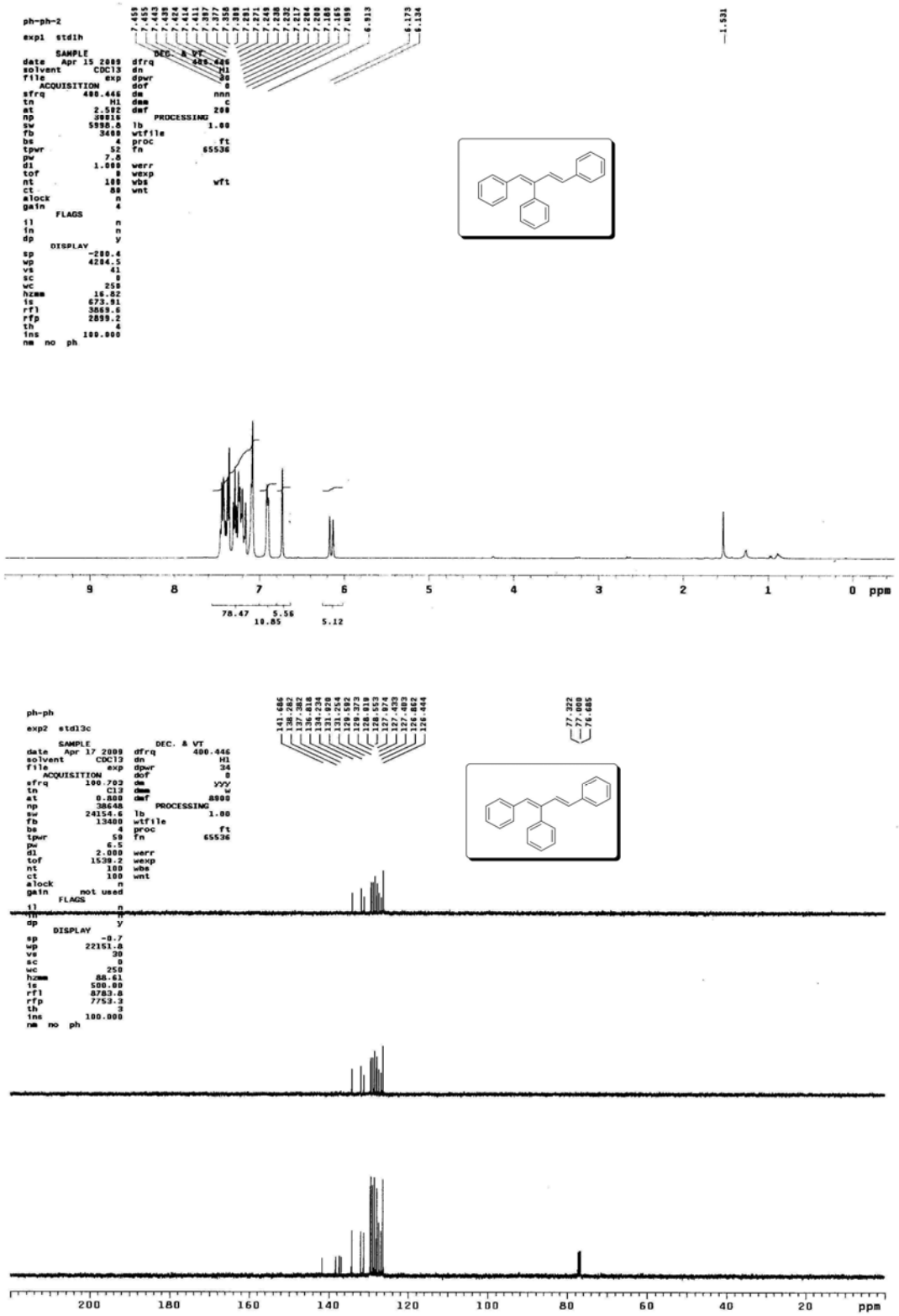
Irradiation at	Observed enhancement (%)
H_a (δ 6.95, d)	H_d (8.85), no NOE for H_c
H_b (δ 6.56, d)	H_c (10.42), H_f (2.19)
H_c (δ 2.10, s)	H_b (3.18)
H_d (δ 6.66, s)	H_a (8.17), H_e (3.37), no NOE for H_c



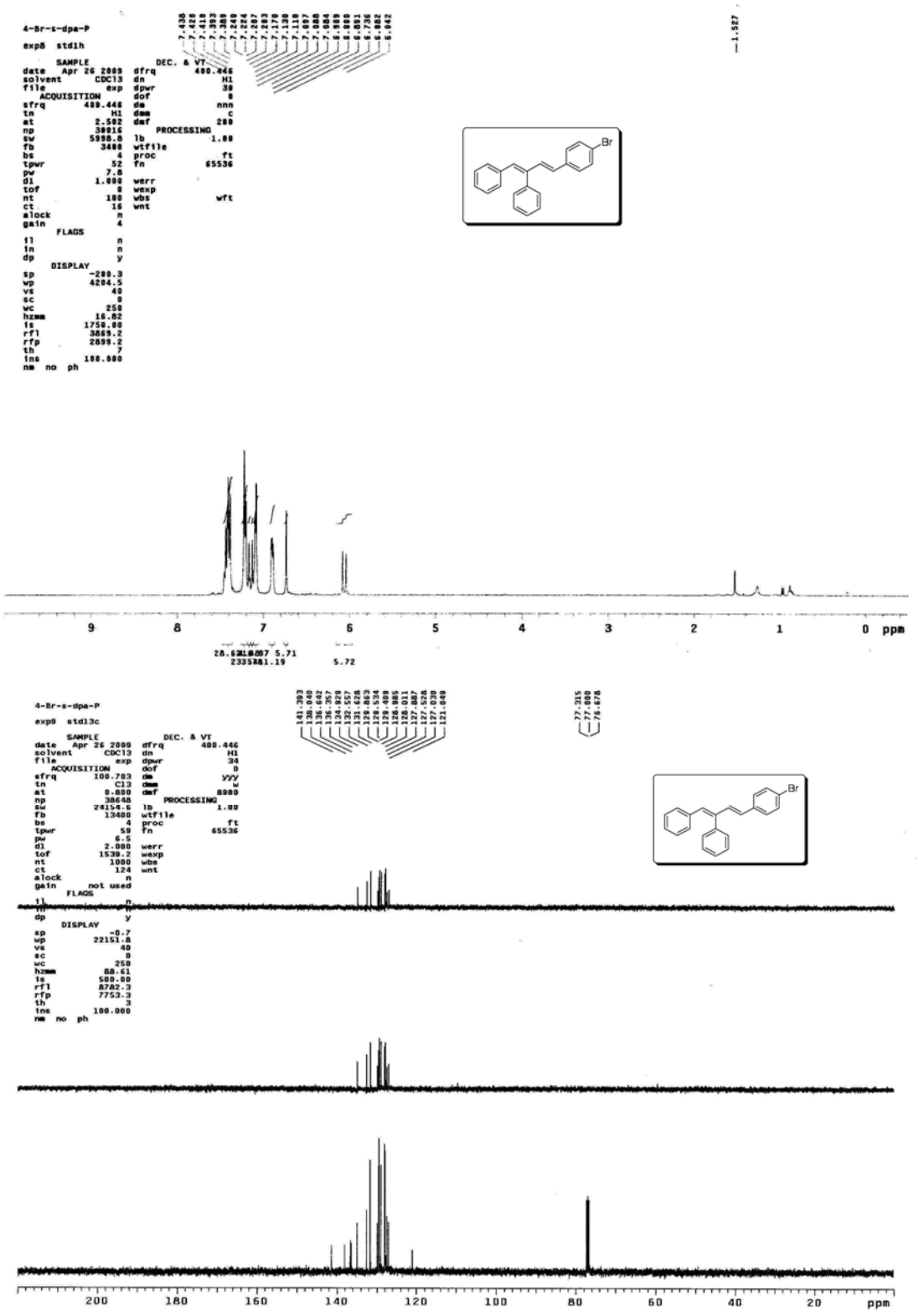
3p

Irradiation at	Observed enhancement (%)
H_a (δ 7.03, d)	H_c (10.73), no NOE for H_e and H_f
H_b (δ 6.35, d)	H_g (5.19)
H_c (δ 6.06, s)	H_a (9.77), no NOE for H_d

