Ruthenium-catalyzed highly regio- and stereoselective hydroarylation of aryl carbamates with alkynes via C-H bond activation

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Electronic Supplementary Information (ESI)

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Experimental Section

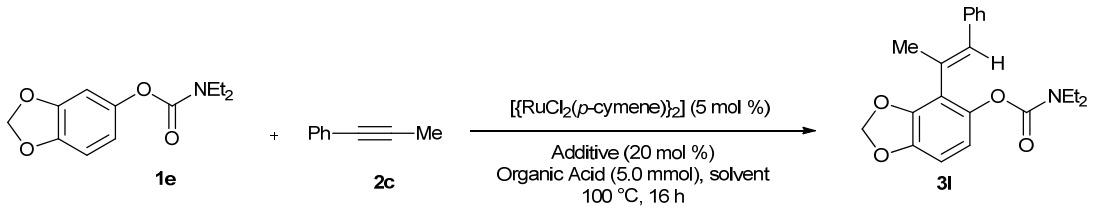
General procedure for the hydroarylation of aryl carbamates with alkynes catalyzed by ruthenium complex.

A 15-mL pressure tube equipped with a magnetic stirrer and septum containing [{$RuCl_2$(*p*-cymene)}$_2$] (0.05 mmol, 5 mol %) and $AgSbF_6$ (0.20 mmol, 20 mol %) was evacuated and purged with nitrogen gas three times. To the tube were then added carbamate (**1**) (1.00 mmol), alkyne **2** (1.50 mmol), pivalic acid (5.00 mmol) and 1,4-dioxane solvent (3.0 mL) via syringes and again the tube was evacuated and purged with nitrogen gas three times. Then, the septum was taken out and immediately a screw cap was used to cover the tube. The reaction mixture was allowed to stir at 100 °C for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **3**.

For the reaction of **1e** with all alkynes **2**, the reaction was done at 100 °C for 16 h.

Spectral data and copies of ^{1}H and ^{13}C NMR spectra of all compounds **3a-v** are listed below.

Table 1 Optimization Studies[a]

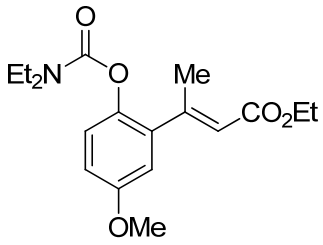


Entry	Solvent	Organic Acid	Additive	Yield of **3a** (%)[b]
1	DME	AcOH	$AgSbF_6$	63
2	DME	Pivalic acid	$AgSbF_6$	74
3	DME	CF_3COOH	$AgSbF_6$	45
4	DME	CF_3SO_3H	$AgSbF_6$	trace
5	DME	$PhSO_3H$	$AgSbF_6$	trace
6	DME	PhCOOH	$AgSbF_6$	52
7	1,4-dioxane	Pivalic acid	$AgSbF_6$	92
8	DCE	Pivalic acid	$AgSbF_6$	45
9	CH_3CN	Pivalic acid	$AgSbF_6$	55
10	THF	Pivalic acid	$AgSbF_6$	81
11	*tert*-BuOH	Pivalic acid	$AgSbF_6$	75
12	Toluene	Pivalic acid	$AgSbF_6$	trace
13	DMF	Pivalic acid	$AgSbF_6$	NR
14	MeOH	Pivalic acid	$AgSbF_6$	79
15	DMSO	Pivalic acid	$AgSbF_6$	NR
16	1,4-dioxane	Pivalic acid	KPF_6	NR
17	1,4-dioxane	Pivalic acid	No	NR

[a] All reactions were carried out under the following conditions: **1e** (1.0 mmol), **2c** (1.5 mmol), [{$RuCl_2$(*p*-cymene)}$_2$] (5 mol %), additive (20 mol %) and organic acid (5.0 mmol) in solvent (3.0 mL) at 100 °C for 16 h under N_2 atmosphere. [b] Yields were determined by the ^{1}H NMR integration method, using mesitylene as an internal standard.

Spectral Data of Compounds 3a-v

(*E*)-Ethyl 3-(2-((diethylcarbamoyl)oxy)-5-methoxyphenyl)but-2-enoate (**3a**).



Colorless semisolid; eluent (12% ethyl acetate in hexanes).

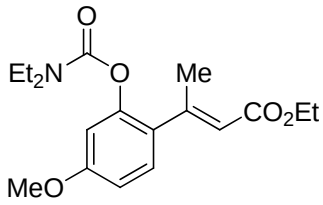
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2959, 1723, 1630, 1270 and 1194.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.01 (d, *J* = 8.0 Hz, 1 H), 6.82 (dd, *J* = 4.0 Hz, 1 H), 6.72 (d, *J* = 4.0 Hz, 1 H), 5.86 (s, 1 H), 4.16 (q, *J* = 8.0 Hz, 2 H) 3.77 (s, 3 H), 3.39 – 3.28 (m, 4 H), 2.43 (s, 3 H), 1.26 (t, *J* = 8.0 Hz, 3 H), 1.18 (t, *J* = 8.0 Hz, 3 H), 1.12 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 156.7, 154.2, 153.8, 141.4, 137.6, 124.1, 119.9, 114.1, 113.6, 59.8, 55.7, 42.2, 41.8, 19.8, 14.3, 14.2, 13.3.

HRMS (ESI): calc. for [($C_{18}H_{25}NO_5$)H] (M+H) 336.1811, measured 336.1812.

(*E*)-Ethyl 3-(2-((diethylcarbamoyl)oxy)-4-methoxyphenyl)but-2-enoate (**3b**).



Pale yellow oil; eluent (12% ethyl acetate in hexanes).

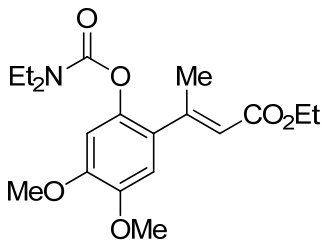
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2979, 1712, 1635, 1457, 1311 and 1163.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.14 (d, *J* = 8.0 Hz, 1 H), 6.73 (dd, *J* = 8.0 Hz, 1 H), 6.65 (s, 1 H), 5.85 (s, 1 H) 4.17 (q, *J* = 8.0 Hz, 2 H), 3.79 (s, 3 H), 3.39 – 3.30 (m, 4 H), 2.42 (s, 3 H), 1.26 (t, *J* = 8.0 Hz, 3 H), 1.20 (t, *J* = 8.0 Hz, 3 H), 1.15 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 160.1, 153.8, 153.6, 148.9, 129.3, 129.2, 119.3, 111.5, 108.8, 59.7, 55.5, 42.0, 41.8, 20.0, 14.4, 14.2, 13.3.

HRMS (ESI): calc. for [($C_{18}H_{25}NO_5$)H] (M+H) 336.1811, measured 336.1814.

(*E*)-Ethyl 3-(2-((diethylcarbamoyl)oxy)-4,5-dimethoxyphenyl)but-2-enoate (**3c**).



Pale yellow oil; eluent (10% ethyl acetate in hexanes).

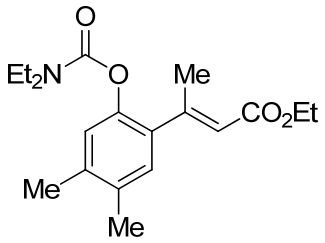
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2965, 1719, 1637 and 1155.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.69 (s, 1 H), 6.63 (s, 1 H), 5.87 (s, 1 H), 4.16 (q, *J* = 8.0 Hz, 2 H), 3.85 (s, 6 H) 3.39 – 3.28 (m, 4 H), 2.43 (s, 3 H), 1.27 (t, *J* = 4.0 Hz, 3 H), 1.19 (t, *J* = 8.0 Hz, 3 H), 1.15 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 154.0, 153.7, 149.1, 146.2, 141.4, 128.2, 119.4, 110.7, 107.0, 59.6, 56.2, 56.0, 42.0, 41.6, 19.8, 14.3, 14.1, 13.2.

HRMS (ESI): calc. for [($C_{19}H_{27}NO_6$)H] (M+H) 366.1917, measured 366.1917.

(*E*)-Ethyl 3-(2-((diethylcarbamoyl)oxy)-4,5-dimethylphenyl)but-2-enoate (**3d**).



Pale yellow oil; eluent (20% ethyl acetate in hexanes).

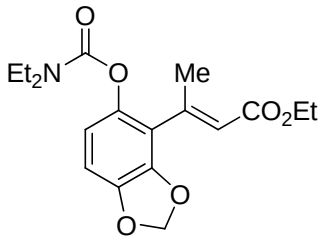
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2945, 1723, 1627, 1429 and 1155.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.97 (s, 1 H), 6.87 (s, 1 H), 5.85 (s, 1 H), 4.16 (q, *J* = 8.0 Hz, 2 H), 3.39 – 3.29 (m, 4 H), 2.42 (s, 3 H), 2.21 (s, 3 H), 2.20 (s, 3 H), 1.26 (t, *J* = 8.0 Hz, 3 H), 1.18 (t, *J* = 8.0 Hz, 3 H), 1.12 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.4, 153.0, 152.9, 144.4, 136.4, 132.8, 132.5, 128.3, 122.9, 118.2, 58.5, 40.9, 40.6, 18.7, 18.4, 17.9, 13.2, 12.9, 12.1.

HRMS (ESI): calc. for [($C_{19}H_{27}NO_4$)H] (M+H) 334.2018, measured 334.2014.

(*E*)-Ethyl 3-(5-((diethylcarbamoyl)oxy)benzo[*d*][1,3]dioxol-4-yl)but-2-enoate (**3e**).



Pale yellow semisolid; eluent (12% ethyl acetate in hexanes).

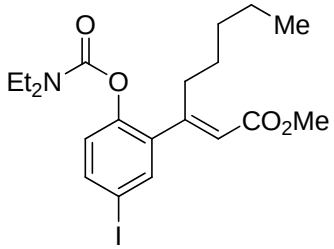
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2978, 1722, 1639, 1469, 1271, 1181, 1105 and 1034.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.68 (d, *J* = 8.0 Hz, 1 H), 6.54 (d, *J* = 8.0 Hz, 1 H), 5.94 (s, 2 H), 5.88 (s, 1 H), 4.14 (q, *J* = 8.0 Hz, 2 H), 3.36 – 3.25 (m, 4 H), 2.41 (s, 3 H), 1.24 (t, *J* = 8.0 Hz, 3 H), 1.15 (t, *J* = 8.0 Hz, 3 H), 1.09 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 154.1, 148.3, 144.98, 144.92, 142.4, 121.4, 120.2, 115.4, 107.3, 101.8, 59.8, 42.2, 41.8, 19.0, 14.3, 14.1, 13.2.

HRMS (ESI): calc. for [($C_{18}H_{23}NO_6$)Na] (M+Na) 372.1423, measured 372.1434.

(*E*)-Methyl 3-(2-((diethylcarbamoyl)oxy)-5-iodophenyl)oct-2-enoate (**3f**).



Colorless semisolid; eluent (18% ethyl acetate in hexanes).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2977, 1726, 1642, 1280, 1177 and 1045.

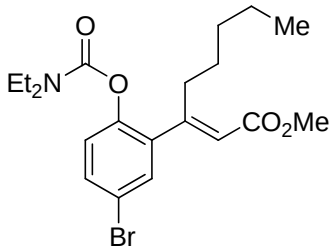
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (dd, *J* = 8.0, Hz, 1 H), 7.47 (s, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 5.78 (s, 1 H), 3.69 (s, 3 H), 3.36 – 3.28 (m, 4 H), 2.88 (d, *J* = 8.0 Hz, 2 H), 1.32 – 1.26 (m, 2 H), 1.25 – 1.23 (m, 4 H), 1.17 – 1.11 (m, 6 H), 0.81 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.1, 156.1, 152.2, 146.9, 136.5, 136.2, 124.3, 118.8, 87.9, 50.0, 41.1, 40.7, 31.4, 30.6, 26.7, 21.2, 12.9, 12.8, 12.0.

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.1, 156.1, 152.2, 146.9, 136.5, 136.2, 131.7, 129.8, 124.3, 118.8, 50.0, 41.1, 40.7, 31.4, 30.6, 26.7, 21.2, 12.9, 12.8, 12.0.

HRMS (ESI): calc. for [($C_{20}H_{28}INO_4$)H] (M+H) 474.1141, measured 474.1143.

(*E*)-Methyl 3-(5-bromo-2-((diethylcarbamoyl)oxy)phenyl)oct-2-enoate (**3g**).



Colorless semisolid; eluent (18% ethyl acetate in hexanes).

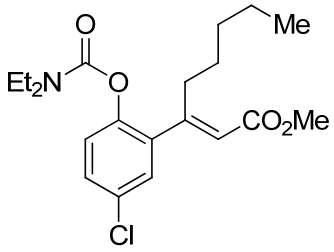
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2926, 1724, 1638, 1425, 1263 and 1121.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (dd, *J* = 8.0 Hz, 1 H), 7.28 (d, *J* = 4.0 Hz, 1 H), 7.02 (d, *J* = 8.0 Hz, 1 H), 5.78 (s, 1 H), 3.68 (s, 3 H), 3.33 – 3.29 (m, 4 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 1.32 -1.27 (m, 2 H), 1.25 – 1.22 (m, 4 H), 1.16 – 1.09 (m, 6 H), 0.80 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 157.3, 153.4, 147.2, 137.4, 131.7, 131.5, 125.2, 120.1, 118.1, 51.1, 42.3, 41.8, 32.6, 31.8, 27.9, 22.4, 14.1, 14.0, 13.2.

HRMS (ESI): calc. for [($C_{20}H_{28}BrNO_4$)H] (M+H) 426.1280, measured 426.1268.

(*E*)-Methyl 3-(5-chloro-2-((diethylcarbamoyl)oxy)phenyl)oct-2-enoate (**3h**).



Pale yellow semisolid; eluent (14% ethyl acetate in hexanes).

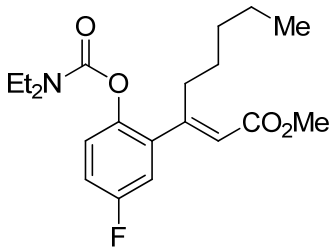
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2979, 1735, 1641, 1423, 1320, 1221, 1154 and 1035.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 (dd, *J* = 8.0, Hz, 1 H), 7.13 (s, 1 H), 7.06 (d, *J* = 8.0, Hz, 1 H), 5.78 (s, 1 H), 3.68 (s, 3 H), 3.36 – 3.27 (m, 4 H), 2.89 (t, *J* = 8.0 Hz, 2 H), 1.33 – 1.27 (m, 2 H), 1.26 – 1.22 (m, 4 H), 1.16 – 1.10 (m, 6 H), 0.80 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 157.4, 153.5, 146.7, 137.0, 130.5, 128.7, 128.6, 124.9, 120.0, 51.1, 42.3, 41.8, 32.6, 31.8, 27.9, 22.4, 14.1, 14.0, 13.2.

HRMS (ESI): calc. for [($C_{20}H_{28}ClNO_4$)H] (M+H) 382.1785, measured 382.1786.

(*E*)-Methyl 3-(2-((diethylcarbamoyl)oxy)-5-fluorophenyl)oct-2-enoateMethyl (**3i**).



Dark brown oil; eluent (12% ethyl acetate in hexanes).

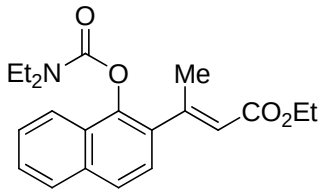
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2978, 1721, 1633, 1427, 1375, 1269, 1182 and 1080.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.09 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.99 (dd, *J* = 4.0, 4.0 Hz, 1 H, F – coupling), 6.87 (dd, *J* = 8.0, 4.0 Hz, 1 H, F – coupling), 5.80 (s, 1 H), 3.69 (s, 3 H), 3.36 – 3.28 (m, 4 H), 2.90 (t, *J* = 8.0 Hz, 2 H), 1.34 -1.32 (m, 2 H), 1.26 – 1.23 (m, 4 H), 1.17 – 1.10 (m, 6 H), 0.81 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 160.8, 158.3, 157.5, 153.8, 144.1 and 144.0 (F – coupling), 137.5 and 136.9 (F – coupling), 125.0 and 124.9 (F – coupling), 120.0, 115.57 and 115.52 (F – coupling), 115.52 and 115.3 (F – coupling)), 51.5, 42.2, 41.8, 32.6, 31.8, 27.9, 22.4, 14.1, 14.0, 13.2.

HRMS (ESI): calc. for [($C_{20}H_{28}FNO_4$)H] (M+H) 366.2081, measured 366.2076.

(*E*)-Ethyl 3-(1-((diethylcarbamoyl)oxy)naphthalen-2-yl)but-2-enoate(**3j**).



Pale yellow oil; eluent (18% ethyl acetate in hexanes).

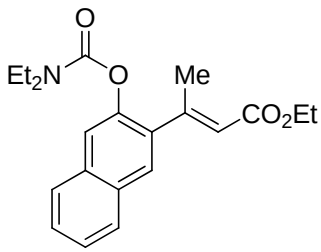
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2969, 1721, 1615, 1505, 1419, 1266, 1159 and 1033.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, *J* = 8.0 Hz, 1 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.70 (d, *J* = 8.0, Hz, 1 H), 7.53 – 7.46 (m, 2 H), 7.32 (d, *J* = 8.0 Hz, 1 H), 5.98 (s, 1 H), 4.19 (q, *J* = 8.0 Hz, 2 H), 3.55 (q, *J* = 8.0 Hz, 2 H), 3.37 (q, *J* = 8.0 Hz, 2 H), 2.53, (s, 3 H), 1.34 (t, *J* = 8.0 Hz, 3 H), 1.28 (t, *J* = 8.0 Hz, 3 H), 1.17 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 153.9, 153.6, 143.2, 134.1, 133.1, 128.1, 127.8, 126.8, 126.6, 125.6, 125.4, 122.0, 120.3, 59.8, 42.4, 42.1, 19.9, 14.4, 14.2, 13.3.

HRMS (ESI): calc. for [($C_{21}H_{25}NO_4$)H] (M+H) 356.1862, measured 356.1860.

(*E*)-Ethyl 3-(3-((diethylcarbamoyl)oxy)naphthalen-2-yl)but-2-enoate (**3k**).



Dark yellow semisolid; eluent (12% ethyl acetate in hexanes).

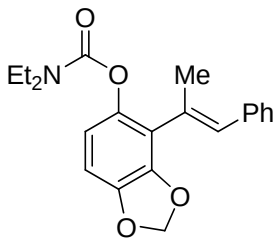
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2975, 1723, 1637, 1178 and 1054.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 8.0 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 1), 7.63 (s, 1 H), 7.52 (s, 1 H), 7.39 – 7.36 (m, 2 H), 5.92 (s, 1 H), 4.14 (q, *J* = 8.0 Hz, 2 H), 3.40 – 3.27 (m, 4 H), 2.48 (s, 3 H), 1.23 (t, *J* = 8.0 Hz, 3 H), 1.17 (t, *J* = 8.0 Hz, 3 H), 1.10 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 154.0, 153.8, 145.9, 136.5, 133.3, 130.9, 127.7, 127.2, 126.7, 125.8, 120.1, 120.0, 59.7, 42.1, 41.8, 20.1, 14.2, 14.1, 13.2.

HRMS (ESI): calc. for [($C_{21}H_{25}NO_4$)H] (M+H) 356.1862, measured 356.1860.

(*E*)-4-(1-Phenylprop-1-en-2-yl)benzo[*d*][1,3]dioxol-5-yl diethylcarbamate (**3l**).



Colorless semisolid; eluent (12% ethyl acetate in hexanes).

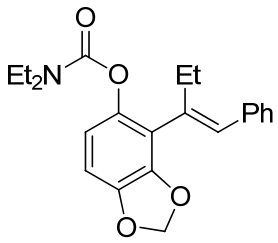
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2928, 1638, 1469, 1318, 1273, 1160, 1103 and 1035.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 – 7.32 (m, 4 H), 7.24 – 7.20 (m, 1 H), 6.70 (d, *J* = 8.0, Hz, 1 H), 6.60 (d, *J* = 8.0 Hz, 1 H), 6.54 (s, 1 H), 5.97 (s, 2 H), 3.31 – 3.30 (m, 4 H), 2.18 (s, 3 H), 1.12 – 1.07 (m, 6 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.5, 145.2, 144.7, 143.1, 137.4, 131.4, 129.4, 129.0, 128.1, 126.7, 122.1, 115.3, 106.3, 101.5, 42.1, 41.8, 18.1, 14.1, 13.3.

HRMS (ESI): calc. for [($C_{21}H_{23}NO_4$)H] (M+H) 354.1719, measured 354.1705.

(*E*)-4-(1-Phenylbut-1-en-2-yl)benzo[*d*][1,3]dioxol-5-yl diethylcarbamate (3m).



Pale yellow liquid; eluent (8% ethyl acetate in hexanes).

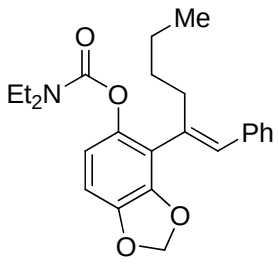
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2959, 1646, 1582, 1329, 1271, and 1175.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 – 7.28 (m, 4 H), 7.22 (t, *J* = 8.0 Hz, 1 H), 6.72 (d, *J* = 8.0 Hz, 1 H), 6.70 (d, *J* = 8.0 Hz, 1 H), 6.52 (s, 1 H), 5.95 (s, 2 H), 3.37 – 3.29 (m, 4 H), 2.61 (q, *J* = 8.0 Hz, 2 H), 1.20 (q, *J* = 8.0 Hz, 3 H), 1.07 (q, *J* = 8.0 Hz, 3 H), 1.02 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.7, 145.6, 144.6, 143.8, 137.4, 135.6, 131.1, 128.8, 128.2, 126.8, 120.5, 115.8, 106.5, 101.5, 42.2, 41.8, 24.5, 14.2, 13.4, 13.1.

HRMS (ESI): calc. for [($C_{22}H_{25}NO_4$)H] (M+H) 368.1862, measured 368.1863.

(*E*)-4-(1-Phenylhex-1-en-2-yl)benzo[*d*][1,3]dioxol-5-yl diethylcarbamate (3n).



Pale yellow liquid; eluent (8% ethyl acetate in hexanes).

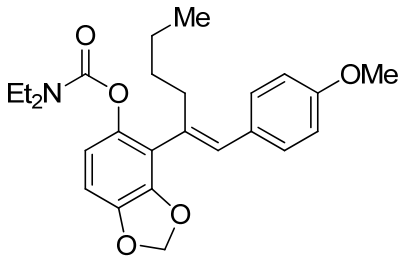
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2959, 1636 and 1229.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 – 7.27 (m, 4 H), 7.21 (t, *J* = 8.0 Hz, 1 H), 6.71 (d, *J* = 8.0 Hz, 1 H), 6.62 (d, *J* = 8.0 Hz, 1 H), 6.53 (s, 1 H), 5.96 (s, 2 H), 3.38 – 3.30 (m, 4 H), 2.57 (t, *J* = 8.0 Hz, 2 H), 1.41 – 1.38 (m, 2 H), 1.31 – 1.25 (m, 2 H), 1.15 – 1.07 (m, 6 H), 0.83 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.7, 145.5, 144.6, 143.6, 137.5, 134.5, 131.5, 128.9, 128.2, 126.7, 120.8, 115.9, 106.5, 101.5, 42.2, 41.8, 31.1, 30.6, 22.8, 14.2, 13.9, 13.4.

HRMS (ESI): calc. for [($C_{24}H_{29}NO_4$)H] (M+H) 396.2175, measured 396.2189.

(*E*)-4-(1-(4-Methoxyphenyl)hex-1-en-2-yl)benzo[*d*][1,3]dioxol-5-yl (**3o**).



Colorless semisolid; eluent (13% ethyl acetate in hexanes).

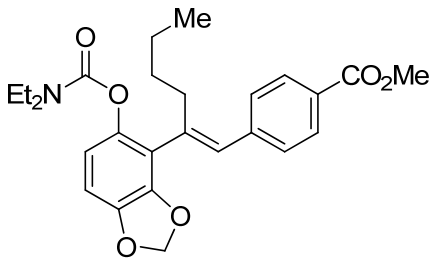
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2978, 1637, 1319, 1277, 1163 and 1107.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (d, *J* = 8.0 Hz, 2 H), 6.86 (d, *J* = 8.0 Hz, 2 H), 6.70 (d, *J* = 8.0, Hz, 1 H), 6.61 (d, *J* = 8.0, Hz, 1 H), 6.44 (s, 1 H), 5.95 (s, 2 H), 3.80 (s,, 3 H), 3.32 – 3.28 (m, 4 H), 2.56 (t, *J* = 8.0 Hz, 2 H), 1.40 – 1.35 (m, 2 H), 1,31 – 1.28 (m, 2 H), 1.13 – 1.05 (m, 6 H), 0.83 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 154.7, 145.4, 144.5, 143.6, 132.9, 130.9, 130.0, 121.0, 115.8, 113.6, 106.3, 101.4, 55.2, 42.1, 41.7, 31.0, 30.6, 22.8, 14.1, 13.9, 13.3.

HRMS (ESI): calc. for [($C_{25}H_{31}NO_5$)H] (M+H) 426.2280, measured 426.2275.

(*E*)-Methyl4-(2-(5-((diethylcarbamoyl)oxy)benzo[*d*][1,3]dioxol-4-yl)hex-1-en-1-yl)benzoate (**3p**).



Colorless semisolid; eluent (17% ethyl acetate in hexanes).

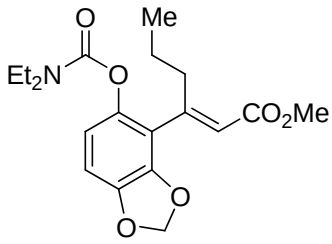
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2977, 1719, 1637, 1469, 1267, 1177 and 1068.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 6.72 (d, *J* = 8.0 Hz, 1 H), 6.61 (d, *J* = 8.0 Hz, 1 H), 6.54 (s, 1 H), 5.96 (s, 2 H), 3.90 (s, 3 H), 3.32 – 3.28 (m, 4 H), 2.55 (t, *J* = 8.0 Hz, 2 H), 1.38 – 1.36 (m, 2 H), 1.30 – 1.26 (m, 2 H), 1.12 – 1.04 (m, 6 H), 0.81 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.0, 154.6, 145.4, 144.6, 143.4, 142.2, 136.7, 130.6, 129.5, 128.7, 128.2, 120.3, 115.8, 106.7, 101.5, 52.1, 42.1, 41.7, 31.2, 30.4, 22.7, 14.2, 13.9, 13.3.

HRMS (ESI): calc. for [($C_{26}H_{31}NO_6$)H] (M+H) 454.2236, measured 454.2227.

(*E*)-Methyl 3-(5-((diethylcarbamoyl)oxy)benzo[*d*][1,3]dioxol-4-yl)hex-2-enoate (**3q**).



Colorless oil; eluent (12% ethyl acetate in hexanes).

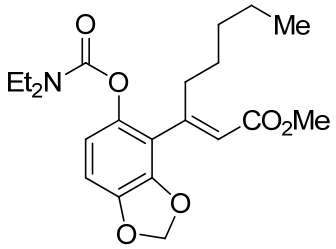
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2967, 1631, 1639, 1279, 1177 and 1064.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.70 (d, *J* = 8.0 Hz, 1 H), 6.57 (d, *J* = 8.0, Hz, 1 H), 5.94 (s, 2 H), 5.89 (s, 1 H), 3.68 (s, 3 H), 3.34 – 3.27 (m, 4 H), 2.90 (t, *J* = 8.0 Hz, 2 H), 1.43 -1.37 (m, 2 H), 1.16 – 1.09 (m, 6 H), 0.88 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 154.3, 153.0, 145.1, 144.7, 142.8, 121.1, 118.9, 115.9, 107.3, 101.7, 51.1, 42.2, 41.7, 34.0, 21.6, 14.19, 14.11, 13.2.

HRMS (ESI): calc. for [($C_{19}H_{25}NO_6$)Na] (M+Na) 386.1580, measured 386.1593.

(*E*)-Methyl 3-(5-((diethylcarbamoyl)oxy)benzo[*d*][1,3]dioxol-4-yl)oct-2-enoate (**3r**).



Colorless semisolid; eluent (15% ethyl acetate in hexanes).

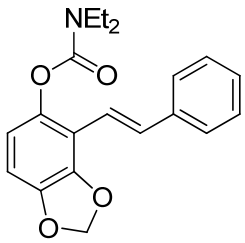
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2975, 1640, 1631, 1455 and 1078.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.68 (d, *J* = 8.0, 1 H), 6.55 (d, *J* = 8.0, 1 H), 5.90 (s, 2 H), 5.85 (s, 1 H), 3.65 (s, 3 H), 3.32 – 3.24 (m, 4 H), 2.90 (t, *J* = 8.0 Hz, 2 H), 1.37 – 1.33 (m, 2 H), 1.25 – 1.22 (m, 4 H), 1.13 – 1.07 (m, 6 H), 0.78 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 154.2, 153.2, 145.0, 144.7, 142.7, 120.9, 118.9, 115.9, 107.3, 101.7, 51.0, 42.2, 41.7, 32.0, 31.8, 27.9, 22.4, 14.1, 14.0, 13.2.

HRMS (ESI): calc. for [($C_{21}H_{29}NO_6$)H] (M+H) 392.2073, measured 392.2094.

(*E*)-4-Styrylbenzo[*d*][1,3]dioxol-5-yl diethylcarbamate (3s).



Pale yellow oil; eluent (10% ethyl acetate in hexanes).

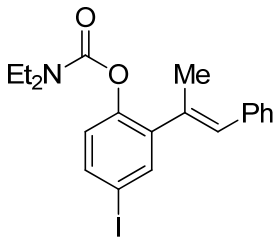
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2976, 1718, 1457, 1316, 1271, 1158 and 1065.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, *J* = 16.0 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 8.0 Hz, 2 H), 7.24 (t, *J* = 8.0 Hz, 1 H), 6.95 (d, *J* = 16.0 Hz, 1 H), 6.68 (d, *J* = 8.0 Hz, 1 H), 6.58 (d, *J* = 8.0 Hz, 1 H), 6.07 (s, 2 H), 3.51 (q, *J* = 8.0 Hz, 2 H), 3.39 (q, *J* = 8.0 Hz, 2 H), 1.31 (t, *J* = 8.0 Hz, 3 H), 1.20 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.5, 145.6, 145.1, 143.6, 137.9, 133.9, 128.7, 127.9, 126.6, 118.1, 115.3, 115.1, 106.6, 101.8, 42.4, 41.9, 14.6, 13.5.

HRMS (ESI): calc. for [($C_{20}H_{21}NO_4$)Na] (M+Na) 362.1368, measured 362.1370.

(*E*)-4-Iodo-2-(1-phenylprop-1-en-2-yl)phenyl diethylcarbamate (**3t**).



Colorless semisolid; eluent (10% ethyl acetate in hexanes).

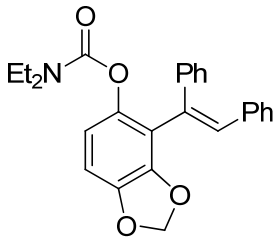
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2978, 1635, 1325, 1167 and 1049.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (s, 1 H), 7.54 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.36 – 7.30 (m, 4 H), 7.23 (t, *J* = 8.0, Hz, 1 H), 6.88 (d, *J* = 8.0, Hz, 1 H), 6.46 (s, 1 H), 3.36 – 3.30 (m, 4 H), 2.15 (s, 3 H), 1.14 – 1.10 (m, 6 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.8, 148.5, 141.1, 138.1, 137.5, 136.8, 133.9, 130.7, 128.9, 128.3, 126.8, 125.3, 89.4, 42.3, 41.9, 19.2, 14.2, 13.4.

HRMS (ESI): calc. for [($C_{20}H_{22}INO_2$)H] (M+H) 436.0773, measured 436.0779.

(*E*)-4-(1,2-Diphenylvinyl)benzo[*d*][1,3]dioxol-5-yl diethylcarbamate (3u).



Pale yellow liquid; eluent (8% ethyl acetate in hexanes).

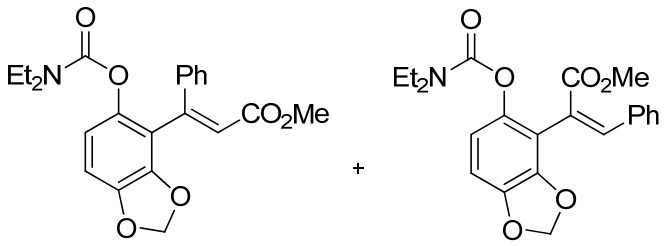
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2979, 1639, 1572 and 1227.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 – 7.23 (m, 2 H), 7.19 – 7.17 (m, 3 H), 7.11 – 7.07 (m, 5 H), 6.80 (s, 1 H), 6.70 (d, *J* = 8.0 Hz, 1 H), 6.58 (d, *J* = 8.0 Hz, 1 H), 5.87 (s, 2 H), 3.17 (q, *J* = 8.0 Hz, 2 H), 2.98 (q, *J* = 8.0 Hz, 2 H), 0.99 – 0.94 (m, 6 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.3, 148.2, 146.4, 144.9, 143.9, 139.3, 136.9, 132.8, 132.6, 129.7, 129.6, 128.1, 127.9, 127.3, 127.0, 115.6, 106.9, 101.6, 41.9, 41.5, 13.9, 13.2.

HRMS (ESI): calc. for [($C_{26}H_{25}NO_4$)H] (M+H) 416.1862, measured 416.1859.

Mixtures of 3v and 3v'.



Pale yellow liquid; eluent (16% ethyl acetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 – 7.25 (m, 5 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 6.54 (d, *J* = 8.0 Hz, 1 H), 6.22 (s, 1 H), 5.89 (s, 2 H), 3.60 (s, 3 H), 3.19 (q, *J* = 8.0 Hz, 2 H), 2.96 (q, *J* = 8.0 Hz, 2 H), 1.06 – 0.99 (m, 6 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 153.9, 146.8, 146.6, 145.0, 143.4, 137.7, 128.8, 128.7, 127.6, 122.0, 118.8, 115.8, 108.3, 101.8, 51.3, 41.9, 41.4, 13.9, 13.2.

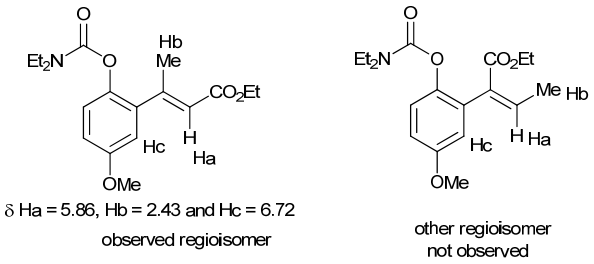
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 – 7.28 (m, 5 H), 7.14 (s, 1 H), 6.74 (d, *J* = 8.0, Hz, 1 H), 6.59 (d, *J* = 8.0, Hz, 1 H), 5.97 (s, 2 H), 3.65 (s, 3 H), 3.28 (q, *J* = 8.0 Hz, 4 H), 1.13 – 1.05 (m, 6 H).