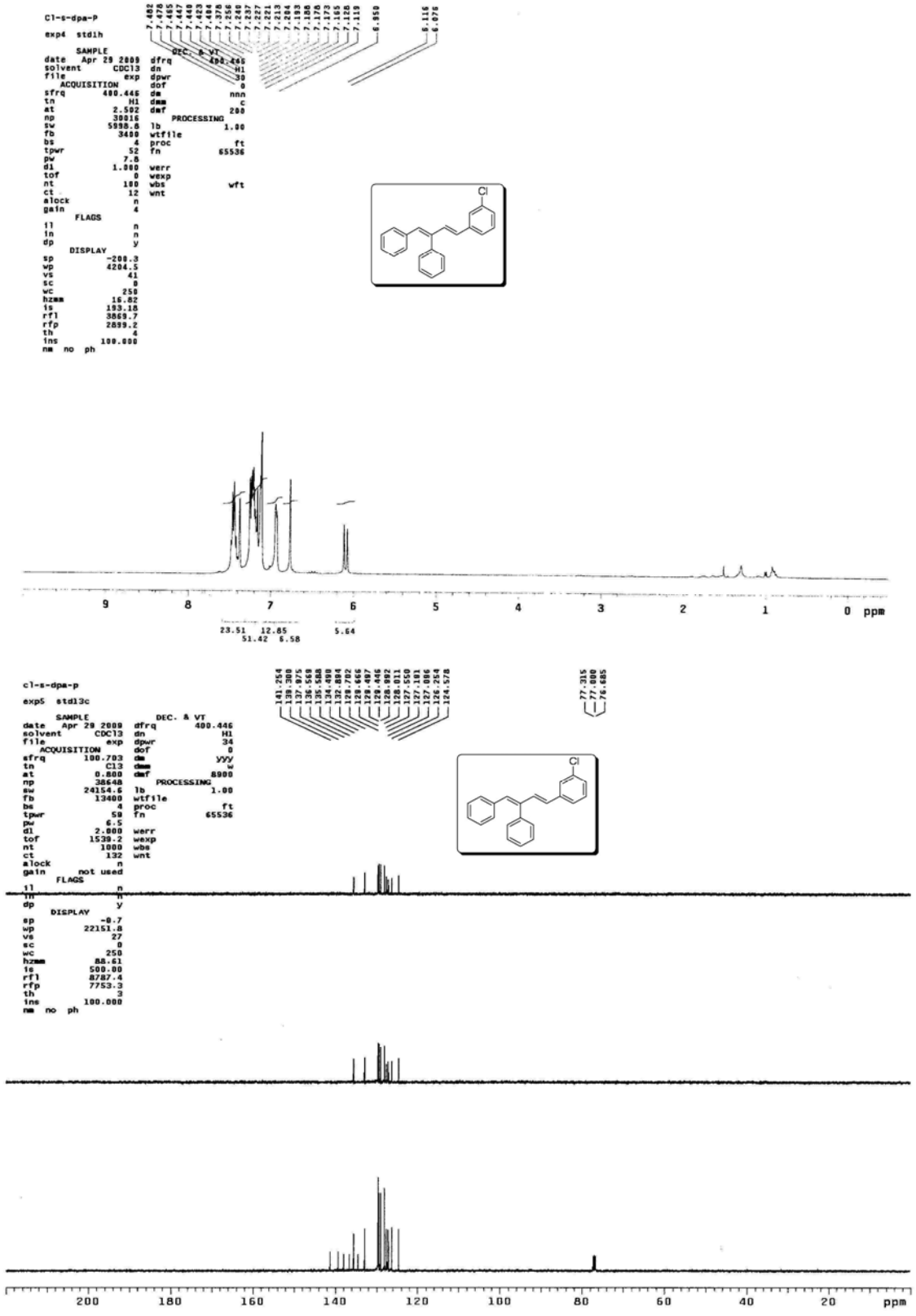
^{1}H and ^{13}C NMR spectra of compound **3a**



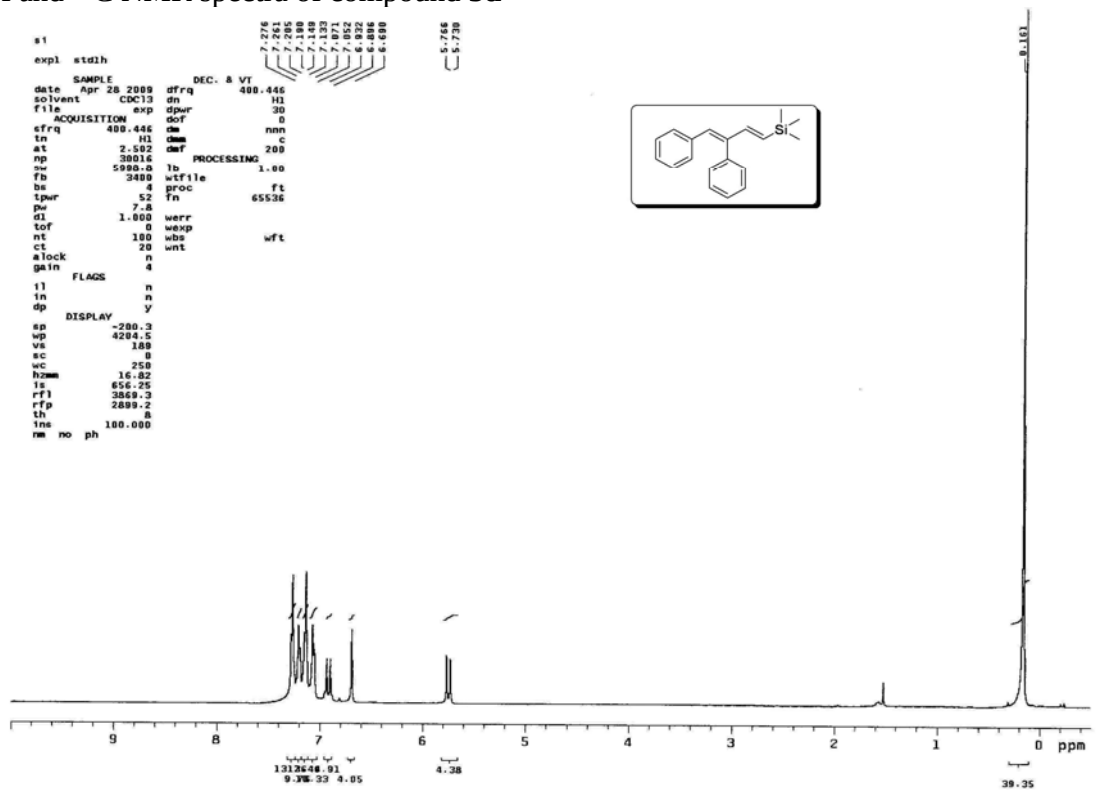
^{1}H and ^{13}C NMR spectra of compound **3b**