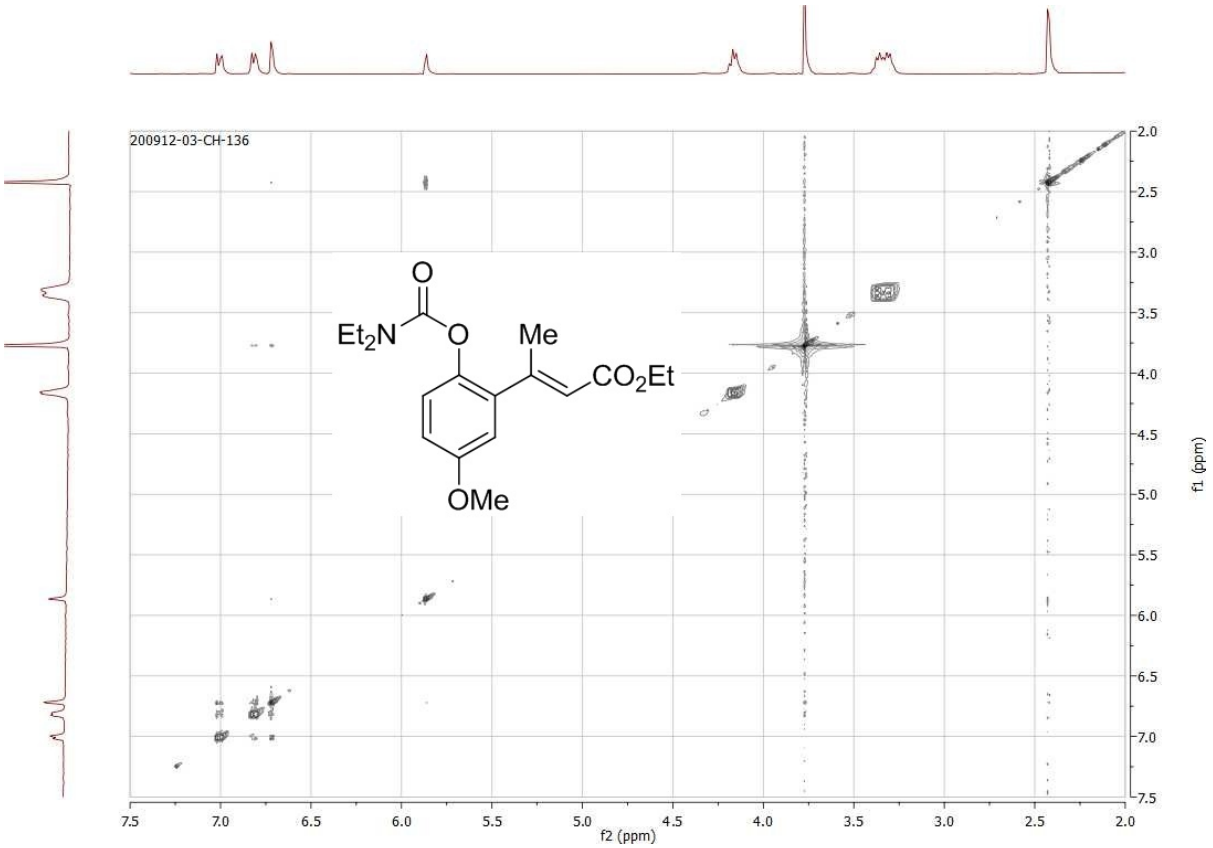
HRMS (ESI): calc. for [($C_{22}H_{23}NO_6$)H] (M+H) 398.1604, measured 398.1601.

Regioselective studies (2D-NOE analysis)

Regioselective studies of compound 3a.

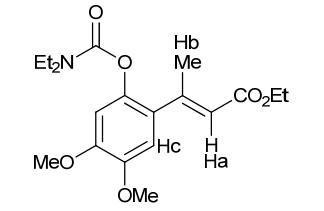
The regiochemistry of hydroarylation product **3a** was confirmed by ^{1}H NMR spectroscopy. Alkene Ha (δ 5.86, s) was observed as a singlet. Alkene Me (δ 2.43, s) was also observed as a singlet. Further, the regiochemistry of **3a** was confirmed by NOESY experiment. There is a NOE signal between protons Ha and Hb. There is a strong NOE signal between Hb and Hc protons. If the other regioisomer is formed, there should not be signal between Hb and Hc. Also, there is no NOE signal between ester CH_2 with Hc protons. There is a very weak NOE signal between Ha and Hc. It is clearly indicated that alkene H (Ha) and cabamate are *cis* to each other. These results clearly revealed that the regiochemistry of compound **3a** is correct.



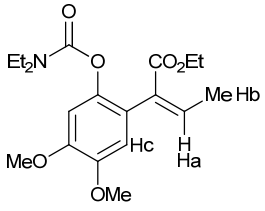


Regioselective studies of compound 3c.

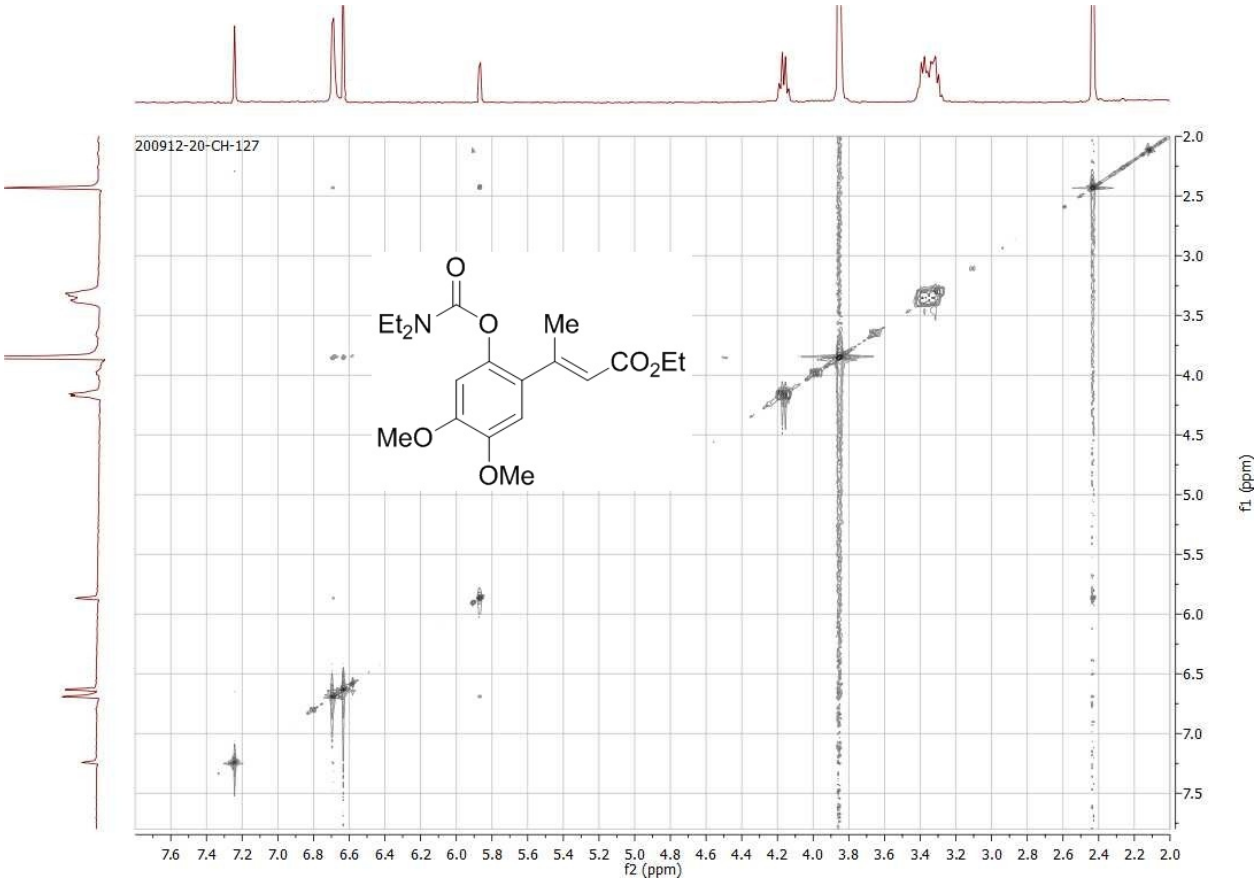
The regiochemistry of hydroarylation product **3c** was confirmed by ^{1}H NMR spectroscopy. Alkene Ha (δ 5.87, s) was observed as a singlet. Alkene Me (δ 2.43, s) was also observed as a singlet. Further, the regiochemistry of **3c** was confirmed by NOESY experiment. There is a NOE signal between protons Ha and Hb. There is a strong NOE signal between Hb and Hc (δ 6.69, s) protons. If the other regioisomer is formed, there should not be signal between Hb and Hc. Also, there is no NOE signal between ester CH_2 with Hc protons. There is a very weak NOE signal between Ha and Hc. It is clearly indicated that alkene H (Ha) and aromatic cabamate are *cis* to each other. These results clearly revealed that the regiochemistry of compound **3c** is correct.



δ Ha = 5.87, Hb = 2.43 and Hc = 6.69
observed regioisomer

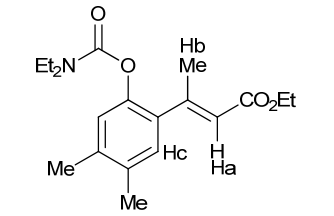


other regioisomer
not observed

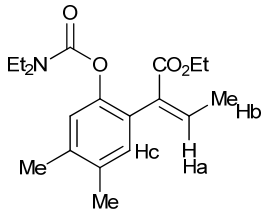


Regioselective studies of compound 3d.

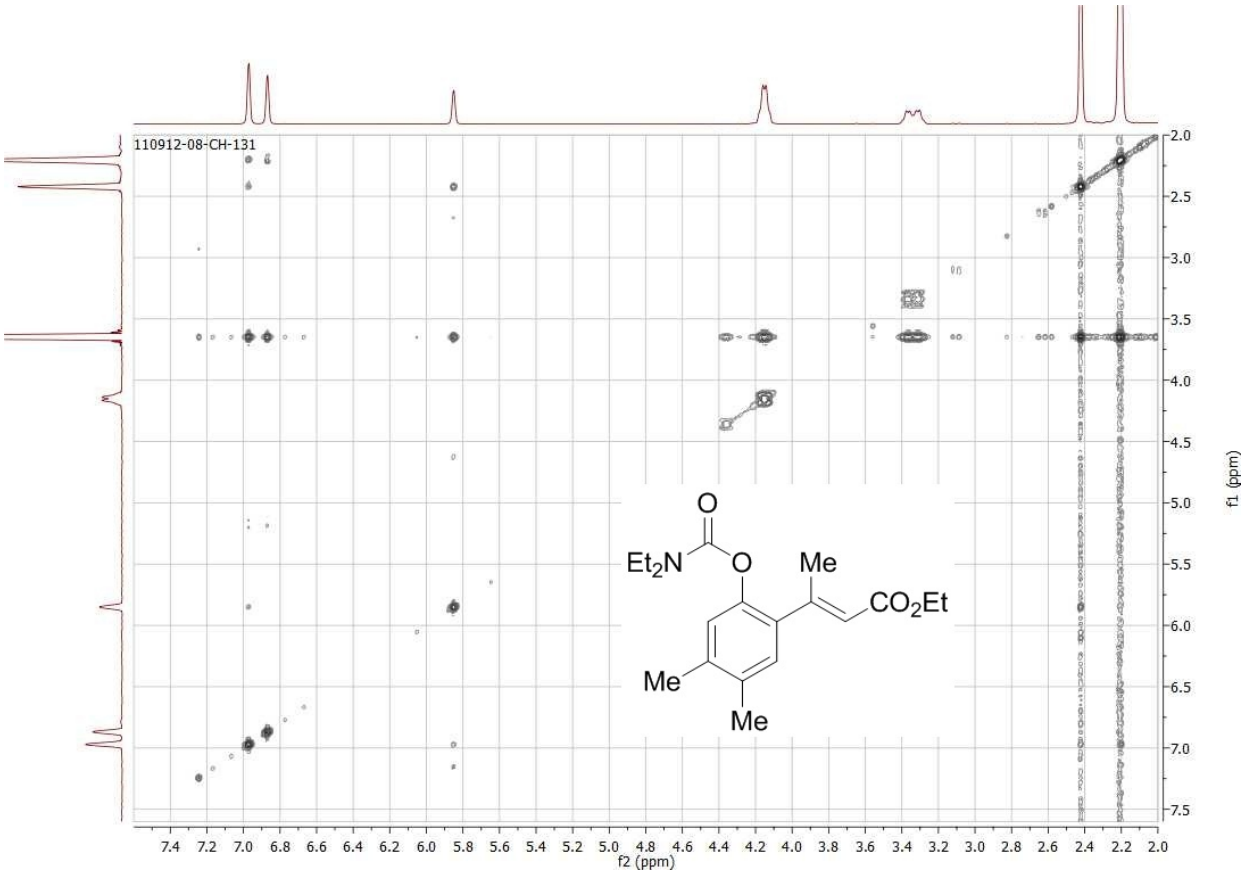
The regiochemistry of hydroarylation product **3d** was confirmed by ^{1}H NMR spectroscopy. Alkene Ha (δ 5.85, s) was observed as a singlet. Alkene Me (δ 2.42, s) was also observed as a singlet. Further, the regiochemistry of **3d** was confirmed by NOESY experiment. There is a NOE signal between protons Ha and Hb. There is a strong NOE signal between Hb and Hc (δ 6.97, s) protons. If the other regioisomer is formed, there should not be signal between Hb and Hc. Also, there is no NOE signal between ester CH_2 with Hc protons. There is a very weak NOE signal between Ha and Hc. It is clearly indicated that alkene H (Ha) and aromatic cabamate are *cis* to each other. These results clearly revealed that the regiochemistry of compound **3d** is correct.



δ Ha = 5.85, Hb = 2.42 and Hc = 6.97
observed regiochemistry

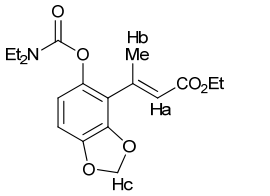


other regiochemistry
not observed

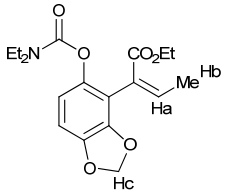


Regioselective studies of compound 3e.

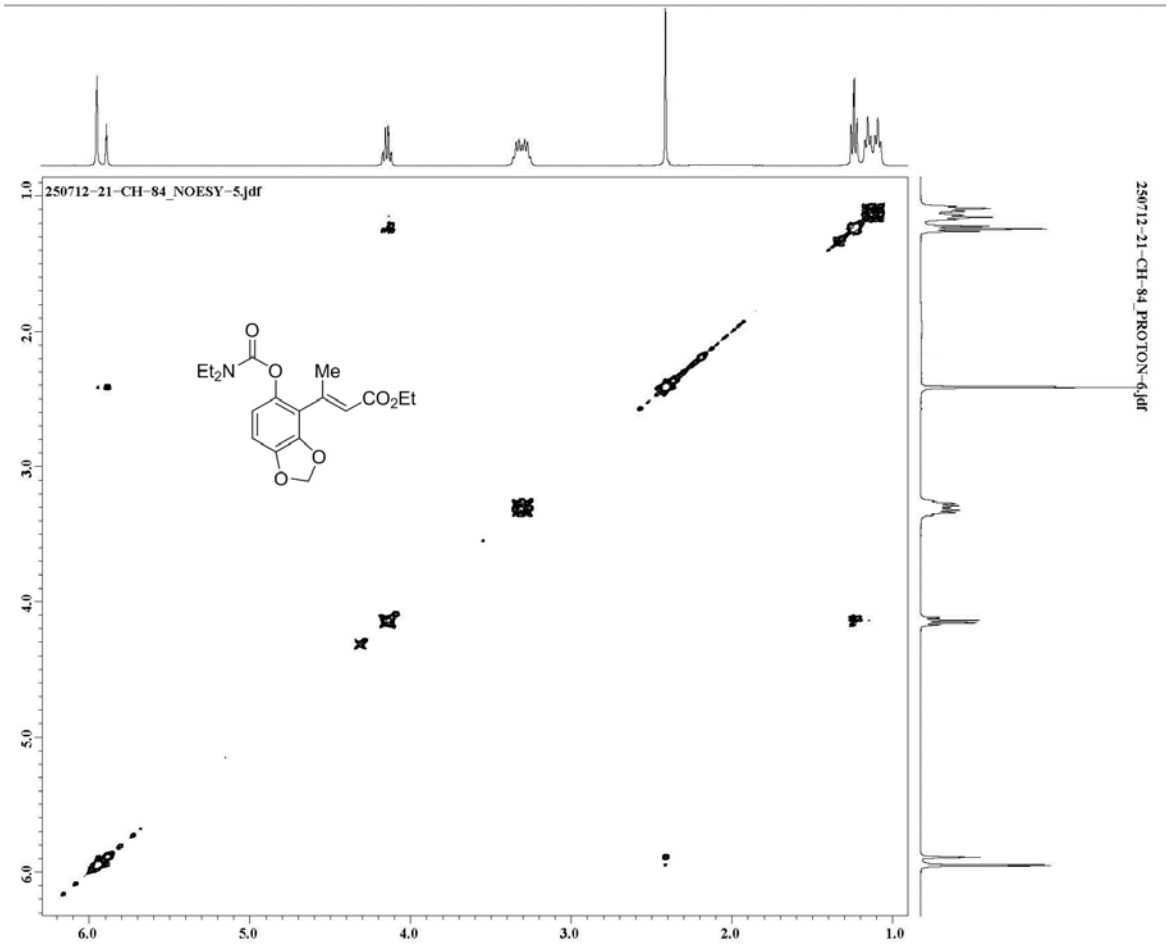
The regiochemistry of hydroarylation product **3e** was confirmed by ^{1}H NMR spectroscopy. Alkene Ha (δ 5.94, s) was observed as a singlet. Alkene Me (δ 2.41, s) was also observed as a singlet. Further, the regiochemistry of **3e** was confirmed by NOESY experiment. There is a NOE signal between protons Ha and Hb. There is also a NOE signal between Hb and Hc (δ 5.85, s) protons. If the other regioisomer is formed, there should not be signal between Hb and Hc. Also, there is no NOE signal between ester CH_2 with Hc protons. These results clearly revealed that the regiochemistry of compound **3e** is correct.



δ Ha = 5.94, Hb = 2.41 and Hc = 5.88
observed regiochemistry

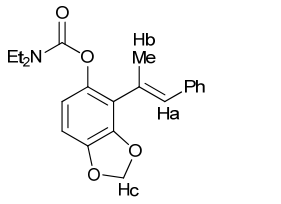


other regiochemistry
not observed

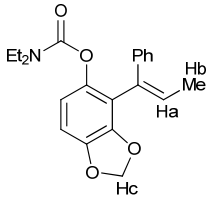


Regioselective studies of compound 3l.

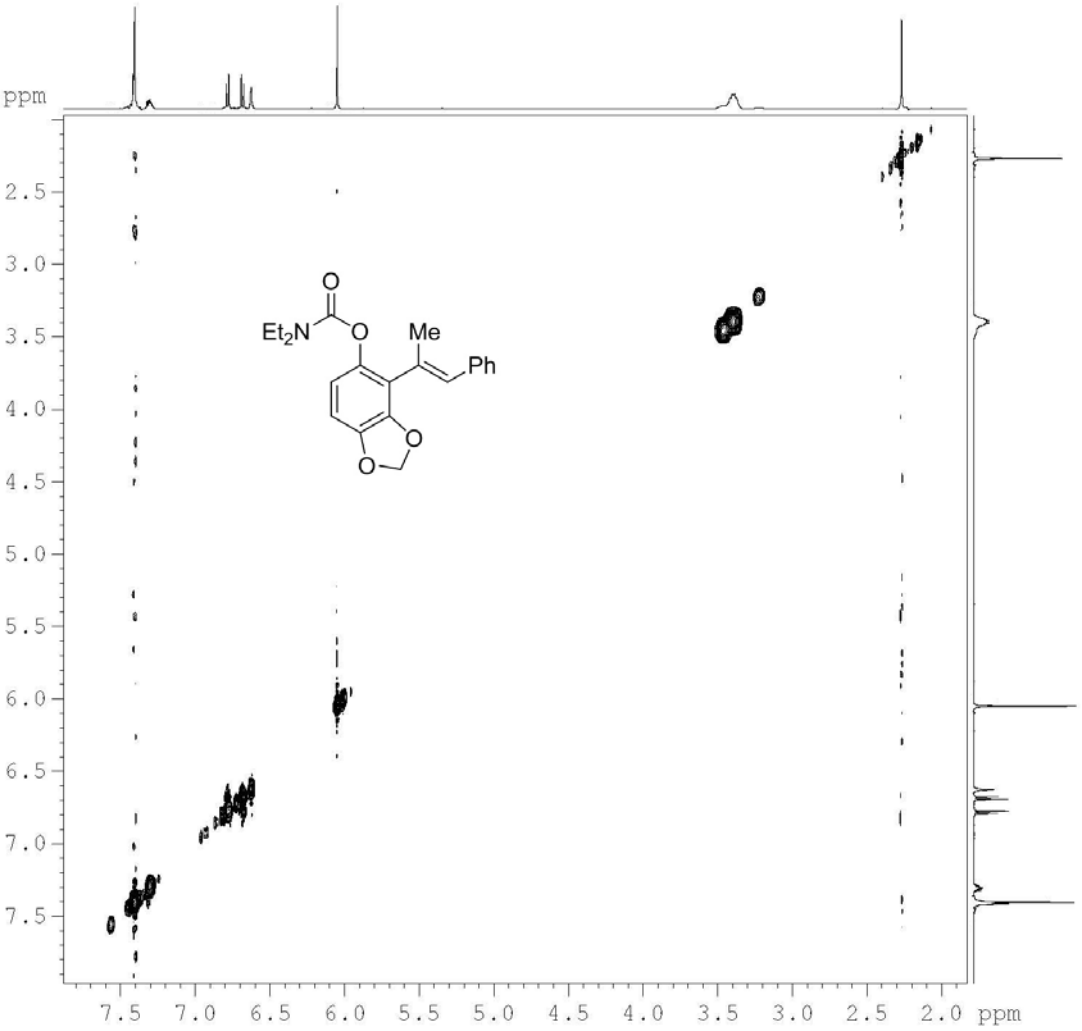
The regiochemistry of hydroarylation product **3l** was confirmed by ^{1}H NMR spectroscopy. Alkene Ha (δ 6.54, s) was observed as a singlet. Alkene Me (δ 2.18, s) was also observed as a singlet. Further, the regiochemistry of **3l** was confirmed by NOESY experiment. There is a NOE signal between Hb and Hc (δ 5.97, s) protons. If the other regioisomer is formed, there should not be signal between Hb and Hc. These results clearly revealed that the regiochemistry of compound **3l** is correct.



δ Ha = 6.54, Hb = 2.18 and Hc = 5.97
observed regiochemistry

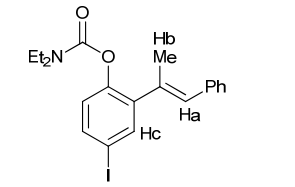


other regiochemistry
not observed

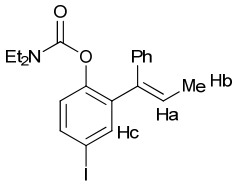


Regioselective studies of compound 3t.

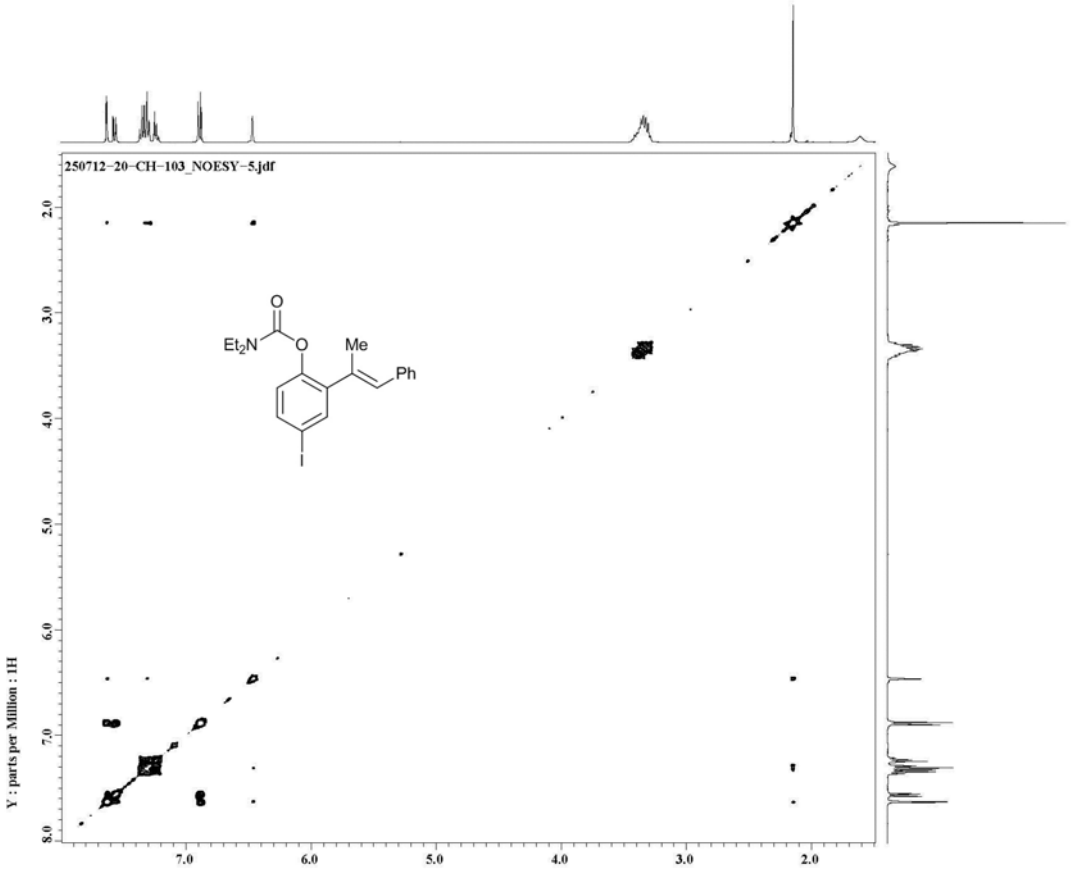
The regiochemistry of hydroarylation product **3t** was confirmed by ^{1}H NMR spectroscopy. Alkene Ha (δ 6.46, s) was observed as a singlet. Alkene Me (δ 2.15, s) was also observed as a singlet. Further, the regiochemistry of **3t** was confirmed by NOESY experiment. There is a NOE signal between Ha and Hb protons. There is a strong NOE signal between Hb and Hc (δ 7.63, s) protons. If the other regioisomer is formed, there should not be signal between Hb and Hc. Also, there is no NOE signal between Hc and Ph group of **3t** (δ 7.36 – 7.30). There is a weak NOE signal between Ha and Hc protons. It is clearly indicated that alkene H (Ha) and aromatic cabamate are *cis* to each other. These results clearly revealed that the regiochemistry of compound **3t** is correct.



δ Ha = 6.46, Hb = 2.15 and Hc = 7.63
Ph = 7.36 – 7.30
observed regiochemistry

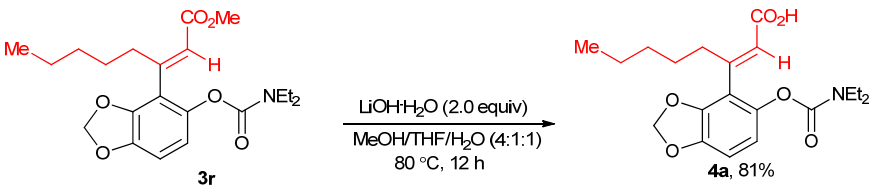


other regiochemistry
not observed

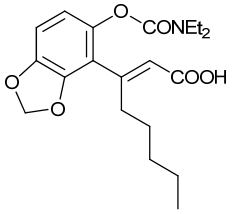


Regioselective studies (X-ray analysis)

The regiochemistry of coupling product **3** was further confirmed by X-ray studies. The coupling products **3** are in liquid form. In order to take X-ray diffraction, the derivative of the corresponding coupling product was used. The ester group of product **3r** was converted into the corresponding carboxylic acid derivative **4a** in the presence of LiOH base. The structure of **4a** was confirmed by single crystal X-ray diffraction.



View



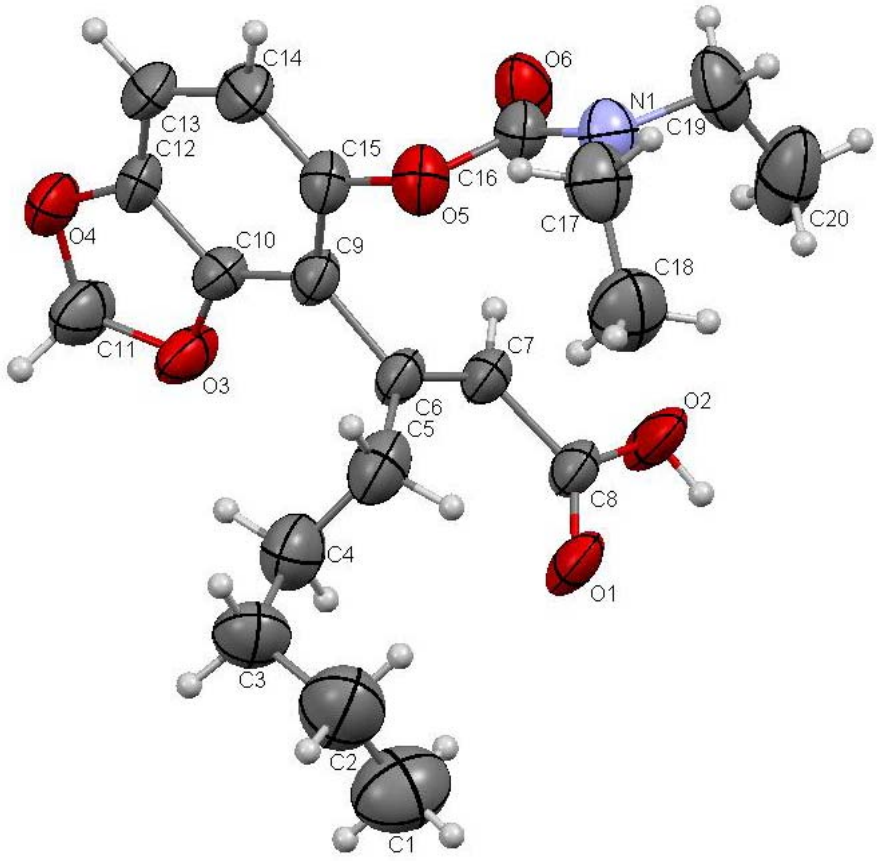
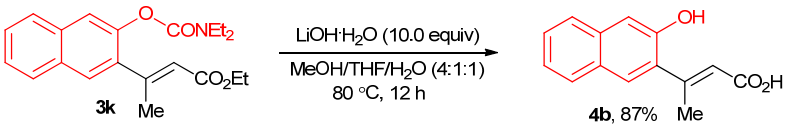


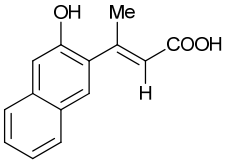
Table 1. Crystal data and structure refinement for **4a**.

Identification code	**4a**	
Empirical formula	C20 H27 N O6	
Formula weight	377.43	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.065(2) Å	α= 92.523(4)°.
	b = 12.172(2) Å	β= 99.861(5)°.
	c = 13.880(3) Å	γ = 95.377(4)°.
Volume	1995.7(6) $Å^3$	
Z	4	
Density (calculated)	1.286 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	820	
Crystal size	0.43 x 0.25 x 0.09 mm^3	
Theta range for data collection	1.49 to 25.00°.	
Index ranges	-14<=h<=14, -14<=k<=14, -16<=l<=15	
Reflections collected	28845	
Independent reflections	7050 [R(int) = 0.0478]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.992 and 0.972	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7050 / 67 / 495	
Goodness-of-fit on F^2	1.828	
Final R indices [I>2sigma(I)]	R1 = 0.0956, wR2 = 0.2683	
R indices (all data)	R1 = 0.1416, wR2 = 0.2977	
Largest diff. peak and hole	0.912 and -0.601 $e.Å^{-3}$	

Whereas, 10.0 equiv of LiOH cleaved both ester and carbamate moieties of compound **3k**, giving phenol derivative **4b** in 87% yield. The structure of phenol derivative **4b** was confirmed by single crystal x-ray diffraction.



View



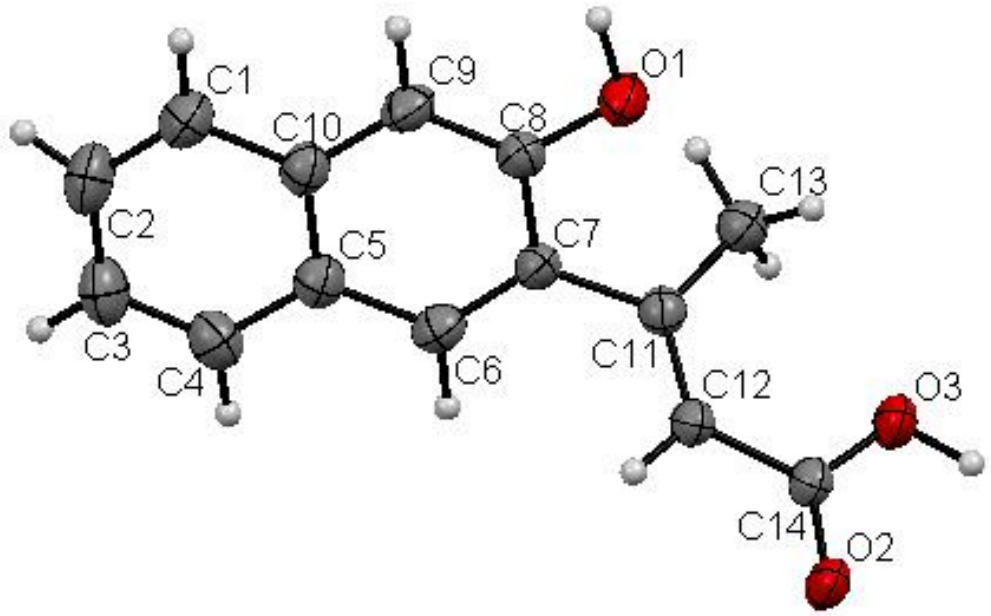


Table 1. Crystal data and structure refinement for **4b**.