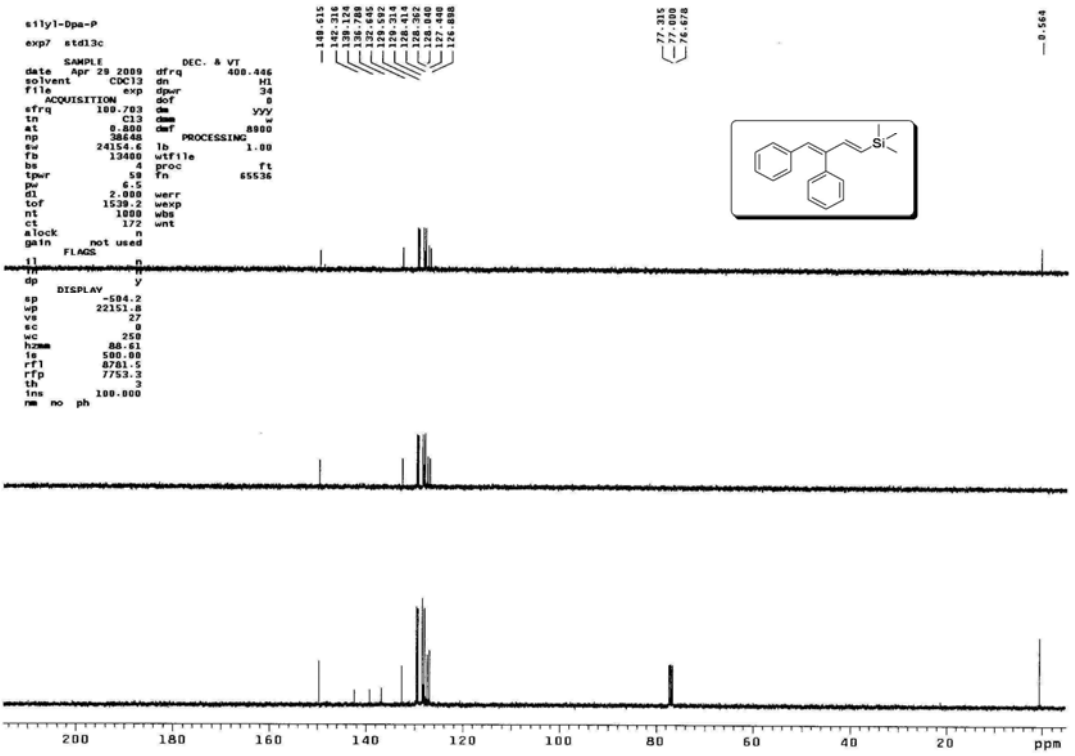


^{1}H and ^{13}C NMR spectra of compound **3c**

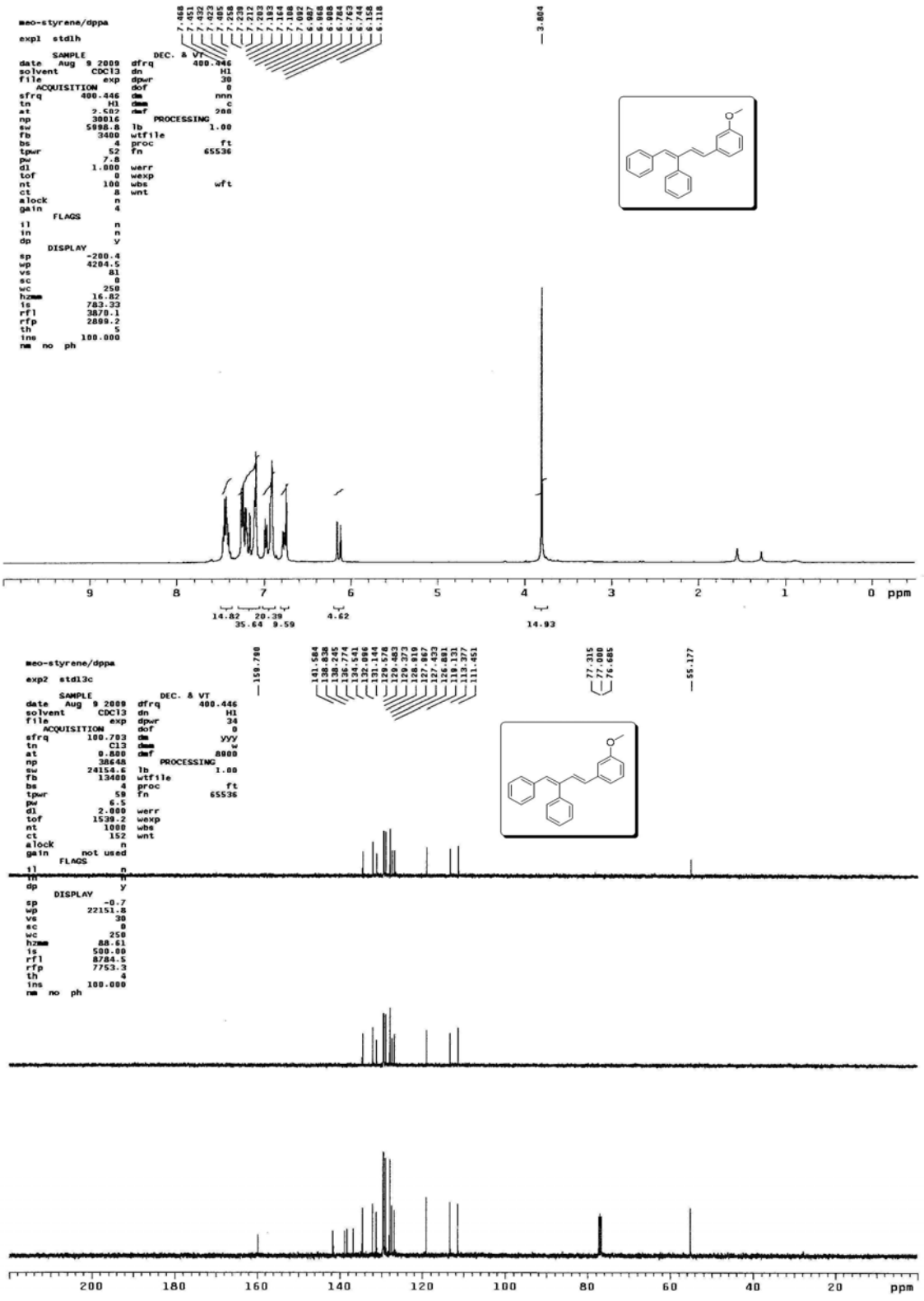


^{1}H and ^{13}C NMR spectra of compound **3d**

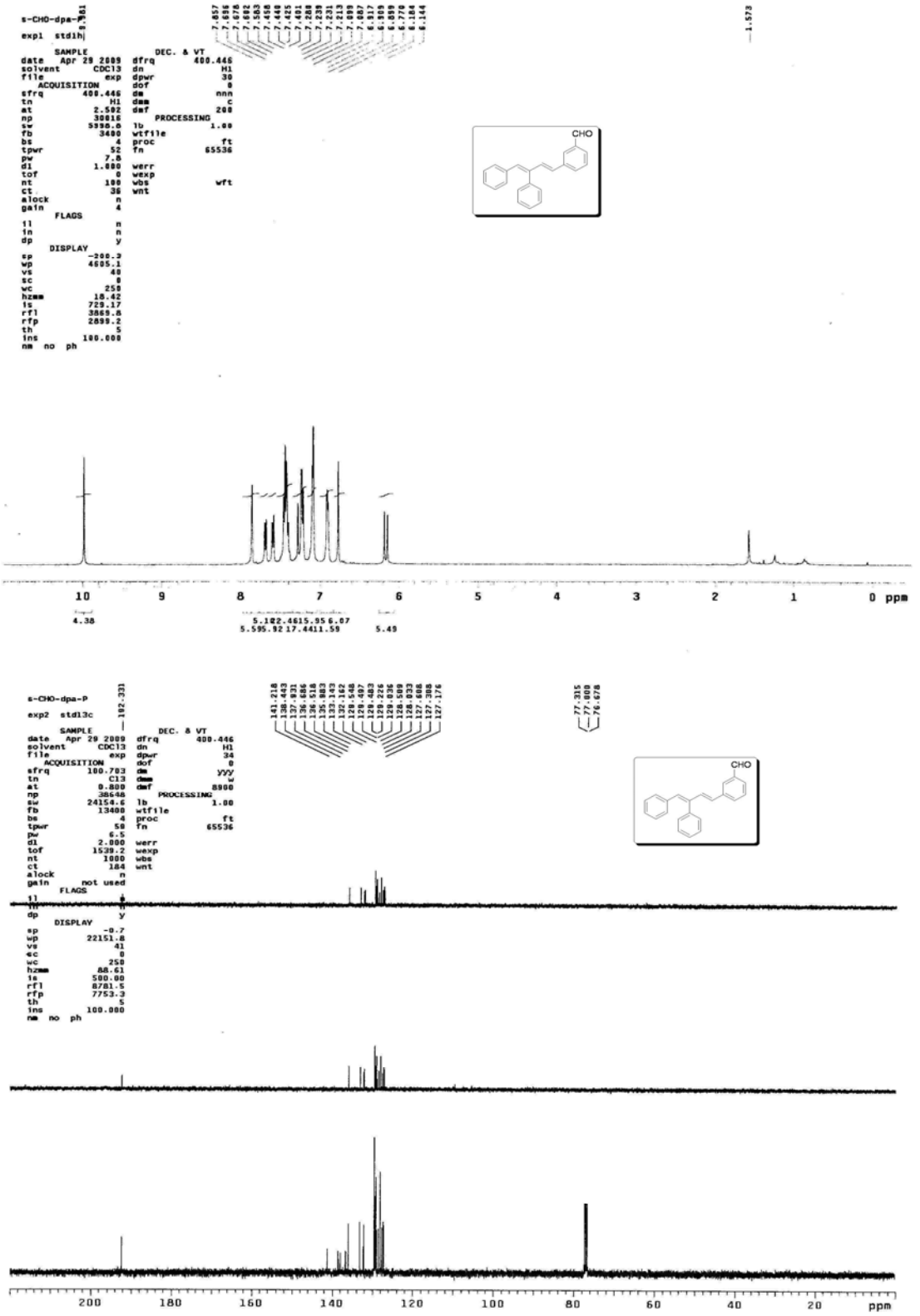