Identification code	**4b**
Empirical formula	C14 H12 O3
Formula weight	228.24
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	C2/c	
Unit cell dimensions	a = 23.015(7) Å	α= 90°.
	b = 5.8478(19) Å	β= 112.391(6)°.
	c = 17.370(6) Å	γ = 90°.
Volume	2161.6(12) $Å^3$	
Z	8	
Density (calculated)	1.403 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	960	
Crystal size	0.13 x 0.08 x 0.02 mm^3	
Theta range for data collection	1.91 to 28.35°.	
Index ranges	-15<=h<=30, -7<=k<=7, -23<=l<=21	
Reflections collected	18133	
Independent reflections	2703 [R(int) = 0.1097]	
Completeness to theta = 28.35°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9980 and 0.9873	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2703 / 0 / 202	
Goodness-of-fit on F^2	0.869	
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1305	
R indices (all data)	R1 = 0.1649, wR2 = 0.1865	
Largest diff. peak and hole	0.219 and -0.215 $e.Å^{-3}$	

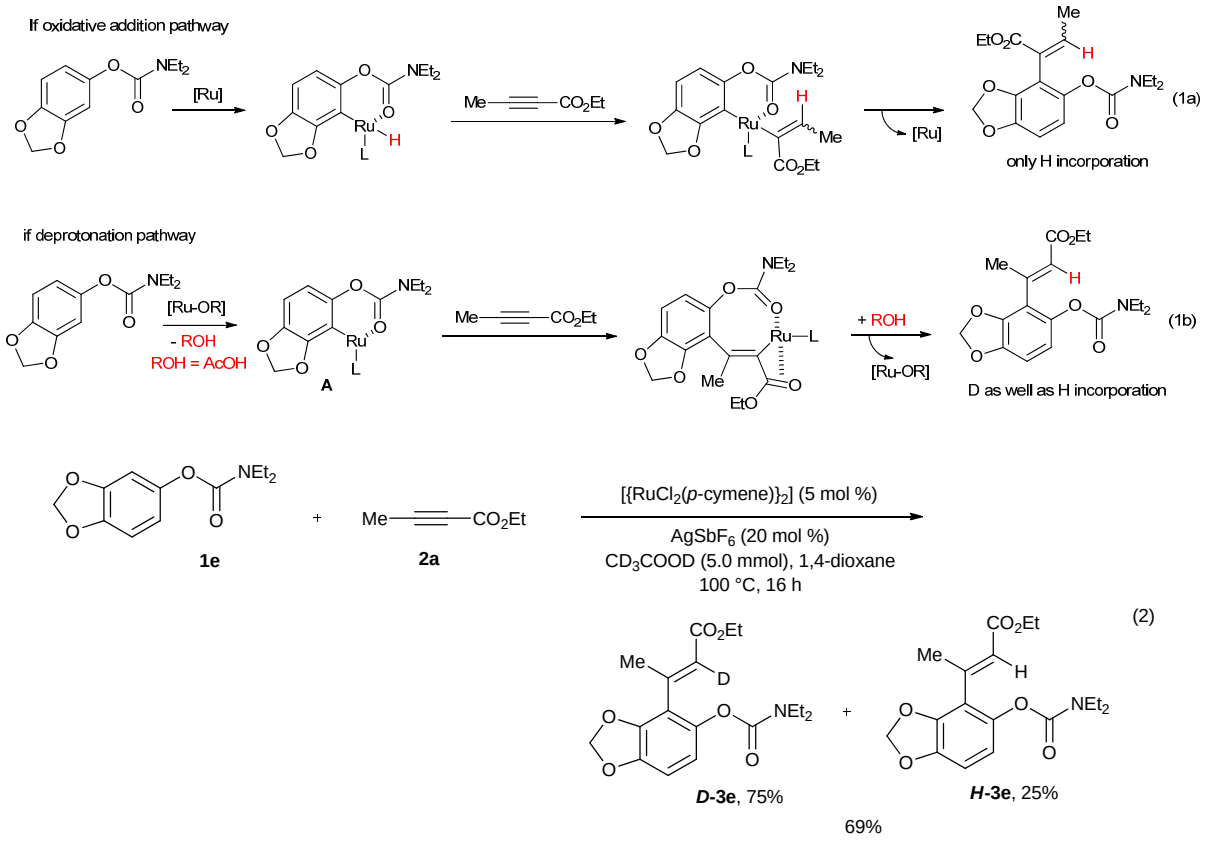
General procedure for the preparation of compounds 4a-b.

A two-neck 50 mL round bottom flask fitted with a condenser and a septum containing a mixture of **3r** (100 mg) and $LiOH{\cdot}H_2O$ (2.0 equiv) in 6 mL of MeOH/THF/H_2O (4:1:l). The reaction mixture was refluxed at 80 °C for 12 h. After the reaction, reaction mixture was allowed to cool to room temperature and the reaction mixture was neutralised (pH = 6) using 1N HCl. The product was extracted with ethyl acetate, washed with water and brine. The extract was dried with anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure to give pure **4a** as a colorless solid (purification is not necessary).

A similar procedure was used for the preparation of compounds **4b**. However, 10.0 equiv of $LiOH{\cdot}H_2O$ was used for the reaction.

Mechanistic investigation

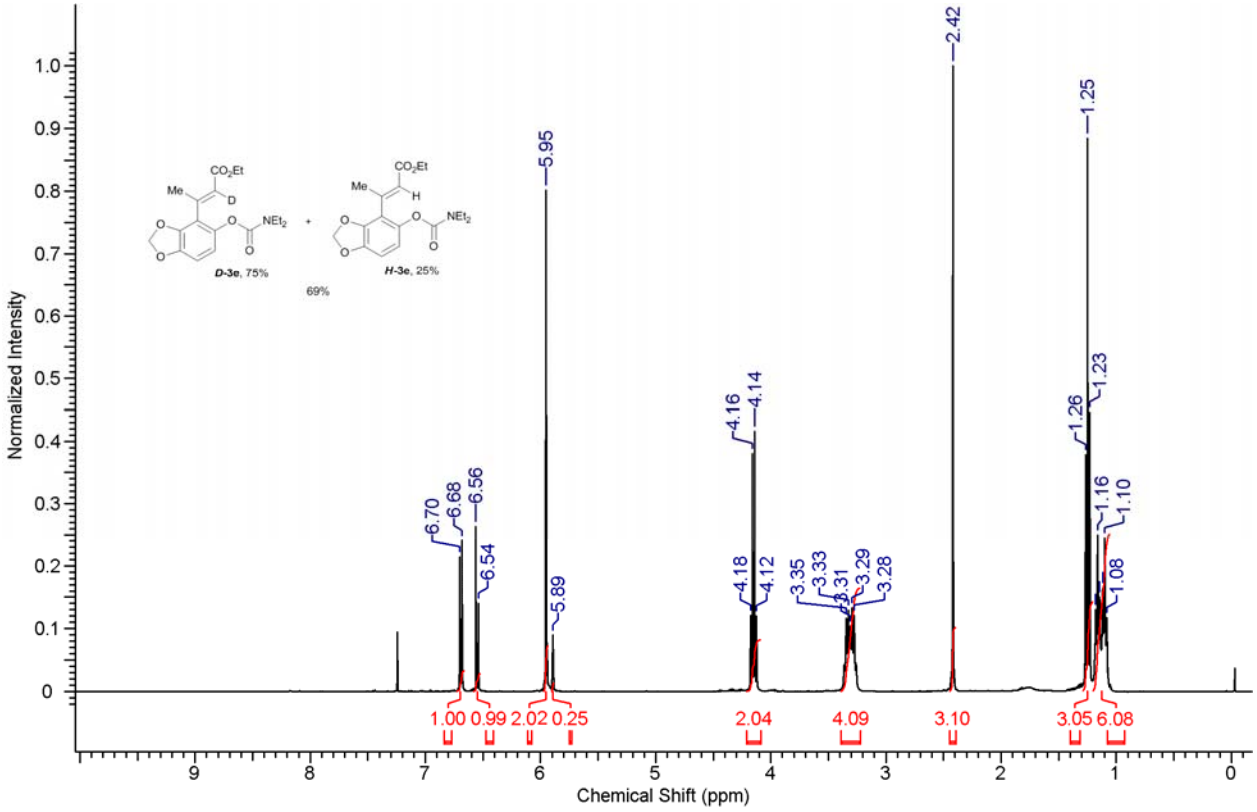
In the present reaction, a six-membered metalacycle **A** is a key intermediate (eq. 1b). The reaction proceeds through an assisted deprotonation by the ruthenium complex (eq. 1b) instead of an oxidative addition on the C-H ortho to the carbamate (eq. 1a). In order to prove the mechanism proceeds via an assisted deprotonation (eq. 2), the following mechanistic studies were done.



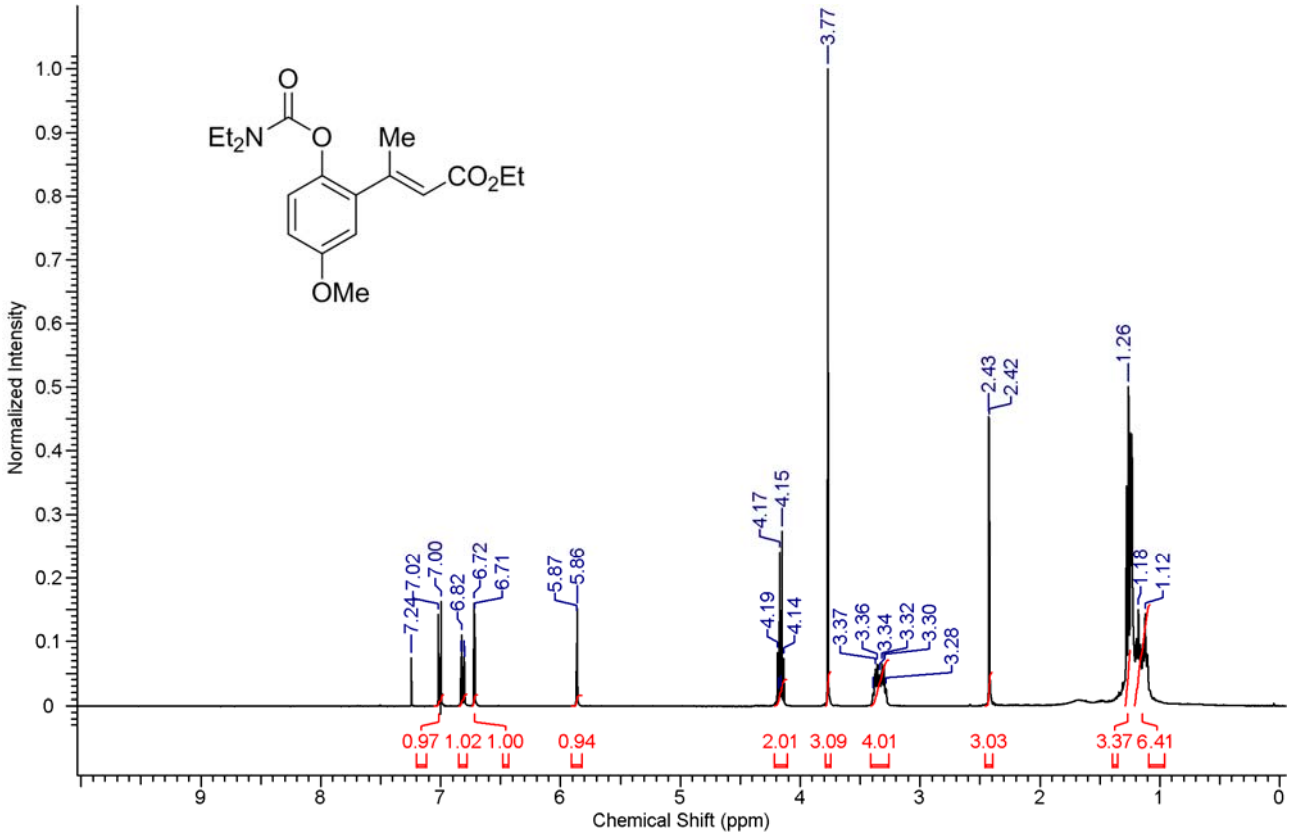
The coupling reaction of sesamol carbamate **1e** with ethyl but-2-ynoate (**2a**) in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (5 mol %), $AgSbF_6$ (20 mol %) and CD_3COOD (5.0 equiv) in 1,4-dioxane at 100 °C for 16 h was examined. In the reaction, instead of pivalic acid, CD_3COOD (5.0 equiv) was used. If the reaction proceeds via oxidative addition pathway (eq. 1a), in the coupling product, no deuterium incorporation would be observed in an alkene C-H bond. If the reaction proceeds via an assisted deprotonation pathway (eq. 1b), in the coupling product, deuterium incorporation should be observed in an alkene C-H bond. In the coupling product, 75% of deuterium incorporation was observed in an alkene C-H bond. In the reaction, CD_3COOH is a side product. It is well known that CD_3COOH is more reactive than CD_3COOD. Although the concentration of CD_3COOD is more in the reaction as compare to

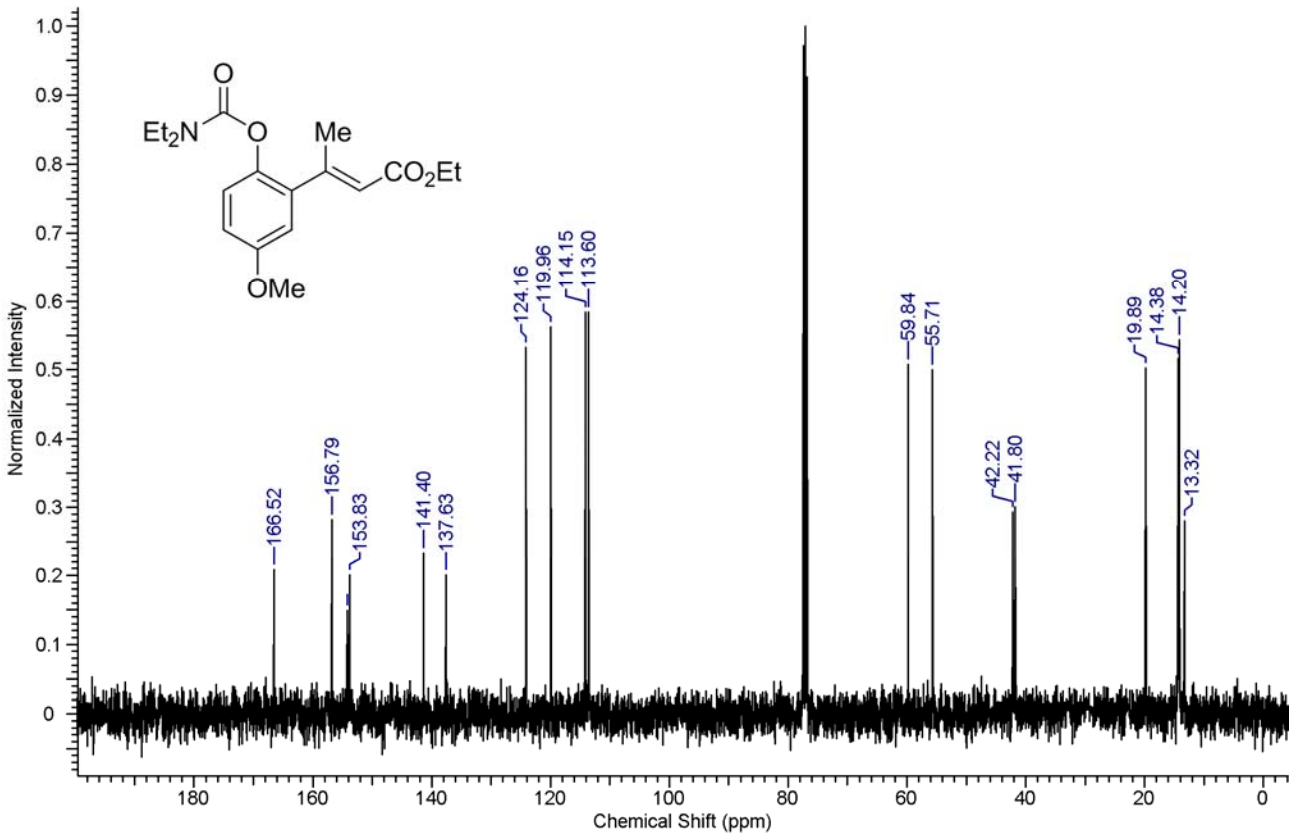
CD_3COOH, due to the less reactivity of CD_3COOD, 25% of hydrogen incorporation was found in the product. This deuterium study clearly revealed that the present reaction proceeds via an assisted deprotonation pathway. In addition, if the reaction proceeds via oxidative addition pathway, a different type of regioisomeric product as explained in eq. 1a should be observed. However, in the reaction such regioisomeric product was not observed (see regioselective studies (X-ray analysis)).

^{1}H and ^{13}C NMR Spectra of Compound **3e.**

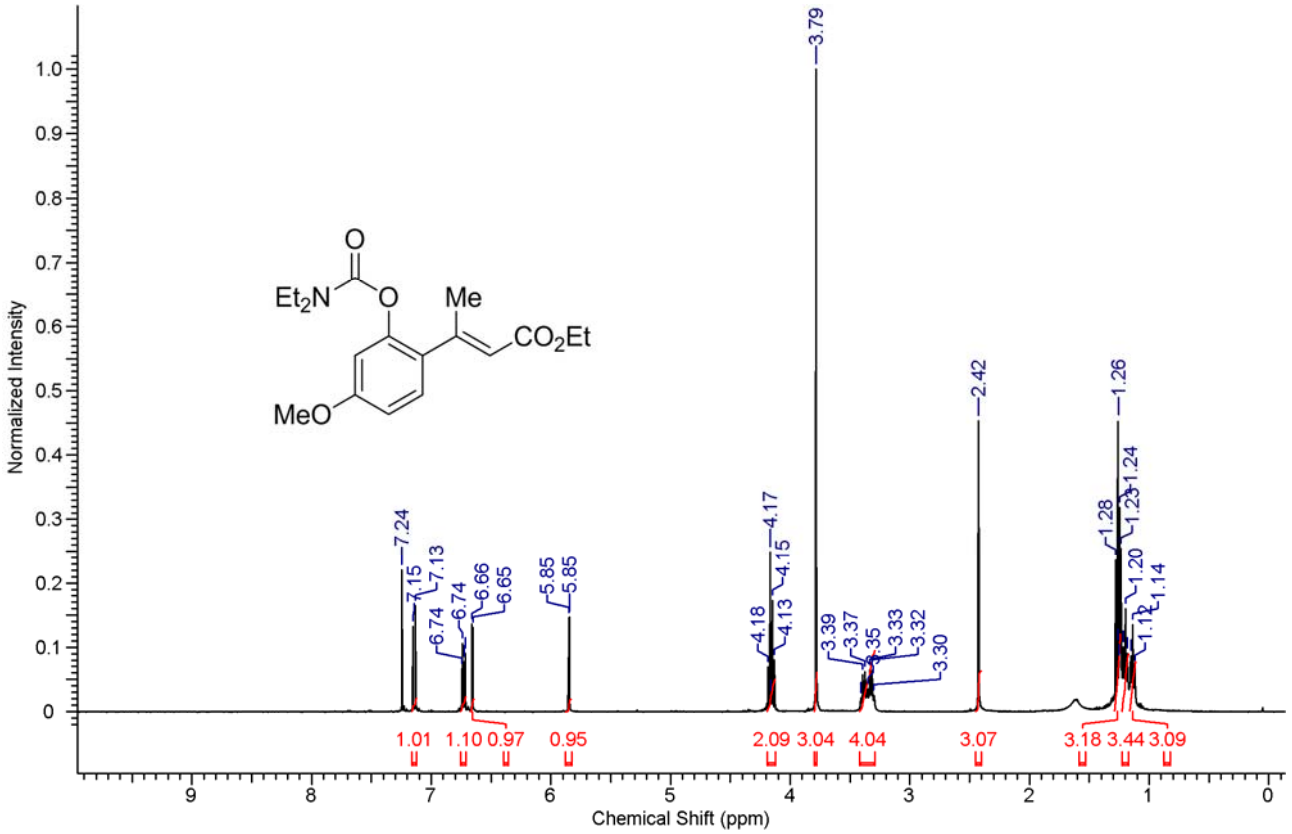


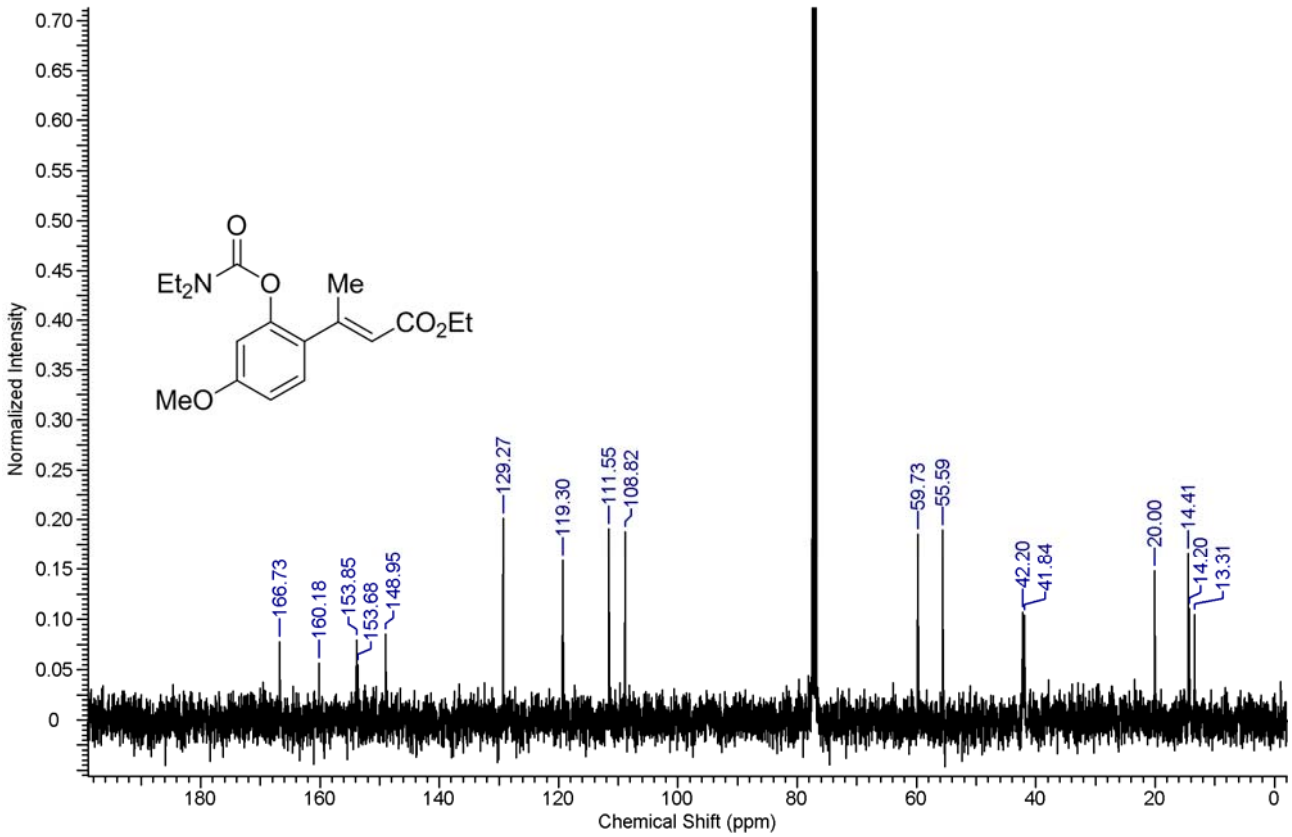
^{1}H and ^{13}C NMR Spectra of Compound **3a.**



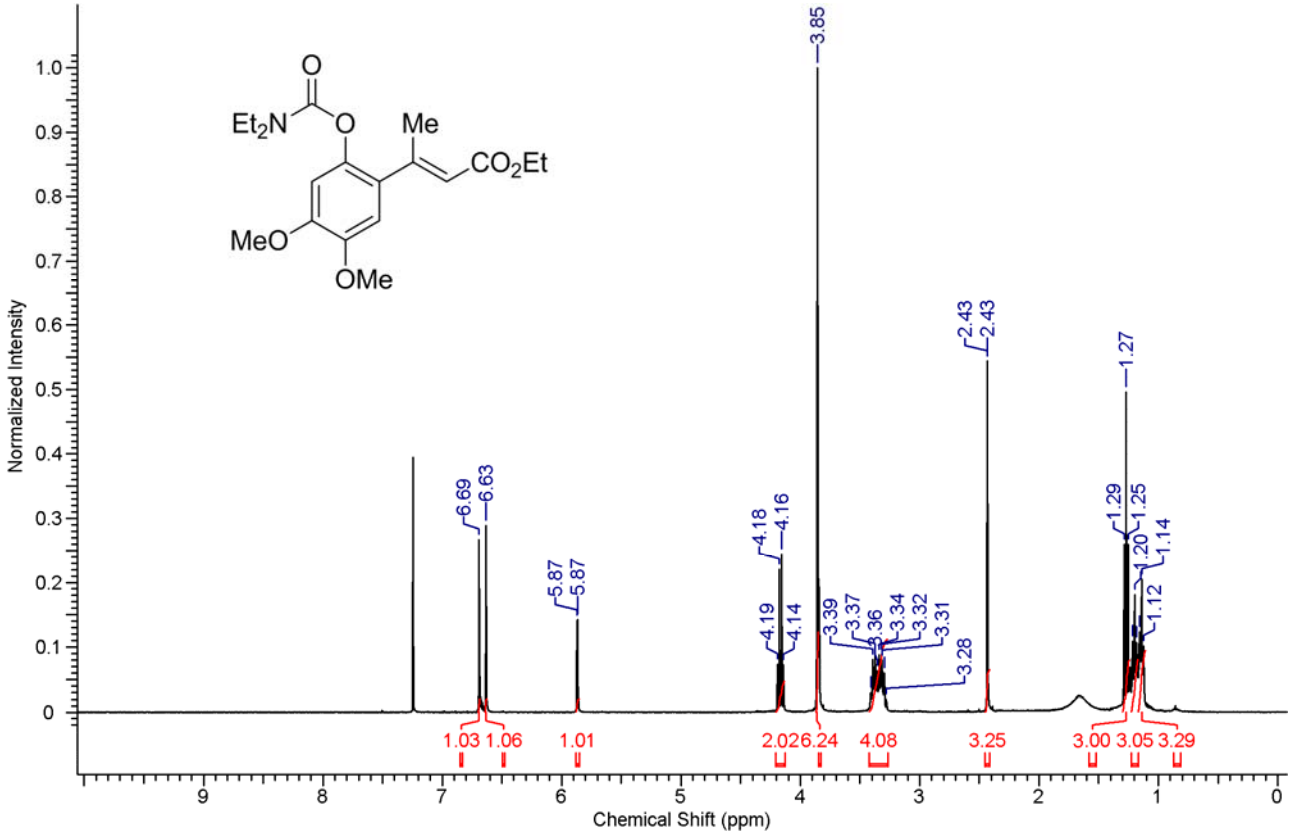


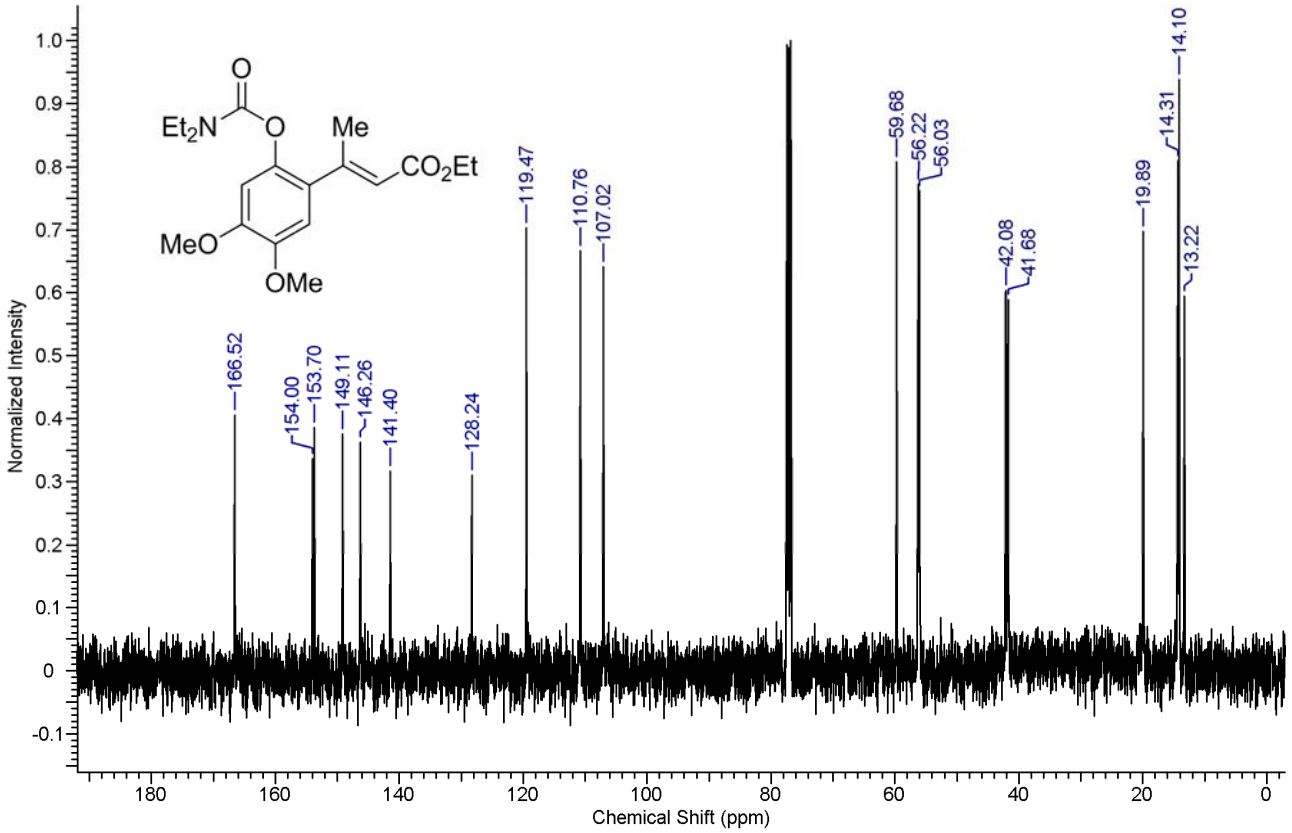
^{1}H and ^{13}C NMR Spectra of Compound **3b.**