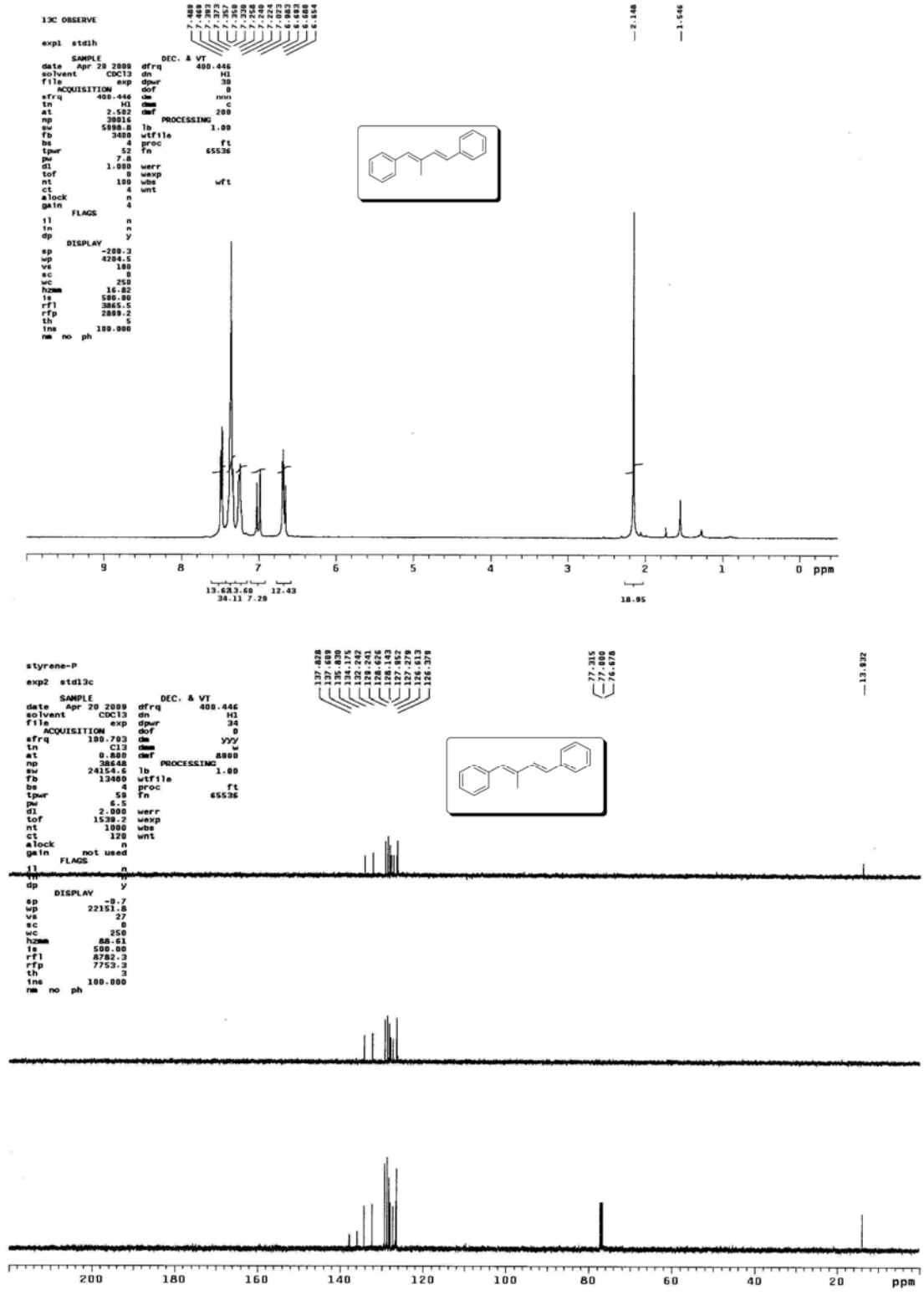
^{1}H and ^{13}C NMR spectra of compound **3e**



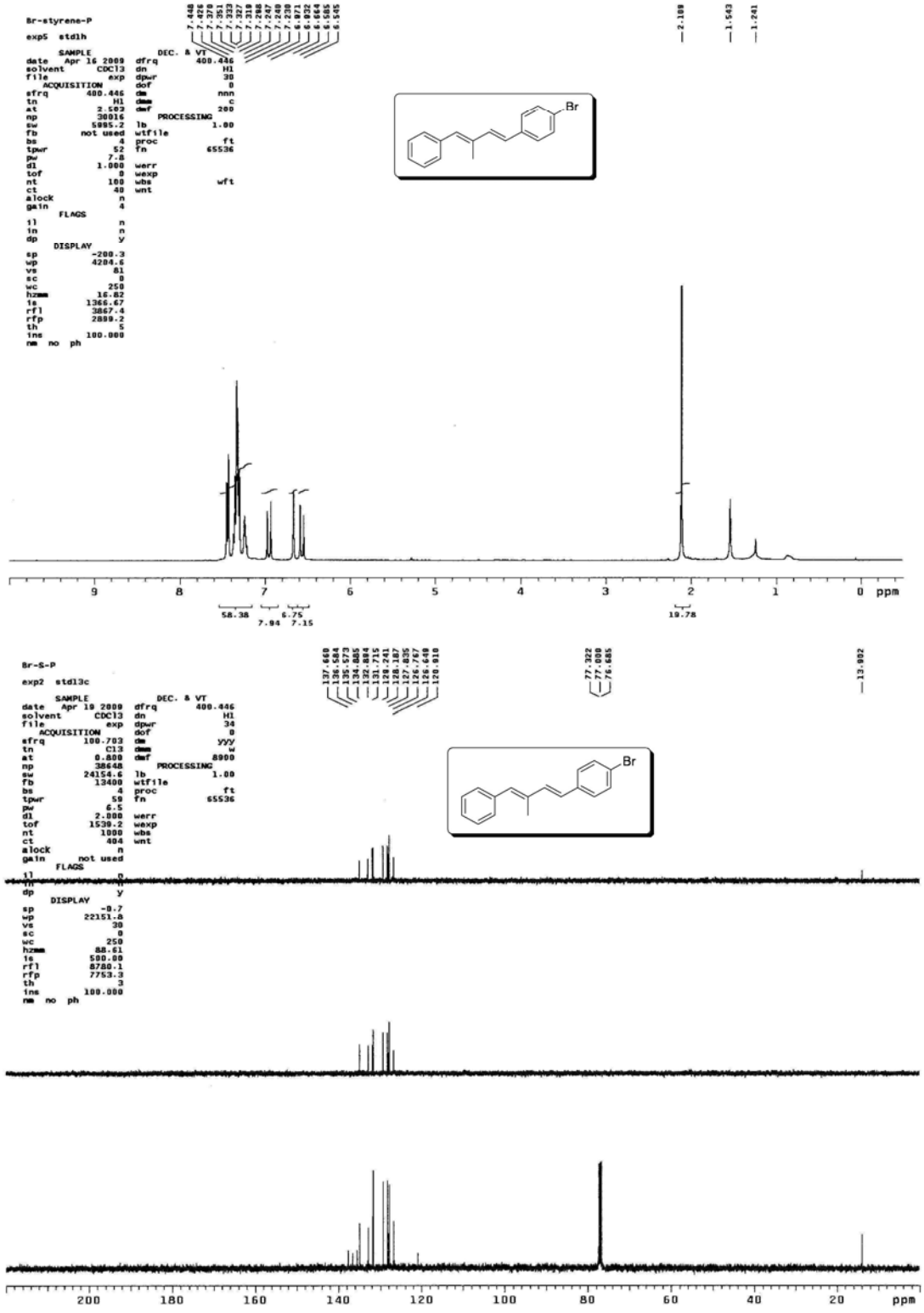
^{1}H and ^{13}C NMR spectra of compound **3f.**