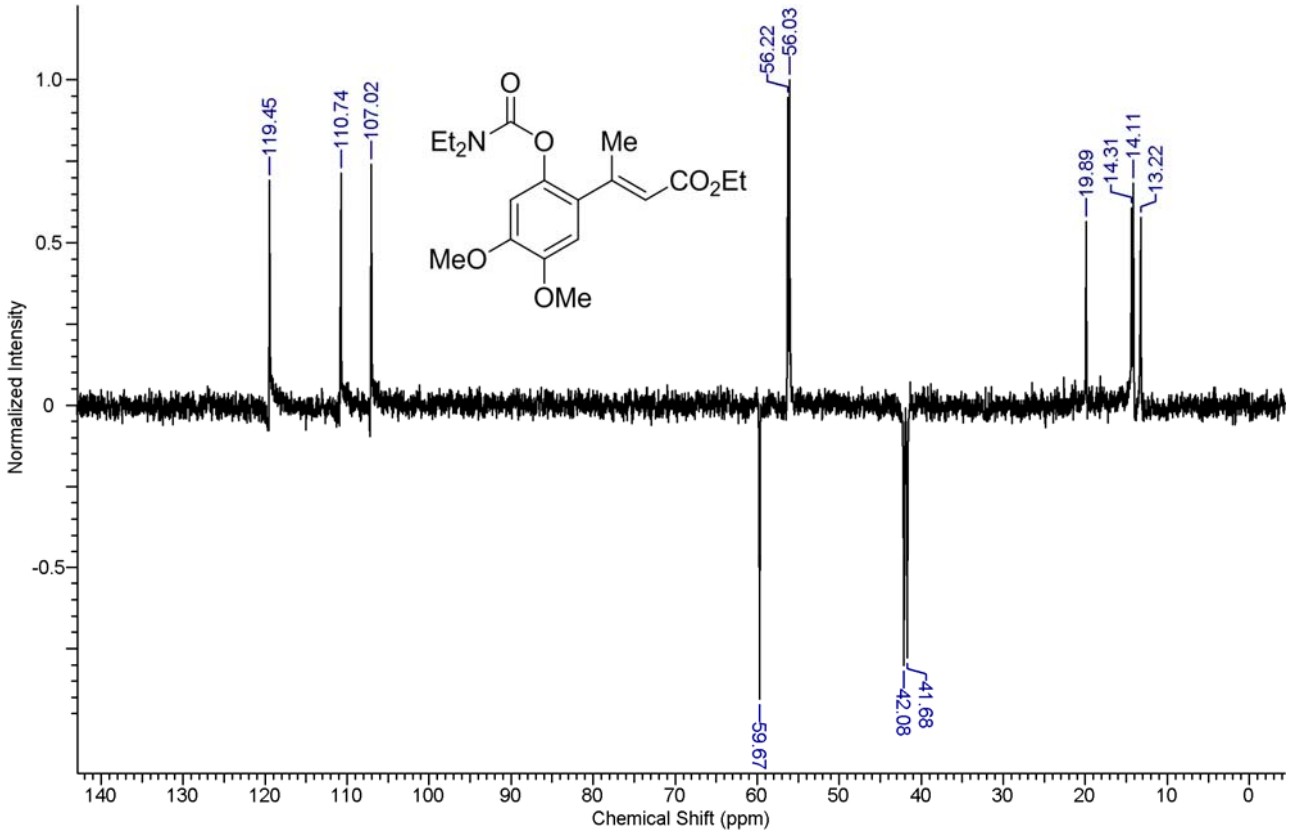


^{1}H and ^{13}C NMR Spectra of Compound **3c.**

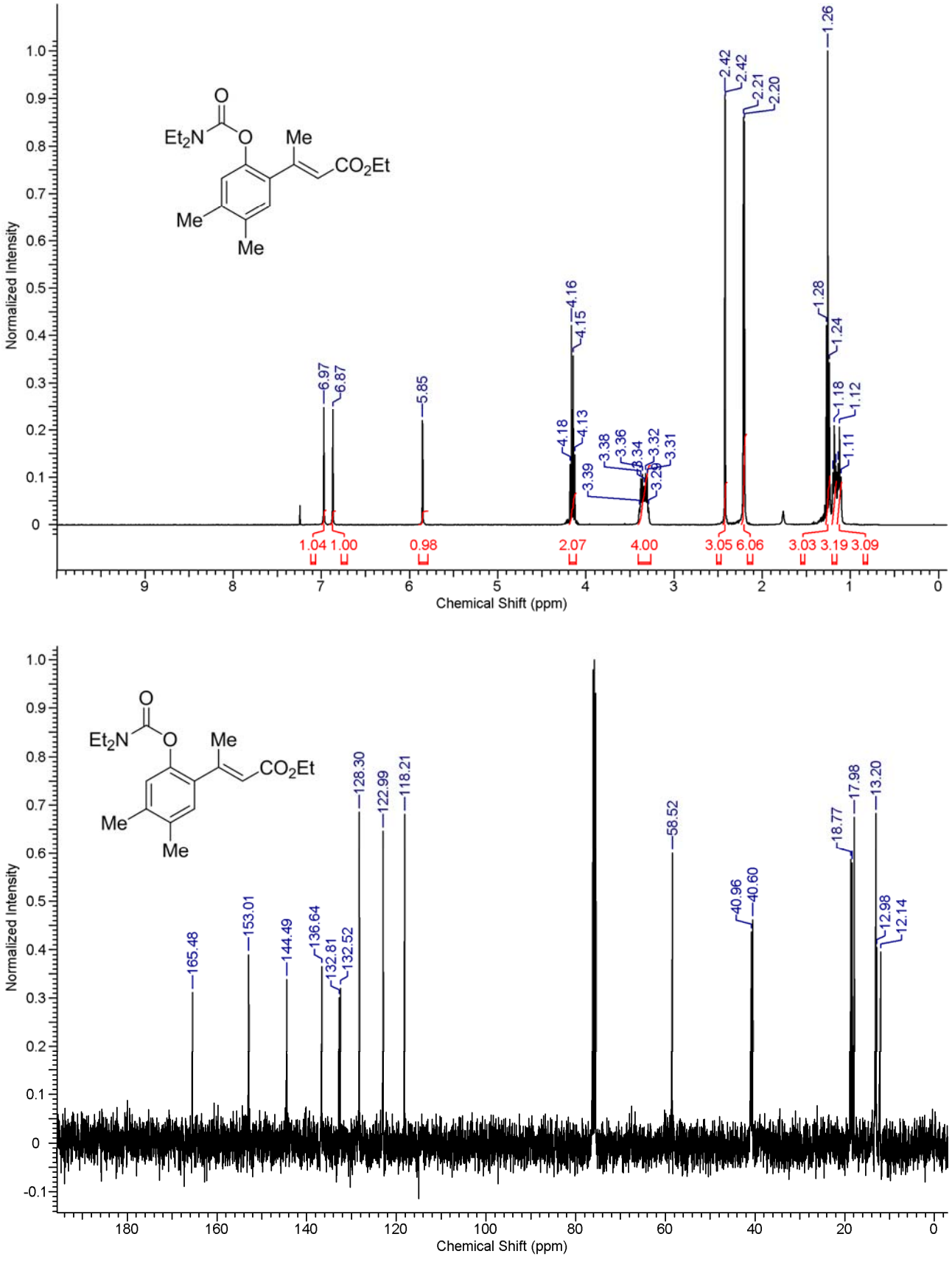




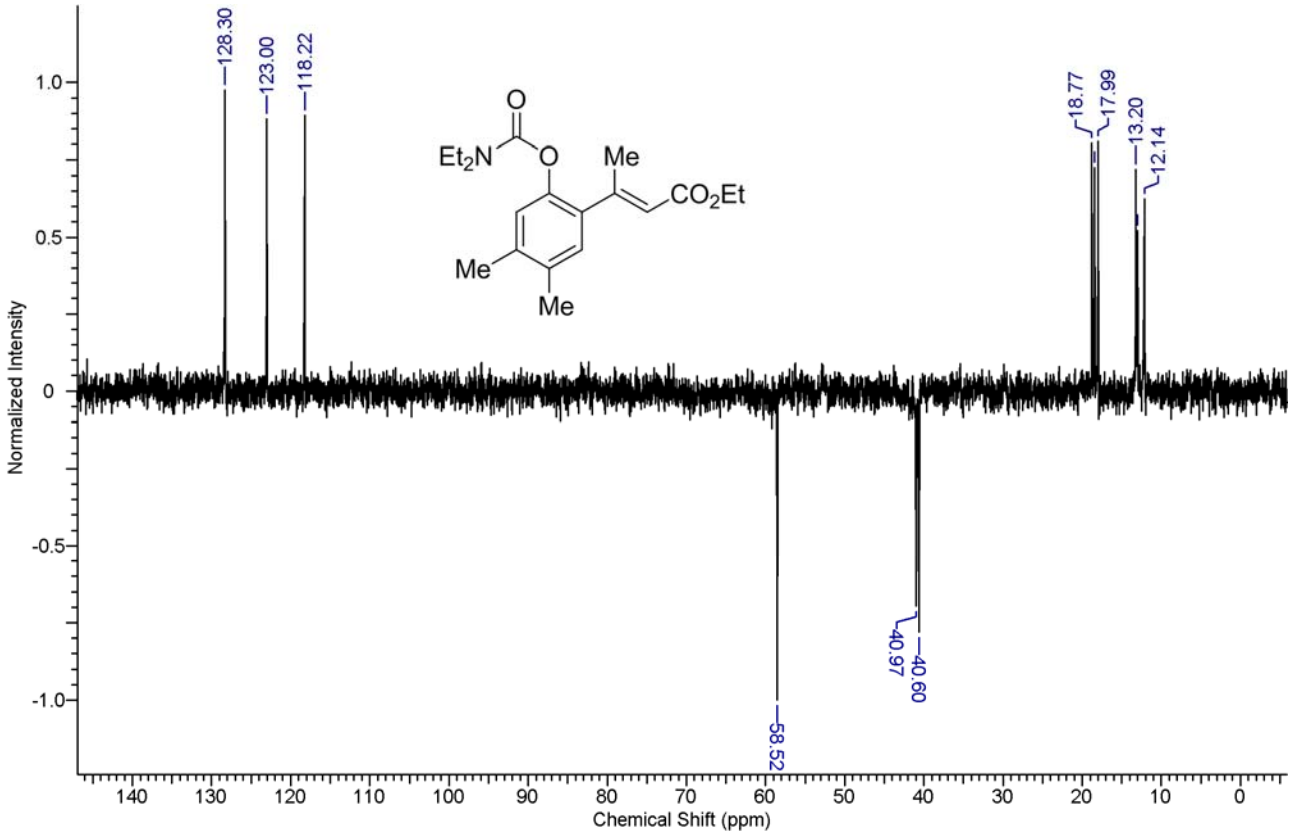
DEPT (135) NMR Spectrum of Compound **3c.**



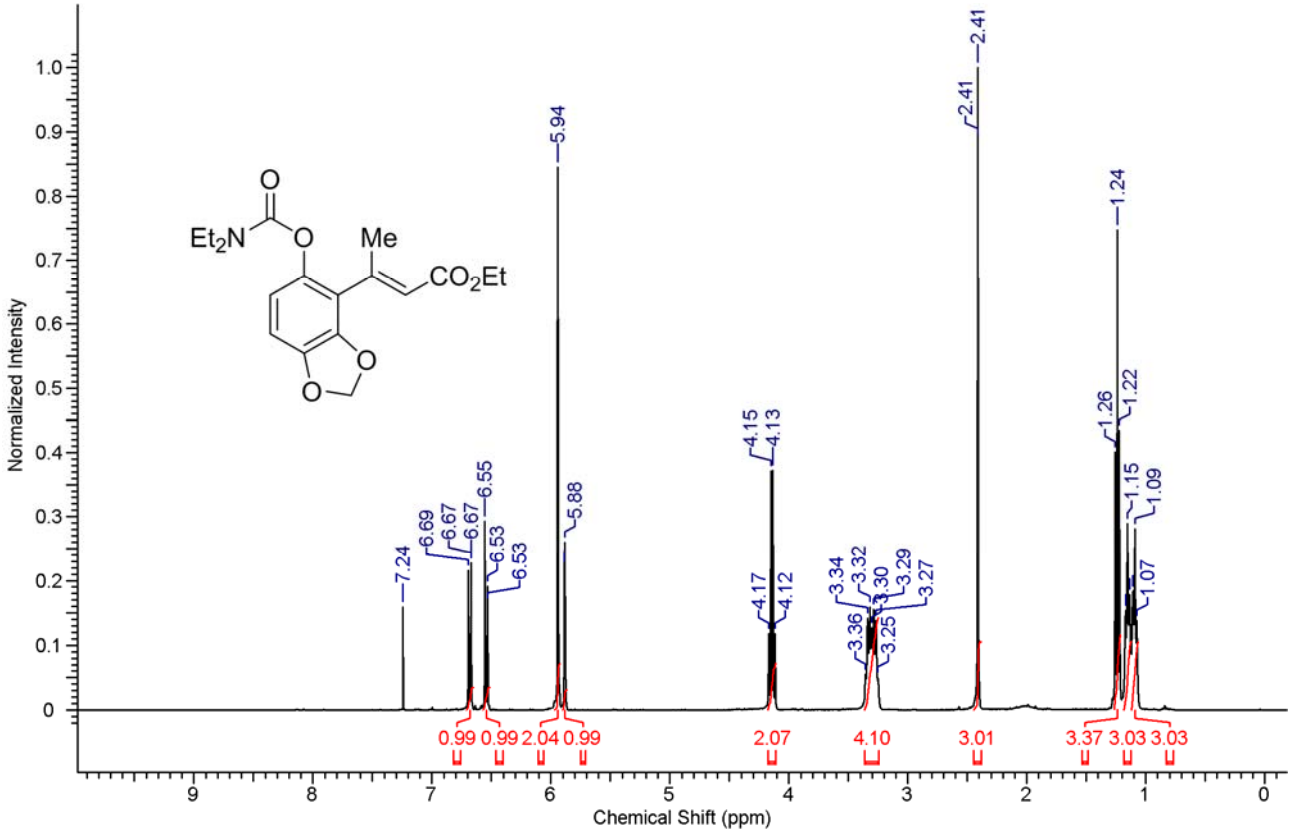
^{1}H and ^{13}C NMR Spectra of Compound **3d.**