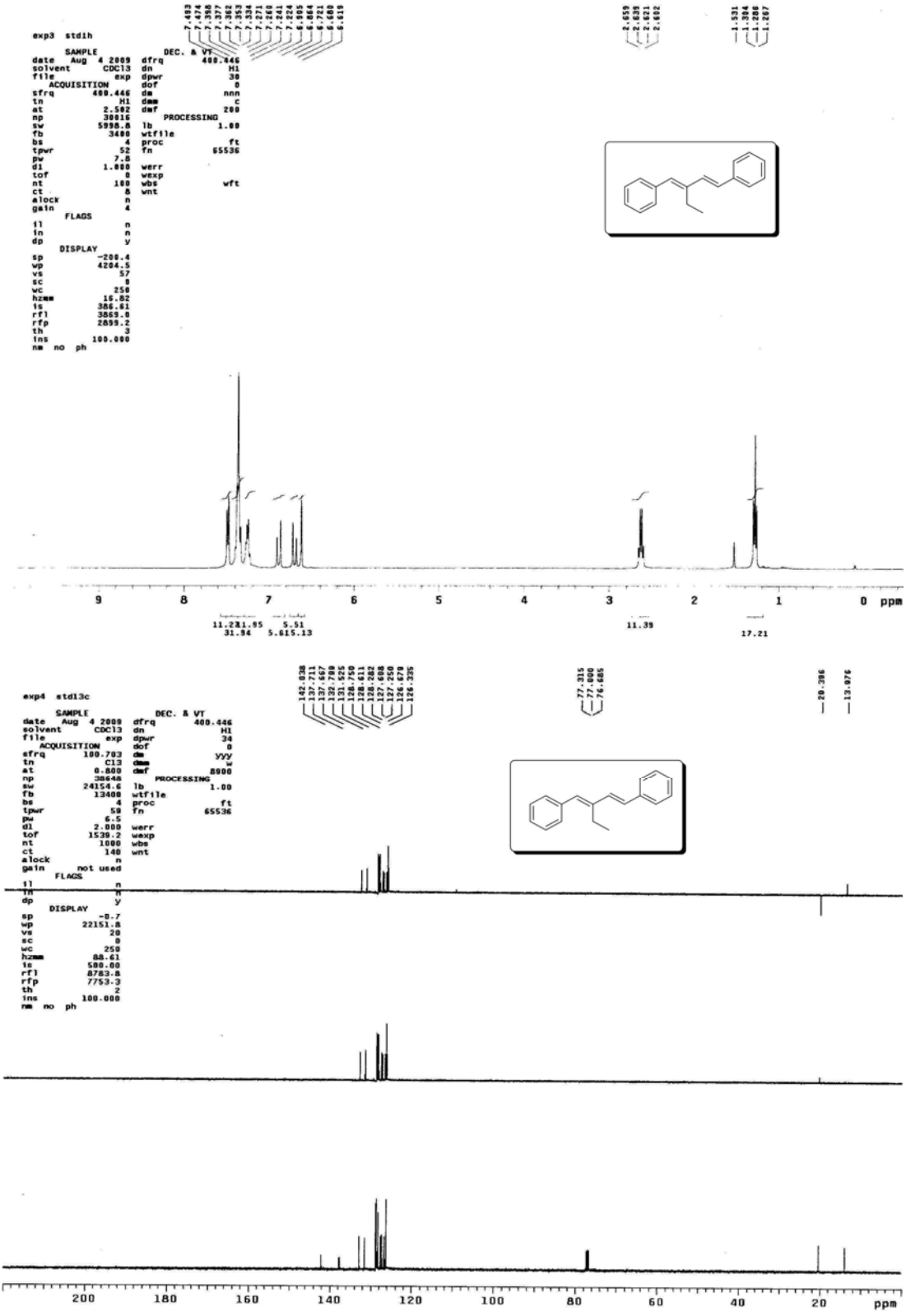
^{1}H and ^{13}C NMR spectra of compound **3g.**



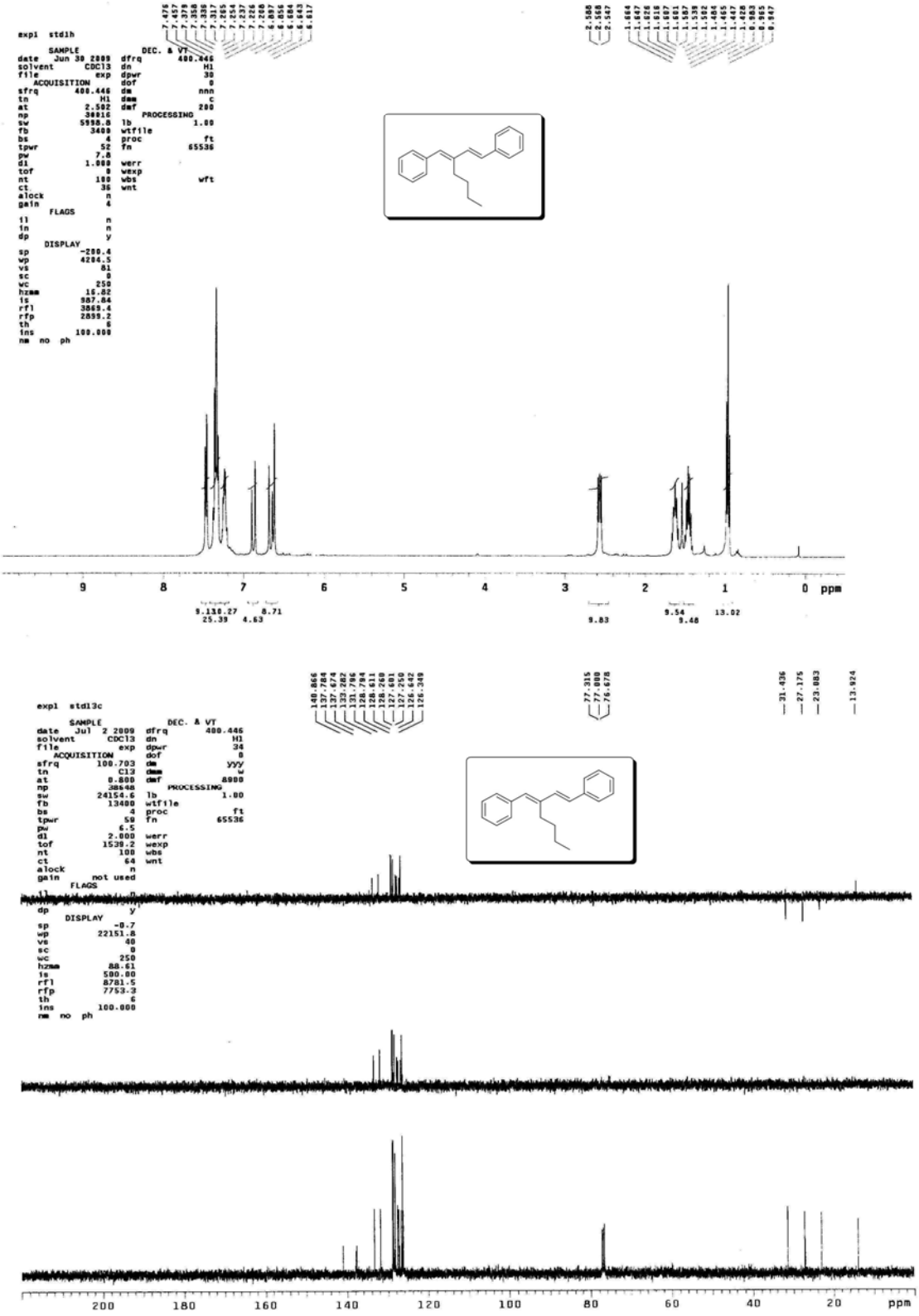
^{1}H and ^{13}C NMR spectra of compound **3h.**



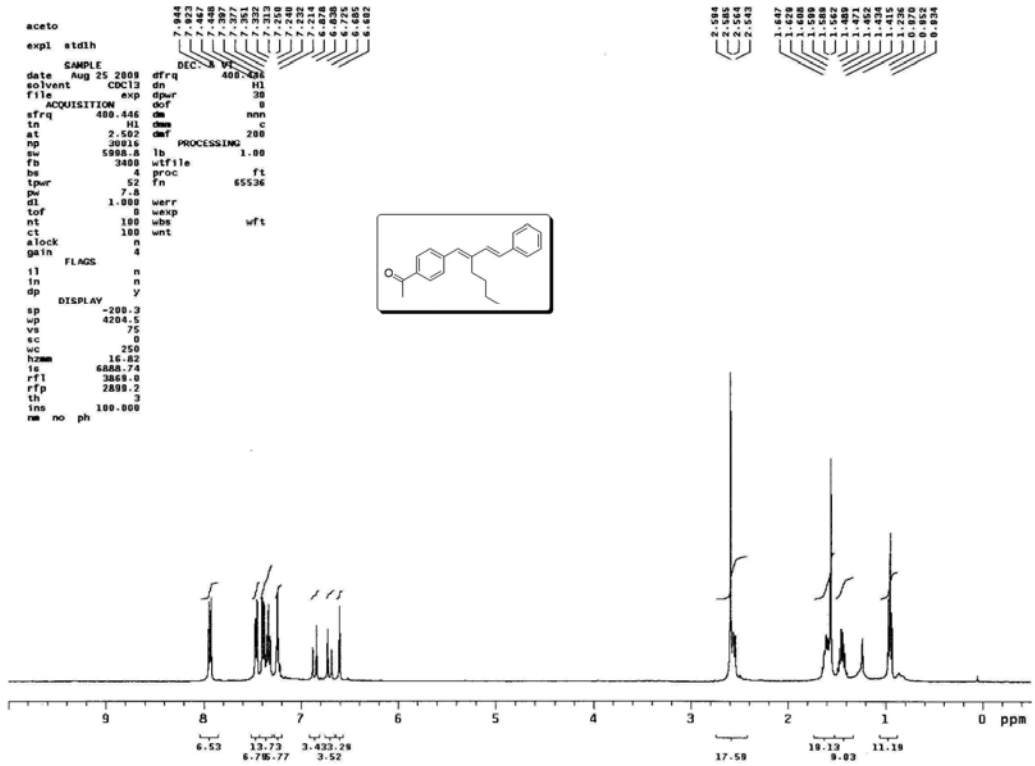
^{1}H and ^{13}C NMR spectra of compound **3i.**