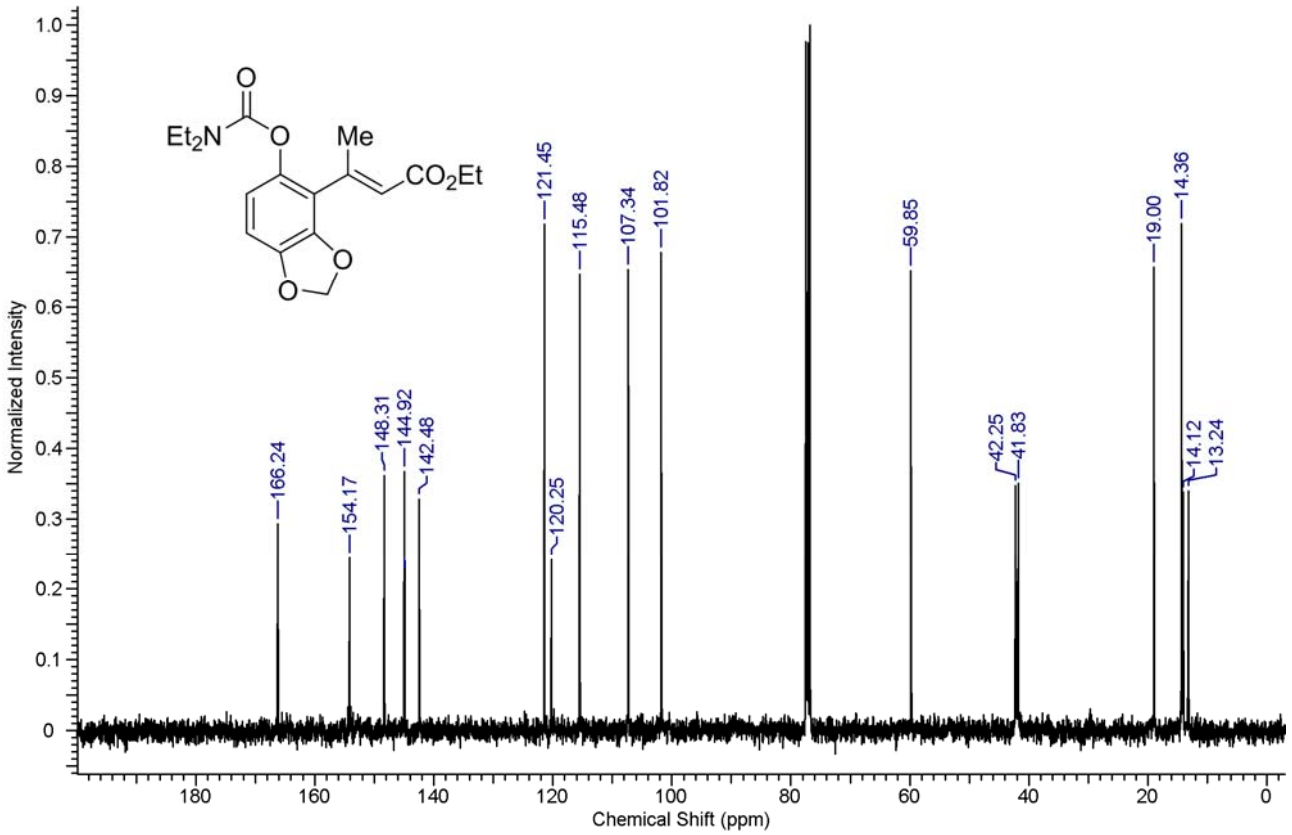


DEPT (135) NMR Spectrum of Compound **3d.**

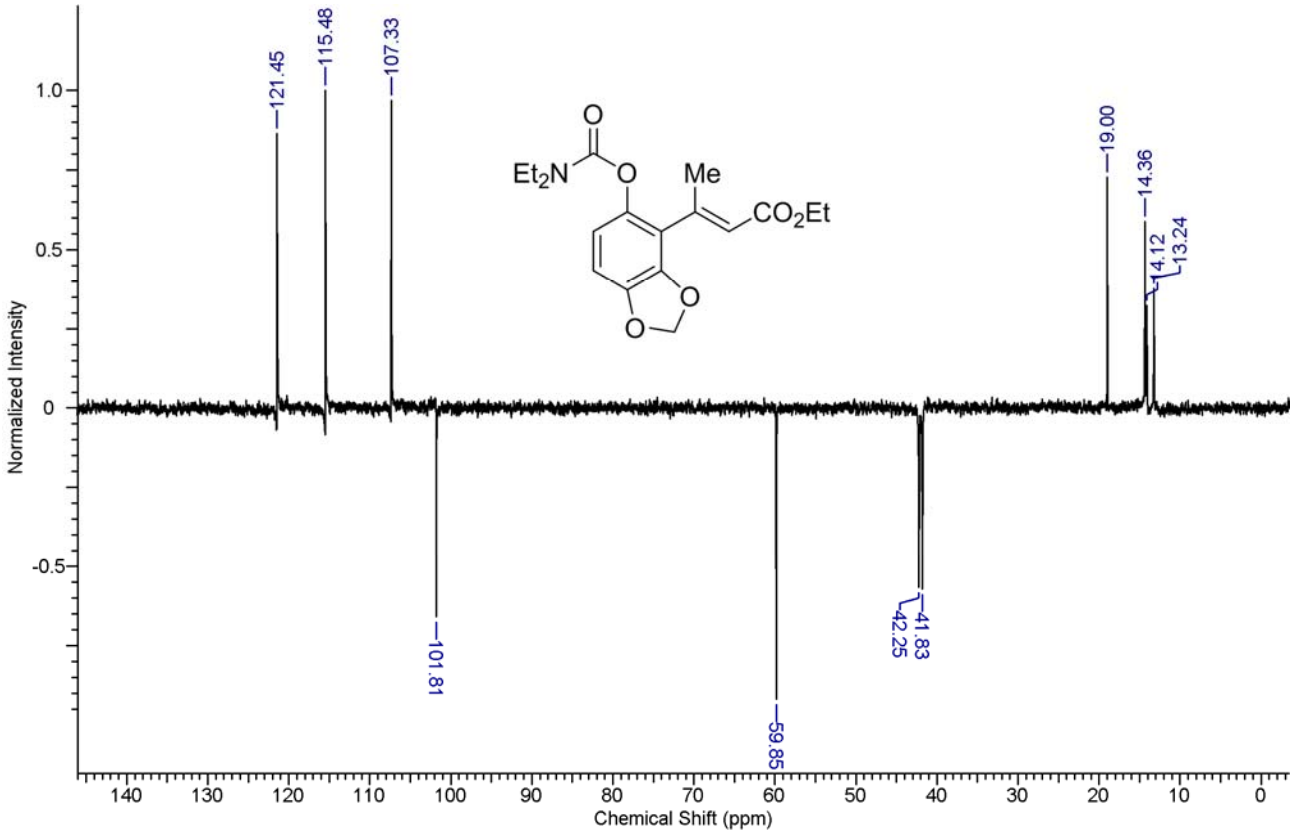


^{1}H and ^{13}C NMR Spectra of Compound **3e.**

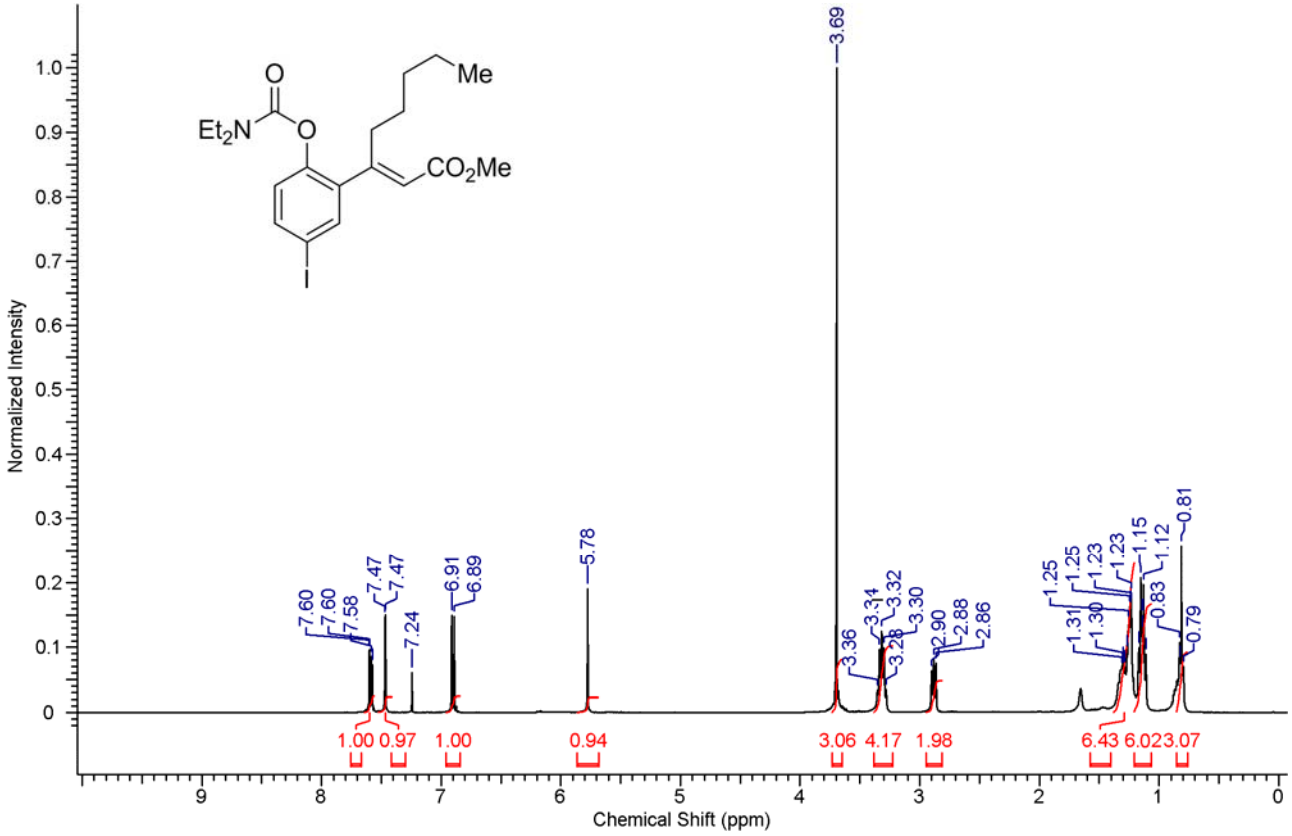


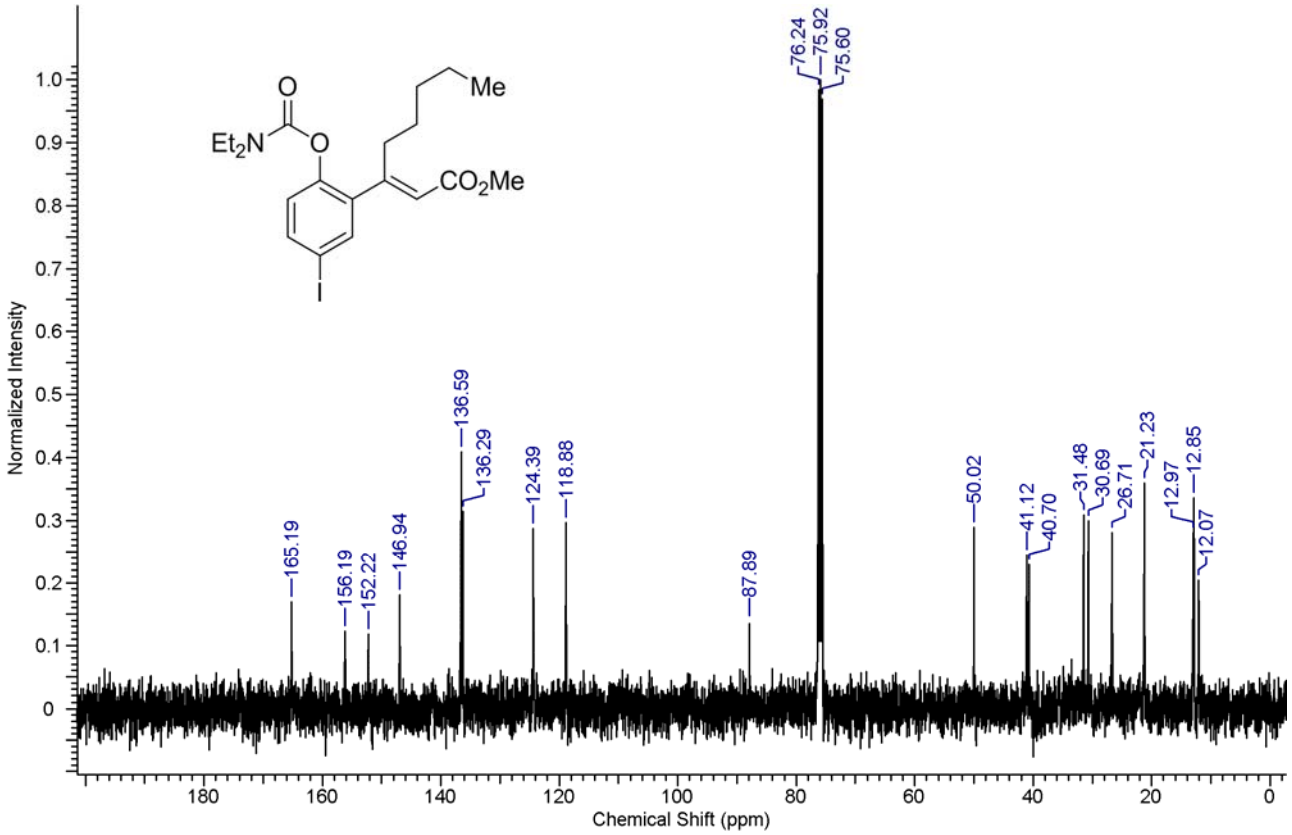


DEPT (135) NMR Spectrum of Compound **3e.**

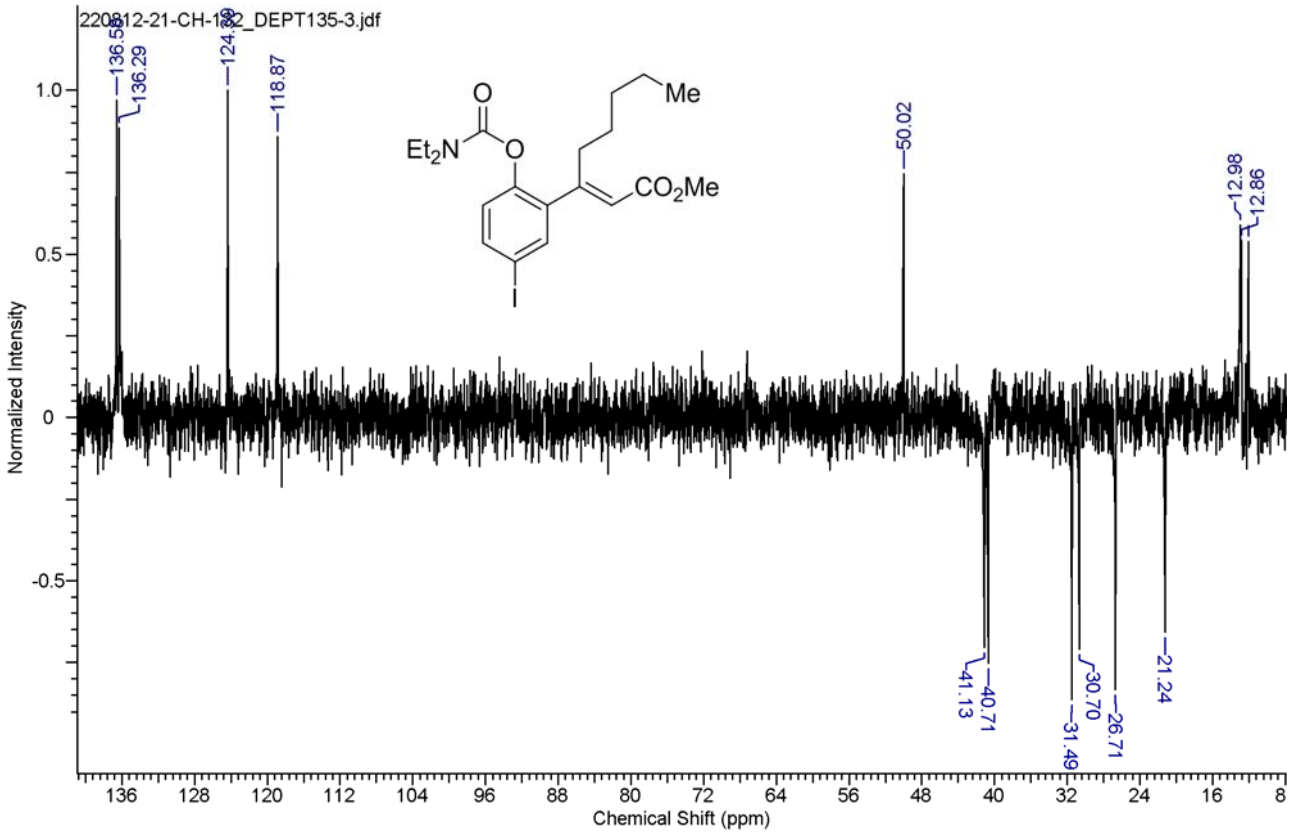


^{1}H and ^{13}C NMR Spectra of Compound **3f.**

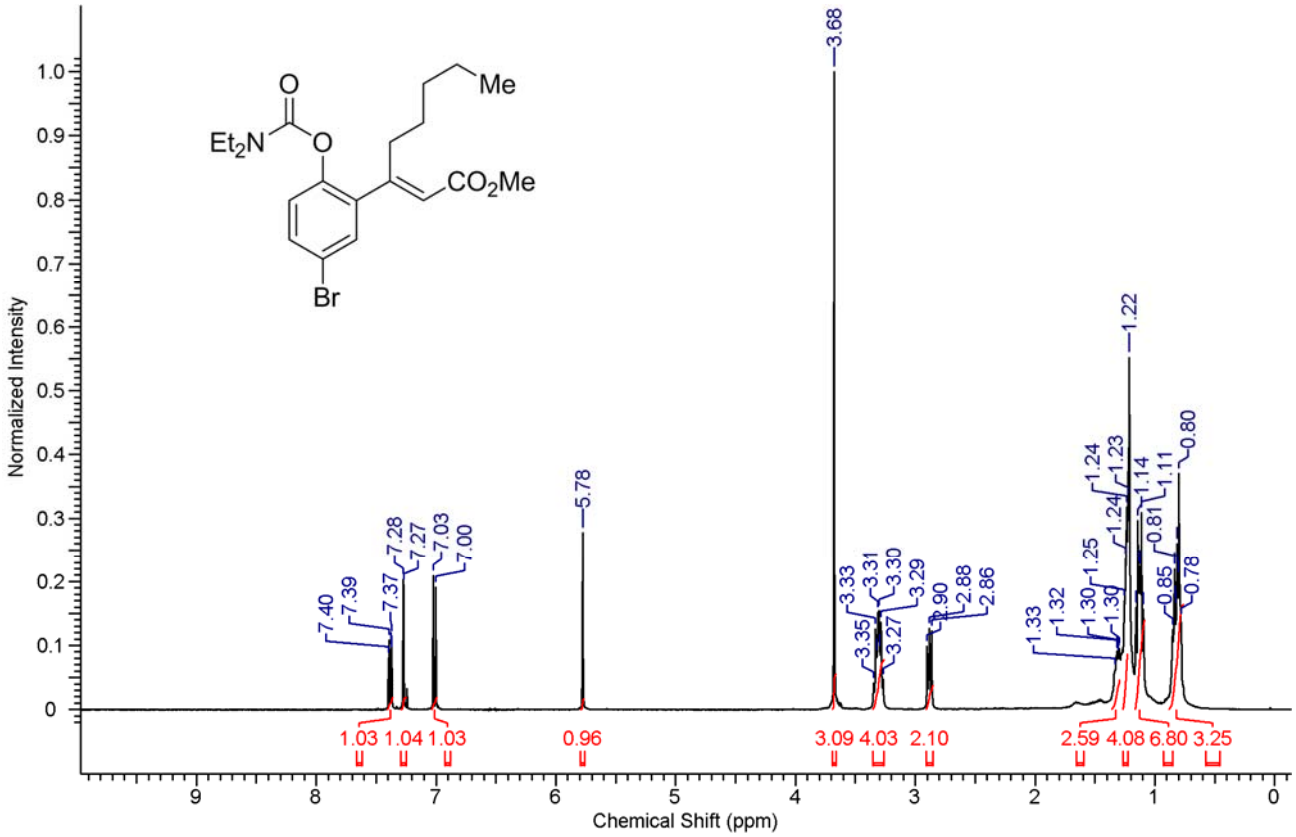


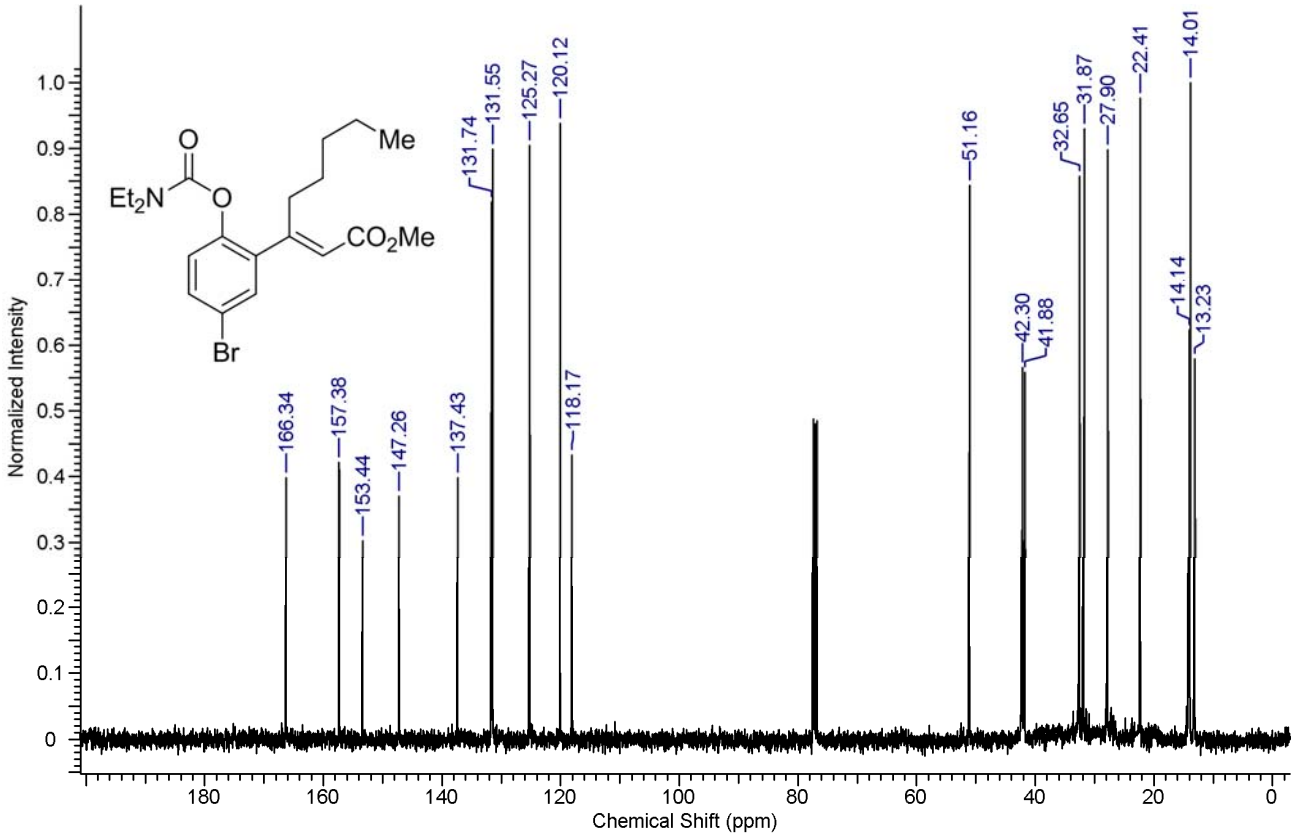


DEPT (135) NMR Spectrum of Compound **3f.**

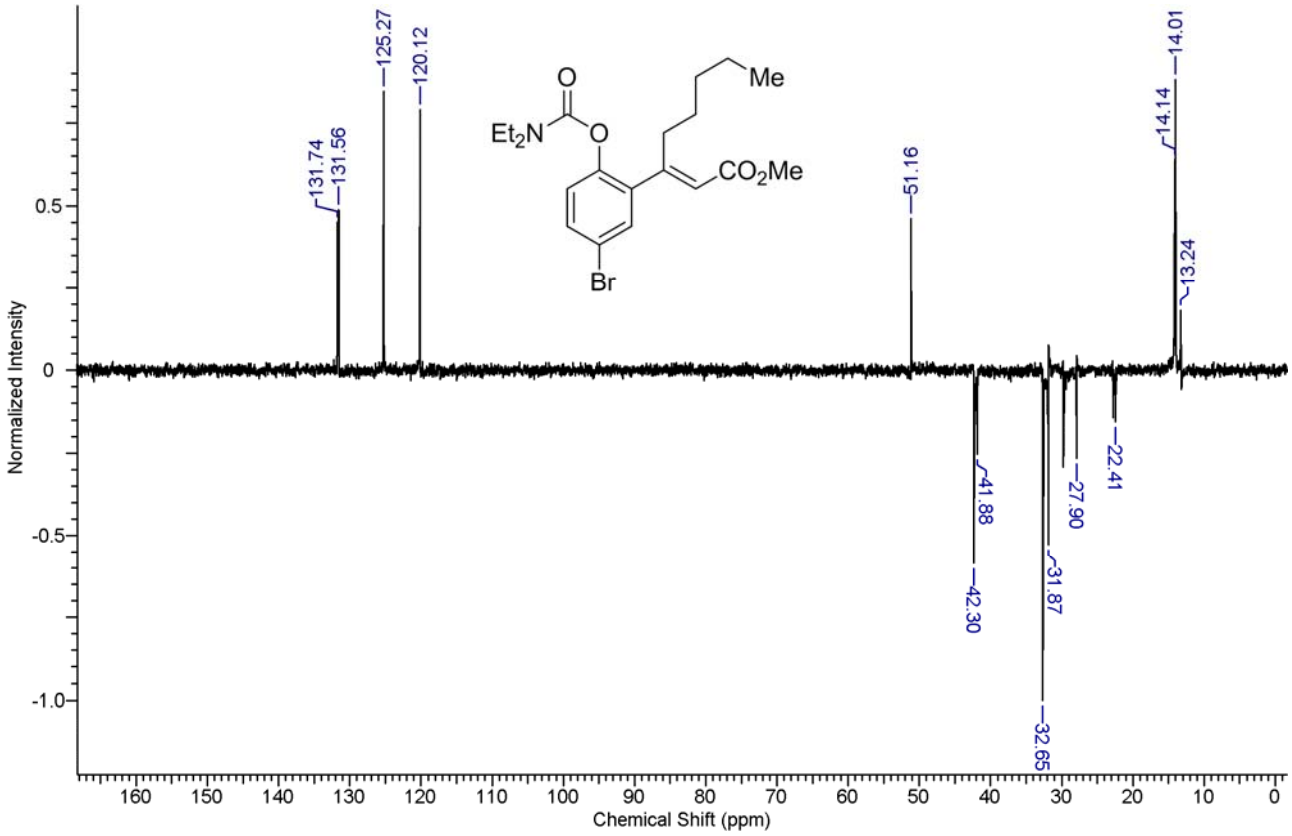


^{1}H and ^{13}C NMR Spectra of Compound **3g.**

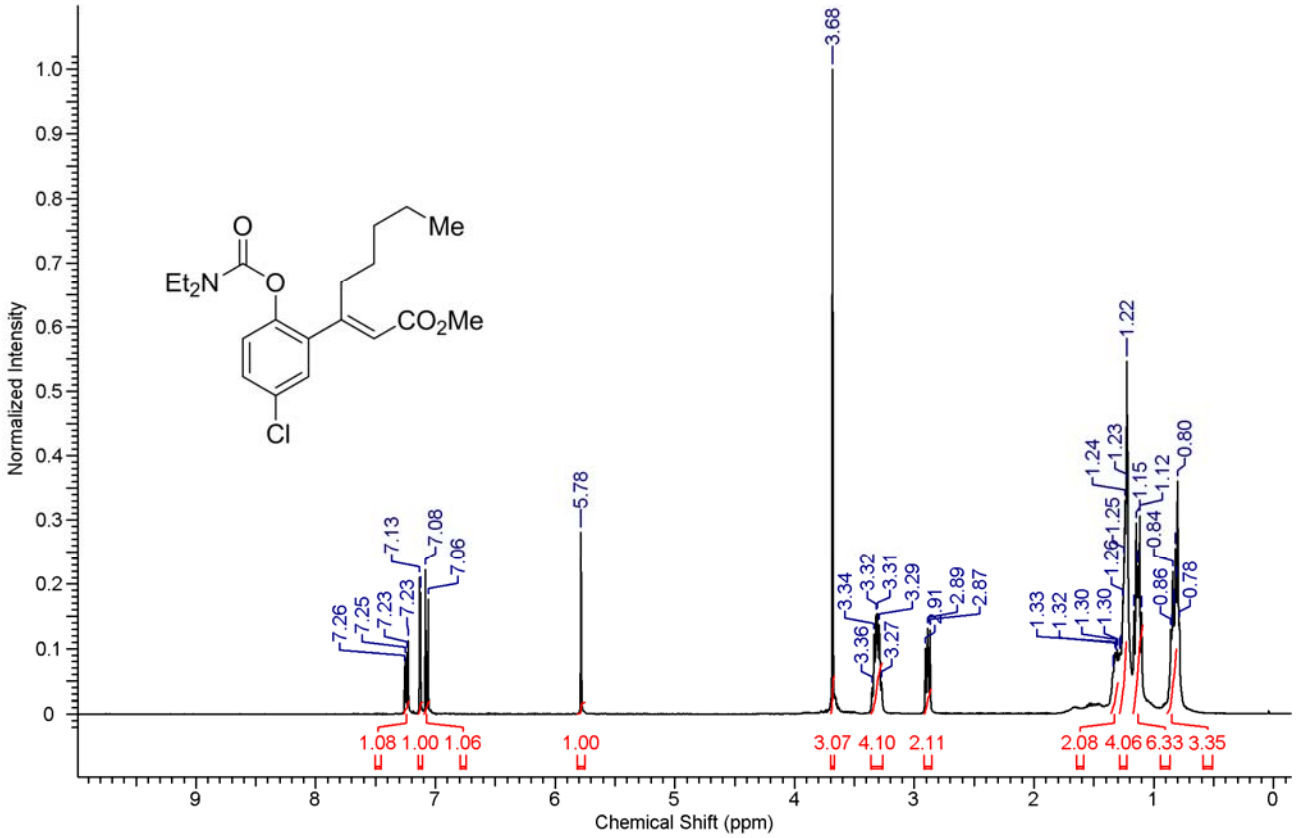


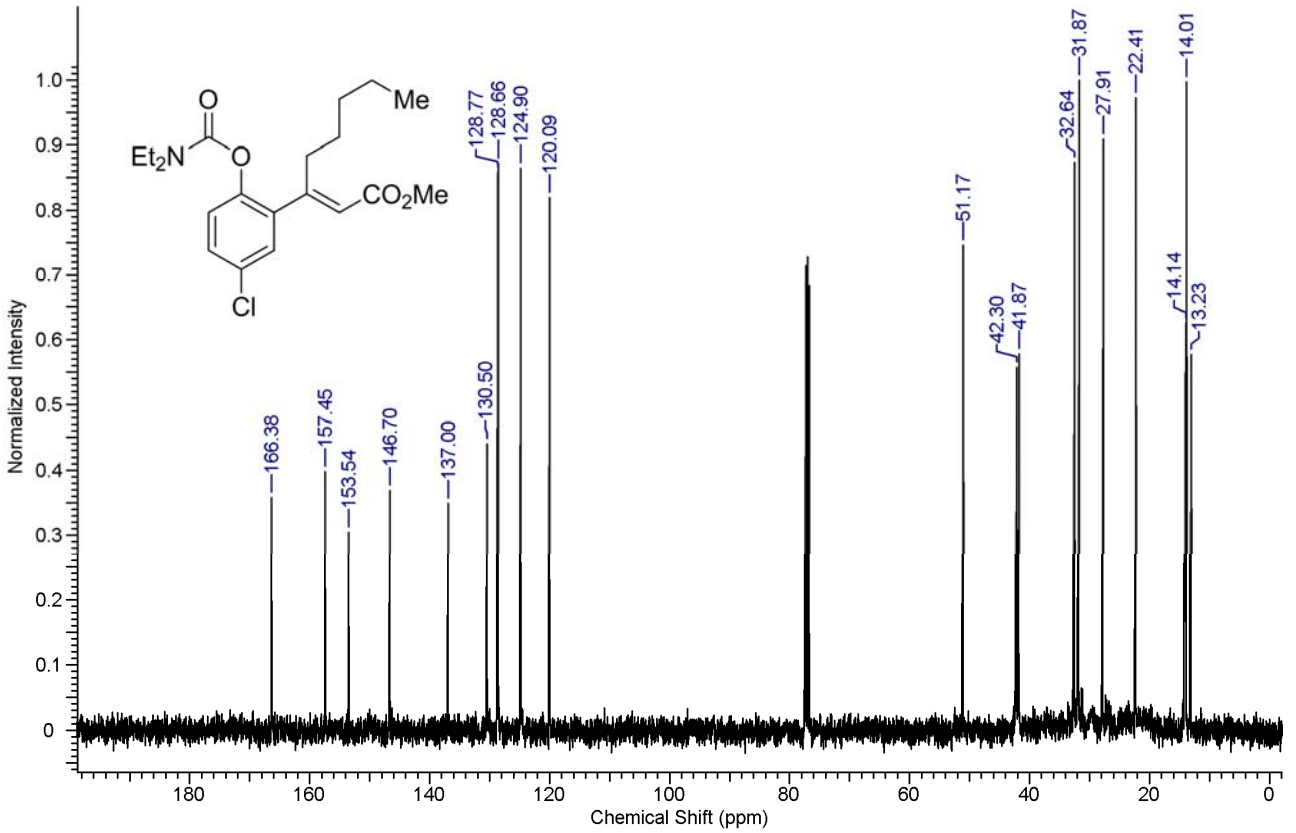


DEPT (135) NMR Spectrum of Compound **3g.**

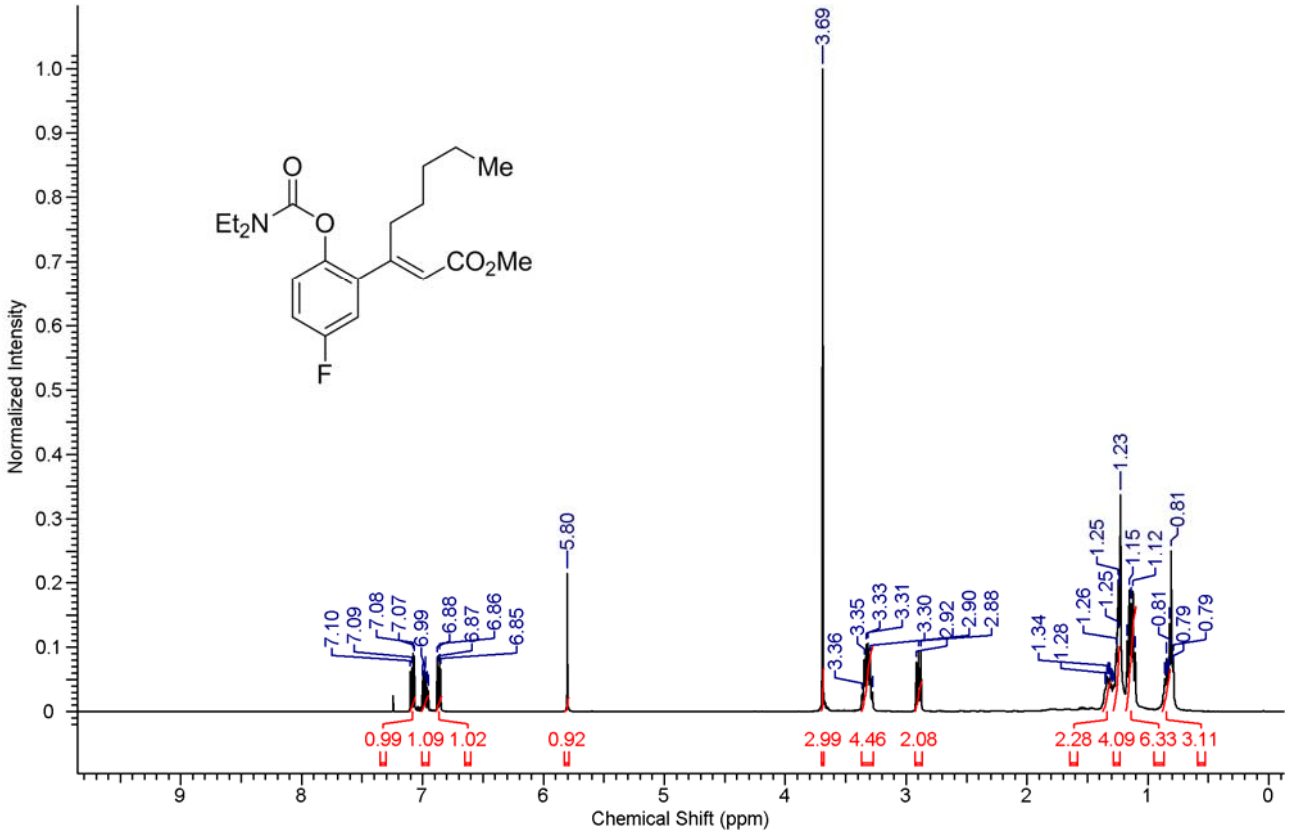


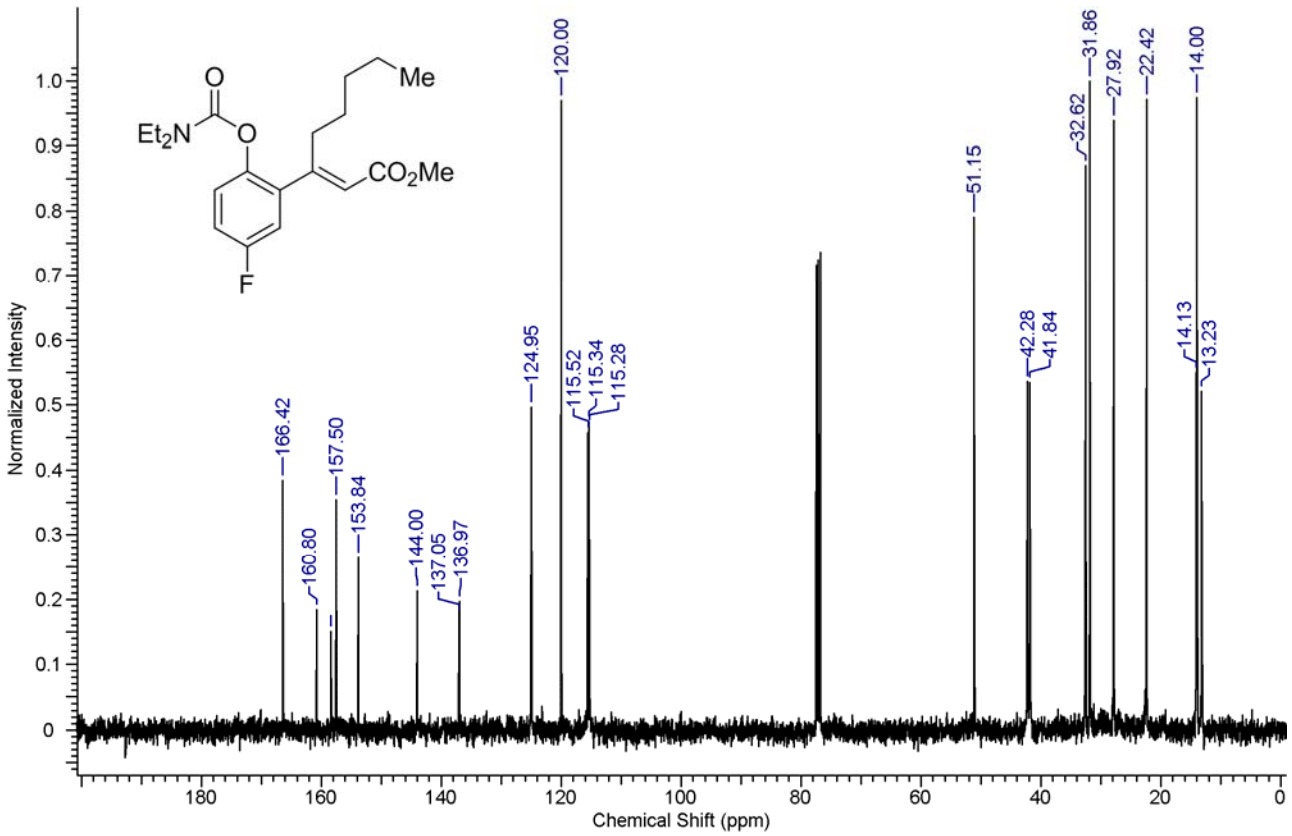
^{1}H and ^{13}C NMR Spectra of Compound **3h.**



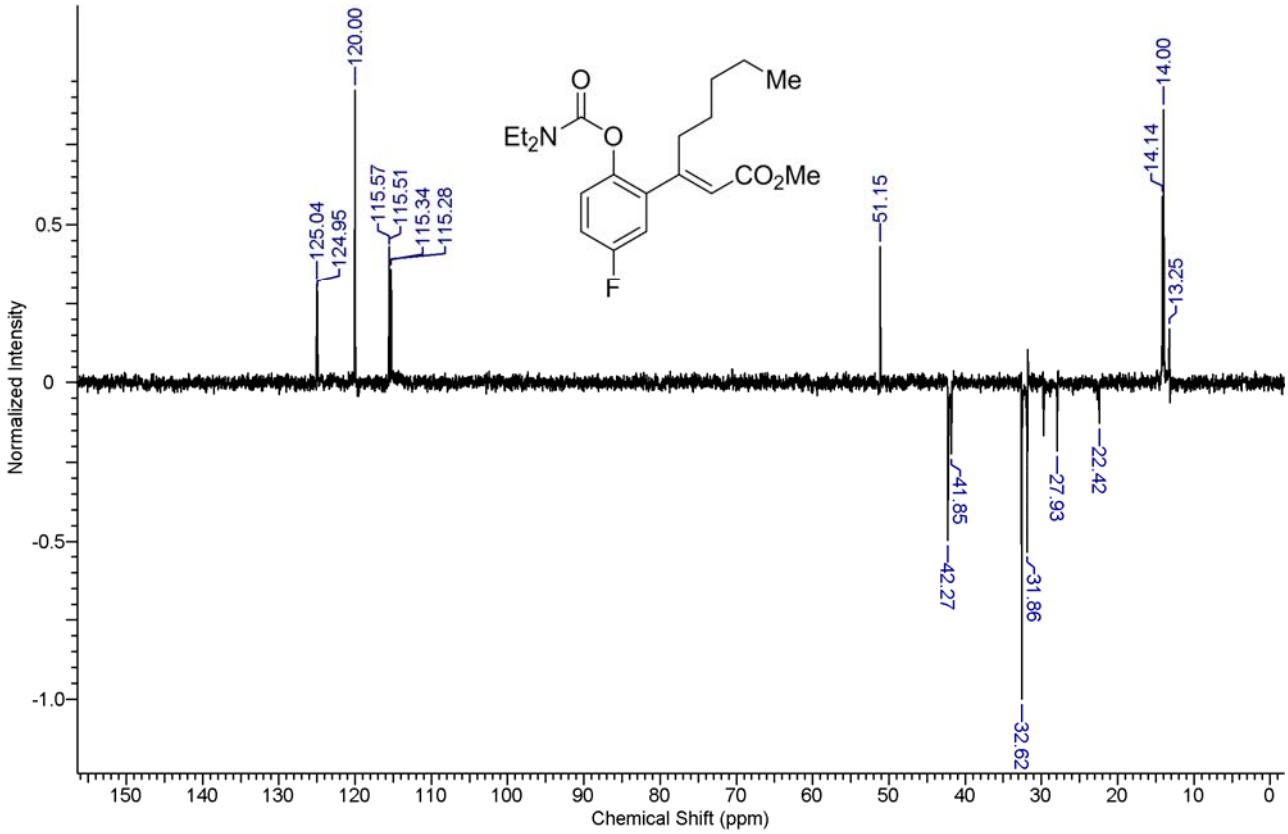


^{1}H and ^{13}C NMR Spectra of Compound **3i.**

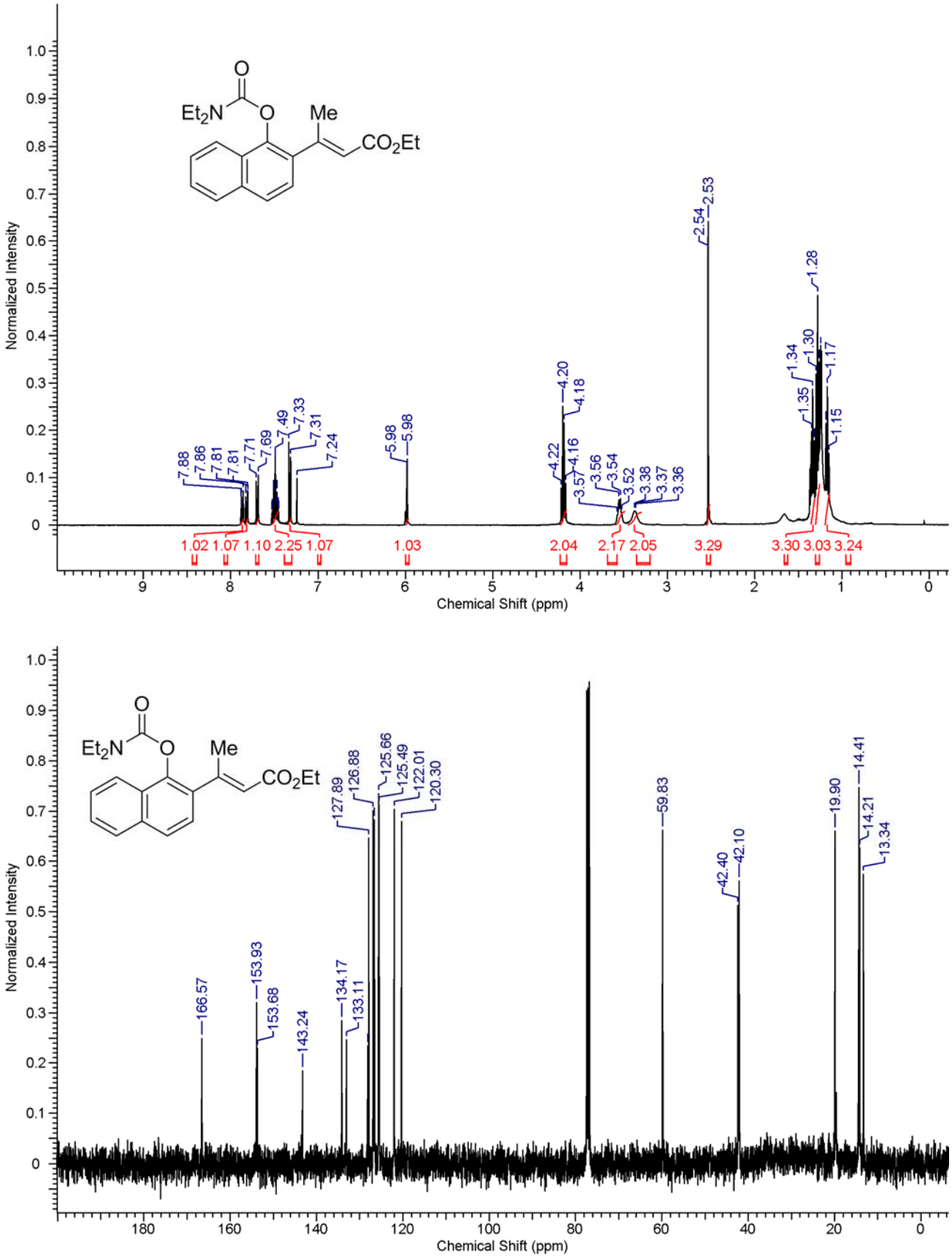




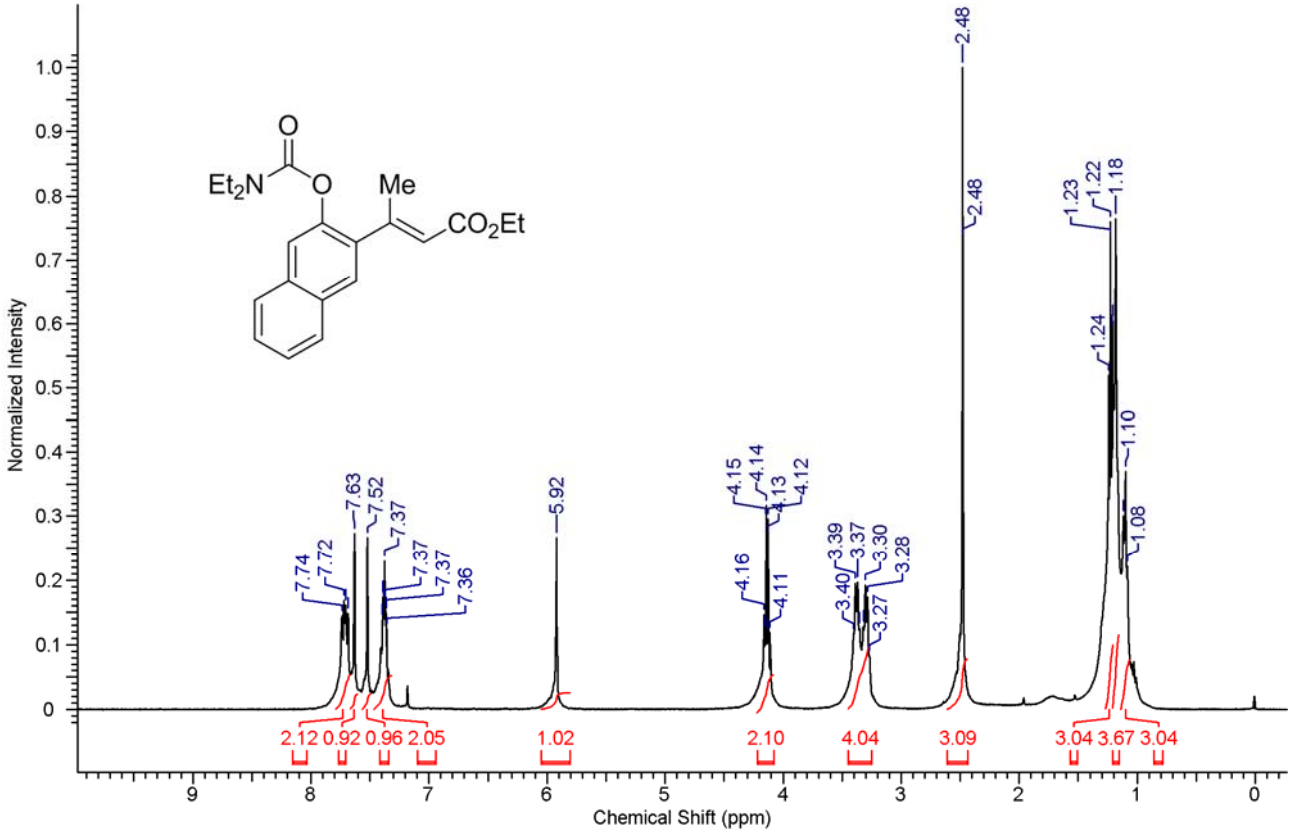
DEPT (135) NMR Spectrum of Compound **3i.**

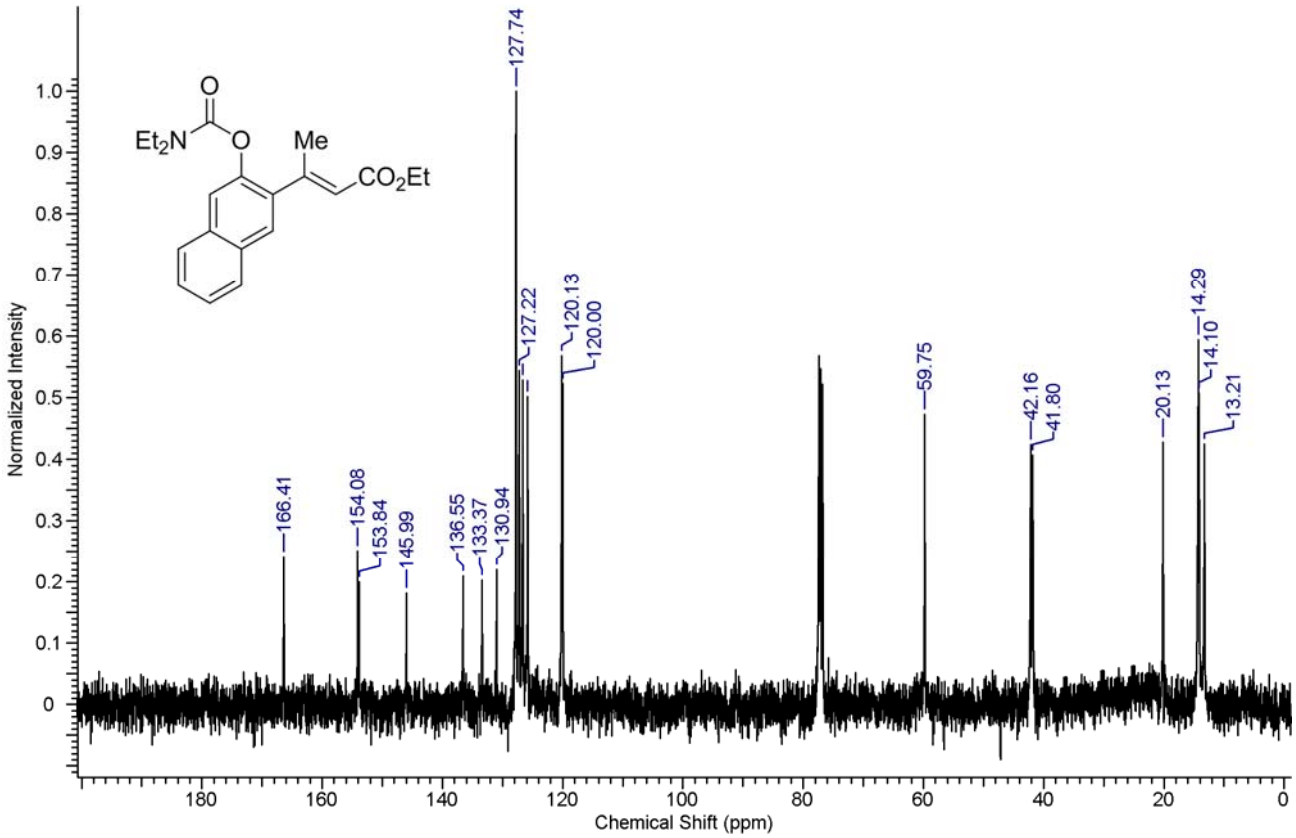


^{1}H and ^{13}C NMR Spectra of Compound **3j.**

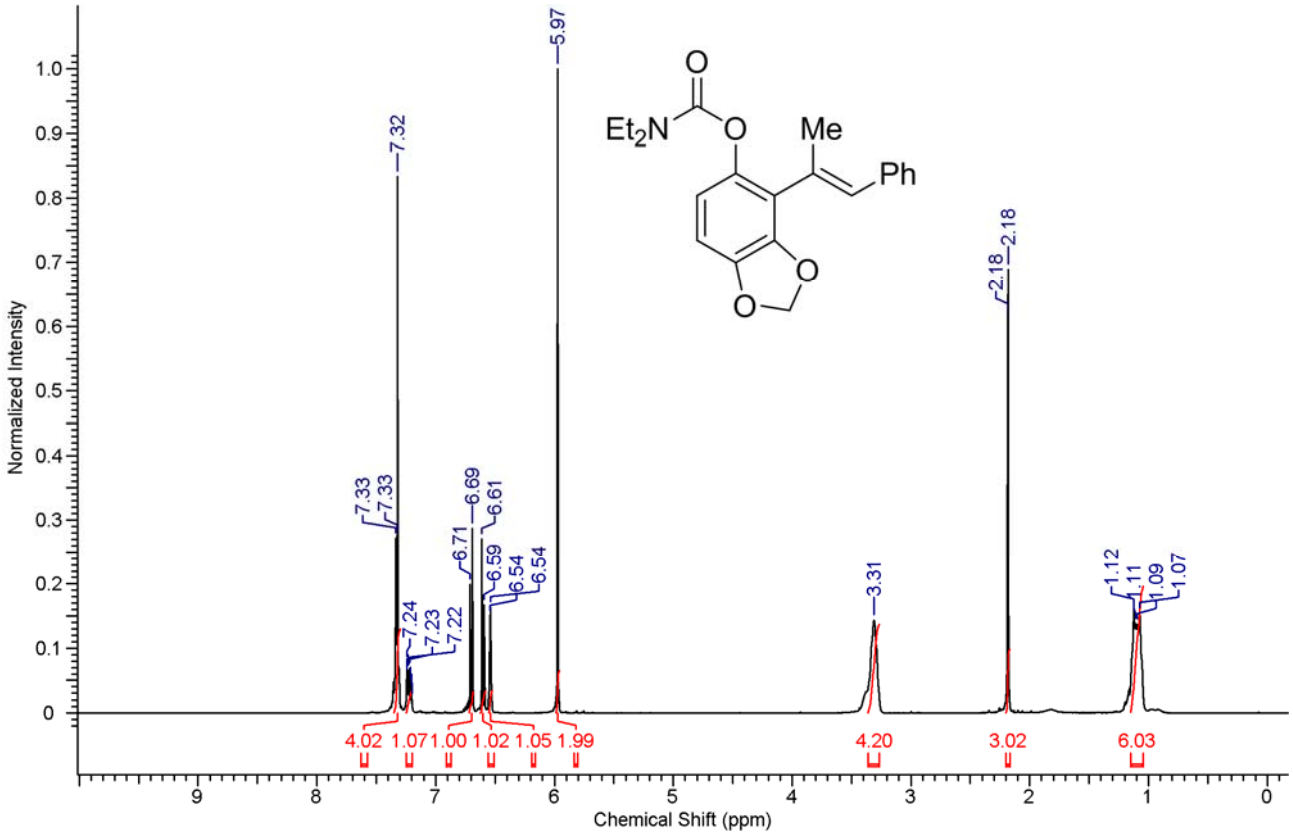


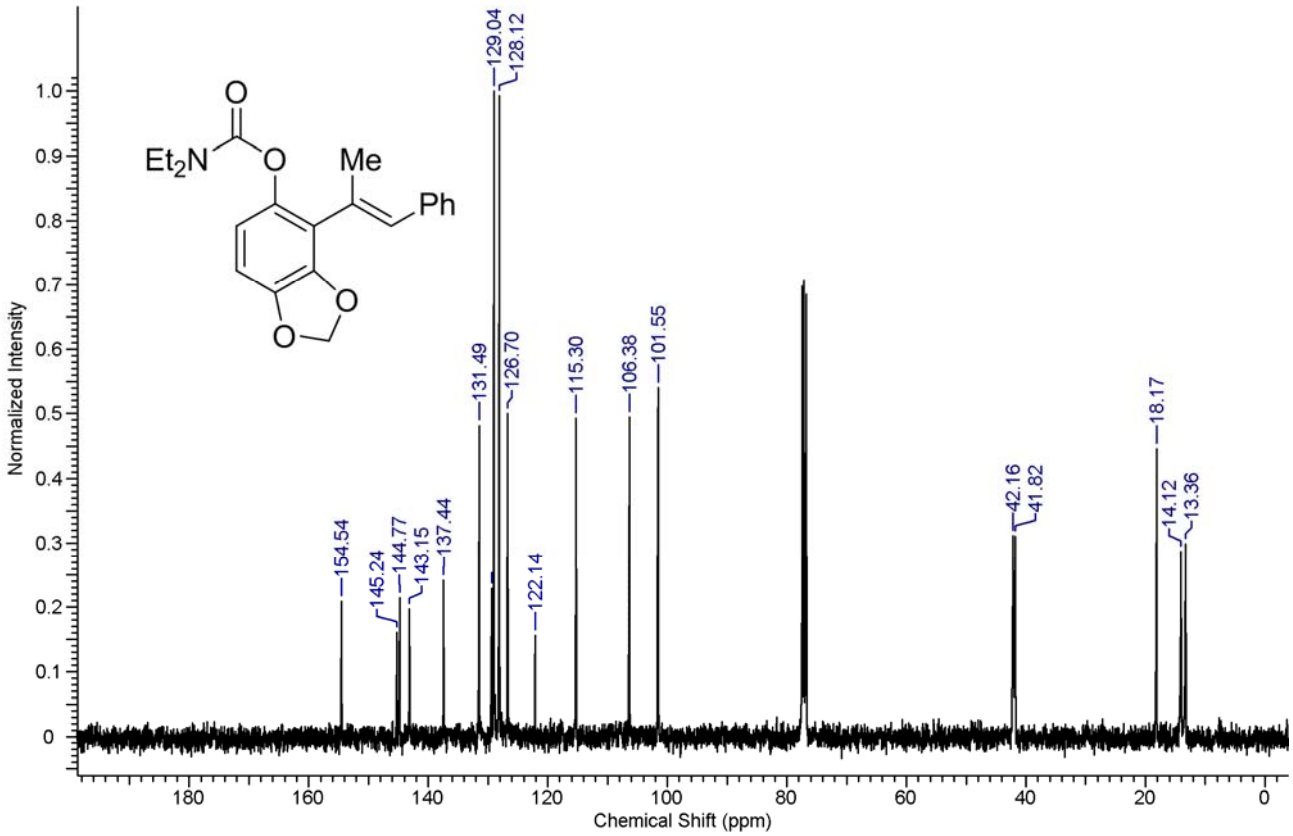
^{1}H and ^{13}C NMR Spectra of Compound **3k.**