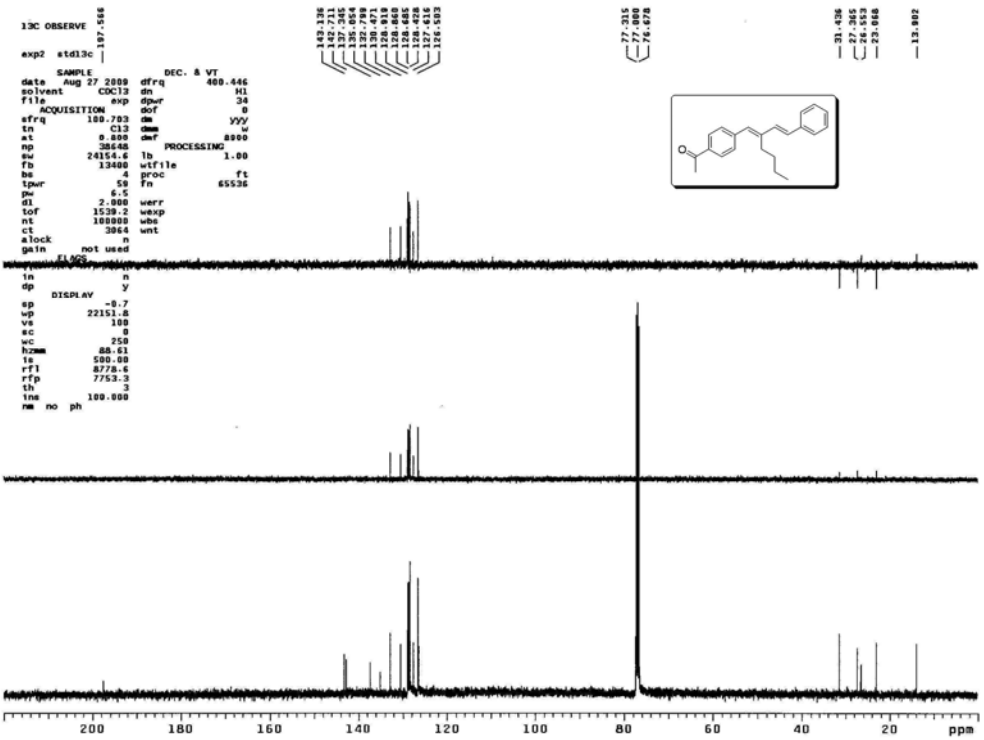


^{1}H and ^{13}C NMR spectra of compound **3j.**

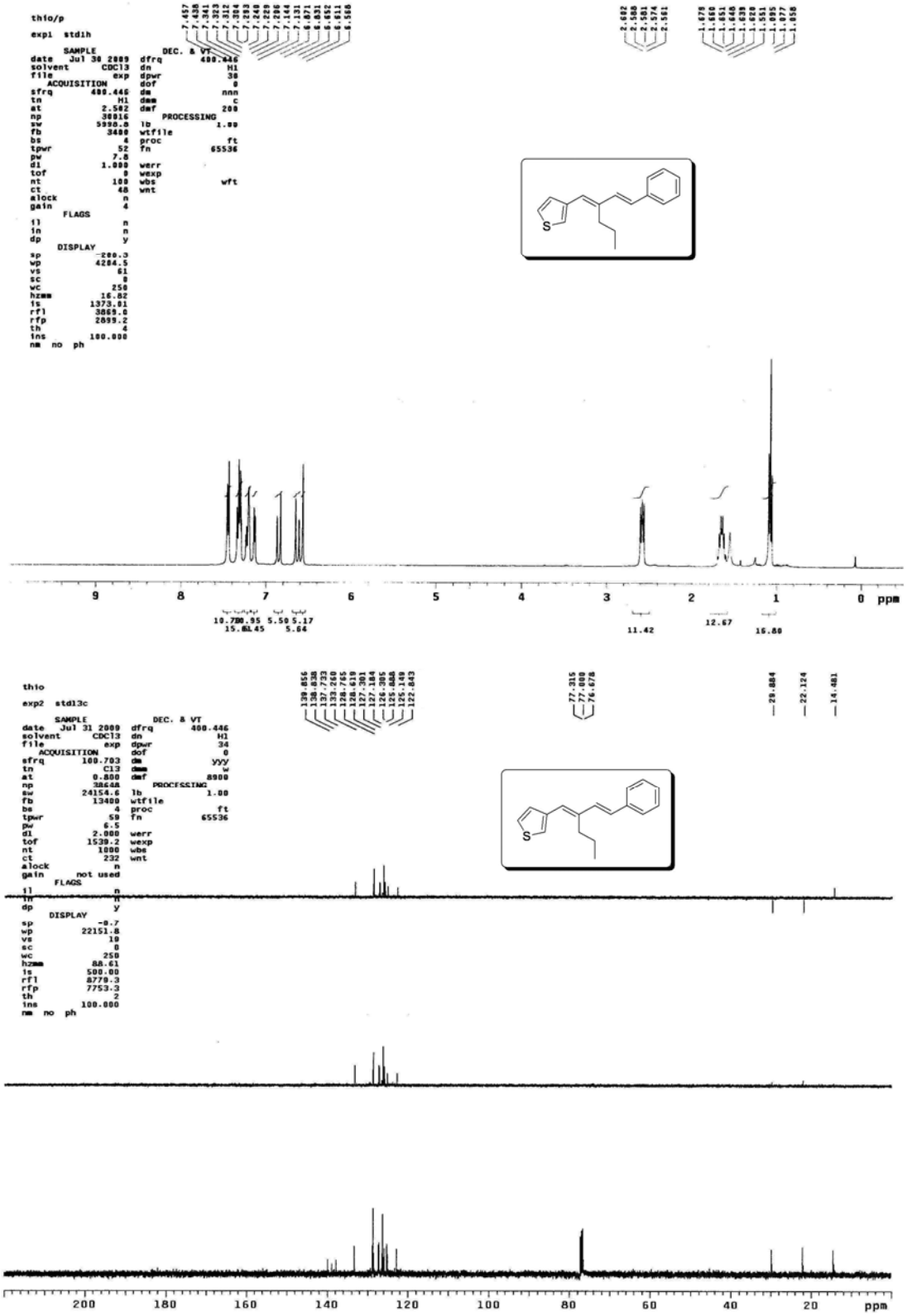


^{1}H and ^{13}C NMR spectra of compound **3k.**

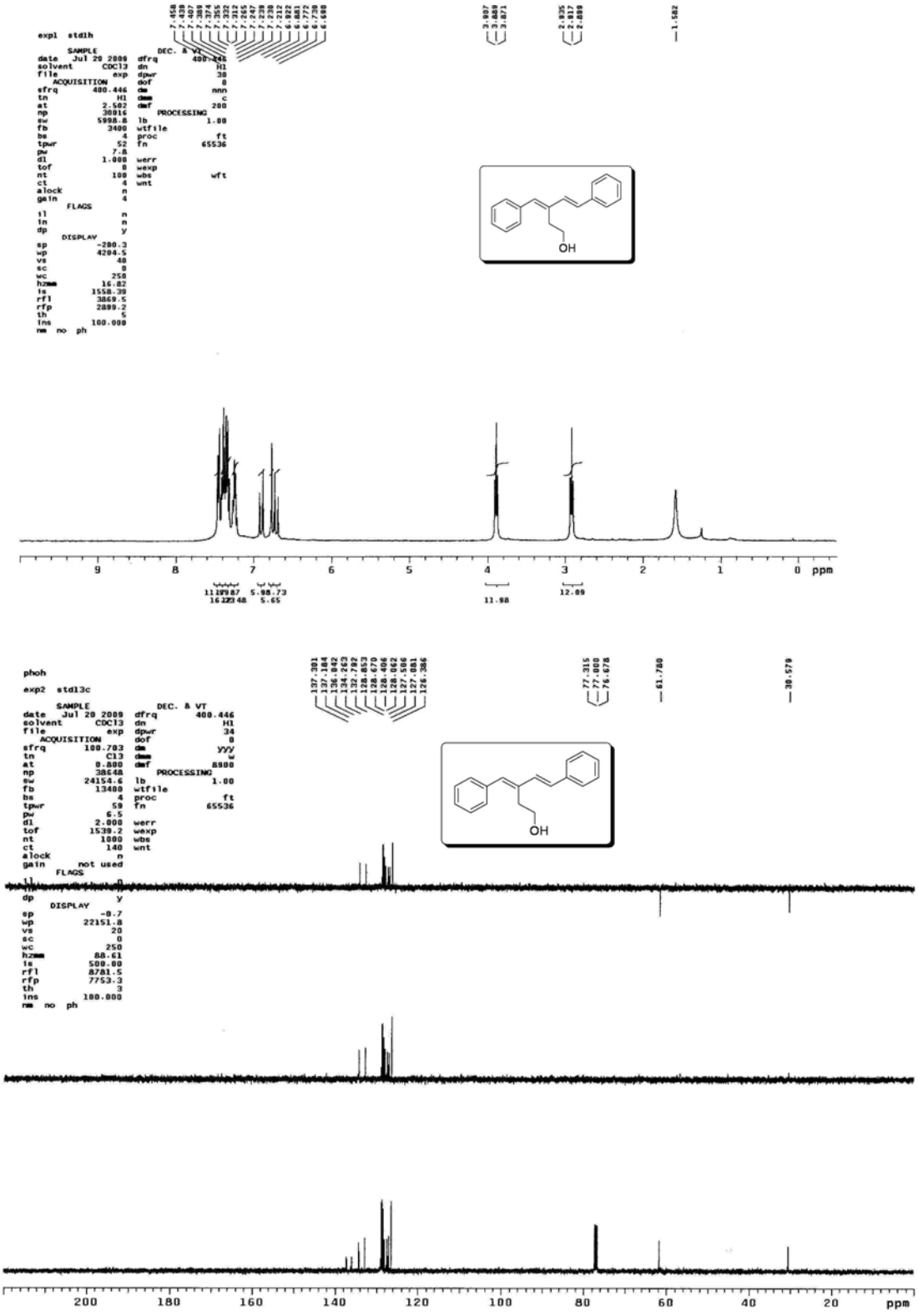




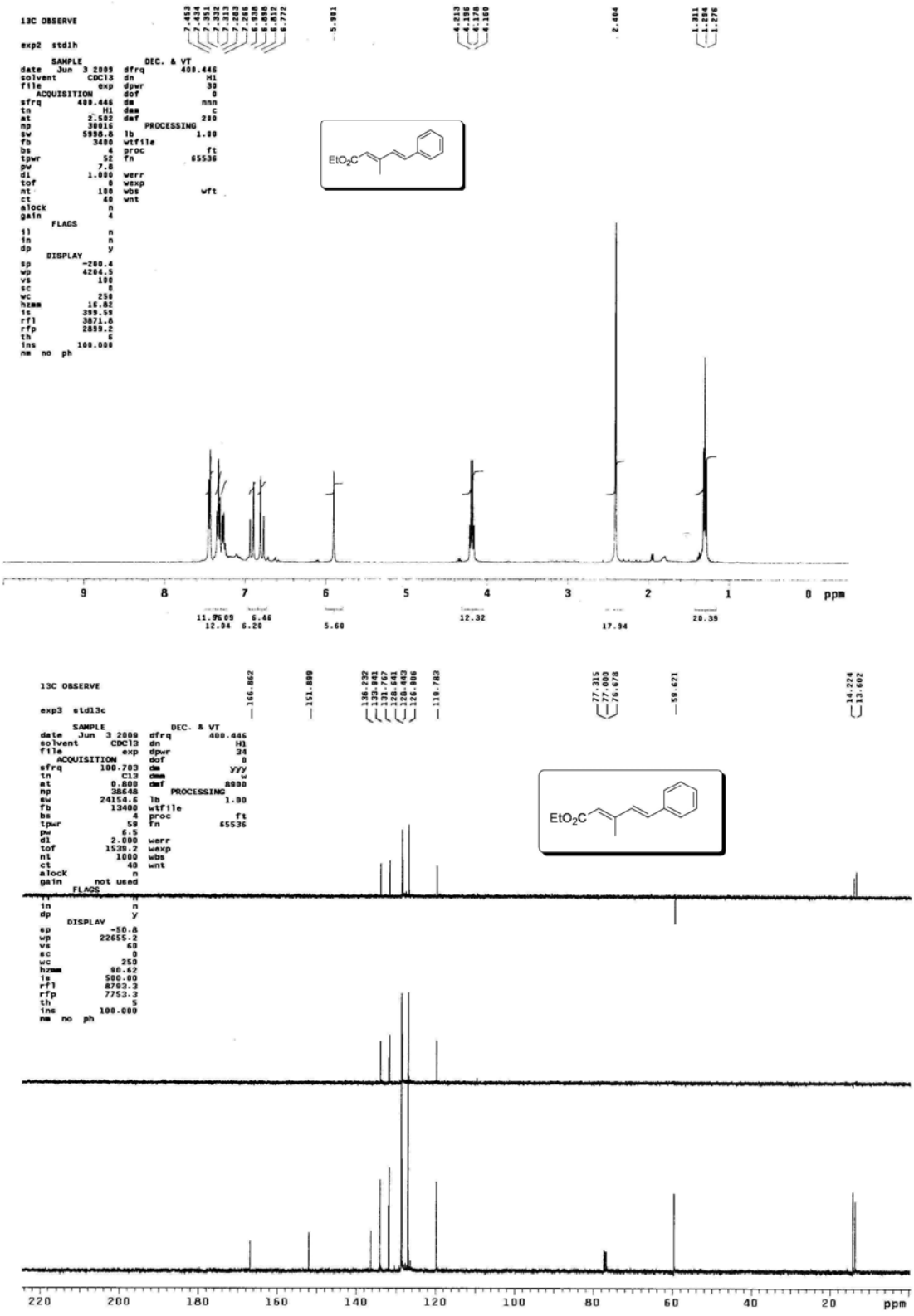
^{1}H and ^{13}C NMR spectra of compound **3l.**



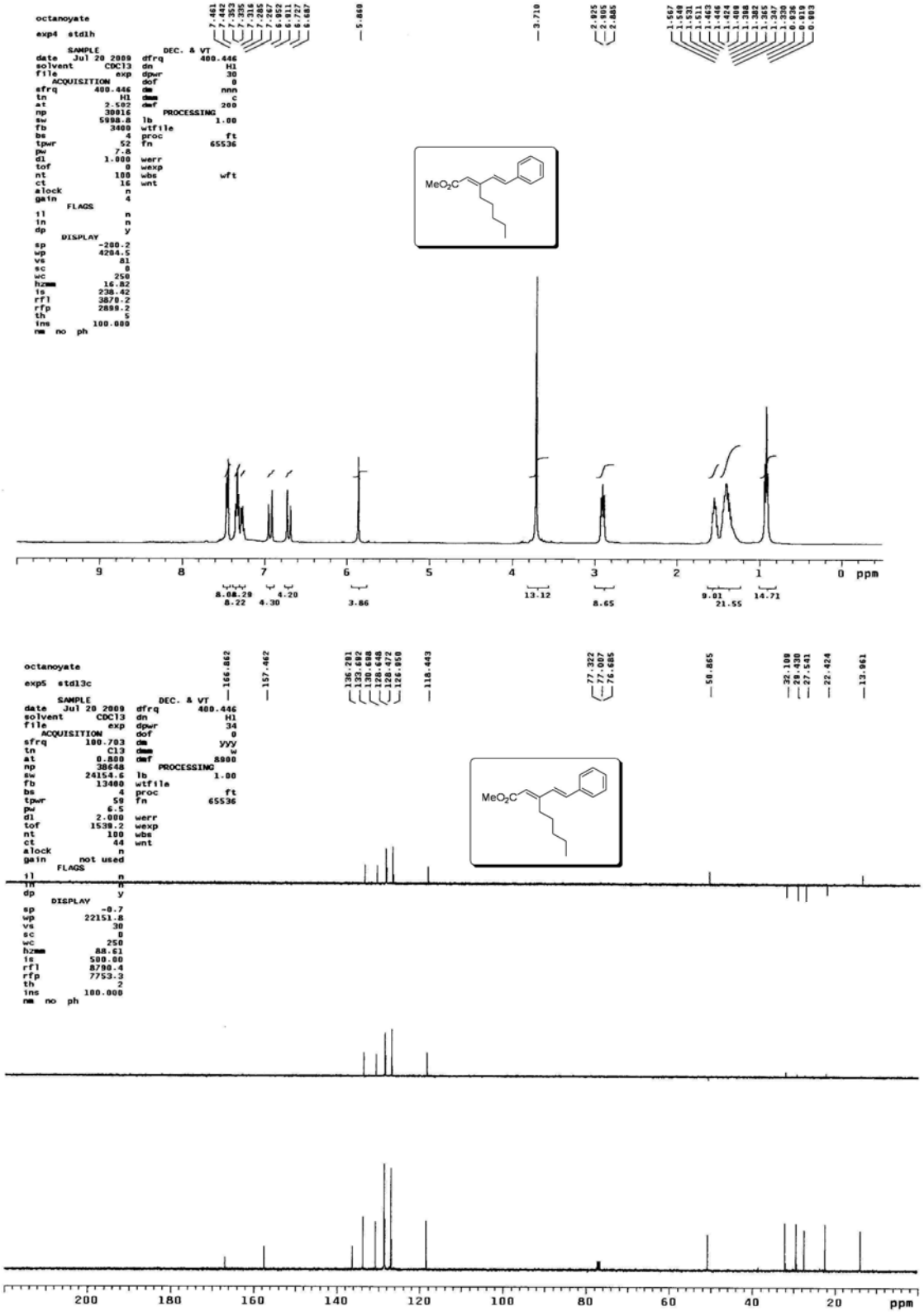
^{1}H and ^{13}C NMR spectra of compound **3m.**



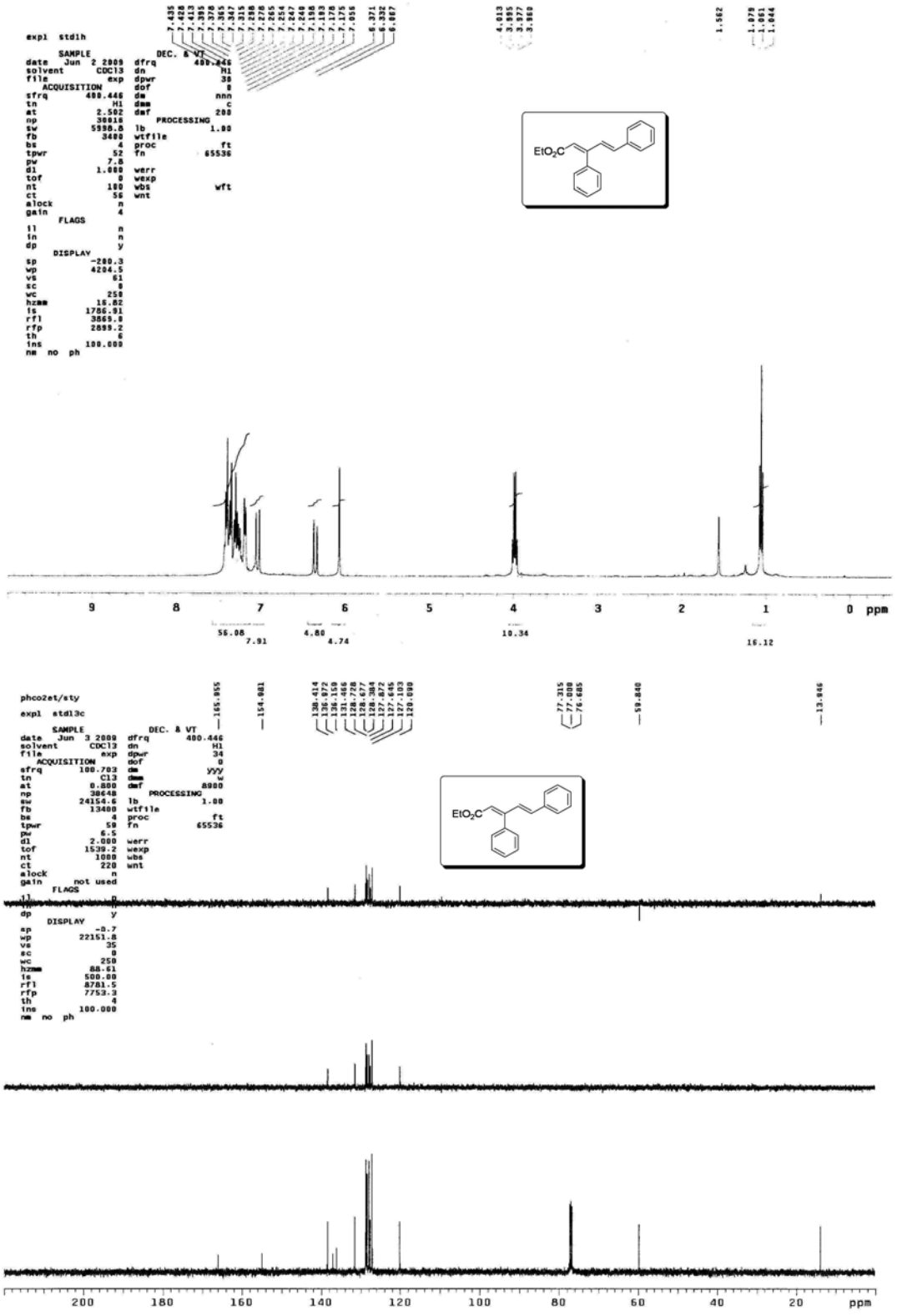
^{1}H and ^{13}C NMR spectra of compound **3n.**



^{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.**