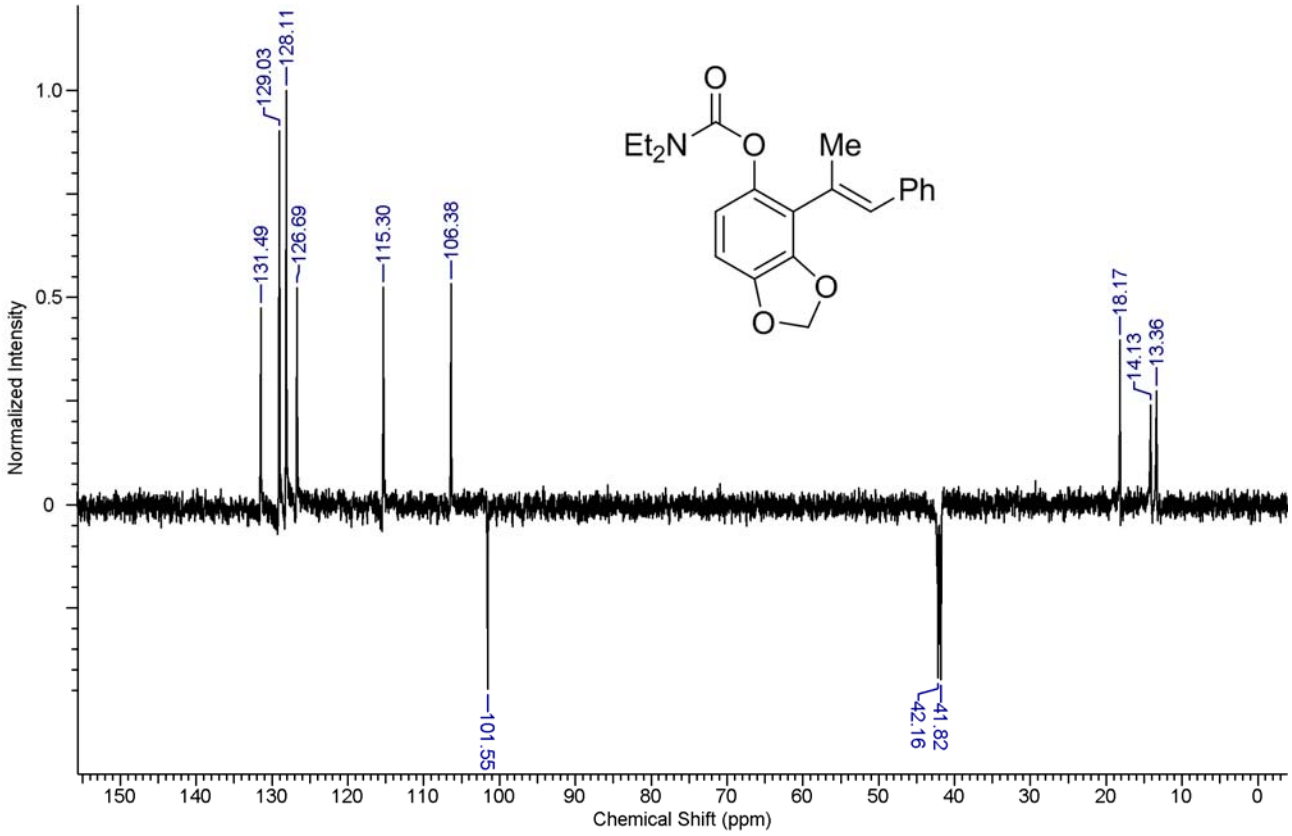


^{1}H and ^{13}C NMR Spectra of Compound **3l.**

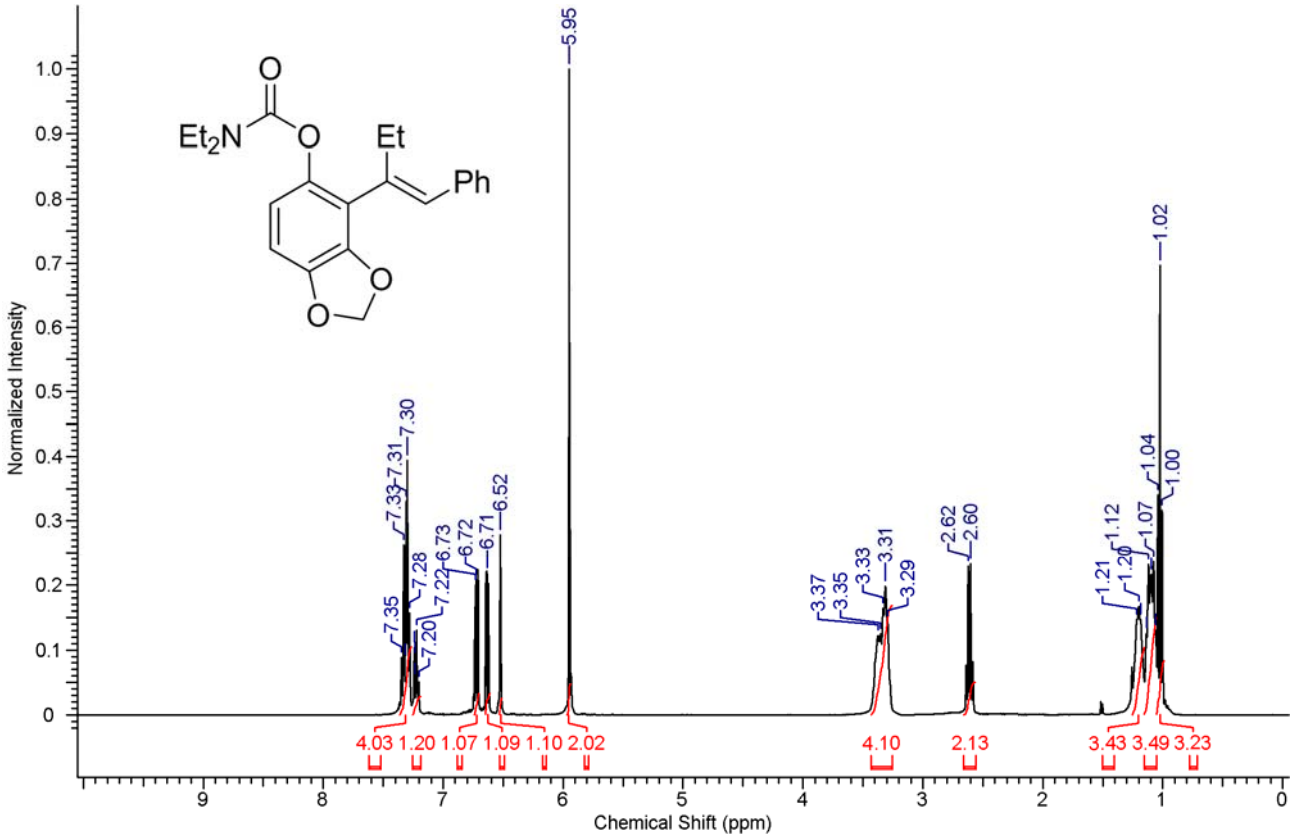


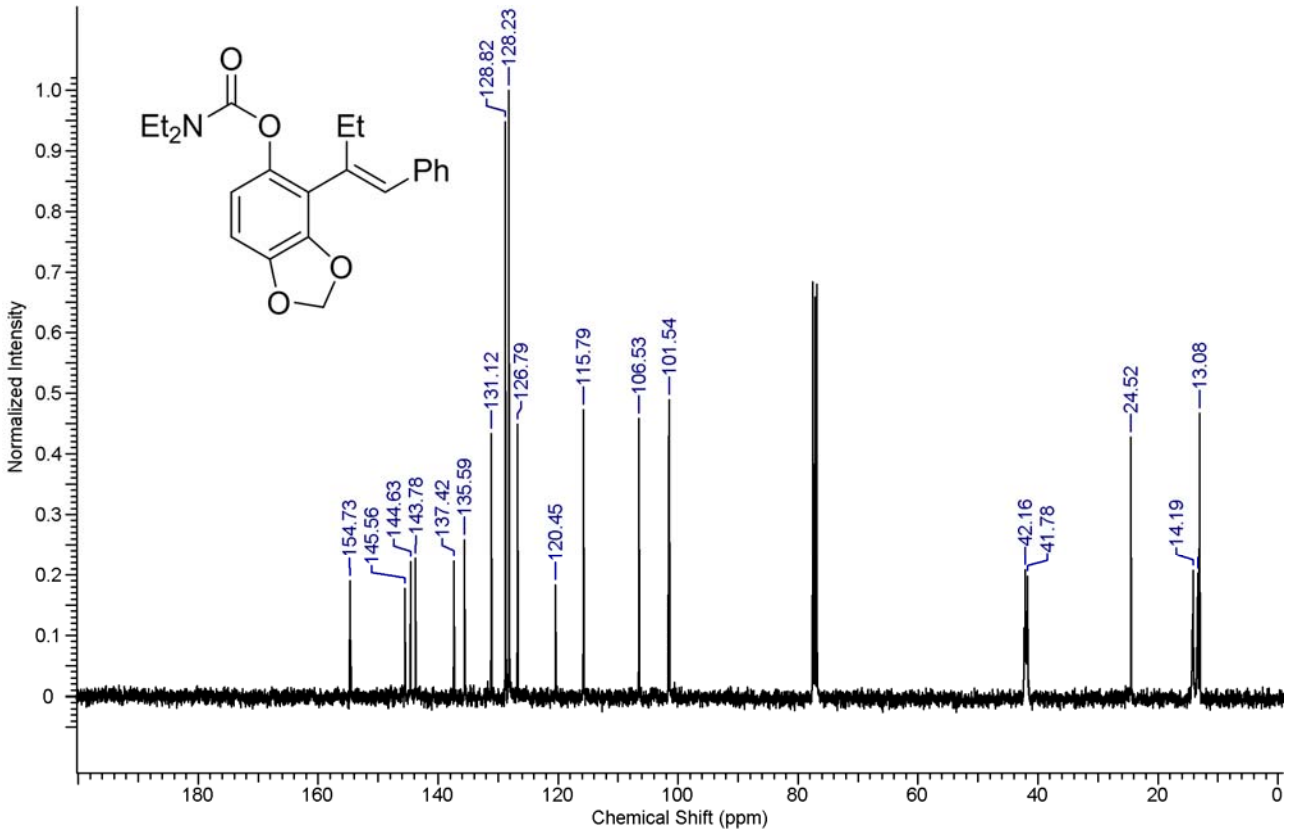


DEPT (135) NMR Spectrum of Compound **3l.**

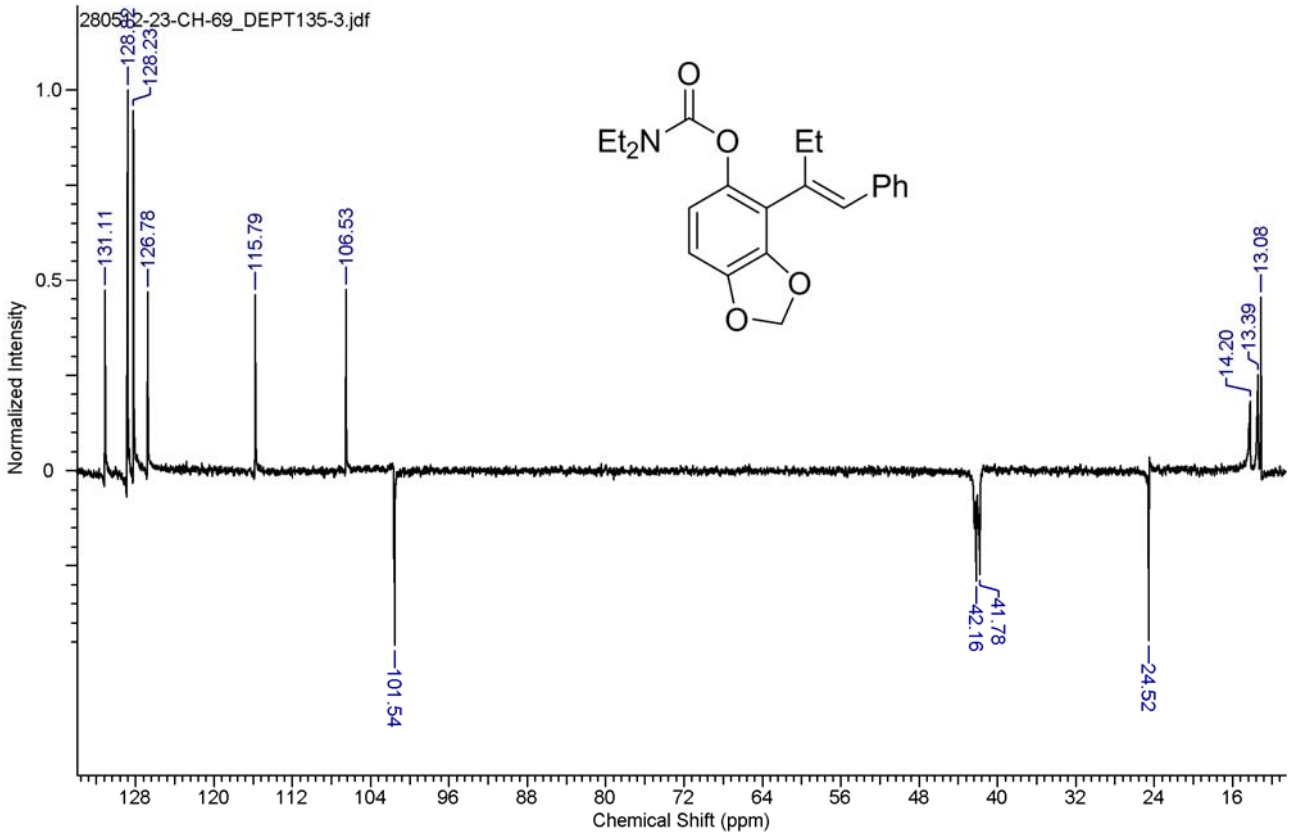


^{1}H and ^{13}C NMR Spectra of Compound **3m.**

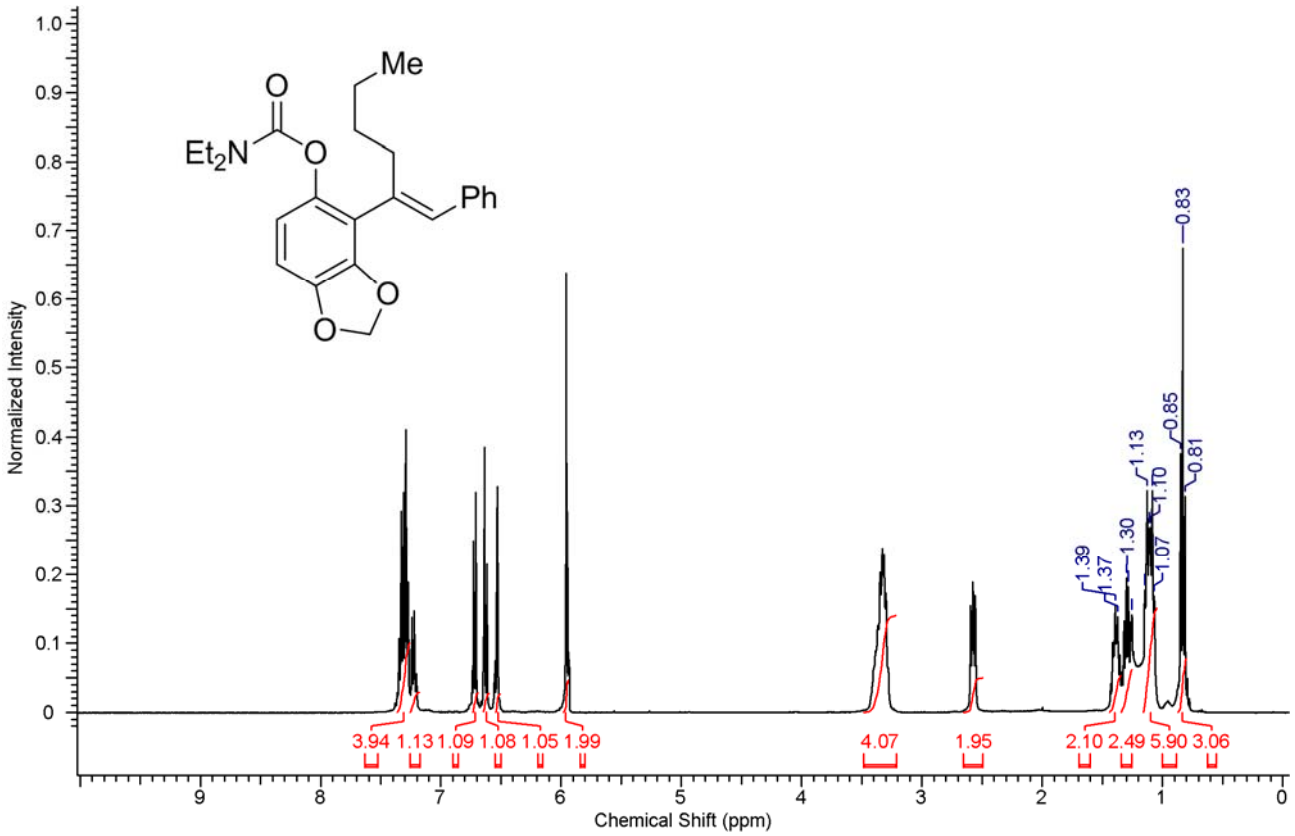


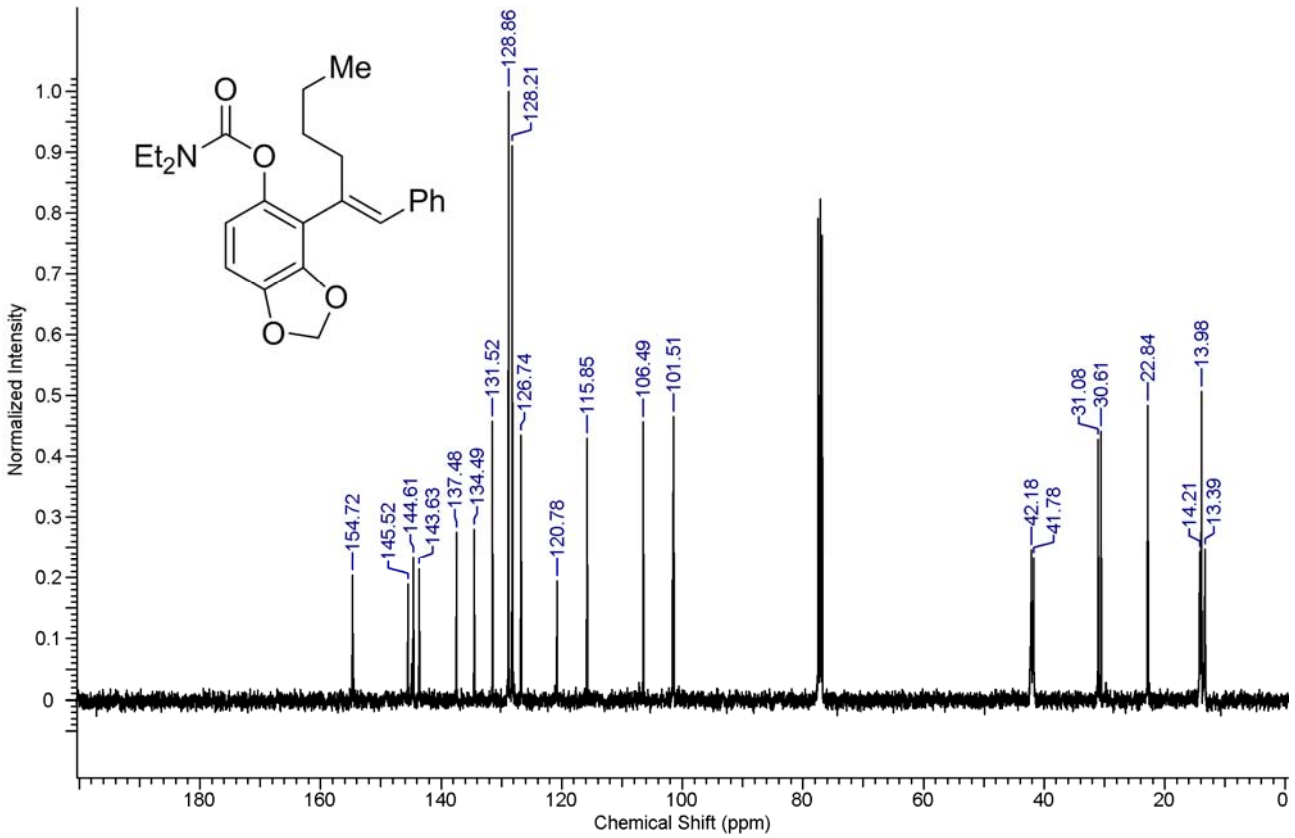


DEPT (135) NMR Spectrum of Compound **3m.**

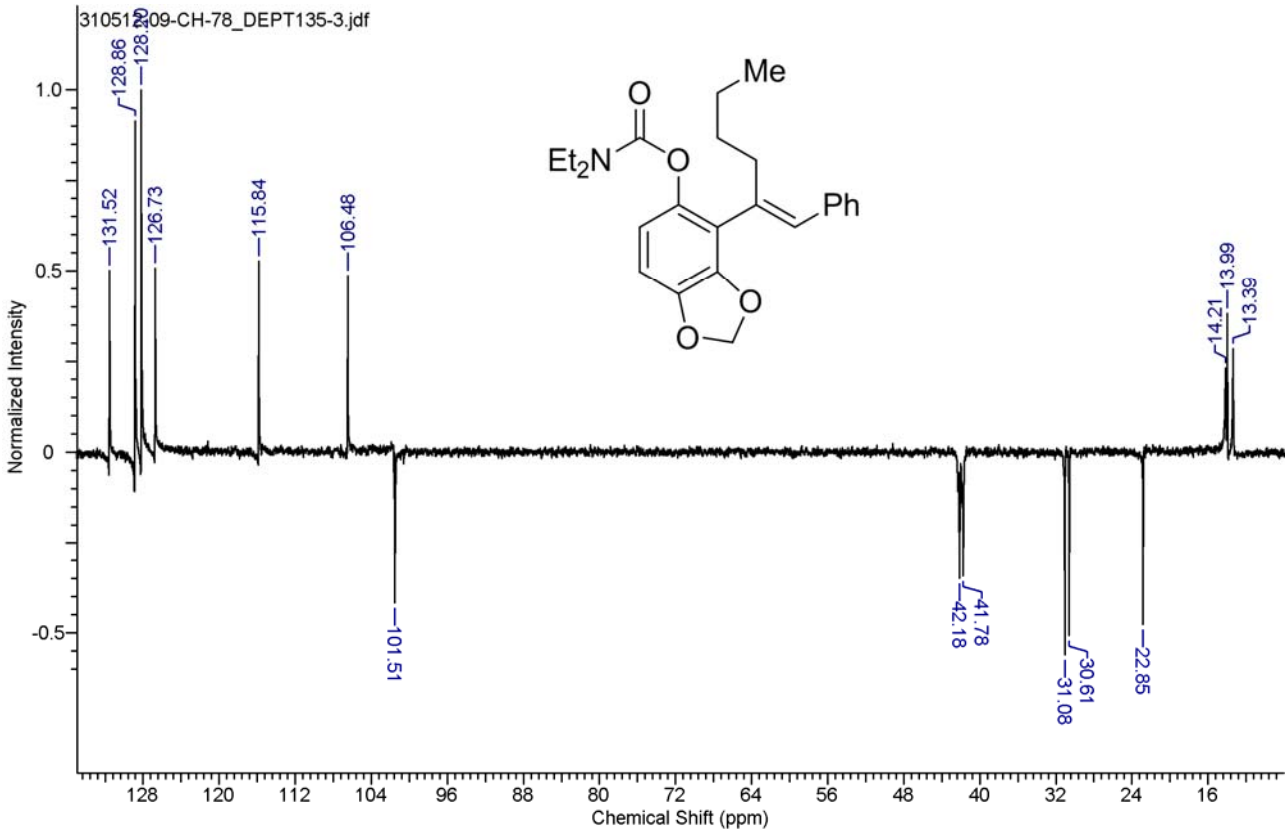


^{1}H and ^{13}C NMR Spectra of Compound **3n.**

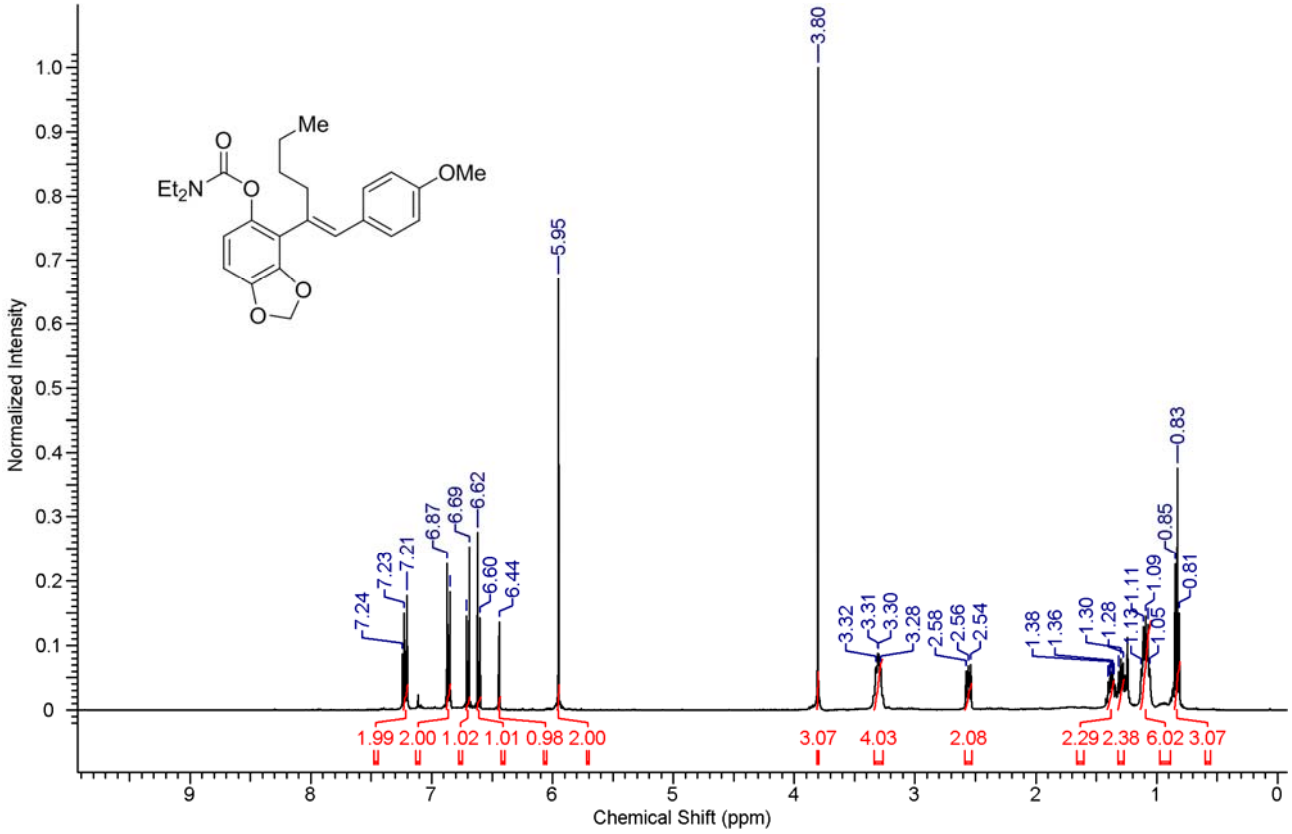


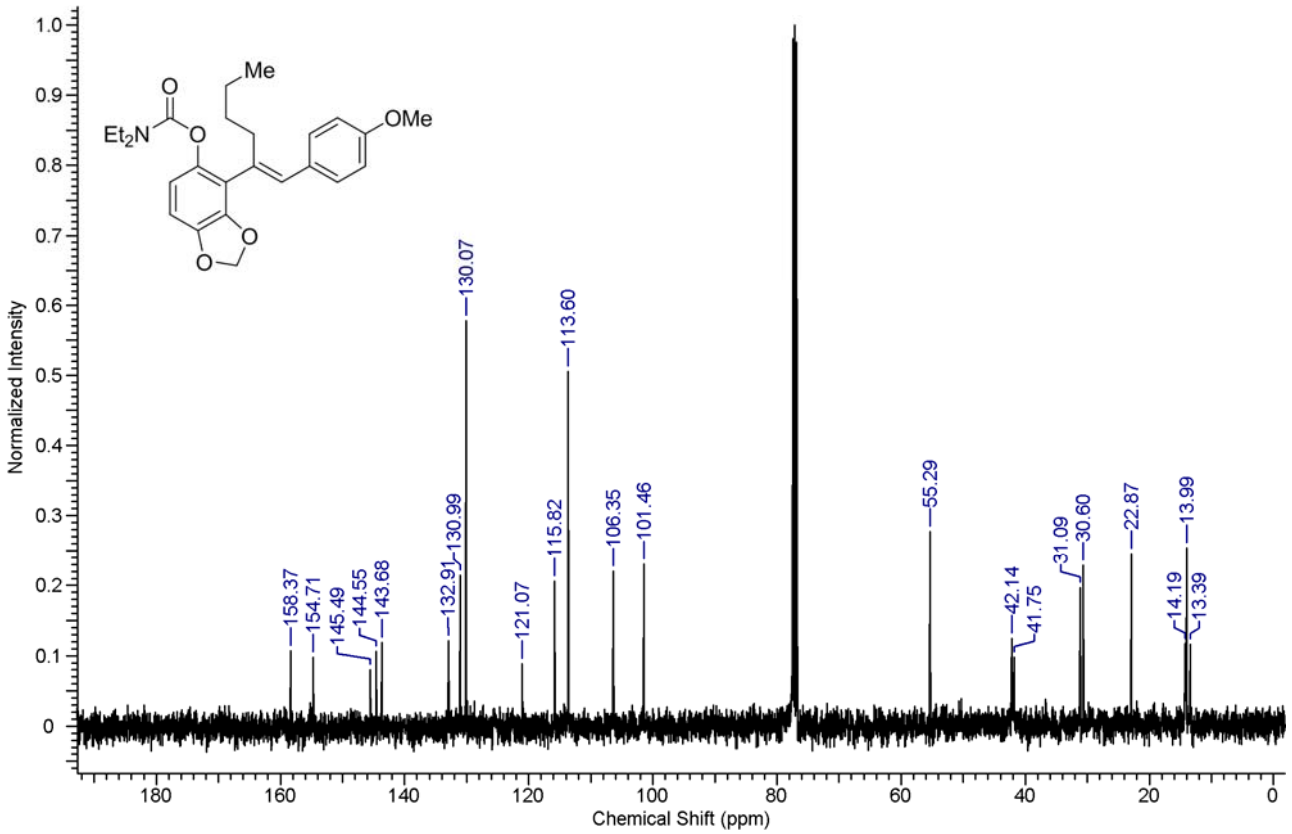


DEPT (135) NMR Spectrum of Compound **3n.**

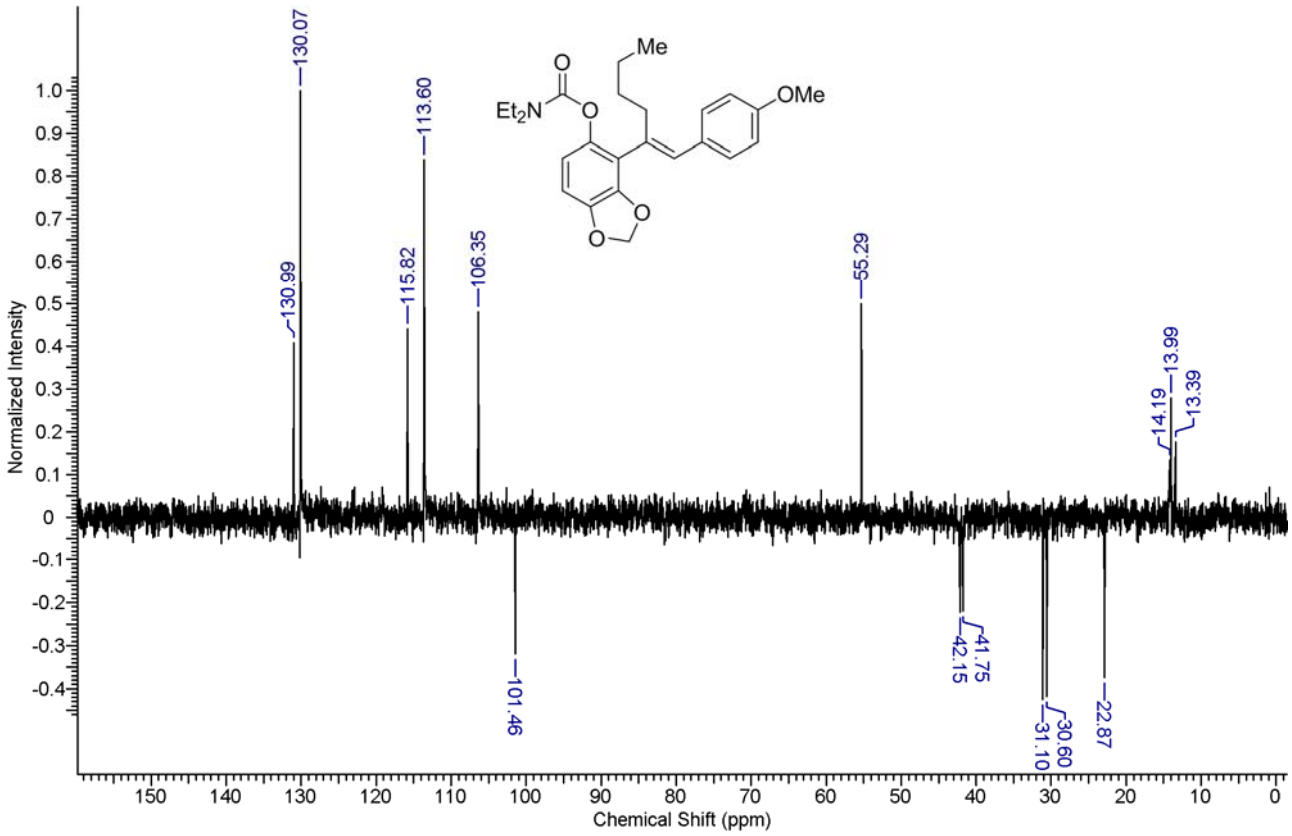


^{1}H and ^{13}C NMR Spectra of Compound **3o.**

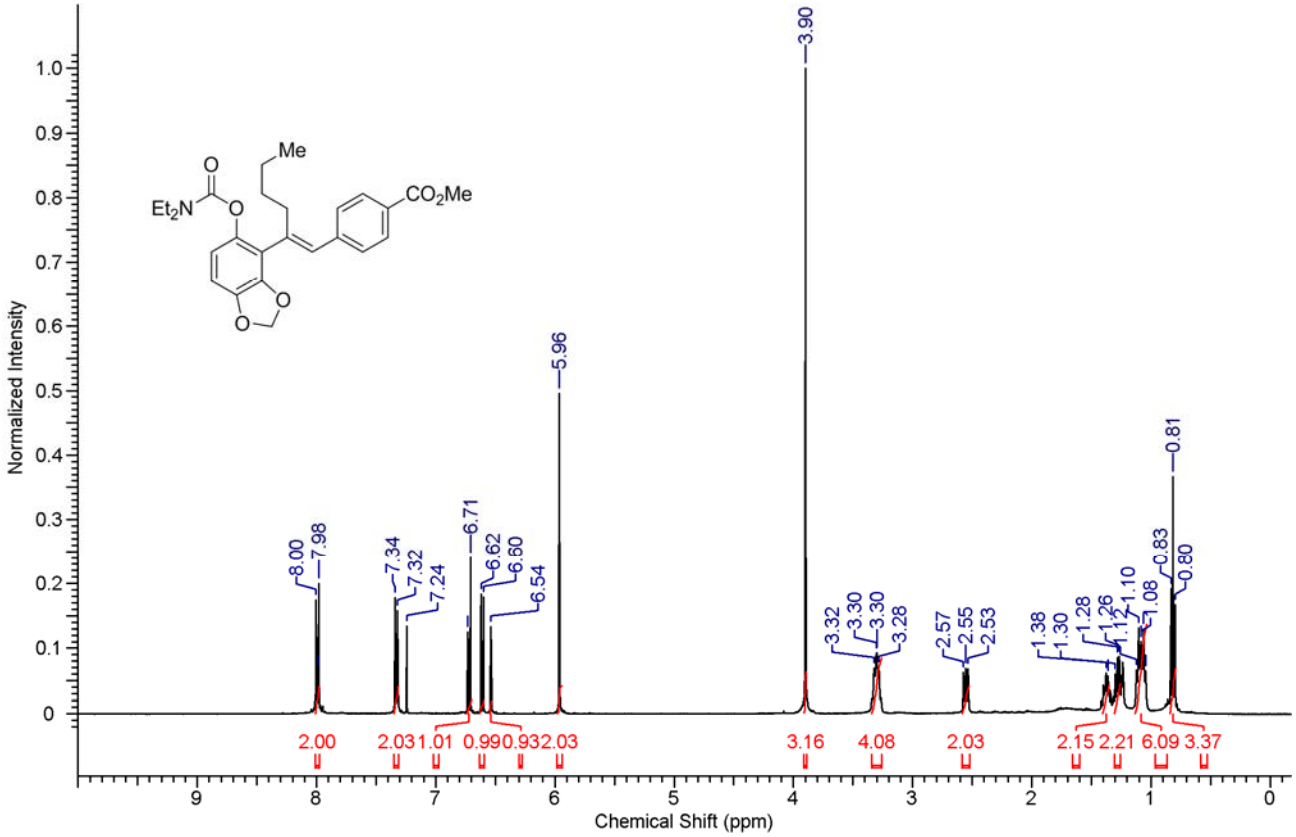


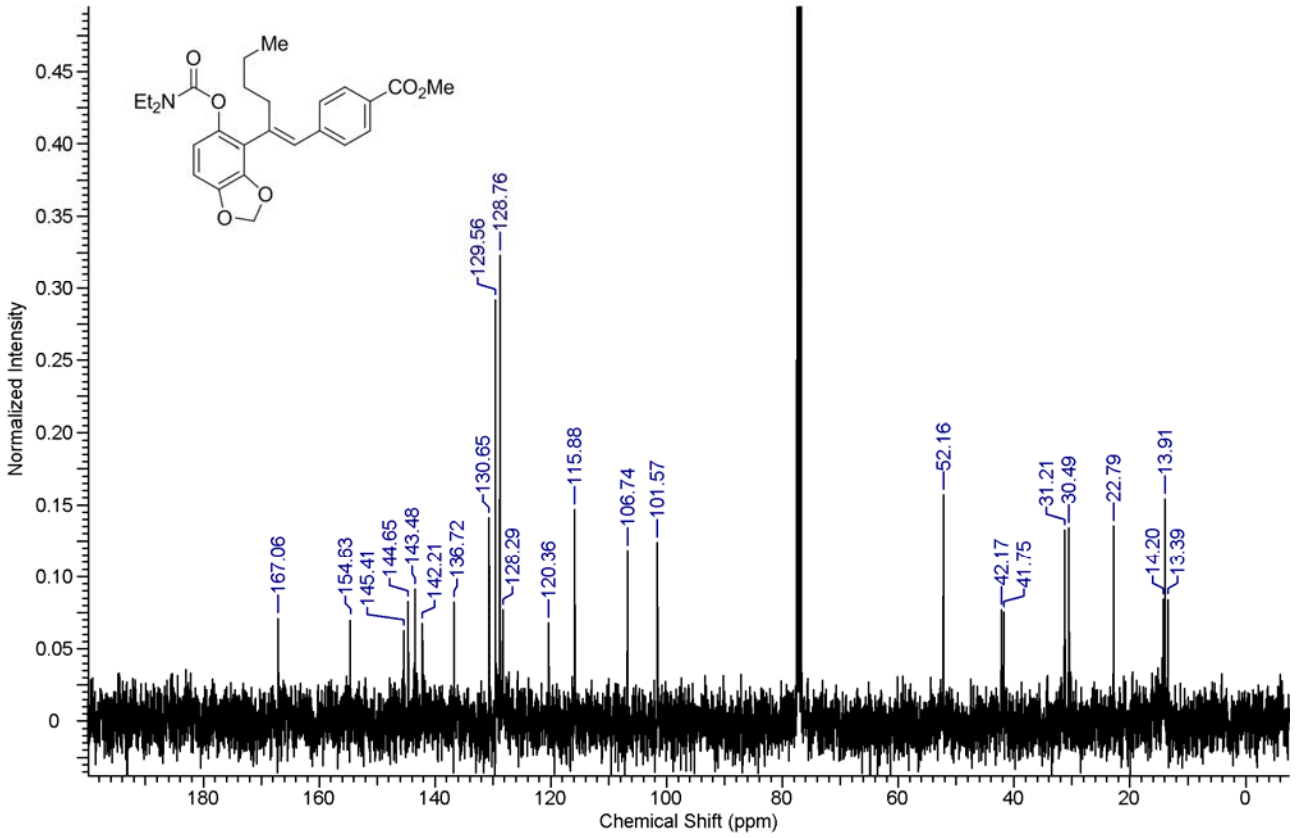


DEPT (135) NMR Spectrum of Compound **3o.**

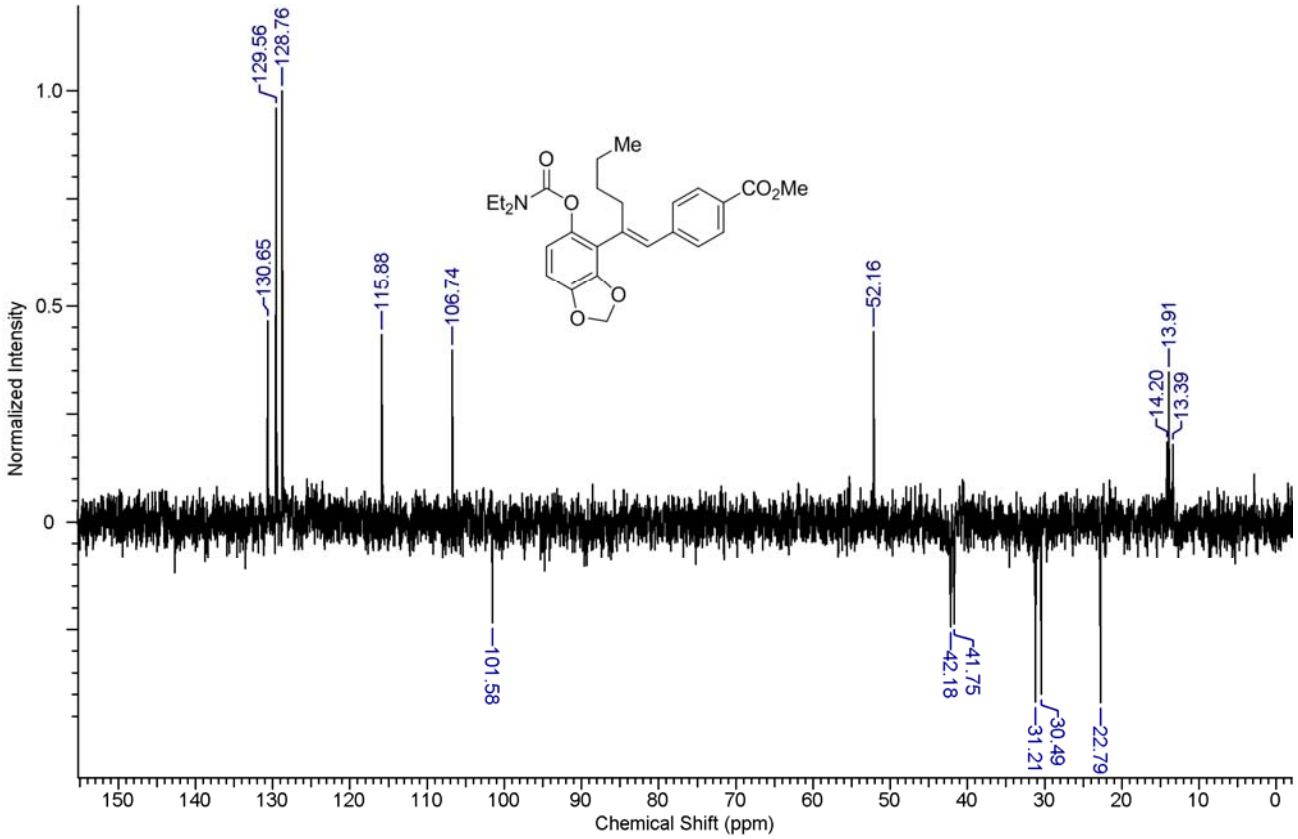


^{1}H and ^{13}C NMR Spectra of Compound **3p.**

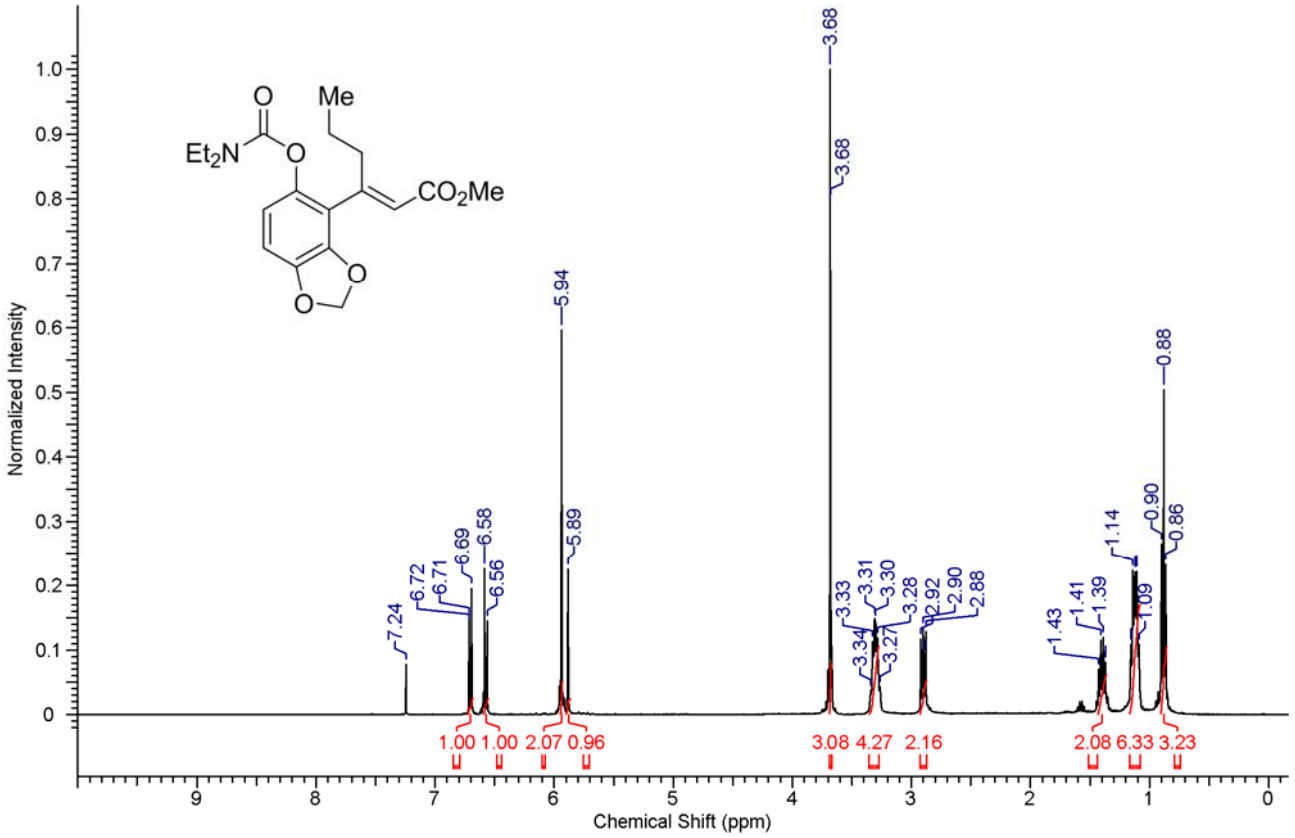


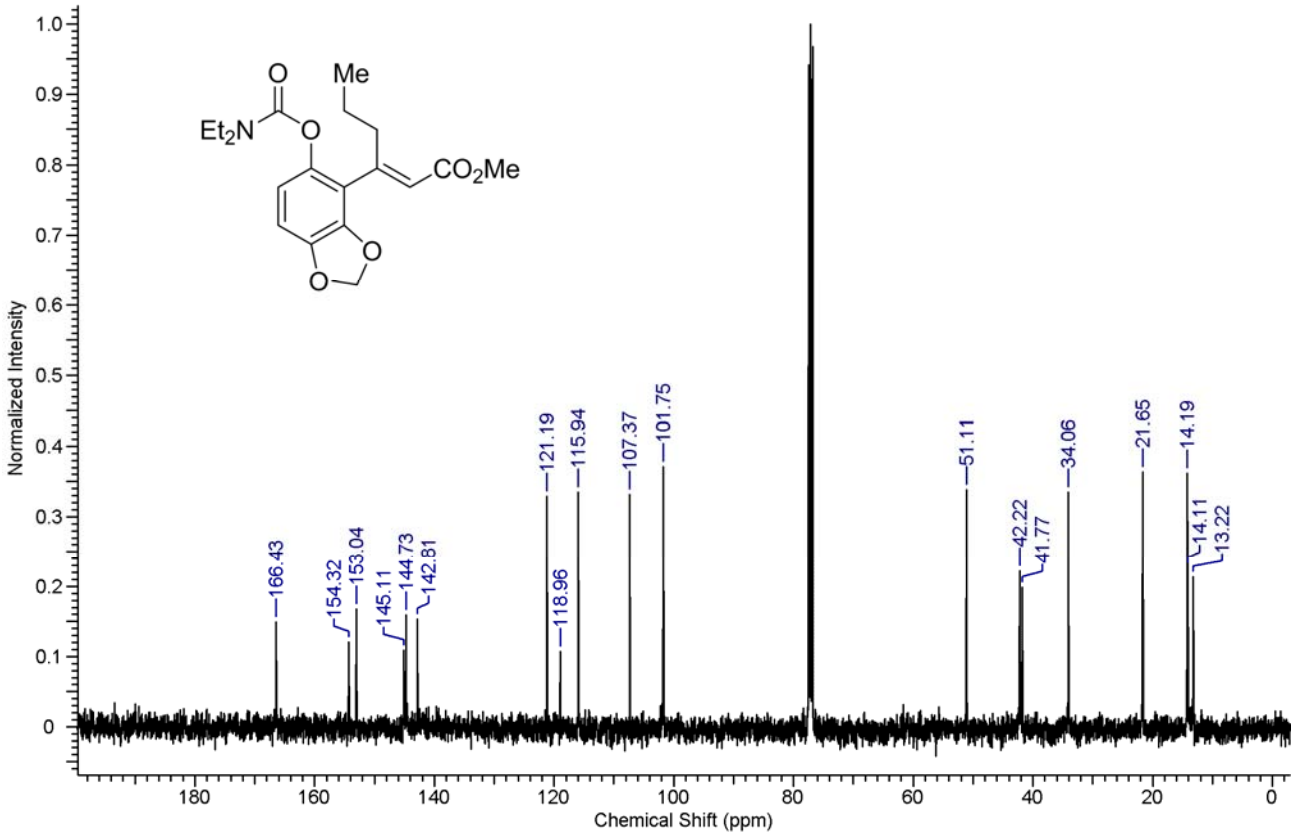


DEPT (135) NMR Spectrum of Compound **3p.**

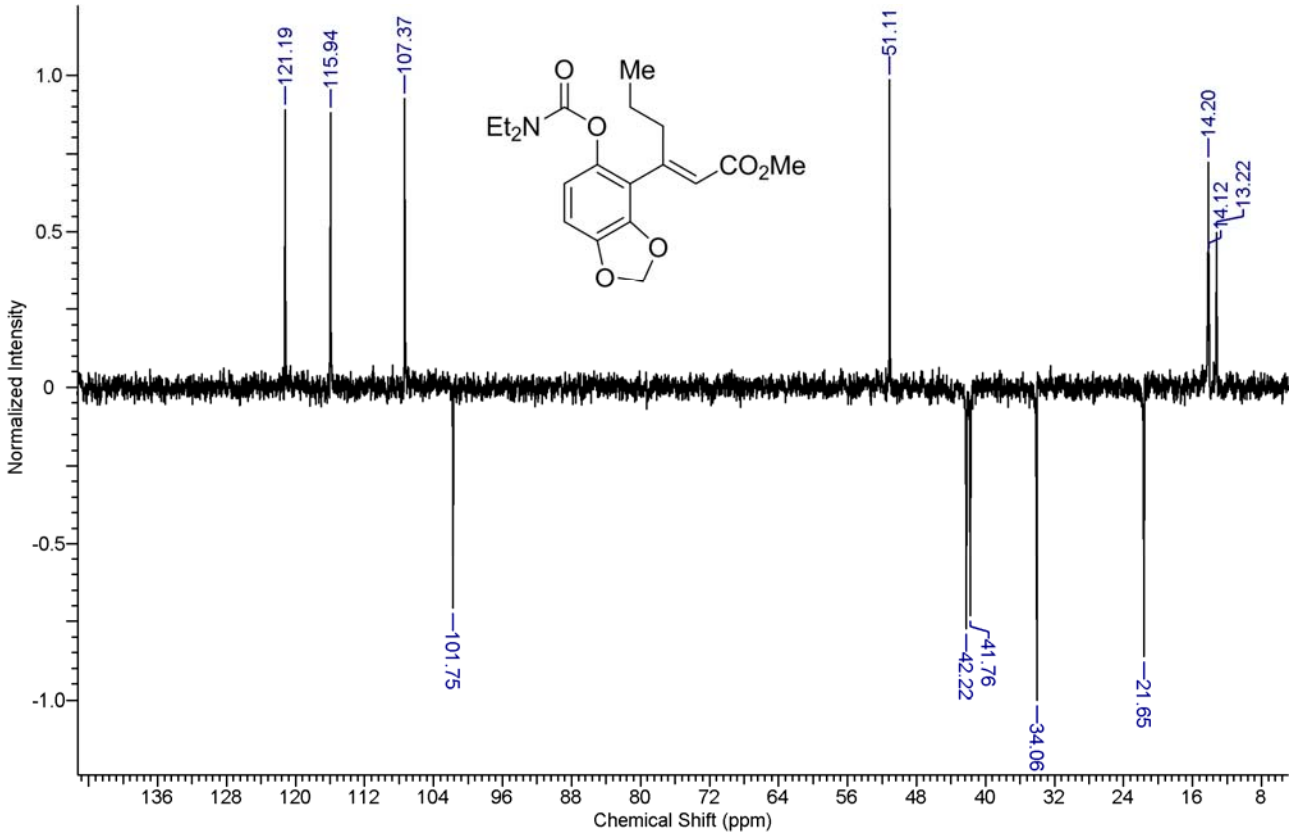


^{1}H and ^{13}C NMR Spectra of Compound **3q.**

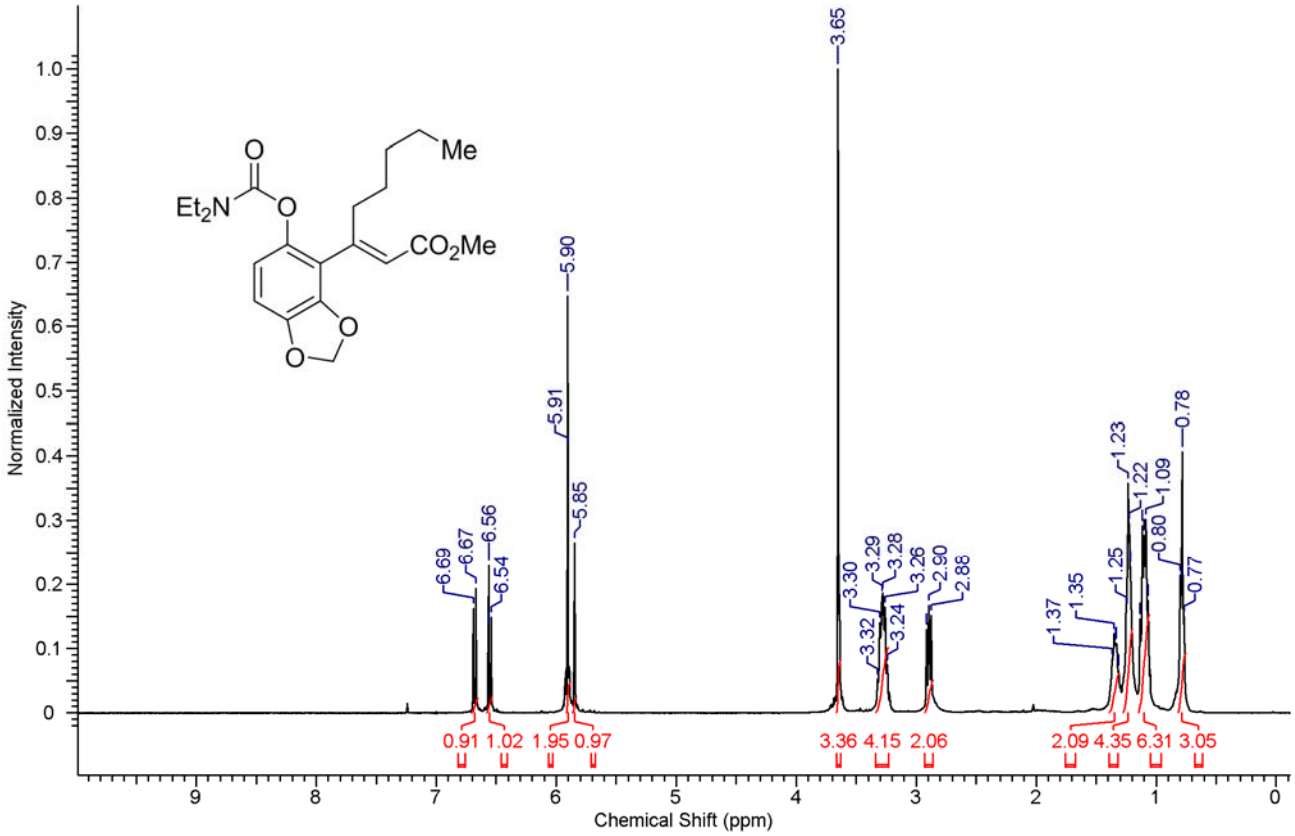


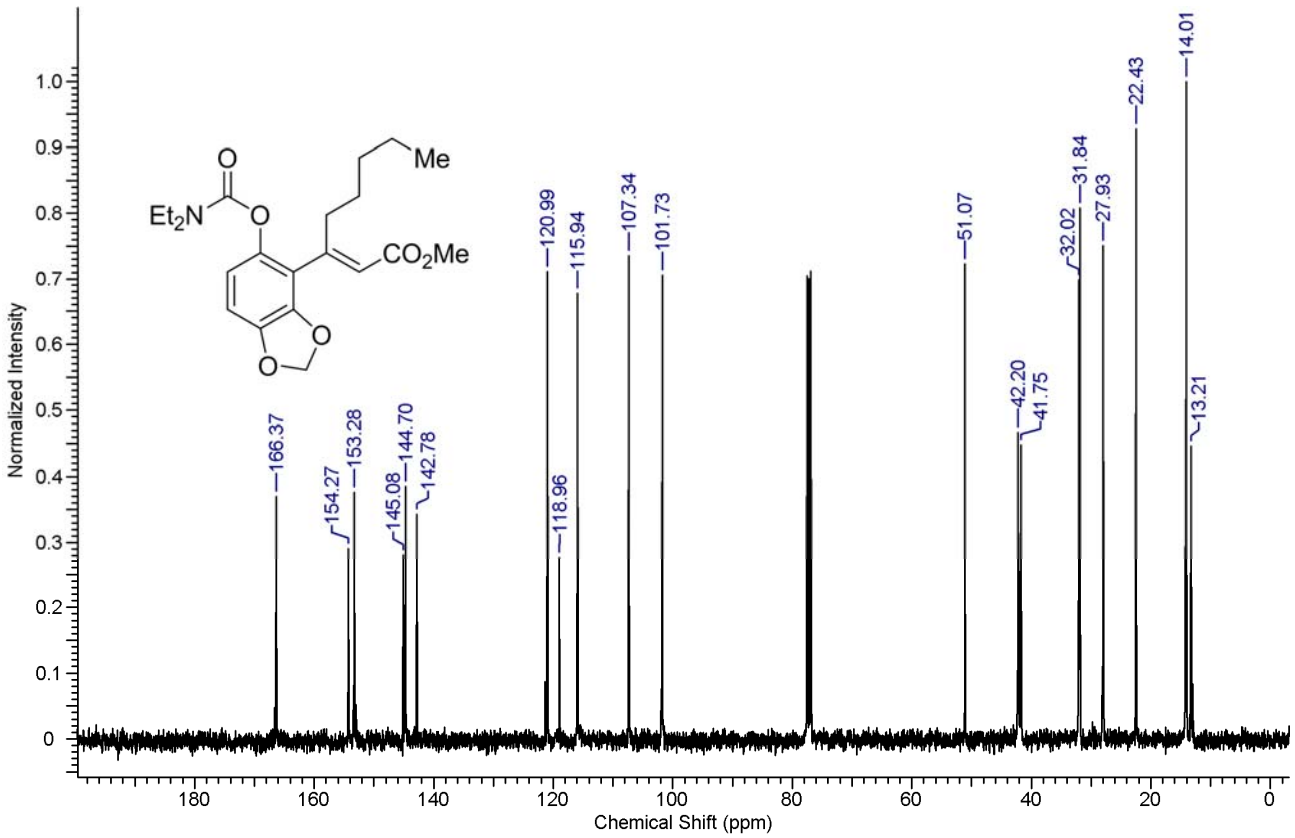


DEPT (135) NMR Spectrum of Compound **3q.**

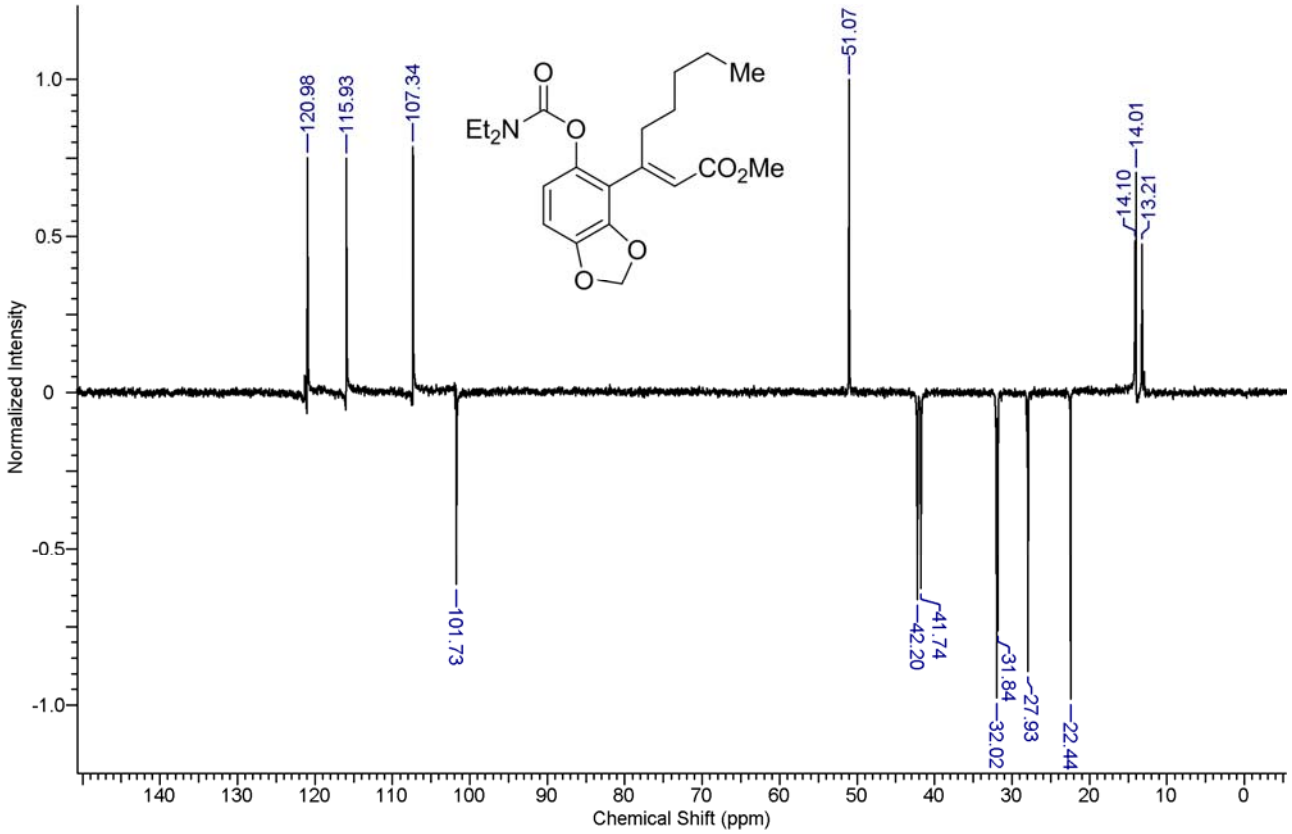


^{1}H and ^{13}C NMR Spectra of Compound **3r.**

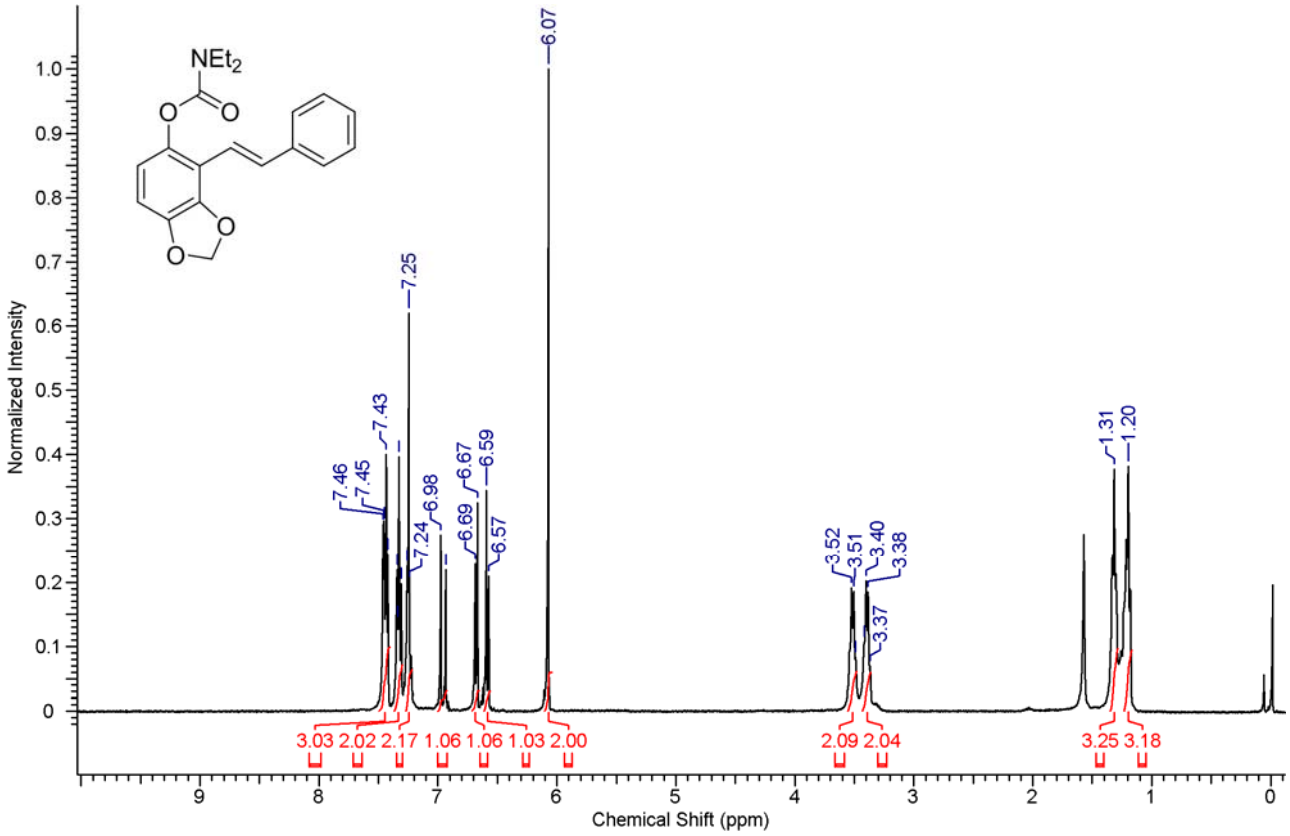


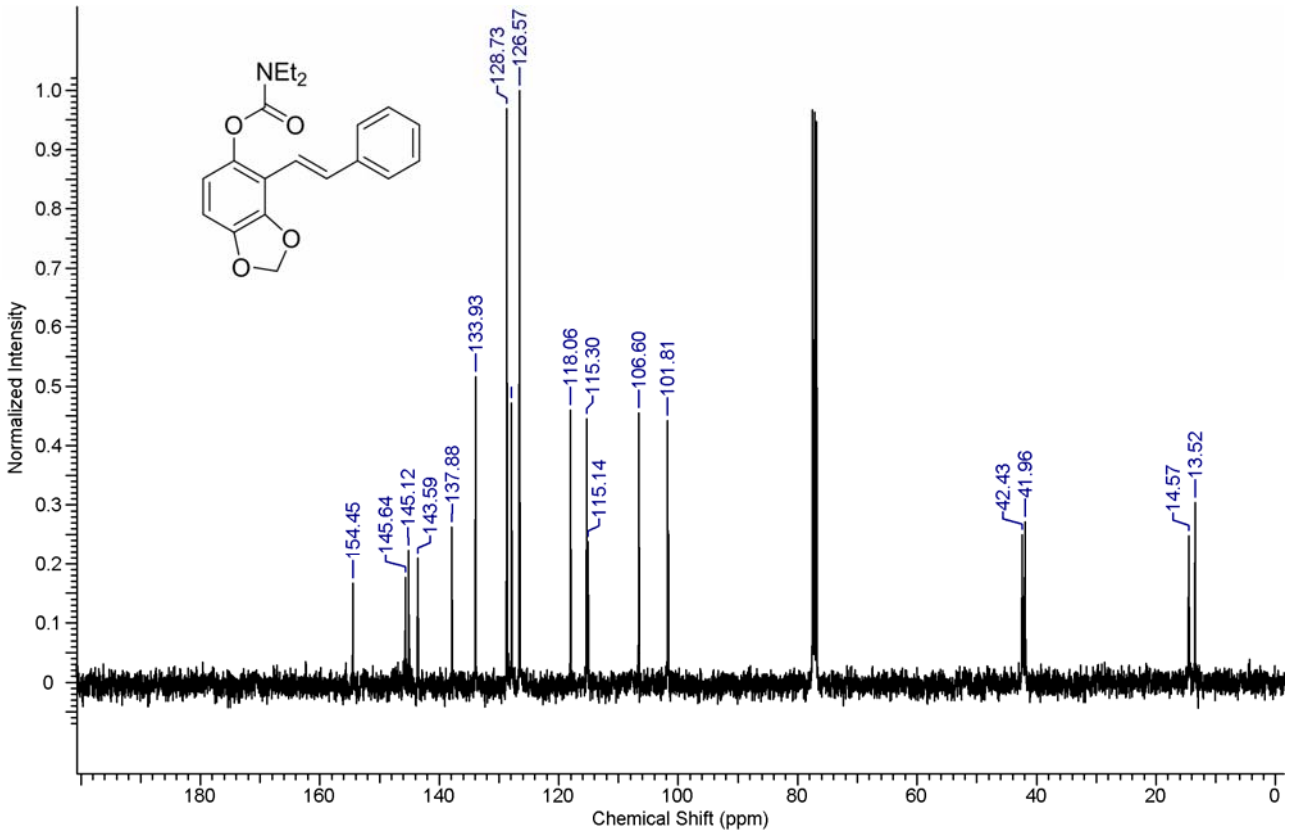


DEPT (135) NMR Spectrum of Compound **3r.**

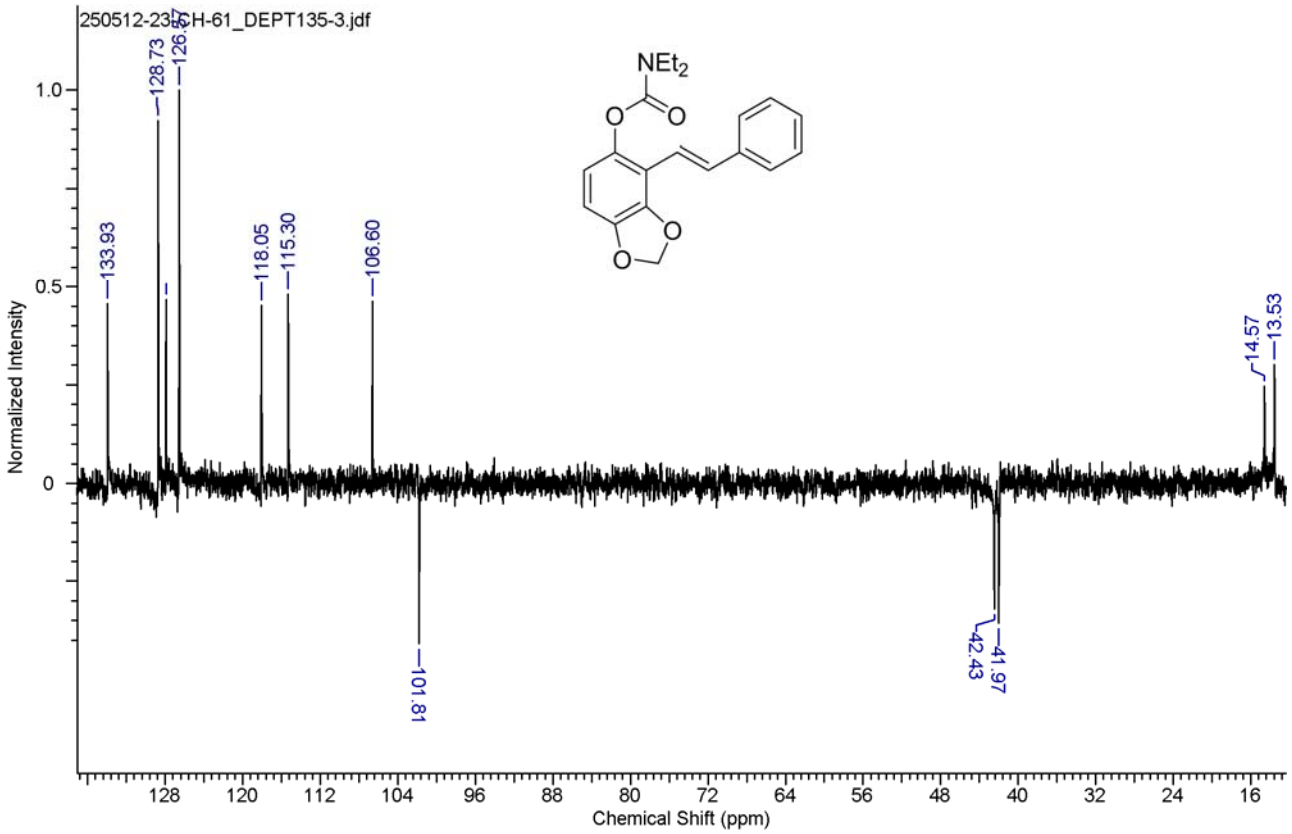


^{1}H and ^{13}C NMR Spectra of Compound **3s.**

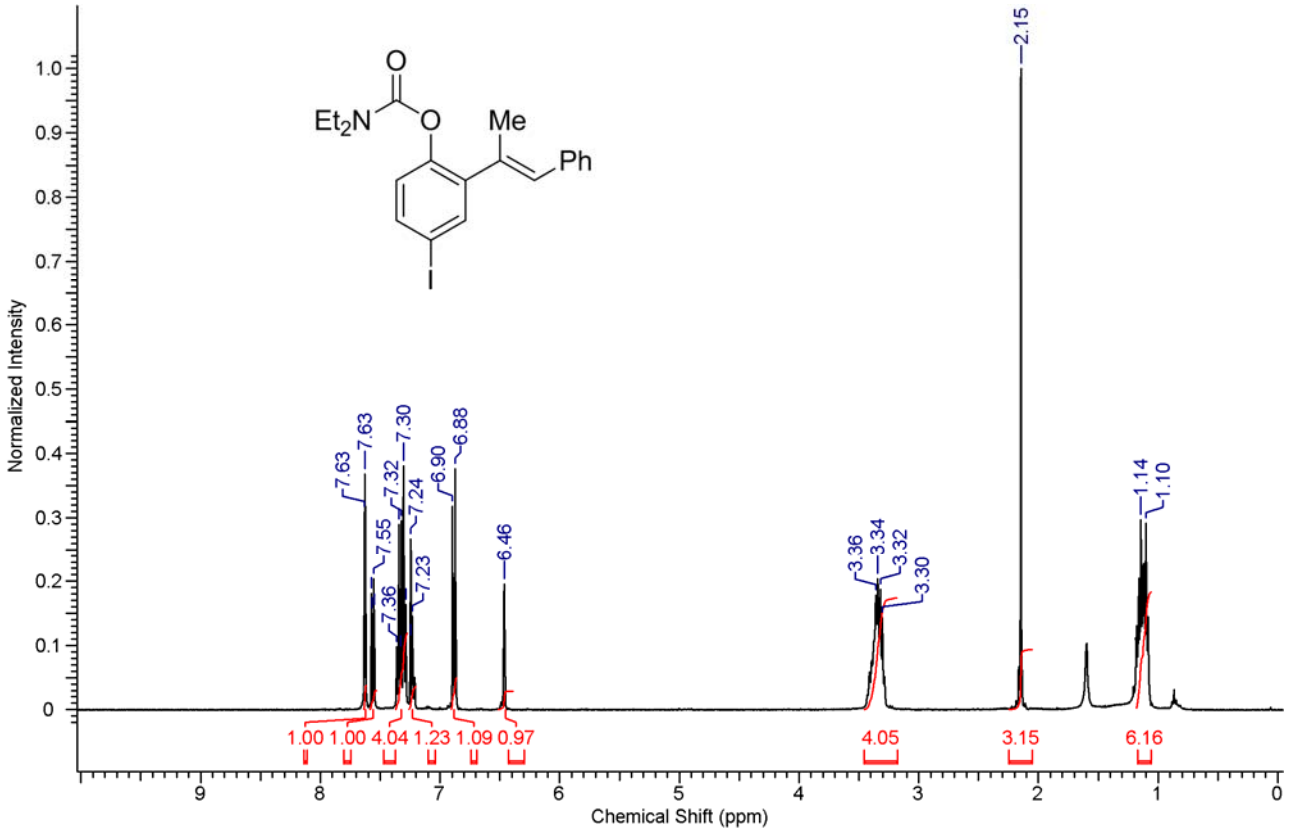


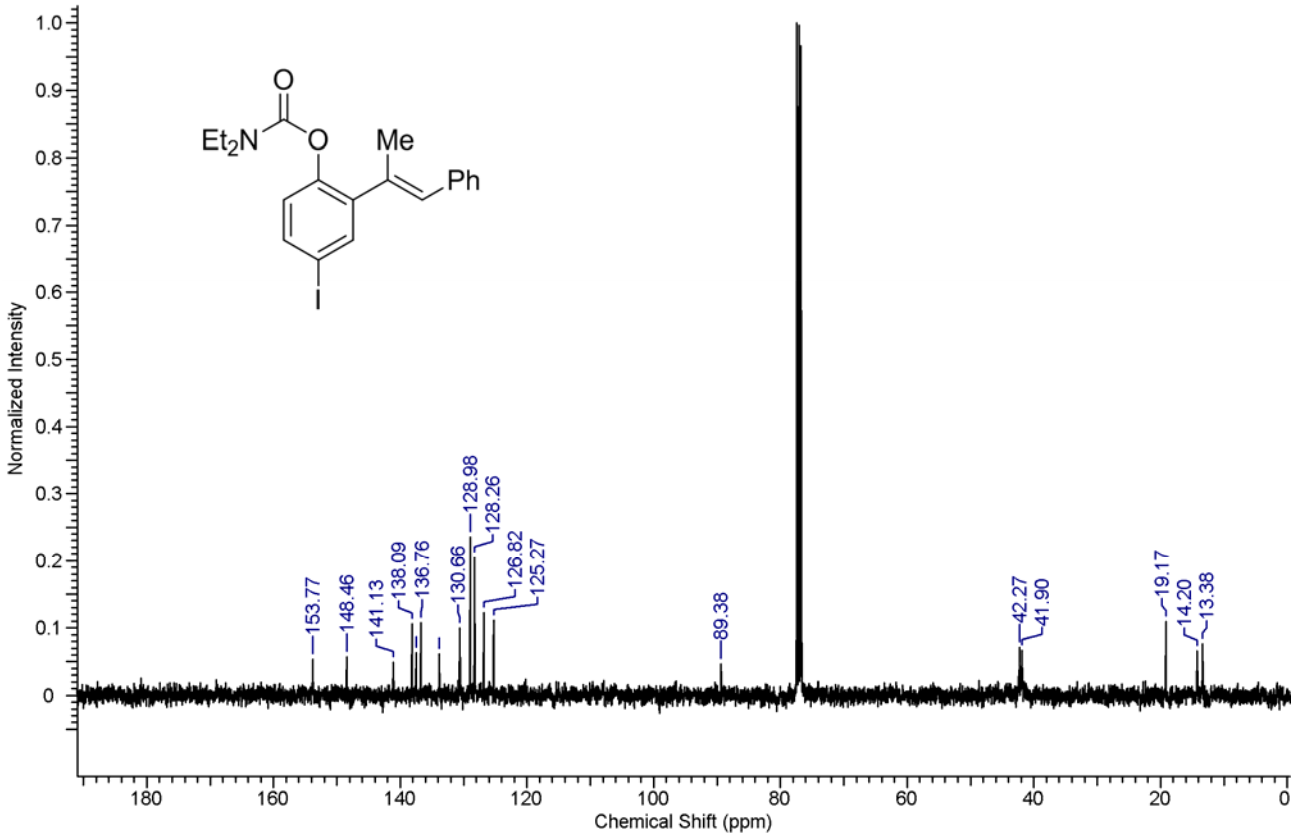


DEPT (135) NMR Spectrum of Compound **3s.**

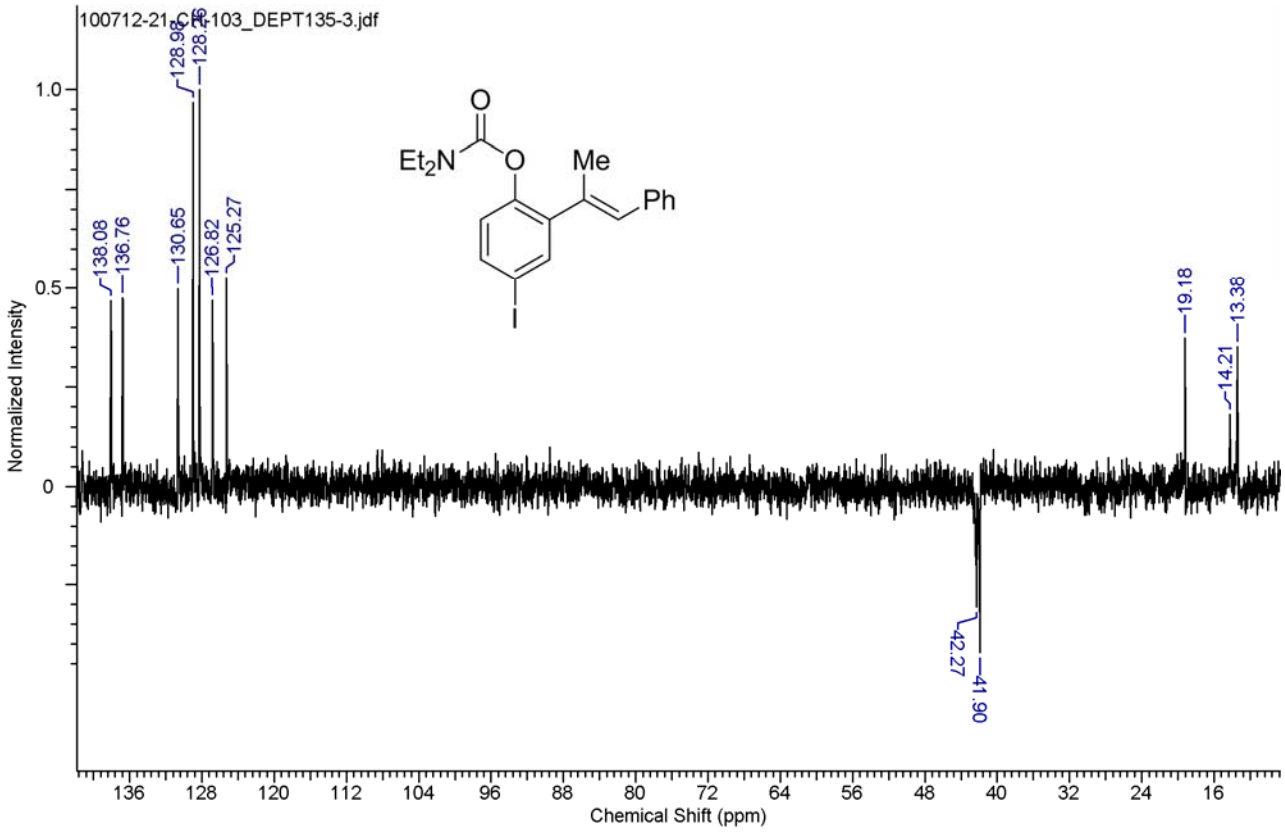


^{1}H and ^{13}C NMR Spectra of Compound **3t.**

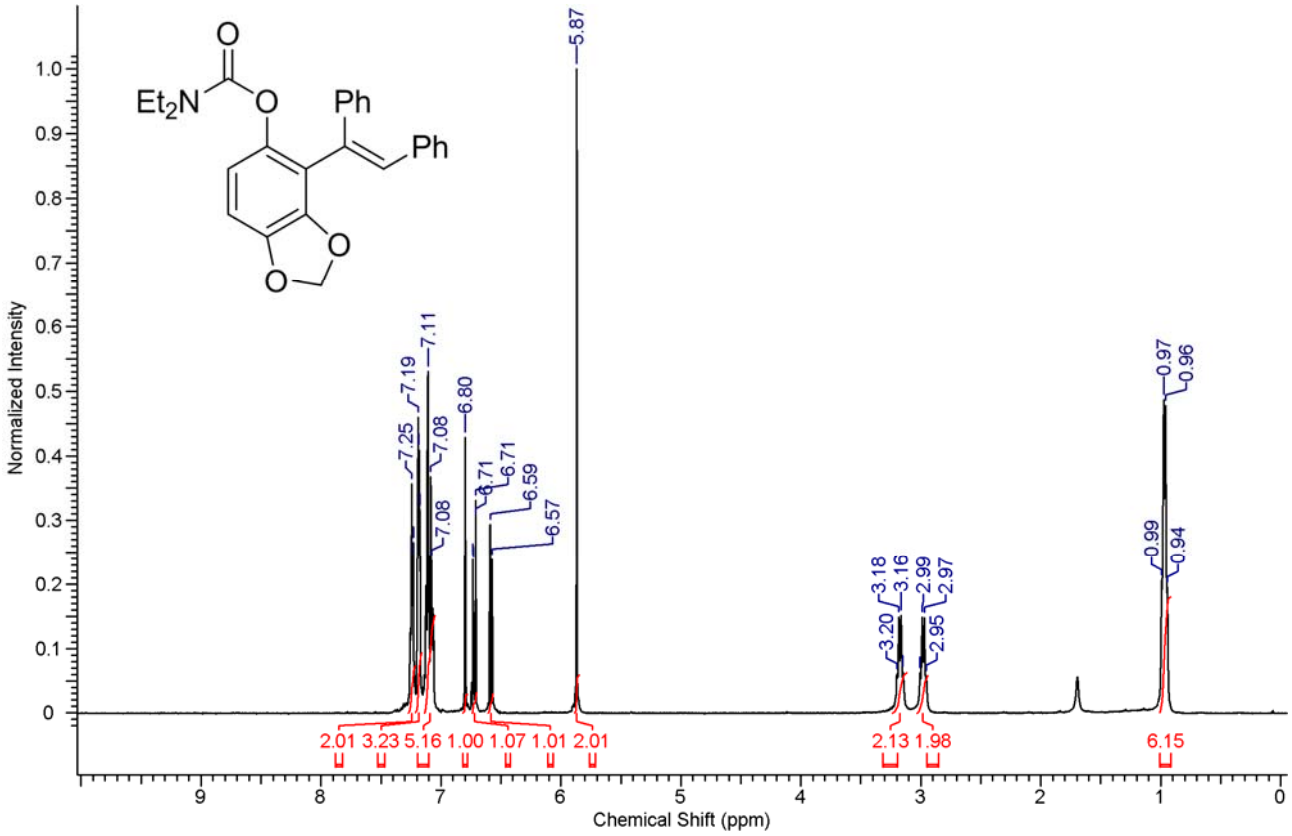


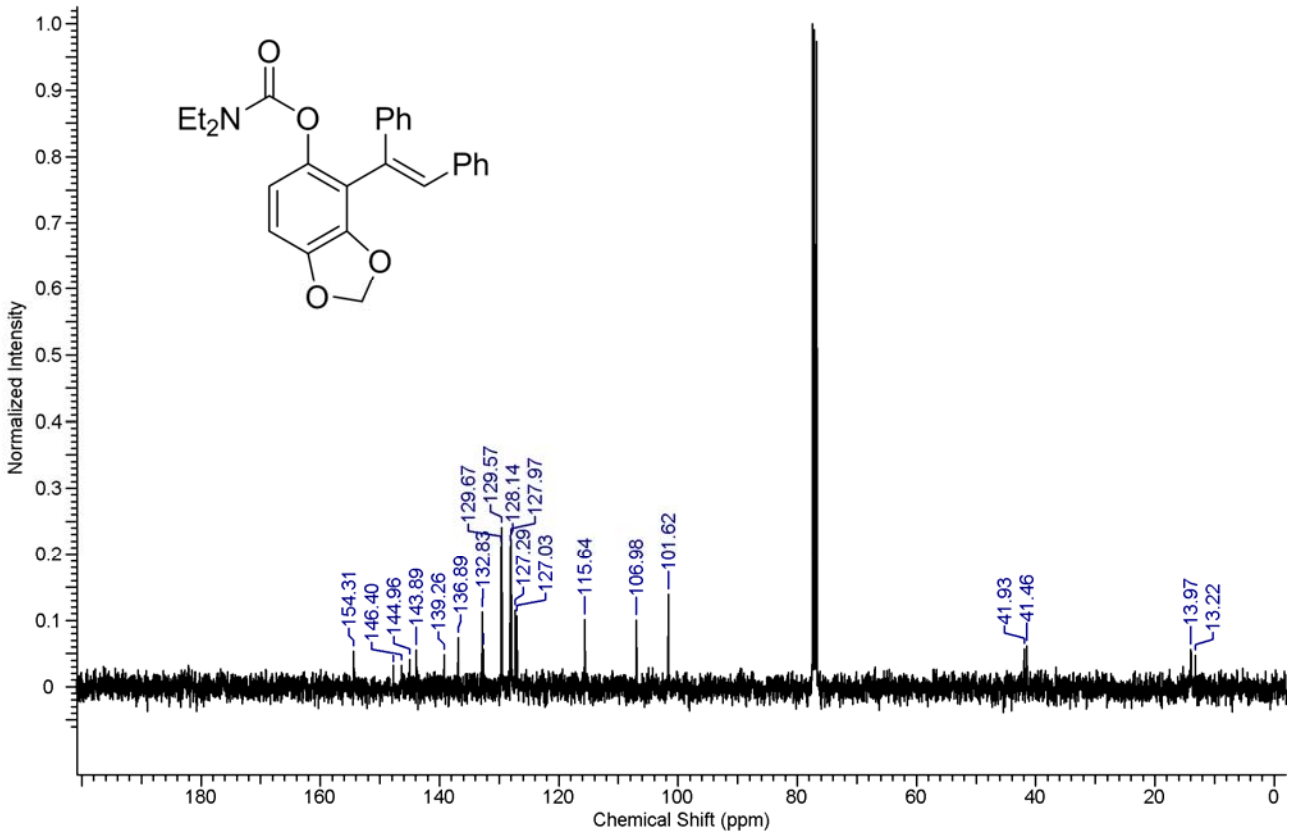


DEPT (135) NMR Spectrum of Compound **3t.**

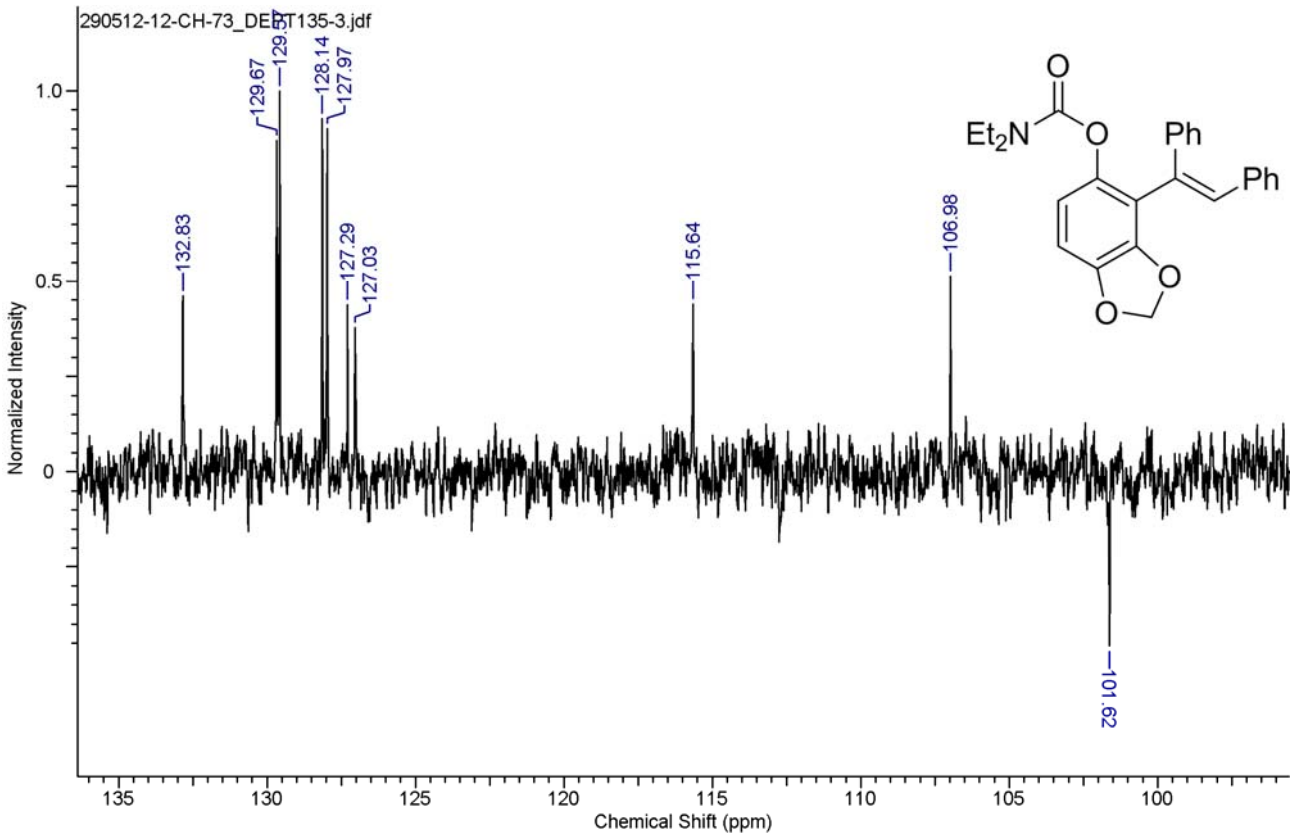


^{1}H and ^{13}C NMR Spectra of Compound **3u.**

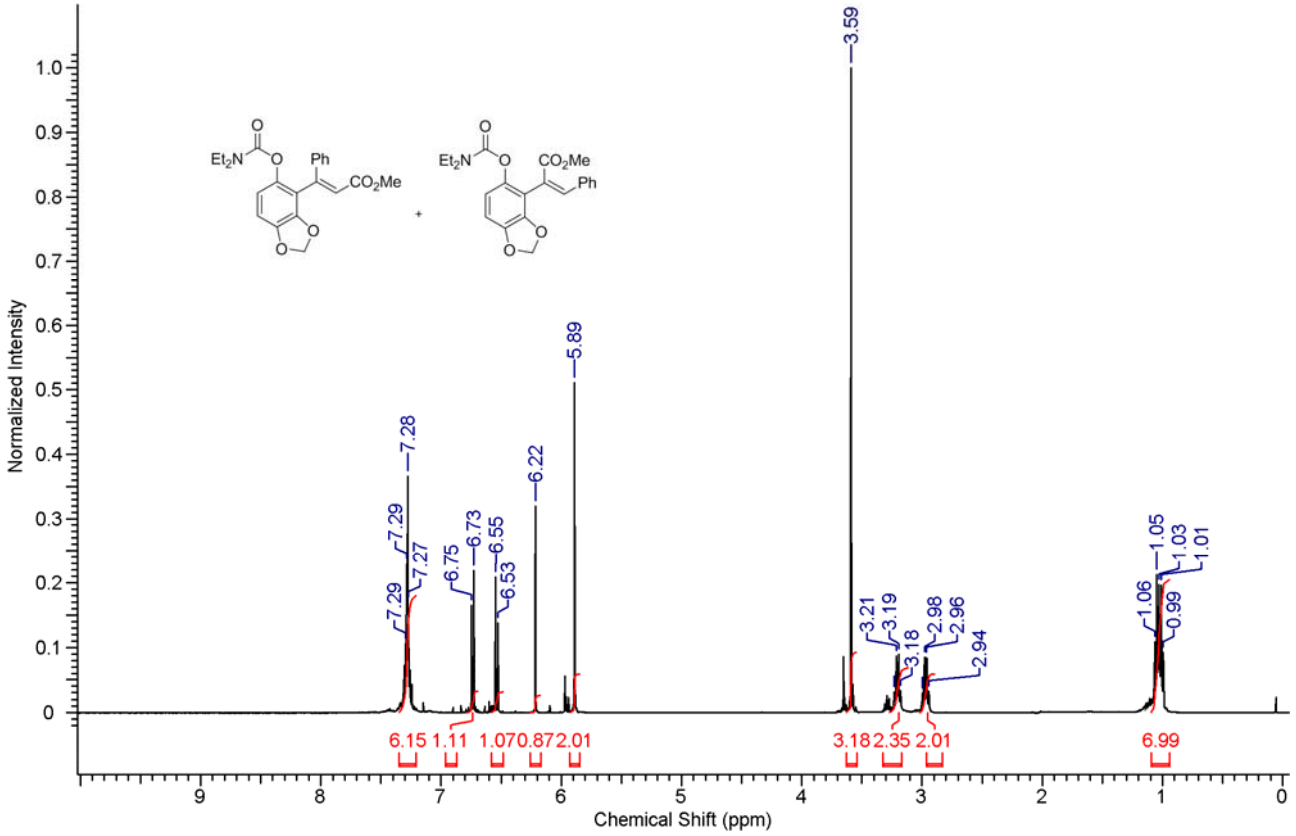


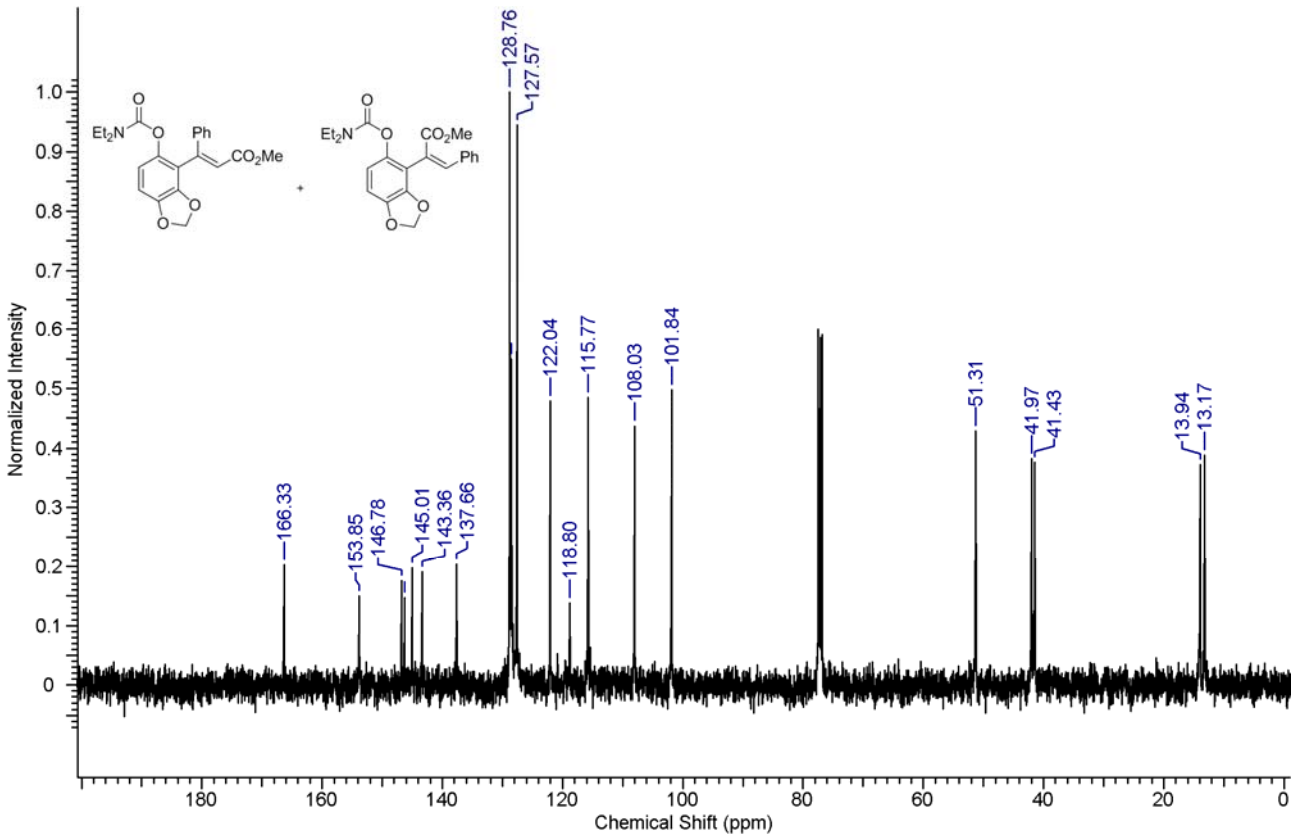


DEPT (135) NMR Spectrum of Compound **3u.**



^{1}H and ^{13}C NMR Spectra of Compounds **3v** and **3v'**.





^{1}H and ^{13}C NMR Spectra of Compounds **3v** and **3v'.**